On the Interplay of Surface Segregation and Bulk Order in Binary Alloys

Structural Investigations of Iron- and Cobalt-Aluminium-based Intermetallics

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Chapter 1

To begin with ...

During routine operation, the turbine blades of an aircraft are exposed to extremely high temperatures and pressures. Of course, any material failure could have fatal consequences, and must be avoided under all circumstances. However, turbine blades must also retain a relatively low weight, if only to save fuel. These conflicting requirements form a prototypical example of the constraints imposed on structural materials in many areas of modern technology: They should perform reliably under thermally, chemically, or otherwise demanding conditions, but do so as cost-efficiently as possible, at manufacturing time as well as during operation. For these reasons, major efforts were dedicated to the development and continued refinement of structural materials throughout history, and in particular throughout the 20th century. Advanced structural applications are but one of several fields in which metallic alloys are routinely used today [Sau95] (for instance, in the above-mentioned case of aircraft turbine blades, major improvements are currently hoped for by the use of Ti-Al-based alloys [App00]). Alloys are applied for tasks as diverse as heterogeneous catalysis, as protective coatings in corrosive environments, or in magnetic devices – in other words, they pervade much of our technology.

The versatility of alloys stems primarily from the ability to manipulate their exact chemical composition, giving profound control over their chemical and physical properties. Apart from the basic ingredients, this also concerns beneficial trace elements, adjustments which often would not seem to change the properties of some hypothetic, homogeneous bulk material very much. Yet, they may affect localised regions of strong compositional inhomogeneity, such as microstructural features (e.g., the distribution and interaction of dislocations, the cohesion of grain boundaries, or the formation and distribution of small-scale precipitates), which determine the mechanical behaviour of a material. Also, this concerns the region which mediates any interaction of a material with its environment – its surface. Obviously, processes such as catalysis or corrosion must necessarily happen there, and it has long been realised that a detailed picture of surface properties is an important building block in understanding and advancing a material’s capabilities as a whole. Much effort has thus been dedicated to the study of solid surfaces, and of alloy surfaces in particular, throughout the past decades, merging the contributions from physicists, chemists, material scientists, and others into what is now simply known as “surface science”.
Chapter 1. To begin with ...

The present work deals with the atomic order and structure of alloy surfaces. Obviously, the preceding paragraphs might well suffice as a general motivation for this type of study. There is, however, a second, more fundamental reason why alloy surfaces form an intriguing class of systems to a solid state physicist: They represent a unique opportunity to “play” with simple Ising-type systems, i.e. the interaction of “spins” on a lattice. Already in bulk alloys, but a few basic ingredients on the atomic scale suffice to create a remarkable complexity of phenomena, and the presence of a surface adds further interesting facets to this picture. In fact, the following chapters address this more fundamental point of view, discussing the physical nature of the mechanisms which govern the arrangement of atoms near a surface, and not their implications for any practical application. Nevertheless, such research always forms part of a larger framework, and so a few sentences near this work’s very end aim to place its results in a broader frame. After all, the study of matter on the atomic scale is ultimately driven by the desire to understand the macroscopic world which surrounds us, and the present work forms no exception to that rule.

The physics of the solid state begins with the description of its structure. Most inorganic solids assume a kind of crystalline order, with their atoms residing on the positions of some basic, periodic lattice. Here, a binary alloy retains a specific degree of freedom: the actual arrangement in which the two different elements are distributed about the lattice. Depending on whether the occupation of neighbouring lattice sites by identical or different atoms is energetically favourable, binary systems are referred to as clustering and ordering alloys, respectively. Both the formation of order on a given lattice and its particular type are determined by short- and long-range interatomic interactions. These, in turn, reflect the precise nature of the chemical bond between the elements, rendering any general predictions of a given alloy’s ordering behaviour quite difficult. An alloy may even form a different basic lattice than either of its elemental constituents, in which case one speaks of an intermetallic compound.
In principle, there is a multitude of different structures which alloys may assume. Three examples are shown in Fig. 1.1: The A2, B2, and D0\textsubscript{3} lattice types, all based on a body-centred cubic (bcc) arrangement, will each play key roles later in this work. In both the B2 and the D0\textsubscript{3} structure, the elements adhere to a kind of long-range order (LRO), i.e. the constituents form an ordered superlattice on the underlying, basic lattice. However, even if an alloy has a tendency to form ordered structures, it may in reality still be found to be substitutionally disordered with both elements randomly distributed about the lattice, as would be the case for an A2-type binary alloy.\footnote{In the following, we will speak of a random alloy or solid solution if no LRO forms at all.} In thermodynamic equilibrium, the dominant interatomic interactions may be irrelevant near specific compositions (e.g. in the dilute limit), entropy may be able to overcome an ordering tendency at finite temperature, or external strain or pressure may modify an alloy’s structural properties. However, an alloy’s constituent elements are rarely distributed about the lattice in a fully random manner even then. Instead, some kind of short-range order (SRO) normally evolves, i.e. there remains a correlation in the elemental occupation of certain lattice sites. Both SRO and LRO are directly linked to an alloy’s macroscopic behaviour, and have formed an active field of study since the early days of crystallography (e.g., the basic structure of Fe\textsubscript{3}Al, FeAl, and CoAl was revealed in the 1930s [Ekm31, Brad32a, Brad32b]).

Of course, no real solid is infinite, and the existence of a surface opens up a variety of additional degrees of freedom to a binary alloy. Apart from the typical geometrical changes, relaxation or reconstruction, that may occur near any solid surface [Hnz94, Wat99], the one possible modification specific to an alloy is surface segregation. In a conventional sense, this denotes the overall enrichment of one constituent in the near-surface region of an alloy, compared to the bulk. Obviously, that definition is somewhat vague regarding the actual arrangement of elements, and thus insufficient for our needs. To deal with atomic order appropriately, we shall therefore formulate it more pointedly.

In the present work, surface segregation denotes any observed deviation from an alloy’s bulk-like composition and order in the vicinity of a surface. Research on such phenomena dates back at least to 1957, when McLean formulated his simple model of interfacial segregation [Lea57], and has remained an active playground for statistical mechanics ever since (recent general reviews include Refs. [Mon97, Vas97, Pol00, Der01]).

The reason for such an inhomogeneity is already inherent in the concept of a surface itself, since it breaks the 3D translational symmetry of the basic bulk lattice. Often-cited qualitative driving forces for segregation are a lower surface free energy of one of the elements involved, the size effect, which drives the “larger” atom out to the surface (relieving some lattice strain in the bulk), or the lower elemental heat of vaporisation (since that element should, on average, contribute less bond energy if located in the bulk). Yet, if one element preferentially occupies the lattice sites near the surface, a conflict must arise for alloys with a noticeable ordering
tendency, provided that the bulk atomic interactions hold near the surface as well. As illustrated very schematically in Fig. 1.2, surface segregation requires the occupation of adjacent sites by identical atoms, whereas ordering favours the exact opposite. So, from a very basic point of view, we must expect the competition of bulk ordering interactions and surface segregation to shape the structure of a crystalline alloy surface.

It is the goal of the present work to provide a detailed picture of the interplay between short- and long-range order on one hand and surface segregation on the other for two particular alloy systems, both transition metal aluminides. Fe-Al and Co-Al are well comparable, as both form phases based on a bcc lattice. Both have a pronounced tendency towards ordering in the bulk. A trend for Al to segregate is consistently reported for Fe-Al [Rue86, Gra95, Elt97, Ham98], while the only available structural study of a Co-Al surface, an earlier work of our group on CoAl(110) [Blu96], reveals a nearly bulk-ordered termination. Also, both Fe-Al and Co-Al form isostructural phases to the often-studied NiAl system (see Chapter 2). Given this background, the present work’s objectives are fourfold, namely

- to study surface segregation and order as a function of bulk composition for \( \text{Fe}_{1-x}\text{Al}_x(100) \) \((x = 0.03, 0.15, 0.30, \text{and } 0.47)\),
- to study surface segregation and order as a function of different bulk ordering forces, by comparing \( \text{Fe}_{1-x}\text{Al}_x(100) \) to CoAl(100),
- to study surface segregation and order as a function of surface orientation, by comparing CoAl(100) and CoAl(111), and
- to create a unified scenario from these results, which also allows a meaningful comparison to related systems – foremost, but not exclusively, to the surfaces of NiAl.

Of course, particularly the last point is an ambitious one, which can hardly be attained in full. Nevertheless, at least some progress towards this goal may be hoped for.

The scientific tool which forms the basis of the following studies is the quantitative analysis of experimental low-energy electron diffraction (LEED) data. In brief, LEED has probably assumed the same fundamental role for surface crystallography that X-ray diffraction (XRD) plays for bulk systems. Since its inception in 1927 [Ger27] and the advent of ultra-high vacuum (UHV) technology in the 1960s, the method has seen considerable progress both on the experimental and theoretical side [Pen74, Hov86, Hov93, Hnz95, Hnz98]. To date, it is the “most productive” method in surface crystallography [Hov00], allowing to solve structures of remarkable complexity [Hov96, Hnz98] with a geometric accuracy approaching the pm level. In particular, it has been applied numerous times to the study of binary alloy surfaces. Even so, its application to the present cases necessitated some further methodological research. Apart from the continued development of existing computer programs in Erlangen, which now form the TensErLEED program package [Blu01], this mainly concerned issues related to parameter correlations, and the accuracy of the method as such (e.g., Ref. [Wal00]). In this respect, Sect. 4.3 deserves particular notice, addressing the factors which influence the chemical precision of LEED.
It should also be emphasised that the work presented in this thesis focuses on the computational evaluation of structural information from LEED intensities. The equally demanding experimental characterisation of the surfaces in question, including the provision of high-quality LEED intensity data, formed part of others’ thesis work, also carried out at the Lehrstuhl für Festkörperphysik (Chair of Solid State Physics) in Erlangen. Dr. H. Graupner, Dipl. Phys. W. Meier, Dipl. Phys. Ch. Müller, Dr. Ch. Rath, and Dipl. Phys. Ch. Schmidt deserve particular credit for their experimental work, on which the current study builds. Their efforts also included the collection of pre-information by methods other than quantitative LEED, which is often drawn upon below. Nevertheless, the reader is referred to the dedicated literature for the description of these other methods, e.g. Refs. [Mue75, Ert85] on Auger electron spectroscopy (AES), Refs. [Nie91, Nie93] on low-energy ion spectroscopy (LEIS), and Refs. [Chn93, Var99] on scanning tunnelling microscopy (STM).

Following this introduction, two chapters intend to acquaint the reader with some necessary background: Chapter 2 addresses the bulk and surface physics of transition metal aluminides in general, and also defines the conditions under which their surfaces are usually studied. Chapter 3 introduces quantitative LEED, and presents the particular approach to structural analyses chosen here. The next two chapters contain the original research of this work, separated into results regarding Fe-Al (Chapter 4) and Co-Al (Chapter 5) surfaces. Based on these findings, Chapter 6 attempts to formulate a broader model of surface order and segregation in Fe-Al and Co-Al, and also touches on related systems in this context. An overview of the progress made concludes this work.
Chapter 2

Prerequisites

Before unravelling the roles of ordering and segregation at Fe-Al and Co-Al surfaces, one should possess a clear understanding of the available background on their properties. To that end, the following two sections introduce the structure of Fe-Al and Co-Al in the bulk, specifically concerning the nature of ordering and defect types, and discuss their (100) and (111) oriented surfaces. Section 2.3 briefly summarises our current understanding of TM-Al surfaces in general. Last, Sect. 2.4 describes the mechanisms which control the equilibration of alloy surfaces, determining their characteristics in an actual experiment. Together, these considerations should enable a clear understanding of the issues faced in the remainder of this work.

2.1 Bulk order in Fe-Al and Co-Al

The thermal equilibrium properties of alloy systems are conveniently visualised by phase diagrams, which map their structural properties as a function of composition and temperature. Those for Fe-Al and Co-Al (and also Ni-Al for comparison – see below) are reproduced in Fig. 2.1, following Ref. [Lan91]. Their Al-rich sides are qualitatively similar: In each case, several well-separated, stable compounds form, which are structurally quite complex. In addition, Ref. [Lan91] also mentions the existence of metastable quasicrystalline (QC) arrangements for both systems between (roughly) 75 % and 85 % Al. The overall bulk structure becomes much simpler close to equiatomic stoichiometry, where both systems switch to a body-centred cubic (bcc) basic lattice. With the exception of the so-called “γ-loop” of face-centred cubic (fcc) Fe at elevated temperature, the entire Fe-rich region of the Fe-Al phase diagram adheres to this arrangement. In contrast, the bcc based region of Co-Al is much narrower. On the Co-rich side, it is bounded by a large miscibility gap which extends up to solid solutions of Al in the hexagonally close-packed (hcp) and fcc bulk modifications of Co (ε Co and α Co, respectively). Due to their direct structural comparability, only bcc-based Fe-Al and Co-Al alloys are investigated in this work. It should be noted that not only the underlying lattice, but also the lattice parameters $a$ of these alloys are very similar. For Fe$_{1-x}$Al$_x$, $a$ rises from 2.866 Å to 2.900 Å between $x = 0$ and 0.2 at room temperature, and then remains approximately constant (between 2.895 Å and 2.905 Å) up to $x = 0.5$ [Lih61]. With $a = 2.862$ Å at $x = 0.5$ [Coo63],
Figure 2.1: Phase diagrams of the Fe-Al, Co-Al and Ni-Al systems, following Ref. [Lan91]. Stability ranges of individual phases are shaded; the white areas inbetween are miscibility gaps in which the adjacent phases coexist.
2.1. Bulk order in Fe-Al and Co-Al

It is noteworthy that Fe-Al and Co-Al alloys are quite exothermic, i.e., their formation enthalpies $\Delta H_f$ (the energy gained by creating the alloy from elemental solids) are relatively high. For instance, $\Delta H_f$ amounts to 0.26 eV per unit cell [Hul73] for stoichiometric FeAl. With 0.55 eV per unit cell [Mes94], that for CoAl is even more than twice as high. Intuitively, $\Delta H_f$ is the result of “bond” formation. In this picture, energy can be gained by maximising the number of Fe-Al and Co-Al “bonds”, i.e., the mutual arrangement of both elements on the bcc lattice must be of great importance. To begin with, it is instructive to consider the relative location of nearest neighbour (NN) sites, second nearest neighbour (2NN) sites, etc., on this lattice. Fig. 2.2 illustrates this relationship for the five closest neighbour shells to a corner atom of the cubic unit cell. Eight NN are located at the centres of the surrounding cubes, in a distance $d_{\text{NN}} = a/\sqrt{2}$ (where $a$ denotes the cubic lattice constant). Six 2NN are located at the adjacent cube corners ($d_{\text{2NN}} = a$), twelve 3NN are located on the face-diagonal cube corners ($d_{\text{3NN}} = \sqrt{2}a$), etc. One might expect the strongest “bond” to form between pairs of NN atoms, and indeed, both stoichiometric phases FeAl and CoAl assume B2 (CsCl) LRO (already shown in Fig. 1.1), where each atom is surrounded by eight NN of the other type, leading to the formation of two inequivalent, primitive cubic sublattices A and B. Denoting the energetic contribution of a bond between two particular atoms by $\epsilon_{\text{NN}}$, the above-given values of $\Delta H_f$ allow a rough estimate of the effective bond strengths in CoAl and FeAl. Assuming only NN interactions to be relevant (which is not quite true, as we shall see), the formation enthalpy of a B2 arrangement is

$$\Delta H_f = 8 \cdot \frac{2\epsilon_{\text{TM-Al}} - \epsilon_{\text{TM-TM}} - \epsilon_{\text{Al-Al}}}{2},$$

(2.1)

per unit cell, i.e., the order of the effective interactions we are dealing with, $2\epsilon_{\text{TM-Al}} - \epsilon_{\text{TM-TM}} - \epsilon_{\text{Al-Al}}$, is roughly 65 meV (140 meV) for FeAl (CoAl).

Returning to the phase diagrams in Fig. 2.1, it is apparent that the B2 structures for Fe-Al and Co-Al are not restricted to exactly equiatomic composition. Rather, each exists for a range of possible concentrations, the extent of which depends strongly on temperature. At low $T$, the Co$_{1-x}$Al$_x$ B2 phase is only stable for $0.48 \leq x < 0.5$, but its phase area expands down to $x \approx 0.21$ for $T$ well above 1000 K. Similarly, the Fe$_{1-x}$Al$_x$ B2 phase exists for compositions $0.23 \leq x \leq 0.55$, depending on $T$. Obviously, each ordered lattice is able to incorporate excess atoms while retaining its positional translational symmetry, i.e., by way of randomly distributed structural defects. The two simplest

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1Of course, one must regard such rough estimates with due caution. First, Eq. (2.1) assumes also the elemental bulk materials to be based on a bcc lattice. Experimentally, this is not true at least for Al and Co. Second, it is by no means obvious that NN interactions should be the only, or even the strongest ones in a given material. For a more rigorous introduction of alloy energetics, see also Section 6.1.1).
possibilities are the formation of “antisite defects” (i.e., excess A atoms on the B sublattice, or vice versa), or “structural vacancies” on one sublattice only. Over the past decades, a consensus has emerged that, in the TM-rich regime, antisites are energetically most favourable for both B2 Fe-Al and Co-Al (Ref. [Bes99] and references therein). The situation is different for Al-rich B2 phases. While B2 Fe-Al also incorporates excess Al atoms as antisite defects, the formation of structural vacancies is advantageous for Co-Al.

Of course, the degree and assumed type of order are also temperature-dependent. Both stoichiometric CoAl and FeAl retain their overall LRO up to their respective melting points, 1921 K and 1488 K. However, the increased presence of antisites appears to destabilise the overall ordering tendency. For stoichiometries below $x = 0.45$, Fe-rich B2 $Fe_{1-x}Al_x$ shows an order-disorder transition: above a critical temperature $T_c$, no LRO survives, reducing the overall lattice symmetry to that of the simple A2 (random bcc) structure (Fig. 1.1, left). In principle, the magnitude of $T_c$ is also indicative of the relative strength of interatomic interactions, since $k_B T$ must reach the magnitude of the effective bond energy to actually destroy LRO. So, no order-disorder transition is reported for the stronger bound B2 Co-Al phase below its melting point, whereas, for instance, the much weaker bound B2 compound CuZn ($\Delta H_f = 0.12$ eV per unit cell) reaches $T_c$ already at 741 K [Hul73].

At lower Al content ($0.22 \lesssim x \lesssim 0.35$), the Fe-Al system assumes a further type of LRO, the D0$_3$ (BiF$_3$) structure (Fig. 1.1, right), which is derived from B2 order. At Fe$_3$Al stoichiometry, exactly half the Al atoms on the B sublattice of the B2 structure are replaced by Fe. According to Fig. 2.2, all B sublattice sites are 2NN to one another, and in the D0$_3$ phase, the Al atoms remaining on the B sublattice order in a checkboard-like arrangement to avoid the formation of 2NN Al-Al pairs. Fig. 2.3 puts this more formally: the original B sublattice (white “atoms”) of the B2 structure now splits into two inequivalent sublattices B and D. For consistency, the original A sublattice (gray “atoms”) may also be viewed as two sublattices A and C, which, however, remain symmetry-equivalent. In stoichiometric Fe$_3$Al, only the D sublattice is still occupied by Al, whereas Fe resides on A, B, and C. The existence of D0$_3$ order clearly shows that interatomic interactions beyond NN are relevant in Fe-Al. However, the 2NN interactions responsible for D0$_3$ formation are apparently weaker than the NN ones: the order-disorder transition temperature only extends up to 825 K at $x = 0.25$, above which the system switches to B2 periodicity. Compositional deviations to either side of $x = 0.25$ again reduce $T_c$, leading to the approximate stability range mentioned above.

Below the D0$_3$ phase area, no further ordered Fe-Al structures exist. With the exception of a small
Bulk order in Fe-Al and Co-Al

2.1. Bulk order in Fe-Al and Co-Al

miscibility gap, Al here simply forms a random, substitutional solid solution in A2 (bcc) Fe. However, the ordering forces between individual lattice sites are active regardless of the overall stoichiometry of a crystal, and the absence of a long-range correlation does not indicate the lack of any order at all. Only, it is now manifest in the form of short-range order, i.e. through a correlation between the occupation of each lattice site and its immediate NN, 2NN, etc. In bulk diffraction experiments, SRO leads to diffuse intensity between the Bragg spots of the underlying lattice, which allows to determine the effective interactions between elements on certain lattice sites.

For instance, Sanchez et al. [San95] extracted the pair interaction energies in a Fe$_{0.80}$Al$_{0.20}$ alloy from neutron diffraction data, reproduced in Table 2.1. Note that these are effective pair interactions $J_{ij}$, related to the above-mentioned, intuitive pair bond energies $\epsilon_{ij}$ by $J_{ij} = (2\epsilon_{ij}^{\text{Fe-Al}} - \epsilon_{ij}^{\text{Fe-Fe}} - \epsilon_{ij}^{\text{Al-Al}}) / 4$ (see Chapter 6 for their exact significance). As already expected from the existence of B2 and D0$_3$ ordered phases, both $J_{\text{NN}}$ and $J_{\text{2NN}}$ are of non-negligible size. In fact, $J_{\text{NN}}$ corresponds reasonably well to the order inferred from $\Delta H_f$ above. In contrast, any higher pair interactions are qualitatively insignificant. Of course, results such as these are subject to considerable experimental error, and depend quite noticeably on the particular calculational method used for their extraction. Nevertheless, the trends agree well with results of a detailed theoretical study [Sta97] (unfortunately, both cannot be quantitatively compared). So, we may safely expect each Al atom to be surrounded almost exclusively by Fe NN in the A2 solid solution, and to have a strong preference for Fe 2NN at low $T$.

Unfortunately, the SRO properties of Co-rich Co-Al alloys have never been studied in a similar fashion, and bulk interaction energies are therefore unavailable in the literature. Qualitatively, the impact of antisite formation is here much more severe than for Fe-Al. At low $T$, the B2 lattice will only tolerate only small antisite concentrations, above which the solid decomposes, forming precipitates of bulk-like fcc or h.c.p Co.

To complement the above considerations of SRO and LRO in Fe-Al and Co-Al, it is worthwhile to take a look at the neighbouring Ni-Al system. Its phase diagram (also shown in Fig. 2.1) is qualitative more similar to that of Co-Al than to the Fe-Al one. A bcc based B2 phase is found around Ni$_{0.5}$Al$_{0.5}$, bounded by several more complex compounds on the Al-rich side, and a fcc-based region on the Ni-rich side. Both the formation enthalpy ($\Delta H_f = 0.60$ eV per unit cell [Hul73]) and its structural defect properties (antisites in Ni-rich NiAl, but vacancies in Al-rich NiAl) further the impression of a close relationship to Co-Al. However, the Ni-Al B2 phase extends over a much larger composition range than Co-Al, and is also much better studied. Other than its B2 phase, Ni-Al does not form any stable bcc-based structures. However, there are reports of a metastable bcc-based phase of Ni$_2$Al stoichiometry [Mur93, Mut93a, Mut93b], i.e. in the region between roughly 30 % and 40 % Al content, where the underlying lattice switches from fcc to bcc with temperature (martensitic phase transition). Its suggested atomic arrangement [Mut93a] is shown in Fig. 2.4. Just like the Fe$_3$Al phase, bcc Ni$_2$Al orders by a rearrangement of Ni antisite atoms on the B sublattice, again avoiding the formation of 2NN homogeneous bonds. However, only every third Al atom in the (111)
Figure 2.4: Schematic depiction of the metastable, bcc-based Ni$_2$Al phase [Mut93a]. Compared to Figs. 1.1 and 2.3, the original A and B sublattices of the B2 structure have been switched for better visibility. Ni atoms are now found in every third (111) oriented plane of the original Al lattice, breaking its cubic symmetry.

direction is now replaced by Ni, i.e. Ni$_2$Al can also be visualised as an ordered stacking sequence of (111) oriented crystal planes, ...-Al-Ni-Ni-Al-Ni-... So, although Ni$_2$Al LRO is consistent with significant NN and 2NN energy terms, it is an example of an ordered structure which requires a further interaction for stability.

This brief summary should demonstrate that the bulk physics of TM aluminides is an interesting, feature-rich field of its own. Although the remainder of this work is dedicated to their surfaces, we shall see that bulk-like order properties play a decisive role also there.

### 2.2 Basic aspects of bcc-based surfaces

For a basic understanding of the surface properties of Fe-Al and Co-Al alloys, the following section introduces the surface orientations of interest in this work, (100) and (111), in the context of the three basic order types A2, B2, and D0$_3$. For greatest generality, we shall use the terminology of the D0$_3$ structure in all illustrations. The left side of Fig. 2.5 shows the location, and a top view, of the (100) orientation. Its 2D unit mesh is quadratic, with the lattice parameter of the bulk cubic cell, $a$, and the spacing between adjacent bulk planes amounts to $d_{100}^b = a/2$. Obviously, the NN and 2NN environments of near-surface lattice sites are considerably modified compared to the bulk. So, each top layer atom has only four NN, located in the second layer, instead of eight in the bulk, and additionally lacks one 2NN, perpendicularly above in two layers distance. Of the remaining 2NN, four are located within the surface plane, and one resides in the third layer, directly below.
2.2. Basic aspects of bcc-based surfaces

For the (111) orientation, sublattice D resides perpendicularly below sublattice A.

The surface affects also second layer atoms directly, through the lack of one 2NN (again, two layers above).

The (100) surface of a B2 ordered bulk structure keeps these basic properties. Its sublattices A and B are alternatingly stacked, i.e. there are two inequivalent possible surface terminations. $D_0^3$ symmetry leads to a further splitting of the original lattice. As seen in Fig. 2.5, each layer is now subdivided into two checkboard-ordered sublattices, stacked in the alternating sequence ...-(A/C)-(B/D)-... Compared to a simple bcc(100) surface, the 2D surface unit mesh thus forms a $c(2 \times 2)$ superstructure with a lateral lattice constant of $\sqrt{2}a$, and still two inequivalent terminations. However, as in the bulk, the A and C sublattices are symmetrically equivalent, so that the superstructure is really only due to the B/D sublattice split.

The analogous, (111) oriented surface termination is also depicted in Fig. 2.5 (right panel). Most importantly, it is decidedly more open that its (100) counterpart. Each top layer lattice site lacks four NN, but now also three 2NN, with three remaining NN in the second, one NN in the fourth, and three 2NN in the third layer. Every lattice site in the second layer still lacks one NN and three 2NN, and even third layer atoms still miss one NN. (111) planes are of hexagonal symmetry, with a lateral lattice constant of $\sqrt{2}a$. The stacking of layers perpendicular to the surface reduces this symmetry to threefold, with an interlayer stacking vector

$$d_{111}^v = \left( \frac{a}{\sqrt{2}}, \frac{a}{\sqrt{6}}, \frac{a}{2\sqrt{3}} \right)$$

This work uses the conventional Wood notation [Woo64, Hov86] to characterise surface superlattices wherever possible. For a depiction of a $c(2 \times 2)$ arrangement, see also Fig. 3.2.
i.e. the interlayer spacing, \( d_{111} = a/(2\sqrt{3}) \), is smaller by a factor \( \sqrt{3} \) than for (100). A (111) oriented B2 surface again leads to an alternating stacking sequence of A and B planes, with two possible bulk-like terminations. Further, Fig. 2.5 illustrates that a D\( _0 \)\( _3 \) bulk structure may also be visualised as a (111)-oriented superlattice of its sublattices A,B,C,D. So, a (111) oriented surface has four different possible terminations, and the A and C sublattices become formally inequivalent.

In return, the D\( _0 \)\( _3 \) structure does not break the lateral translational symmetry of a (111) surface, i.e. there are no mixed layers, and no superstructure forms. We shall encounter the consequences of this fact in the different behaviour of CoAl(100) and (111) in Section 6.2.3.

The preceding considerations also allow us to define the structural quantities of interest in a LEED analysis more precisely. Of course, in an alloy, the occupation probability of different layers and sublattices is of interest. In the following, \( x^i \) denotes the Al concentration in layers composed of equivalent sites. In case a layer is made up of several different sublattices, these must of course be treated separately (e.g., \( x^iB \) and \( x^iD \) in (B,D) layers of D\( _0 \)\( _3 \)(100)). Geometrically, the most important phenomenon is usually the relaxation of interlayer spacings \( d_{i;i+1} \). However, if equivalent lattice sites are occupied by different elements, these may reside at slightly different average vertical positions. In a D\( _0 \)\( _3 \)-ordered (100) surface, positional differences may additionally occur between sublattices of the same layer. Under these circumstances, the term “interlayer distance” is not well defined. Instead, the proper approach would be to account for absolute positions \( h \) relative to some common origin of the coordinate system. In layers \( i \) with only equivalent sites, one must then distinguish element-dependent positions \( h^i_{\text{TM}} \) and \( h^i_{\text{Al}} \). In the (B,D) layers of a D\( _0 \)\( _3 \)(100) surface, a sublattice dependence \( h^i_{\text{TM}} \), \( h^i_{\text{Al}} \), \( h^i_{\text{TM}} \), and \( h^i_{\text{Al}} \) should strictly be added. Fortunately, the last level of generalisation proved unnecessary throughout this work: it sufficed to determine either element-dependent positions \( h^i_{\text{TM}} \) and \( h^i_{\text{Al}} \) or sublattice positions \( h^i_{\text{B}} \) and \( h^i_{\text{D}} \).

To quantify the deviation of real surfaces from bulk-truncated ones more directly, we shall adopt the following notation throughout this work. Interlayer distances \( d_{i;i+1} \) are always defined by their average value, i.e.

\[
d_{i;i+1} := \left( x^i h^i_{\text{Al}} + (1 - x^i) h^i_{\text{TM}} \right) - \left( x^{i+1} h^{i+1}_{\text{Al}} + (1 - x^{i+1}) h^{i+1}_{\text{TM}} \right).
\]

Positional differences within individual layers lead to a buckling, denoted

\[
b^i := h^i_{\text{Al}} - h^i_{\text{TM}},
\]

i.e. counted positive if Al buckles outward. Analogous definitions are used for (100) layers with different sublattices (B,D), with B replacing “TM”, D replacing “Al”, and 1/2 replacing \( x^i \). While these definitions may seem somewhat formal at this point, their use in Chapters 4 and 5 should show that they allow a rather intuitive description of the surfaces under study.

2.3 “Prior art” for TM-Al alloy surfaces

Over the years, a large number of studies were dedicated to the surface properties of transition metal aluminides, often initiated by their candidate role as a class of “new materials”, mentioned in
the introductory chapter. Apparently, most of this research revolves around the Ni-Al system, even though at least Ti-Al-based alloys are of equal technological interest, and might have warranted similar efforts. Still, a number of other materials have also been subject to study. For instance, the segregation of Al in polycrystalline Fe$_{0.90}$Al$_{0.10}$ was already proven by means of AES in 1971 [Buc71]—the earliest work in the field known to the author. In the following, we shall briefly review the existing literature on the structure of single crystalline TM-Al surfaces. More detailed accounts can be found in the references cited, or in several excellent review articles on alloy surface physics [Vas97, Pol00, Der01].

The various phenomena observed near TM-Al surfaces can be summarised as follows:

- **Bulk-truncated termination.**
  Surface terminations which adhere to the order of the underlying crystal have been reported for several Ni-Al alloys. Among these, the Ni$_3$Al(100) and Ni$_3$Al(110) surfaces, which belong to the fcc-based L1$_2$ phase (see also Fig. 6.10), would allow for two inequivalent bulk-like terminations. Both prefer the variant richer in Al [Son86a, Son86c]. The truncation of the bulk is unique for Ni$_3$Al(111) and B2 NiAl(110), which both surfaces were found to retain [Son86b, Dav85a, Dav85b, Yal88, Mul88, Dav88, Tor01]. In contrast, some disagreement remains for NiAl(100) and NiAl(111), which will therefore be discussed separately below. Terminations consistent with their bulk lattice were also reported for surfaces of QC AlCoCu [Rae90], AlCoNi [Shi00, Gie00], AlCuFe [She98], and AlPdMn [She98, She00]. In these cases, the respective compositions were not exactly determined, but an Al-rich bulk-like termination was established for the fivefold surface of QC Al$_{0.70}$Pd$_{0.21}$Mn$_{0.09}$ [Gie98]. Also, a metastable B2 Al(CuFe)(110) film formed on a fivefold QC AlCuFe surface displayed a bulk-like termination similar to NiAl(110) [Shi98].

- **Bulk truncation with near-surface defects.**
  Some TM-Al alloys surfaces are almost bulk-truncated, except for a few additional defects in the surface region. These cases probably belong to the class of bulk-like terminations in general, given that most of the above-cited studies did not check for defects explicitly. For instance, compositional deviations in Ni$_3$Al(110) and (111) were not tested for, although AES shows some additional Al segregation for $T \gtrsim 1000$ K. This was explained as an equilibrium phenomenon which cannot be frozen in at RT where the crystallographic analyses were done. A LEED study of B2 CoAl(110), conducted earlier in our group [Blu96], found a bulk-ordered arrangement similar to NiAl(110), but with some excess Co on the Al sublattice of the second layer. Its presence was explained by incomplete annealing, rather than as a property of full equilibrium with the faraway bulk. In Chapter 6, this interpretation of the structure of CoAl(110) will be shown to be fully consistent with results for CoAl(100) and (111). In contrast, B2 Fe$_{0.53}$Al$_{0.47}$(100) was first found to be bulk-like Al-terminated [Wan93], but small amounts of second layer Al antisites were reported later [Ktk96, Ham98]. We shall address Fe$_{0.53}$Al$_{0.47}$(100) in Sect. 4.4.3, showing that the original bulk-like termination with an enhanced second layer Fe vibrational amplitude seems the most likely explanation.
Chapter 2. Prerequisites

- **Al segregation.**
  Al segregation beyond any bulk-like truncation characterises the majority of studied systems. A full Al top layer is reported for D0₃ Fe₃Al(100) [Ktk96], Fe₃Al(110) [Vog92], and L1₀ TiAl(010) [Wan95]. At least partial Al segregation is found for fcc random Ni₀.₉₆Al₀.₁₀(100), (110), and (111) [Sul94a, Sul94b, Pol97], and bcc Fe₀.₈₇Al₀.₁₅(100) [Elt97], while only slight Al segregation occurs for fcc random Cu₁₋ₓAlₓ(100) (Ref. [Zhu96] and references therein). Often, Al segregation is accompanied by the formation of non-bulklike superstructures, e.g. for fcc random Cu₀.₈₄Al₀.₁₆(111)-(√3 × √3)R30° [Bai86], bcc random Fe₀.₉₇Al₀.₀₃-c(2×2) [Rue86], and B2 FeAl(210)-(1×3) [Ham98]. Even several different, preparation-dependent superstructures are reported for TiAl(010) [Wan95], FeAl(111), FeAl(110) [Gra95, Bad96, Ham98], and B2 Al₀.₄₈Pd₀.₄₁Mn₀.₁₁(110) [Hei99]. The two latter cases are particularly surprising because Al segregation here leads to an incommensurate arrangement – i.e., the driving force for segregation is strong enough to overthrow the underlying basic lattice entirely. Quite apparently, the stabilisation of these superstructures requires strong interactions between the elements involved.

- **TM segregation.**
  To the author’s knowledge, equilibrium TM segregation beyond a bulk-like termination is only found with certainty in one particular case, for fcc random Agₐ₀.₀₃Alₐ₀.₉₇(100) [Wet93]. Here, AES clearly shows Ag to segregate.

In summary, the literature seems to suggest a relatively simple picture. With the exception of Ag₀.₀₃Al₀.₉₇(100), either Al segregation or a bulk-truncated, ordered termination (Al-rich, if possible) characterise each example satisfactorily. Nevertheless, some systems (FeAl(111), FeAl(110), Al₀.₄₈Pd₀.₄₁Mn₀.₁₁(110), TiAl(010)) show a marked preparation dependence – a surprising behaviour, given the simplicity of the projected “Al-rich, if possible” driving force. In the following, we will highlight two more cases which also hint to a greater complexity of TM-Al surface physics: The equilibrium structures of B₂ NiAl(100) and (111). Both are closely related to CoAl(100) and (111) investigated below, and subject to long-standing debates.

**NiAl(100)**

Already the first study of NiAl(100) noted the dependence of its structure on the exact preparation conditions and sample history [Mul88]. The standard preparation involves ion sputtering to remove any residual impurities, which also depletes the surface of Al through preferential sputtering (see also next section). Annealing at low T only leads to a low-quality (1×1) LEED pattern (“LP”). A different arrangement forms at intermediate T, characterised by a c(√2 × 3√2)R45° superstructure (“MP”). Finally, another (1×1) arrangement (“HP”) is observed after heating to very high T [Mul88, Blm96, Roo96, Tag98]. The surface structure changes with rising T_{anneal} are irreversible – e.g., after preparing the HP structure, the MP structure can not be restored by another anneal at lower T. Unfortunately, thus ends the literature consensus. Already the reported stability ranges of the MP superstructure vary, with 750 K ≤ T_{anneal} ≤ 950 K [Mul88], 600 K ≤ T_{anneal} ≤ 1300 K [Blm96], and 700 K ≤ T_{anneal} ≤ 900 K [Roo96, Tag98]. Likewise, different groups arrive at quite different results for the top layer stoichiometry of each phase:
2.3. “Prior art” for TM-Al alloy surfaces

Figure 2.6: Published structural models for NiAl(100). (a) \((1 \times 1)\) “LP” phase according to Refs. [Blm96, Tak99]. (b) \((1 \times 1)\) “HP” phase (bulk-like Ni-termination with top layer vacancies) after Ref. [Sti00].

Figure 2.7: Published structural models for NiAl(100)-c\((\sqrt{2} \times 3\sqrt{2})R45^\circ\) “MP” (diagonal and top views). The top views also show the centred (dashed) and the primitive (full line) unit mesh of the arrangement. (a) Mixed NiAl\(_2\) top layer according to Ref. [Mul88]. (b) Top Al layer with vacancies according to Ref. [Blm96].
Two studies of the LP (1×1) structure exist. Ref. [Blm96] concludes an Al-termination with defects from LEIS (Fig. 2.6a). The same data are evaluated quantitatively in Ref. [Tak99]. Generally, a good fit to experiment can be obtained by an assumed bulk-like Al-termination; however, one Ni-associated peak cannot be made to fit.

For the MP superstructure, early LEIS experiments suggest a top layer stoichiometry of \( \text{Ni}_{0.35}\text{Al}_{0.65} \) [Mul88], leading to the model in Fig. 2.7a. Refs. [Roo96, Tag98] corroborate this result. In contrast, evidence from LEIS and STM by other workers [Blm96, Blm98] shows a top layer of Al, but with 1/3 vacancies arranged in (011)-oriented rows (Fig. 2.7b).

An early LEED study finds the HP phase to be bulk-like Al-terminated [Dav88], with the Ni-terminated alternative clearly ruled out. However, while the authors mention remnants of the MP superstructure, they did not test for any near-surface defects. According to Ref. [Mul88], the HP surface is indeed nominally Al-terminated, but the top layer includes between 0 % and 30 % Ni atoms – strangely, the top layer composition shows a long-term drift with the number of subsequent preparations over several months (!). Refs. [Roo96, Tag98] support an Al-termination with Ni antisites, but with rising Ni content for increasing annealing temperature between 1300 K and 1700 K. In contrast, a bulk-like Ni-terminated surface is found by LEIS in Ref. [Blm96] after flash-heating at 1400 K. This model is supported by a very recent SXRD study [Sti00], which also finds 1/3 randomly distributed vacancies in the top layer (Fig. 2.6b).

In total, a contradictory picture results, which leaves much room for speculation. All groups used samples of exactly the same nominal stoichiometry, very similar preparation procedures, and highly trusted analysis methods. Yet, their findings span the whole range of possible terminations. It is hard to believe that half the authors should have arrived at outrightly wrong conclusions for no apparent reason. Rather, some subtle dependence on preparation conditions must exist for NiAl(100). The present work suggests such a mechanism, described in Chapter 6.

\( \text{NiAl}(111) \)

The behaviour of NiAl(111) is less complicated than that of NiAl(100), although similar preparation constraints result from preferential sputtering and subsequent annealing. All authors find a (1×1) arrangement under almost all circumstances, with the exception of the very first work [Noo87] which additionally claims a weak \((\sqrt{3} \times \sqrt{3})R30^\circ\) superstructure for \( T_{\text{anneal}} \gtrsim 1173 \) K. Nevertheless, some dissent over the actual surface structure persists. LEED indicates a bulk-ordered surface, but with both possible terminations (Al and Ni) coexisting [Noo87, Noo88, Dav88]. This observation is supported by two LEIS studies [Nie88, Ove90], and by recent, preliminary LEED results [Han97]. In contrast, the analysis of LEED spot profiles (SPA-LEED) [Wen90] yields an average step height of two bulk interlayer spacings on this surface, which rather indicates a single termination. An STM study [Nie90] confirms this result, attributing any residual single-step-high islands to a contamination by oxygen. LEIS experiments in the same work prove a Ni-termination when annealing high enough \((T \approx 1400 \text{ K})\) for O to desorb. \textit{Ab initio} calculations [Kan90] approximately confirm the geometry of the Ni-terminated domain in the original LEED study [Noo87, Noo88, Dav88], but the respective Al-terminated geometries are at variance. In total, two opposing factions exist for NiAl(111), and
2.4. Alloy surfaces and thermal equilibrium

again, both claim very similar surface conditions and present sound evidence for their findings. Moreover, both proposed results are unexpected in the light of our previous remarks. Considering the overwhelming number of Al-rich TM-Al surfaces, a Ni termination would be quite unusual. A mixed termination with two coexisting domains is even less appealing – it seems a strange quirk of nature to provide two very different domains with so similar surface free energies that thermodynamics fail to discriminate between them. Our investigations of CoAl(111) add another twist to the story, and we shall revisit NiAl(111) in Sects. 5.5 and 6.3.1.

2.4 Alloy surfaces and thermal equilibrium

The conceptually simplest state in which to study matter is that of thermal equilibrium. For the “favourite” systems of early surface science, the close-packed surfaces of pure metals, this is relatively easily attained. Once such a surface has been cleaned, its variables of state (geometric relaxation, vibrational properties, electronic structure etc.) are normally not subject to any strong kinetic limitations, and can be studied in “equilibrium” by quenching to any temperature. However, kinetic constraints exist for virtually any other kind of surface, rendering their investigation more complicated. For instance, the additional variables of state of a binary alloy surface are their near-surface composition and order. Both are shaped by diffusion processes with distinct barriers, and any corresponding results can only be interpreted correctly by taking these into account. To put it in a nutshell, we must define the development of “thermal equilibrium” precisely to place our anticipated findings in the broader picture of equilibrium ordering and segregation.

The standard procedure to achieve well-defined surface conditions consists of three steps, beginning with ion sputtering. As a side effect, one of the elements is preferentially removed from the surface by this method in most alloy systems. For TM-Al alloys, this is Al, leading to the formation of an Al-deficient zone which may extend several nm into the surface [Tho83]. Next, the near-surface region and the surface selvedge must be brought back into “global” compositional equilibrium with the underlying bulk by annealing at sufficiently high temperature. However, an upper limit for $T_{\text{anneal}}$ is set where one of the alloy components (Al in the case of TM-Al alloys) begins to evaporate preferentially from the surface. Above, the surface stoichiometry would again be distorted away from thermal equilibrium. Finally, many experimental techniques to characterise the surface are difficult to use at high $T$, so that quenching to low $T$ is required before achieving structural information.

The mechanisms which control the equilibration process of (100) oriented Fe$_{1-x}$Al$_x$ alloy surfaces ($x = 0.03, 0.15, 0.30,$ and $0.47$) were recently described in detail by our group [Mei01]. Fig. 2.8 shows the development of their near-surface stoichiometry, monitored by the ratio of AES peak-to-peak intensities for Al (68 eV) and Fe (47 eV), $r_{\text{AES}} = I_{\text{Al},68\,\text{eV}}/I_{\text{Fe},47\,\text{eV}}$, as a function of the annealing temperature. Each surface was initially sputtered using 2 keV Ar$^+$ ions, and then step-wise annealed for constant time intervals $\Delta t = 2$ min, with increasing $T_{\text{anneal}}$ for each step. Between successive steps, the sample was quenched to $T \approx 100$ K, and $r_{\text{AES}}$ was determined. Above $T \approx 1200$ K, significant amounts of Al begin to evaporate from the surface [Gra95b], and measurements were stopped there to avoid permanent compositional changes of the samples.
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Figure 2.8: Development of the AES peak-to-peak ratio $r_{\text{AES}} = I_{\text{Al,68 eV}} / I_{\text{Fe,47 eV}}$ with increasing annealing temperature ($\Delta t = 2 \text{ min annealing time for each step}$) after initial Ar$^+$ ion sputtering. Also indicated are the characteristic LEED patterns which develop in certain $r_{\text{AES}}$ ranges.

In Fig. 2.8, the sputter-induced depletion level is similar for $x = 0.03$, 0.15, and 0.30. All three show a relatively well-defined “transition range” of annealing temperatures in which $r_{\text{AES}}$ rises strongly, ending in a plateau of approximately constant $r_{\text{AES}}$ at high $T_{\text{anneal}}$. Only the $x = 0.47$ sample deviates slightly from this trend. Here, the onset of the transition regime seems to lie below the lowest experimental temperature, 400 K, i.e. the initial depletion level was not observed at all. The transition range extends up to the point where, again, a high-temperature plateau is reached. It must be stressed that these experiments do not monitor equilibrium segregation. For the latter task, $r_{\text{AES}}$ would have to be measured at $T_{\text{anneal}}$ itself instead of at 100 K, because quenching is usually not fast enough to freeze out the exact high-$T$ surface composition [Son86b, Son86c]. Here, we are not dealing with true equilibrium features. The average near-surface Al-concentration increases irreversibly between subsequent annealing steps, and the constant level of $r_{\text{AES}}$, reached above a certain annealing temperature, indicates only that compositional equilibrium with the bulk is largely re-established, but the actual equilibrium segregation at these temperatures might still differ from our quenched samples. We will come back to this point below.

Interestingly, the LEED patterns associated with the transition regimes of Fig. 2.8 indicate an already remarkably well-developed near-surface order, despite the fact that all samples’ near-surface concentrations still change drastically with increasing $T_{\text{anneal}}$. Each sample shows a series of different LEED patterns (distinguished by their $I(E)$ spectra), denoted $(1 \times 1)^I$, $c(2 \times 2)^I$, $(1 \times 1)^{II}$, $c(2 \times 2)^{II}$, and $(1 \times 1)^{III}$ in Fig. 2.8. It is particularly noteworthy that

- the same superstructure corresponds to the same approximate $r_{\text{AES}}$ for different samples,
although quite different annealing temperatures may be required to bring it about,

- the same superstructures on different samples are of the same structural origin, according to their $I(E)$ spectra,

- the superstructures occur in the same sequence for each sample, but the higher the bulk composition, the more structures are run through,

- each superstructure is associated with the high-temperature plateau of a certain sample, with the exception of $(1\times1)_1$, whose $I(E)$ spectra are similar to those of clean Fe(100).

Moreover, the intermediate c($2\times2$)$^{\text{II}}$ phase of the $x = 0.47$ sample was already investigated by quantitative LEED. Within the accessible “information depth” (strictly, $\gtrsim 6$ layers), its structure corresponds to a bulk Fe$_3$Al crystal with a segregated layer of Al on top [Ktk96]. In fact, this is also the termination observed for a true bulk D$_0_3$ Fe$_{0.70}$Al$_{0.30}$(100) sample in Sect. 4.4.2.

Figure 2.9: Left: The length scales and processes which govern the equilibration of preferentially sputtered Fe$_{1-x}$Al$_x$(100) surfaces.

So far, the observations suggest a refined scenario of the equilibration process of Fe-Al surfaces, illustrated in Fig. 2.9. Initial preferential sputtering subdivides the system into an Al-depleted near-surface region (including the very surface – the selvedge), and the remaining crystal (bulk). Only the former region is “seen” by low-energy electron probes such as AES or LEED, since its thickness, certainly greater than 1 nm, exceeds their information depth. The subsequent equilibration is a twofold process: First, the formation of local order within the near-surface region itself (at its momentary stoichiometry), and second, its compositional equilibration with the faraway bulk. Local ordering is a fast process, and occurs already at low annealing temperatures, where individual atoms become mobile on our experimental time scale. In particular, this local ordering also includes the segregation of Al to the selvedge, and a possible multilayer segregation. In contrast, long-range equilibration is relatively slow as it requires a net mass transport over relatively large distances. For each annealing step, this is the throttle which determines the average Al concentration $x^{\text{av}}$ reached in the near-surface region on our experimental time scale. The local order assumed within the near-surface region and the segregation profile at the selvedge correspond to the true equilibrium state of a bulk crystal of composition $x^{\text{av}}$ and $T_{\text{anneal}}$.

Compared to its state at $T_{\text{anneal}}$, the surface seen by a low-temperature measurement is once more modified. During quenching, the near-surface composition $x^{\text{av}}$ itself should no longer change. However, short-range diffusion processes will initially stay active, adjusting the surface’s structure to thermal equilibrium as $T$ decreases, until they finally freeze out at some lower temperature $T_{\text{eq}}$. Of course, $T_{\text{eq}}$ can not be defined exactly, since quenching is really a non-equilibrium process, and different diffusion mechanisms will freeze at slightly different temperatures. Yet, it should be emphasised that $T_{\text{eq}}$ is qualitatively different from both $T_{\text{anneal}}$ or $T_{\text{meas}}$ in general.
We can now proceed to define the significance of the onset and the end temperatures of the transition ranges in Fig. 2.8, $T_o$ and $T_e$, more clearly. For this, we must remember that $T_{AES}$ does not directly reflect the average near-surface composition, but rather the layerwise concentration profile associated with $x^{av}$. So, $T_o$ denotes the point where Al first starts to segregate to the selvedge, even if $x^{av}$ still remained unchanged. In a broader sense, $T_o$ marks the onset of near-surface atomic mobility in a system with a segregation trend, and not necessarily the onset of mass transport from the bulk. In contrast, $T_e$ indicates the point where the selvedge segregation profile stabilises as a function of $x^{av}$. In this sense, the composition profiles associated with the high-temperature plateaus in Fig. 2.8 must be characteristic of full compositional equilibrium with the underlying bulk. Vice versa, the beginning of these plateaus would be delayed to higher $T_e$ if the segregation profile was extremely sensitive to $x^{av}$ for some reason. Of course, exact values of $T_o$ and $T_e$ are hard to extract from Fig. 2.8, but an interesting qualitative trend arises. Roughly, $T_o$ decreases continuously with increasing $x$; $T_e$ shows the same tendency for $x = 0.03$, 0.15, and 0.30, but then appears to rise again as $x = 0.47$. In fact, bulk diffusion shares the same behaviour [Lar75, Ven90, Hel99]. So, it seems reasonable to assume that bulk-like diffusion processes control the long-range Al transport necessary for compositional equilibration. Inverting this statement, the behaviour of $T_o$ suggests that near-surface atomic diffusion reflects additional influences, such as near-surface defects, and enhanced near-surface mobility. In particular, these might then also be relevant during quenching.

In total, we now understand that any structural findings at low $T$ (i.e., all results presented in this work) contain contributions from three different regimes of local equilibrium. As visualised in Fig. 2.10,

1. the overall composition of the near-surface region, $x^{av}$, is controlled by $T_{anneal}$, and is the product of long-range, bulk-like diffusion processes. The higher $T_{anneal}$, the smaller is the remaining Al depletion (if any) from the initial, preferential sputtering treatment.

2. the local order of the near-surface region (which is the region “seen” by LEED, AES, etc.) and the segregation profile near the selvedge are those which would be found for a fully equilibrated bulk crystal of composition $x^{av}$ at $T_{eq}$.

3. effects related to the local environment of each lattice site are not expected to be kinetically limited at all. So, any geometric relaxations, thermal vibrations etc. should indeed correspond to thermal equilibrium at $T_{meas}$, but for the atomic arrangement which was frozen at $T_{eq}$.

Although this scenario was derived for Fe$_{1-x}$Al$_x$ surfaces, the underlying mechanisms are quite general, and may well apply to other alloy surfaces, too. E.g., metastable superstructures during step-wise annealing have been found for sputtered Pt$_3$Sn(111) [Atr93], NiAl(100) [Mul88, Blm96], TiAl(010) [Wan95], or B2 AlPdMn(110) [Hei99]. Their origin was mostly attributed to the top layer
only, but might really be due to the local equilibration of the whole, compositionally modified near-surface region. Apparently, this model holds even if the entire underlying lattice must be destroyed to reach the state equivalent to the momentary near-surface composition: As mentioned in Sect. 2.3, sputter-depleted QC surfaces are commonly reported to form thin films of B2-ordered material with well-defined surface orientations. The original QC lattice is reclaimed only as subsequent annealing to higher $T$ restores the overall surface composition [She98, Zur98].

We shall use the preceding concepts to link our findings for Fe$_{1-x}$Al$_x$(100), CoAl(100), and CoAl(111) to equilibrium thermodynamics in Chapter 6.

2.5 Summary

With the present chapter at hand, the necessary physical foundations for the structural investigations of Fe$_{1-x}$Al$_x$(100), CoAl(100), and CoAl(111) should be established. Both bcc based Fe-Al and Co-Al alloys belong to the class of strongly ordering materials, with the certain activity of NN and 2NN interactions in Fe-Al, and probably similar but stronger ordering forces in Co-Al. From the general properties of TM-Al alloy surfaces, one might expect simple Al terminations for Fe-Al and Co-Al (100) and (111). After all, this element is preferentially located at the surface of most other TM aluminides, and no direct contradiction to bulk-like ordering arises. On the other hand, similar arguments could have applied to NiAl(100) and NiAl(111), but their termination is as yet controversial, and certainly depends on details of their preparation. For our work, the example of Fe$_{1-x}$Al$_x$(100) can serve as a showpiece which clarifies many preparation-related aspects of aluminides. In fact, we shall draw on the resulting model often in the following chapters.

Nevertheless, we still lack one important prerequisite before tackling the physics of Fe-Al and Co-Al surfaces itself. We must yet define the principal method used in this work, the quantitative analysis of low-energy electron diffraction data. The next chapter addresses this issue.
Chapter 3

Surface crystallography by LEED

A clear description of the method of investigation is an obvious necessity in any scientific work. Here, this method is quantitative low-energy electron diffraction (LEED). Essentially, LEED has been the principal method to extract detailed structural information from crystalline surfaces for the past thirty years. The present chapter introduces its essentials, and how it can be used to provide crystallographic information. Further details should be sought in several excellent, introductory review articles [Hov93, Hnz95, Hnz98] and books [Pen74, Hov86].

Below, we will first outline the phenomenology of LEED and its experimental side, placing particular emphasis on the extraction of high-quality intensity data. The following section then introduces the corresponding theory in greater detail. Since actual structural information is extracted by comparing experimental and calculated diffraction intensities, a separate section deals with data fitting in LEED. The final section describes the practical method of structure analysis used in this work. Here, the Tensor LEED approximation [Rou86, Rou89, Rou92] plays a central role, allowing the fast calculation of the $I(E)$ spectra of model surfaces within a whole portion of the parameter space, and a partial automation of the optimisation procedure.

3.1 A LEED experiment

By definition, low-energy electron diffraction comprises all phenomena associated with elastically and coherently scattered electrons between $20 \lesssim E \lesssim 600$ eV.\footnote{Similar experiments with $E \lesssim 20$ eV belong to very low energy electron diffraction (VLEED), while medium energy electron diffraction (MEED) begins somewhere above 600 eV.} For surface structural studies, the advantage of electrons in this energy range is their low inelastic mean free path length in matter, generally below 10 Å. Typically, the structural changes which distinguish a surface from the bulk are localised within this range, i.e. the LEED signal is sensitive to exactly what we are looking for. Additionally, the electron wave length is of the order of the lattice parameter at these energies. The resulting diffraction angles are rather large, facilitating the measurement of LEED intensities.

Fig. 3.1 shows the schematic setup of a LEED experiment. A collimated beam of monoenergetic
electrons is directed at the surface of a sample, the elastically backscattered ones are singled out and then collected by a detector. Typically, the latter is a luminescent screen, allowing for a simultaneous, two-dimensional overview of the LEED pattern. Already this simple design imposes an important restriction. Due to the strong interaction of low-energy electrons with matter, the space between the electron gun, sample, and detector must be evacuated. However, this is necessary for most problems of surface science anyways: In order to maintain a well-defined, contamination-free surface over reasonable measurement times (≈ 30 min), any adsorption from the residual gas surrounding the sample must be negligible. To fulfill this condition safely, pressures of only $p < 10^{-10} \text{ mbar}$ (ultra-high vacuum, UHV) are required. For TM-Al alloy surfaces, this is particularly critical: Metallic Al is extremely reactive, accumulating any available oxygen to ultimately form a film of $\text{Al}_2\text{O}_3$, and thereby destroying the surface stoichiometry and order properties of interest.

For a well-oriented crystalline surface, the LEED pattern consists mainly of a regular array of diffraction spots, corresponding to electron beams reflected by the surface. This spot pattern results directly from elementary symmetry considerations: Any translational symmetry of a system automatically leads to the conservation of momentum in that direction. Here, this translational symmetry (the periodicity of the crystalline surface) is discrete, i.e. the conservation of the lateral momentum component $k_\parallel$ is also discrete, as prescribed by Bloch’s theorem [Ash76]. For an incident wave with $k_\parallel$, the outgoing wave’s momentum $k_{\text{out}}$ obeys

$$k_{\text{out},\parallel} - k_\parallel = g$$

with $g$ the lateral component of a reciprocal lattice vector of the surface.\footnote{Strictly speaking, $g$ should be a two-dimensional vector which belongs to the “dual space” of the surface point lattice (which is also two-dimensional).} We shall write $k_g^-$ for $k_{\text{out}}$ in the following (i.e., an outgoing beam travels in the negative $z$ direction by definition). While the
3.1. A LEED experiment

![Diagram of a surface with a quadratic unit cell and a c(2×2) superstructure in real space (left), and the corresponding schematic LEED pattern, including the indexing of LEED spots (right). Spots which originate only from the superstructure are drawn smaller.](image)

The observed diffraction pattern is directly determined by the surface’s lateral unit mesh in real space, energy conservation fixes the perpendicular momentum component of each beam:

\[ k_{g,\|}^2 + k_{g,\perp}^2 = \frac{2mE}{\hbar^2}, \]  

(3.2)

In contrast to 3D diffraction, no further criterion restricts \( k_{g,\perp} \), i.e. a LEED spot can exist at any energy above a certain threshold, \( E \geq \frac{\hbar^2}{2m}(k_{\|} + g)^2 \). Of course, a surface’s 2D unit mesh need not be the same as that derived directly from the truncated bulk. A reconstructed surface has a larger unit cell than prescribed by the bulk itself. Nevertheless, LEED spots are indexed in units of the bulk-truncated surface’s reciprocal lattice by convention, leading to the nomenclature defined in Fig. 3.2 for a quadratic surface with a c(2×2) superstructure\(^3\) (which we will encounter for Fe\(_{1-x}\)Al\(_x\)(100) below).

In order to obtain quantitative structural information by LEED, the diffraction pattern produced by a surface must somehow be inverted. In practice, this task consists of two parts. First, the geometry of the unit mesh may normally be inferred directly from a given spacial diffraction pattern. Second, the distribution of atoms within the unit mesh determines the intensity distribution, \( I_g(E) \), of the diffraction pattern, which naturally depends on the electron energy \( E \). Unfortunately, “direct” crystallographic methods of inversion as used, e.g., in XRD, usually rely on some phase information hidden in the diffracted wave, and must therefore assume some kind of quasi-kinematic scattering (see, e.g., Refs. [Mar98, Shn01]). For LEED, this means a severe restriction: Since the interaction of electrons with matter is strong, the diffracted intensities may contain dominant multiple scattering contributions. So, the precise evaluation of LEED intensities requires a full multiple scattering theory. Crystallographic information is then usually obtained in an indirect approach, i.e. by comparing diffracted intensities calculated for a given structural model with a set of measured ones.

Since a surface’s structural information is hidden in the intensities \( I_g(E) \), their precise measurement is the crucial experimental prerequisite of quantitative LEED. The provision of high-quality LEED data for a computational analysis is a complex field of its own. Since this task was not part of the

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\(^3\)Wood’s notation [Woo64, Hov86]
present work, the necessary data refinement steps are here treated in a rather superficial manner, aiming only for some basic understanding, and highlighting some issues relevant in the present work. Assuming the availability of a well-defined sample surface, a state-of-the-art LEED measurement must still pay attention to several demands:

- **Short measurement times.**
  To avoid changes of the surface’s chemical state by residual gas adsorption during the LEED experiment, it should be kept as short as possible. The fastest means today is the parallel measurement of the entire LEED pattern, either by a video image of the luminescent screen [Hnz98], or by a channel plate detector [Ogl92]. The former approach was chosen here. The latest video based systems stream their data directly to the hard drive of a standard PC, thus achieving the fastest possible throughput. Since such systems were not yet available when the present work was begun, the established, commercial AUTOLEED system [Hnz88, Gem90] was used instead. The $I_g(E)$ data for CoAl(100) and (111) were obtained by recording the entire LEED pattern on video tape for each energy step, integrating individual spot intensities off-line. In contrast, $I_g(E)$ spectra for Fe$_{1-x}$Al$_x$(100) were directly measured for each beam, with the total measurement time still below 30 min. Test measurements before and after data set collection ensured that the adsorption of particles during measurement remained negligible at residual gas pressures $p \leq 10^{-10}$ mbar.

- **Elimination of background intensities.**
  The diffraction spots $g$ always ride on some instrumental background intensity, increased by that from thermal diffuse scattering and surface defects. As this background may depend on $E$ in subtle ways, it must be removed carefully. Fortunately, the AUTOLEED system performs a reliable, automated background subtraction, using the border of the measurement window to be integrated over.

- **High S/N ratio.**
  There are several ways to improve the overall signal-to-noise ratio $S/N$ of $I_g(E)$. As usual, their relative statistical error decreases with increasing intensity and measurement time. Since important diffraction information is often carried by intensity minima or weak superstructure spots, low-intensity regions can not simply be neglected. Rather, a good $S/N$ ratio must be achieved there, too. So, one must attempt a trade-off by increasing the measurement time per energy step (“averaging”). Also, one may exploit data correlations in the measured $I_g(E)$. Within a single beam, $I_g$ varies smoothly with $E$, and typical feature widths around 10 eV are dictated by inelastic damping [Hov86]. Any higher-frequency variations must be noise, which may be removed by numerically smoothing $I_g(E)$. In the present case, this was done by repeatedly applying a standard three-point smoothing formula to the data (measured with an energy step width of 0.5 eV). For symmetrical incidence of the primary beam, certain diffraction spots become equivalent. Then, $I_g(E)$ can be averaged for groups of symmetry-equivalent beams, enhancing $S/N$ further. In fact, all $I_g(E)$ used below were measured at normal incidence to maximise this benefit.\(^4\) Finally, it should be noted that significant $S/N$
improvements can be achieved with high-sensitivity detection equipment, i.e. the camera in video-based systems. The introduction of 12- or even 16-bit grayscale resolution reduces even lowest-intensity noise remarkably by multiple-measurement averaging. Unfortunately, such equipment was unavailable when the data below were measured, and a standard 8-bit camera was used.

- **Consistent normalisation of $I_g(E)$**.
  Any comparison of measured LEED intensity data with calculated ones requires their consistent normalisation across the entire energy range. So, $I_g(E)$ must be corrected for both variations of the incident electron current and, strictly, for the curvature of the luminescent screen (the “cosine correction”).

Obviously, modern LEED measurements warrant some perfectionism before passing $I_g(E)$ data to a “theoretician” for structural evaluation. A typical example of the available data quality in this work is given in Fig. 3.3, showing $I_g(E)$ of a Fe$_{0.85}$Al$_{0.15}$(100) sample’s (1,0) LEED spot (see also Sect. 4.3). Fig. 3.3a shows the raw intensities of three symmetry-equivalent diffraction spots (the
fourth was hidden by the electron gun) without any corrections. Obviously, all three agree very well overall, but still contain some noise in low-intensity regions. Fig. 3.3b contains the processed $I_g(E)$ spectrum used in the analysis (full line). Obviously, a considerable reduction of noise was achieved inbetween. Its reproducibility is demonstrated by the second spectrum in Fig. 3.3b, a remeasurement for control purposes separated from the original by several days (broken line). Both agree remarkably well, showing that statistical errors in the final data are small (at least for high-intensity beams). Of course, this says nothing about possible systematic errors. In particular, this concerns the relative intensities of peaks. The three raw curves still show some disagreement in the low-energy region, and the responsible instrumental properties should also be present in a remeasurement. To avoid biasing structural results by such effects, the “standard” data fitting criterion in LEED, Pendry’s R-factor (Sect. 3.3.2), places its primary emphasis on feature positions, and less on relative intensities.

Of course, any real surface contains deviations from perfect translational symmetry, which strictly break the applicability of Bloch’s theorem, assumed above. In general, the effect of such deviations will not be measurable as long as the periodic areas in the surface are of the order of the apparatus’ transfer width $w_0$, a measure of the lateral coherence within the LEED beam. Unless specific precautions are taken, $w_0 \approx 100-200$ Å goes as a common rule of thumb. So, if two entirely different structural domains A and B with individual patches $\gtrsim w_0$ coexisted within the same surface, no coherence of amplitudes diffracted from each exists. In that case, LEED spot intensities simply add up according to their respective area fractions $s$ and $(1 - s)$:

$$I_g(E) = s \cdot I_{A,g} + (1 - s) \cdot I_{B,g}. \quad (3.3)$$

The ordered LEED pattern is retained unless the connected areas of each domain are much smaller than $w_0$.

In contrast, surface defects on a much smaller length scale (impurities, steps, islands, etc., but also thermally induced atomic vibrations at elevated temperature) lead to measurable modifications of LEED spot shapes, or even to diffuse intensity — electrons diffracted away from the LEED spots $k_g$ altogether. Indeed, a whole branch of LEED is concerned with the study of surface defect properties by means of spot profile analysis LEED (SPA-LEED) [Hen94, Hen97]. Diffuse intensities have also been used successfully to investigate properties of disordered adsorption, e.g. at low coverage, in diffuse LEED (DLEED) [HNz95, Sta96]. For binary alloys, diffuse intensity has a special significance. Strictly, any possible random substitutional disorder in the surface breaks its 2D translational symmetry, and one might naively expect its (ordered) LEED pattern to vanish entirely. In fact, this is not the case – as long as the underlying geometrical lattice remains periodic, even fully random alloys produce sharp diffraction patterns. Nevertheless, chemical disorder allows to scatter some of the overall intensity away from the diffraction spots. This diffuse background is generally inhomogeneous, and reflects the SRO among the randomly distributed atoms. In bulk diffraction, kinematic theories [Kri69, Fen87] are used to determine SRO properties of binary alloys even quantitatively from diffuse intensities (e.g. the pair interaction parameters of Table 2.1). Unfortunately, no similar description exists for LEED as yet, and we will use diffuse intensities only as a qualitative indicator of SRO within the surface. The following discussion of the theory of LEED will focus on diffraction spot intensities only.
3.2 Computing model LEED intensities

For all practical purposes, LEED is a typical scattering problem, and we shall treat it as such throughout this work. However, before outlining the foundations of the particular scattering theory behind LEED intensity calculations, we shall take a step back for an even more basic perspective.

Any quantum-mechanical problem may be formulated by Schrödinger’s equation, and so also in the present case:

\[(T + V)|\Psi\rangle = E|\Psi\rangle \quad (3.4)\]

As usual, \(T\) here denotes the kinetic energy operator, \(V\) a potential operator, and we have chosen the time-independent approach, focusing on eigenstates \(|\Psi\rangle\) of energy \(E\). However, we are here dealing with a solid surface, which consist of many nuclei and electrons, onto which a continuous flux of electrons impinges. Thus, Eq. (3.4) really describes a many-particle problem, with \(E\) the total energy of the entire system, and \(V\) due to both electron-nucleus and electron-electron interaction. \(|\Psi\rangle\) is a many-particle wave function \([Mah90]\) which accounts for the correlated motion of the incident electrons and those in the solid. Moreover, we are not simply interested in the system’s ground state, but in a specific excited state which contains electrons far above the solid’s Fermi level. Since an excited state must decay with time, we must also account for the consequences of this possibility in our time-independent approach — i.e., we must have a way for inelastic scattering to occur. Of course, the many-particle formulation is impractical, and we shall henceforth choose to deal with a suitable, effective single-particle approach instead. Yet, some aspects of the latter picture are much easier understood by remembering that we are really confronted with an excited-state many-particle problem.

In a narrower sense, the LEED problem can be reduced to a single-particle Schrödinger equation

\[(H_0 + V_s)|\Phi^+(k_{||})\rangle = E|\Phi^+(k_{||})\rangle \quad (3.5)\]

Here, \(H_0\) denotes a free electron’s Hamilton operator, and \(V_s\) is the effective single-particle potential for the LEED state \(|\Phi^+(k_{||})\rangle\). \(V_s\) includes the electrostatic interaction between LEED electrons and the surface nuclei and electrons, accounts for correlations of their motion, and for possible inelastic effects. \(|\Phi^+(k_{||})\rangle\) is defined by the boundary condition of an incident wave \(|\epsilon(k_{||})\rangle\) of lateral momentum \(k_{||}\), and our foremost interest is to determine those parts of \(|\Phi^+(k_{||})\rangle\) which are reflected by the surface. In the following, we will first define the conventional approximation to formulate \(V_s\) for LEED, the muffin-tin model, and then turn to the multiple-scattering formalism (full dynamical LEED) which allows to calculate actual \(I_g(E)\) spectra reliably. The description includes the effects of thermal and chemical disorder, and an outline of LEED computations in practice. This theory is well-established, and more complete accounts should be sought elsewhere \([Pen74, Hov86, Hnz95]\).

\(^5\)Actually, this should even be Dirac’s equation. Relativistic effects have some influence in LEED for heavy atomic nuclei \([Jen75, Fed78, Fed84, Mat95]\), and are partially included in the calculations below.

\(^6\)The notation adopted here is that used by Rous and Pendry \([Rou89]\) in their formal derivation of the Tensor LEED approximation (see also Sect. 3.4). Of course, \(|\epsilon(k_{||})\rangle\) is strictly defined through both the electron energy \(E\) and the lateral momentum \(k_{||}\).
3.2.1 The muffin-tin approximation

As mentioned, we must first design a local single-particle potential $V_s(r)$ which allows to efficiently calculate LEED intensities reflected from a solid surface. In this task, many helpful simplifications can be made because of the large energy difference between the incident electrons and those of the solid, typically above 30 eV. However, these approximations must break down at low $E$. In practice, this occurs in the VLEED range and below, whereas the present work should only be affected by slight deviations between calculated and measured $I(E)$ spectra at the lowest energies used, if at all.

For convenience, let the solid fill one half of the coordinate system. $V_s$ is relatively simple on the vacuum side. Far away from the surface, and assuming no interaction among incident or reflected electrons themselves, we have a true single-particle problem – no correlation with other electrons, no channel for inelastic losses. Hence, $V_s$ is constant and may conveniently be set to zero. Life becomes more complicated as we approach the solid: Already outside, a LEED electron “feels” the surface electrons, the motion of which leads to an image potential-like shape of $V_s$. Within the solid surface, we must account for the electrostatic interaction with all nuclei and other electrons, for their correlated motion, and for inelastic losses. Of course, the electrostatic potential dominates, but the two latter terms still have important implications: In principle, correlation is a non-local, energy-dependent phenomenon. Well-founded local approximations exist [Hed71], but the overall potential $V_s$ will still depend on $E$ in principle. And, the equivalent to an excited state’s decay in time-dependent quantum mechanics is an imaginary component of its single-particle energy in the stationary picture of Eq. (3.4). So, any model potential for $V_s$ should be both energy-dependent and complex within the solid.

The established approximation to $V_s$ in LEED is the muffin-tin (MT) approximation [Pen74],

$$V_s(r) \approx V_{\text{MT}}(r) := \begin{cases} V_0r + iV_{0i} + \sum_i v^i(|r - R^i|) & z \geq 0 \\ 0 & z < 0 \end{cases} \tag{3.6}$$

Here, individual “atoms” $i$ of the solid are modelled by localised potentials $v^i(r)$, each restricted to a sphere of radius $r_{\text{MT}}$ (the muffin-tin radius), and zero outside. They are assumed to be spherically symmetric, centred about an atomic position $R^i$. $V_{\text{MT}}$ is constant between individual atoms, allowing to expand $|\Phi^+(k_{\parallel})\rangle$ in a free-electron basis referenced to $V_0r$ (the muffin-tin constant) there. Obviously, Eq. (3.6) takes no heed of the shape of the potential barrier, assuming a sharp step towards the vacuum instead. As mentioned above, inelastic damping leads to an imaginary part of the electron energy, within the solid, $V_{0i}$. Together, $V_0r + iV_{0i}$ are also referred to as the inner or optical potential.

For a practical LEED calculation, we must devise a “complete” form of $V_s(r)$, and then dissect it into the components $v^i$, $V_0r$, and $V_{0i}$ of the MT approximation for each $E$. To do this correctly, we

\footnote{This property is best visualised by considering a stationary plane wave of momentum $k$. If $E$ is complex, its momentum $k$ also acquires an imaginary component, which automatically makes $\exp(ikr)$ decay along that component.}
must identify those components which crucially influence the LEED state $|\Phi^+(k_\parallel)|$. It is important to realize that $V_s$ is actually positive, strongest near the atomic nuclei, and sharpened by the screening charge of the surrounding electrons. So, the most influential part of the scattering potential is the region occupied by atomic core electrons for almost all solids, and must be represented accurately. Fortunately, this region is also largely unaffected by the crystal, i.e. retains the local spherical symmetry assumed in the construction of $V_{MT}$. In contrast, $V_s$ is weakest in the region occupied by the valence electrons. Hence, assuming a spatially constant interstitial potential $V_0r$ and local spherical symmetry of $v^i$ in this region do not matter much to $|\Phi^+(k_\parallel)|$, although both approximations defy the chemical bond of a solid entirely. In fact, the solid’s charge density is normally even modelled by superimposing the charge densities of free atoms, calculated in the relativistic Hartree-Fock approximation (described e.g. in Ref. [Fis77]). This procedure performs well for the core electrons, i.e. the part of $v^i$ which dominates scattering, and avoids the computational effort of determining either the surface single-particle states of the overall excited state, or at least their ground state in full. Likewise, for LEED energies, the error due a step-like potential barrier to the vacuum is small since $V_s$ is weak in this range. It can be further reduced by assuming ideal transmission in the later multiple-scattering treatment.

A more subtle point concerns the energy dependence of $V_s$. As mentioned, it is due to correlations in the motion of surface and LEED electrons, and can e.g. be treated in the excited-state local-density approximation of Hedin and Lundquist [Hed71]. However, many LEED analyses neglect this $E$ dependence entirely. This is probably reasonable for $V_0r$, which is often approximately constant for $E \gtrsim 50$ eV [Run99, Run99b], and $v^i$, which is typically much larger than the change due to different $E$. However, it is not entirely negligible in $V_0r$, which acts as an offset to $E$ within the solid. A shown recently [Wal00], if $V_0r$ has a term which is linear in $E$, its neglect is approximately equivalent to rescaling space in its entirety. At least, when attempting to determine a crystal’s 3D lattice parameter $a$ in a LEED analysis, this must induce a systematic error. In practice, the effect is small, but relevant in high-precision structure analyses. For instance, $a$ appears contracted by 2 % for Cu(100) when assuming $V_0r(E) = \text{const.}$, while it results correctly with $V_0r(E)$ handled properly. Of course, for systems such as Cu, $a$ is well known from bulk studies at any temperature, and could safely be treated as a fixed quantity. However, $a$ is often not precisely known in more complex systems, e.g. epitaxial films. For binary alloys, literature values for $a$ may exist, but not necessarily at the temperature of the LEED measurement. Then, it is desirable to determine $a$ by LEED itself, and $V_0r(E)$ must be correctly treated at least to first order in $E$.

In total, the MT approximation is a well-tested and versatile means to account for the effective scattering potential in LEED. Nevertheless, with growing refinement and complexity of structures solved, it may sometimes become necessary to go back and correct yet another small effect. Hence, this foundation of LEED theory should be kept in mind when interpreting the structural results obtained.

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8In principle, asphericities of $v^i$ could also be taken into account within the MT model. However, even for a covalent system such as Si(100), an estimate shows their impact to be quite weak [Rub95].

9According to unpublished work of Rundgren [Run01b], the difference between a correct image potential barrier and an ideally transmitting step barrier is fully negligible in practical LEED calculations.
3.2.2 The formalism of multiple scattering

Having set up a suitable single-particle scattering potential for LEED, it remains to calculate the elastically reflected electron flux from the surface. Defining the crystal potential \( V_c(r) := \sum_i v_i(|r-R_i|) \) and \( \tilde{E} := E - V_0 - iV_0 \), we must actually solve

\[
(H_0 + V_c)|\Phi^+(k_\parallel)| = \tilde{E}|\Phi^+(k_\parallel)|
\]

within the crystal, instead of Eq. (3.5) above. This can be done by a scattering path formalism, propagating the incident electrons back and forth between the surface’s atoms, before they eventually leave the crystal again. The following two paragraphs connect the original Schrödinger equation to this intuitive picture of multiple scattering, with Eq. (3.15) as a central result. Since this derivation is quite technical in nature, it is only sketched here. Completely rigorous treatments can be found in the literature; on Green functions in potential scattering, e.g. in Ref. \[Mah90\], on dynamical LEED in the language of the Green function formalism in Ref. \[Hov86\], and on all details of multiple scattering in LEED in a very practical way in Ref. \[Pen74\].

Knowing the incident state \( |\epsilon(k_\parallel)\rangle \), we can invert Schrödinger’s equation (3.7) to its integral form using Green functions. Here, any reflection at the potential barrier is neglected, so that we can conveniently perform all calculations within the crystal only. In the regions of constant potential inside the crystal, the free-space Green function \( G^+_0 := (\tilde{E} - H_0)^{-1} \) transforms the incident wave \( |\epsilon(k_\parallel)\rangle \) to a simple plane wave,

\[
G^+_0|\epsilon(k_\parallel)\rangle = |\tilde{k}_0^+\rangle.
\]

Here,

\[
\tilde{k}_0^+ = \left( k_\parallel, \sqrt{\frac{2m}{\hbar^2} \tilde{E} - k_\parallel^2} \right)
\]

denotes the momentum of the incident wave when referred to the muffin-tin constant inside the crystal.

Similarly, Eq. (3.7) can be written by means of its own Green function \( G^+ \), which by definition includes the full action of \( V_c \),

\[
|\Phi^+(k_\parallel)\rangle = G^+|\epsilon(k_\parallel)\rangle .
\]

Fortunately, \( G^+ \) can be expressed by means of \( V_c \) and \( G^+_0 \) by rearranging Eq. (3.7):

\[
V_c|\Phi^+(k_\parallel)\rangle = (\tilde{E} - H_0)|\Phi^+(k_\parallel)\rangle .
\]

Since \( G^+_0 = (\tilde{E} - H_0)^{-1} \), adding the homogeneous solution \( G^+_0|\epsilon(k_\parallel)\rangle \) to \( |\Phi^+(k_\parallel)\rangle \) on the right hand side and inverting by means of \( G^+_0 \) yields

\[
|\Phi^+(k_\parallel)\rangle = G^+_0|\epsilon(k_\parallel)\rangle + G^+_0V_c|\Phi^+(k_\parallel)\rangle.
\]

This result can be iterated, so that, by comparison with Eq. (3.10), we obtain Born’s series for \( G^+ \),

\[
G^+ = G^+_0 + G^+_0V_cG^+_0 + G^+_0V_cG^+_0V_cG^+_0 + \ldots .
\]
3.2. Computing model LEED intensities

It remains to insert the definition of $V_c$ into Eq. (3.13), turning it into products of multiple sums. Their factorisation is simplified by grouping successive scattering events at the same atom $i$ to the \textit{atomic t-matrix},

\begin{equation}
  t^i = v^i + v^i G^+_0 v^i + \ldots
\end{equation}

$t^i$ summarises the effective scattering properties of atom $i$ completely. By this trick, Eq. (3.13) becomes a simple series of individual scattering events at different crystal atoms $i$, each connected by $G^+_0$ (Fig. 3.4):

\begin{equation}
  G^+ = G^+_0 + \sum_i G^+_0 t^i G^+_0 + \sum_{i,j \neq i} G^+_0 t^i G^+_0 t^j G^+_0 + \ldots
\end{equation}

In principle, Eq. (3.15) contains all which is necessary to solve the LEED problem for a given surface: The remaining work is simply to find practical expressions for the quantities involved.

3.2.3 Positional and chemical disorder in LEED

The preceding sections settle the basic theory of LEED for surfaces of 2D translational symmetry. While this is a convenient approximation, it was already mentioned in Sect. 3.1 that no real surface is \textit{exactly} periodic. Apart from the usual defects (vacancies, steps, ...), this also affects the “ideal” surface areas in two ways. First, any solid is subject to some thermally induced, dynamic positional disorder through the vibrations of atoms around their ground-state positions. Second, and particularly relevant for binary alloys, different elements may be randomly distributed on the sites of an otherwise perfectly periodic crystal lattice. Incidentally, this chemical disorder can then induce displacements of the atoms according to their local chemical environment, i.e. add some \textit{static} positional disorder to the thermal vibrations. Neither modification can be represented by a simple periodic potential as defined in Eq. (3.6), i.e. the rigorous basis leading to the LEED spot pattern no longer holds strictly. Nevertheless, well-defined diffraction spot patterns are usually observed from thermally and/or chemically disordered surfaces.

In fact, both phenomena may be approximated within the scattering path formalism of the previous section, by modifying the \textit{effective t-matrix} of the lattice site in question. The random occupation of (geometrically periodic) lattice sites by different elements A and B still leads to a regular array of deep potential wells, so that the coherence of scattering entirely is not destroyed entirely. Loosely speaking, it is now the averaged potential which scatters coherently. The difference to the true elemental potentials is non-periodic and contributes mainly to the diffuse background (see Sect. 3.1), and is much less relevant to $I_g(E)$. The most convenient way to express the coherent scattering contribution in LEED is the use of configurationally averaged $t$-matrices in Eq. (3.15). If a fraction $x^i$ of all equivalent sites $i$ is occupied by element A, and the remaining fraction $(1 - x^i)$ by B, the \textit{average t-matrix approximation} (ATA) [Gau85, Bau86] prescribes

\begin{equation}
  t^i_{av} = x^i \cdot t^i_A + (1 - x^i) \cdot t^i_B
\end{equation}
Chapter 3. Surface crystallography by LEED

It is even possible to extend this formalism to element-dependent atomic positions. However, this introduces an asphericity into $t_{nv}$, and will therefore only be exploited using the Tensor LEED approximation (Sect. 3.4) in this work. Of course, for two elements to be distinguishable, their $t$-matrices must be sufficiently different. For Fe and Al, Fig. 3.5 illustrates this difference in terms of their scattering factors $f^i$, an equivalent representation of the atomic $t$-matrix [Pen74]:

$$f^i(\cos \theta) = -\frac{2\pi}{k} \sum_l (2l + 1) t_{vl}^i P_l(\cos \theta)$$  \hspace{1cm} (3.17)

Here, $k$ denotes the electron wave number, $\theta$ the scattering angle with respect to the incident plane wave, and $P_l$ the Legendre polynomials. In the far-field approximation, the amplitude of a scattered plane wave with a scattering angle $\theta$ is proportional to $f^i$. In Fig. 3.5, Fe and Al indeed show different scattering characteristics for many energies and angles, most prominently at low $E$, and should be well distinguishable in LEED.

Thermal and static statistical atomic displacements $u^i$ are indistinguishable since thermal motion occurs on a much slower time scale than coherent electron scattering. So, an impinging electron really “sees” a frozen snapshot of a vibrating lattice. As long as the displacements $u^i$ are small, random positional disorder does not destroy the overall coherence of scattering. Yet, the diffracted amplitudes are reduced since contributions from equivalent lattice sites are no longer exactly in

Figure 3.5: Modulus and phase of the scattering factors of Al and Fe, shown as a function of the scattering angle for three different scattering energies.
3.2. Computing model LEED intensities

phase. Positional disorder is then accounted for by a temperature factor \( w^i \), i.e. [Wil75]

\[
\begin{align*}
\int_{\text{eff}}^i = w^i \cdot f^i.
\end{align*}
\]

(3.18)

For harmonic vibrations (i.e. if the probability distribution of \( u^i \) is Gaussian) which are moreover isotropic, \( w^i \) has the well-known form [Wil75]

\[
\begin{align*}
w^i = \exp\left(-\frac{1}{6}\left|\mathbf{q}\right|^2 (u^i)^2\right) \quad .
\end{align*}
\]

(3.19)

Here, \( \mathbf{q} \) denotes the 3D momentum transfer experienced by the scattered electron (determined by both \( E \) and \( \theta \)), and \( u^i = \sqrt{\langle(u^i)^2\rangle} \), the average 3D atomic displacement on site type \( i \). Obviously, \( w^i \) has no influence on forward scattering (\( \theta = 0 \), i.e. \( \mathbf{q} = 0 \)), and most strongly reduces any back-scattered amplitude (\( \theta = \pi \), i.e. \( \mathbf{q}^2 = 4k^2 \)).

Of course, both chemical and positional disorder will occur simultaneously in random binary alloys. Their combined influence is, again, best visualised in the scattering factor picture:

\[
\begin{align*}
f_{\text{av}}^i = x_i \cdot w^i_A \cdot f_A + (1 - x_i) \cdot w^i_B \cdot f_B \quad .
\end{align*}
\]

(3.20)

Again, a direct extension of this equation to element-dependent positions is possible within the Tensor LEED approximation (Sect. 3.4). The representation of positional and chemical disorder by Eq. (3.20) is exact in a kinematic (i.e., single-scattering) approximation [Fen87], as are Eqs. (3.16) and (3.18) themselves. It also holds for most multiple-scattering terms in Eq. (3.15), with the exception of closed scattering paths, which run through the same atom twice [Pen74, Cra91]. However, a comparative study of the ATA and the coherent potential approximation (CPA), which handles closed scattering paths more precisely [Cra91], shows this contribution to be entirely negligible in LEED.

Another issue concerns the influence of local correlations (phonons, SRO) on multiple scattering in Eq. (3.15). For instance, if an electron propagates from an Al atom to its NN site in a random Fe\(_{1-x}\)Al\(_x\) alloy, the probability to encounter another Al atom on that site is practically nil due to SRO, and not \( x \) as prescribed by the ATA.\(^{11}\) The quantitative consequences of this effect were never yet tested to the author’s knowledge. However, they must be small since the ATA has been used with much success in the determination of the surface stoichiometry of many different alloys for the past 15 years, and its precision is well-proven by comparing LEED results to those of other experimental methods [Spo98, Pla99, Pla99b].

Finally, it should be noted that a substitutional disorder on a lattice, as modelled by the ATA, and the occupation of the same basic lattice by coexisting, long-range ordered structural domains, as modelled by Eq. (3.3), should be clearly distinguishable by LEED in principle — even if the overall, layer-dependent near-surface stoichiometry is the same. As an example, consider the

\(^{10}\)\( w^i \) is sometimes loosely referred to as the Debye-Waller factor, but the exact meaning of this term varies between different authors [Wil75, But93]. Here, we shall follow the consistent nomenclature of Ref. [Wil75], denoting \( w^i \) as the “temperature factor” only.

\(^{11}\)In other words, multiple scattering should reflect the true pair correlation function of a binary alloy, rather than just its configurational average.
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Figure 3.6: Comparison of two structural models for CoAl(111) with the same averaged layerwise elemental concentrations, but different long-range order. (a) Mix of two bulk-like, B2-ordered structural domains, each covering half the total surface area. (b) Random occupation of the entire bcc(111) surface by 50% Al and 50% Co on each lattice site.

Figure 3.7: Calculated and measured $I_g(E)$ for the two structural models of CoAl(111) as given in Fig. 3.6, showing the (1,1) and (2,0) beams.
two hypothetical structural arrangements compared in Fig. 3.6: A CoAl(111) surface\[12\] consisting of equal fractions of both ordered, bulk-terminated B2 domains (a) has the same averaged layer concentrations and scattering path lengths as a fully random A2 Co\(0.5\)Al\(0.5\)(111) surface (b). If the long-range elemental order did not play a role, very similar \(I_g(E)\) spectra might be expected from both arrangements. Fortunately, as shown in Fig. 3.7 for the (1,1) and (2,0) beams, this is not the case: Pronounced differences arise both in peak heights and positions. The inequivalence of both cases in LEED can easily be traced back to the basic scattering equations: The intensities for model (a) arise by inserting the t-matrices of Co and Al into the Born series of Eq. (3.15) according to the order of each domain, obtaining \(I_g(E)\) for either one by inserting the result in Eq. (3.21), squaring the obtained amplitudes in (3.23) (as detailed in the next section), and then averaging over the intensities according to Eq. (3.3). In contrast, average t-matrices for arrangement (b) are inserted already into Eq. (3.15), which is then squared by way of Eqs. (3.21) and (3.23) to give the intensity curves depicted in Fig. 3.7. Hence, the difference between large ordered domains and a substitutionally disordered surface arises both in the kinematic terms and in the multiple scattering sequence.

### 3.2.4 Full dynamical LEED calculations

As mentioned, practical LEED calculations aim for the intensities of the set of beams \(\{k_g^-\}\) leaving the surface, \(I_g(E)\). At the vacuum boundary, the LEED wave function takes the form

\[
|\Phi^+(k_\parallel)| = |\tilde{k}_0^- + A_g^-|\tilde{k}_g^-\rangle,
\]

with \(A_g^-\) the amplitude of each outgoing wave \(|\tilde{k}_g^-\rangle\). Note that

\[
\tilde{k}_g^- = \left( k_\parallel + g, -\frac{2m}{\hbar^2} \sqrt{E - (k_\parallel + g)^2} \right)
\]

denotes the momentum of damped plane waves within the surface, which are referenced to the muffin-tin zero. Including the proper flux normalisation outside the crystal, the desired intensities read

\[
I_g(E) = \frac{|k_g^-|}{k_{0,\perp}} \cdot |A_g^-|^2.
\]

Thus, we must focus on obtaining \(A_g^-\) from Eq. (3.15) as efficiently as possible. Although there are ways to tackle this task heads-on (i.e., in real space [Jol92]), the use of other quantum-mechanical representations is normally much more efficient. Typically, the solution of the LEED problem is subdivided into four steps.

1. **The calculation of phase shifts \(\delta_i^j(E)\).**

   The components of the muffin-tin potential form the basis of any LEED calculation. Since

---

\[12\]The choice of CoAl(111) as an example is advantageous because similar structural models – one consisting of ordered domains vs. a laterally homogeneous, but substitutionally disordered surface – are conceivable for that system. We shall therefore briefly return to the present considerations in Sect. 5.4.3.
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the elemental atomic potentials \( v^i \) are spherically symmetric, they are diagonal in a spherical wave basis \( \{ |R^i; l, m \rangle \} \) and do not depend on \( m \). Moreover, the maximum required angular momentum quantum number \( l_{\text{max}} \) is limited since \( v^i(r) = 0 \) for \( r > r_{MT} \) by construction. The scattering properties of \( v^i(r) \) are usually summarized in a set of scattering phase shifts \( \delta^i_l(E) \) [Pen74]. Those used in the present work were calculated relativistically from \( v^i \) by means of Dirac’s equation, and then spin-averaged. However, \( V_0^i \), which enters through \( G^+_{0i} \) in Eq. (3.14), was neglected in this step. Note that \( V_0^i(E) \) should ideally be provided along with \( \delta^i_l(E) \).

2. The calculation of atomic \( t \)-matrices \( t^i \).

The scattering properties of each surface lattice site \( i \) are fully determined by its chemical occupation and the associated temperature factor(s) \( w^i \). Throughout this work, only isotropic temperature factors were used, preserving the spherical symmetry of atomic scattering. For each element, \( t^i_l \) is obtained from \( \delta^i_l \) through the relation

\[
t^i_l = \sin \delta^i_l \exp(i\delta^i_l).
\]

Next, \( w^i \) is included by inverting Eq. (3.17). Finally, Eq. (3.16) accounts for possible substitutional disorder.

3. The calculation of layer diffraction matrices \( M^{\pm\pm}_{g_1g_2} \).

Any crystalline surface can be viewed as a stack of 2D periodic atomic layers, the scattering properties of which are best described using a basis of plane waves \( \{ \tilde{k}^+_g, \tilde{k}^-_g \} \). This set is only strictly limited by the conservation of lateral momentum, Eq. (3.1). Basis functions which violate energy conservation can occur, but \( k^{\pm}_{g, -} \) then becomes strongly imaginary according to Eq. (3.2). So, \( \{ \tilde{k}^+_g, \tilde{k}^-_g \} \) is also finite since evanescent waves need only be considered if they do not decay fast enough between adjacent layers. Since \( t^i \) is best handled in \((l, m)\) space, Eq. (3.15) is solved in this representation for each inequivalent layer type. The resulting Green function is then transformed to a matrix \( M^{\pm\pm}_{g_1g_2} \), which links any plane wave amplitudes incident on that layer to those travelling away. Perturbational [Zim75, Abe75, Ton77, Hnz83, Hnz85] and self-consistent [Pen74, Ton77] approaches exist to calculate \( M^{\pm\pm}_{g_1g_2} \), but only the latter was used in the present work. The calculation is quite fast for layers with only one atom per 2D unit mesh (Bravais layers) [Pen74]. Based on Beeby’s idea, it is also possible to treat composite layers (\( N_a > 1 \) atoms per 2D unit mesh) in \((l, m)\) space [Bee68, Ton77], but the time to compute \( M^{\pm\pm}_{g_1g_2} \) then scales with \( N_a^3 \).

4. The calculation of the surface reflection matrix \( R^{+-}_{0g} \).

With diffraction matrices \( M^{\pm\pm}_{g_1g_2} \) for each layer type at hand, a total reflection matrix \( R^{+-}_{0g} \) of the surface can be computed by matching the plane wave amplitudes of \( |\Phi^+(k_\parallel)\rangle \) at each interlayer boundary. Moreover, \( A^-_g = R^{+-}_{0g} \), since we chose an incident amplitude of 1 in Eq. (3.21). So, the LEED problem is reduced to a set of matrix equations, which can either be solved perturbationally (renormalised forward scattering) [Pen74] or self-consistently through matrix inversions (layer stacking) [Pen74, Hov86]. The latter method is used exclusively in this work. Due to inelastic damping, \( |\Phi^+(k_\parallel)\rangle \) decays into the crystal, so that a slab of finite thickness suffices to model the surface’s scattering properties correctly.
3.3 The multi-parameter problem

By comparing the third step with the fourth, one may note that $R_{0g}^{\pm}$ could also be obtained directly in $(l, m)$ space by means of the composite layer technique. However, the necessary matrix inversions generally require much more computing time than the layer stacking approach in $k$ space. On the other hand, as the distance $d$ between two layers decreases, more and more evanescent waves become relevant for $M_{g_1 g_2}^{\pm \pm}$, i.e. the required matrix dimension rises roughly as $d^2$. As a consequence, handling $M_{g_1 g_2}^{\pm \pm}$ becomes both time-consuming and numerically unstable [Ton77, Ada85]. The failure of the layer stacking scheme for interlayer distances below approximately 1.0 Å is characterised by mostly correct $I(E)$ spectra with abrupt, “spurious” divergences in narrow but unpredictable $(E, d)$ windows. From experience, these unphysical features cannot reliably be avoided by increasing the basis size or the numerical accuracy alone (Ref. [Ada85] contains a concise and instructive summary), and a number of other remedies have been proposed in the literature [Pin90, Zha90, Jon99, Jep99]. The safest approach is to avoid the plane wave approach entirely for problematic $d$, resorting to the composite layer technique instead [Arn98, Ham99, Wal01]. It should be noted that this approach scales quite badly when optimizing structural parameters full-dynamically, but produces no additional overhead when the Tensor LEED method is used (Sect. 3.4).

Today, reliable computer programs exist for full dynamical $I(E)$ calculations. In the present work, phase shifts were obtained by programs long in use in the Erlangen LEED group.\footnote{This program package is a compilation of older work and was originally made available to the Erlangen group by T. Grandke (MPI Stuttgart). It is based on relativistic Hartree-Fock calculations after Ref. [Lib65], and the “Binary compound potential generator” of Koelling (basics given in Ref. [Koe69]). The complete collection of programs was first used in Ref. [Grn77].} For Fe$_{1-x}$Al$_x$, $V_{0g}(E)$ stems from the phase shift package assembled and enhanced by J. Rundgren [Run01]. To the author’s knowledge, the latter collection is the most advanced one available today, but its development is too recent to be incorporated in a fully consistent way below. Any multiple scattering calculations were then performed by the subroutines of van Hove and Tong [Hov79], on which the full dynamical part of the TensErlLEED package [Blu01] (Sect. 3.4) is based.

### 3.3 The multi-parameter problem

The previous sections show how LEED intensities arise from a surface in experiment and theory. As already mentioned, it is generally impossible to invert this theory and calculate a surface’s structure directly from $I_g(E)$ – the different terms in Eq. (3.15) are too far entangled. So, the crystallographer requires an alternative means to infer structural data from $I_g(E)$ alone. The commonly chosen approach in LEED (as in many other fields of physics) is straightforward. Using any previously available information on the system under study, one sets up different classes of basic models, which each contain a number of a priori free parameters. The question to be answered is then, “Which of these models represents the experimental $I_g(E)$ data best, and which parameter values correspond to the best fit between theory and experiment?”

As yet, this question is badly put: Obviously, we must define just what is meant by “best fit”. However, even with this information at hand, there remain two more important questions: “Is the
chosen model adequate at all? And if so, how accurately do the best fit parameter values reflect physical reality?" Fortunately, a whole branch of mathematical statistics is dedicated to these issues. Its methods have long been applied in the field of crystallography, and an excellent introduction to "data fitting" can be found in the book by G. Prince [Pri82]. Generally, two conceptually different sources of possible inadequacies in a structure determination can be distinguished [Pri82]:

1. **Precision.**
   Obviously, we must expect any experimental $I_g(E)$ data to bear some statistical error, leading to uncertainties in the model parameters determined later. This determines the structural precision for which the experimental data quality allows.

2. **Accuracy.**
   Even without any statistical error of measurement, we cannot expect a perfect reproduction of measured $I_g(E)$ by any structural model. A variety of possible reasons for such deviations exist, ranging from simple, forgotten parameters via approximations inherent in the model (e.g. the muffin-tin approximation) to experimental effects such as magnetic stray fields which may affect the angle of incidence. In general, any of these systematic errors could introduce a bias into the fitting procedure if somehow correlated with a model parameter. Furthermore, the tested range of model parameters might not include the real structure at all, but instead give rise to some artifact best fit ("multiple coincidence" is a well-known example in LEED [Hov86]). Finally, any model may be extended to contain more and more free parameters, improving the overall fit quality in an unphysical way. Citing G. Pawley [Paw82], Prince calls such redundant parameters *elephant parameters*, as the saying goes that, by including enough of them, one might "even fit an elephant" (Fig. 3.8). In each case, structural results could have a seemingly high experimental precision, although their accuracy compared to physical reality was really much lower.

The question of precision can be solved by straightforward statistical means, provided that one possesses a reasonable estimate of the experimental uncertainty. The question of accuracy is much more difficult. It depends on details of the structural model itself, and will directly reflect the care taken to eliminate all relevant systematic errors. We shall encounter this question often throughout this work.

In the following, we will concentrate on practical data fitting in LEED only. Our foremost aim must be to limit the possible space of structural models and model parameters properly, including all necessary quantities but not any superfluous ones. We will then introduce Pendry's R-factor $R_P$, the standard measure of fit quality between experimental and theoretical $I_g(E)$ spectra in LEED. A description of how $R_P$ allows to quantify the statistical uncertainty of a LEED measurement, and particularly its use to estimate the experimental precision attained for each fit parameter, concludes this section.
3.3. The multi-parameter problem

Figure 3.8: According to the literature [Pri82], one might even fit an elephant by any model when including enough free parameters. Here, an elephant (right) fits a given set of data (left) (from “Le Petit Prince” [Sai43]).

3.3.1 Physical constraints on the parameter space

In order to obtain crystallographic information by fitting a structural model against experimental \( I_g(E) \), we must first define the model’s physical bounds. Of course, some trivial information is always available, e.g. the nature of the bulk crystal under investigation, and one can normally limit the structural investigation to the topmost few atomic layers of a sample. Furthermore, some specific insights from other experimental methods may exist, e.g. regarding the chemistry and homogeneity of the topmost atomic layer. Beyond this, the most pointed information normally comes from the LEED pattern itself, since the spot positions reveal the shape of a surface’s 2D unit mesh. However, the pattern provides no direct insights into the 3D atomic distribution therein, except in rare cases where systematic spot extinctions give some additional hints on symmetry.

A priori, the set of model classes to be considered in a structural analysis must include all “reasonable” atomic arrangements consistent with this previous knowledge. For each of these model classes, one must then optimize the specific geometric arrangement of atoms, and their vibrational properties. To be precise, some technical quantities need also be fitted – particularly, this concerns possible constant shifts of the energy scale, \( V_{00} \) (to be added to \( V_{0r}(E) \)), the normally unknown damping constant \( V_{0i} \), and the angles of incidence of the primary beam, \( \theta \) and \( \phi \), if these can not be inferred from the symmetry of the LEED pattern itself. In binary alloy surfaces, all these parameters must be determined in addition to those of special interest in the present work: the chemical occupation of individual lattice sites, i.e. the composition and order of the surface region.

Consider the example of a simple random alloy surface such as Fe\(_{0.85}\)Al\(_{0.15}\)(100)-(1×1) (Sect. 4.3), schematically depicted in Fig. 3.9, limited to normal incidence and models retaining the bulk-like bcc lattice and symmetry in principle. As outlined in Sect. 2.2, we should strictly include separate occupation probabilities, plus element-dependent positions and vibrations, for each layer into the fit. Even if we allow for deviations from bulk-like stoichiometry and order of the top four layers only, we have four unknown occupation probabilities \( x^1-x^4 \), eight element-dependent atomic positions \( h^1_{Al}-h^4_{Fe} \) and eight vibrational amplitudes\(^{14}\) \( u^1_{Al}-u^4_{Fe} \) to consider, plus \( V_{00} \) and \( V_{0i} \). Additionally, we may yet need to determine unknown bulk properties such as the \( T \)-dependent lattice parameter \( a \) or the vibrational amplitudes \( u^b_{Al} \) and \( u^b_{Fe} \). In total, these are 25 free parameters to be determined in the LEED analysis. Clearly, this hypothetical number is unreasonably large, and we must constrain

\[^{14}\text{Note that, throughout this work, we shall speak of statistical positional displacements of atoms as vibrational amplitudes, even though these may also contain a static component if random chemical disorder occurs, due to variations of each atom’s local environment.}\]
Figure 3.9: Structural parameters associated with a $\text{Fe}_{0.85}\text{Al}_{0.15}(100)-(1\times1)$ random alloy surface as described in the text. The listed parameters are those which would have to be considered at maximum; in the actual analysis of Sect. 4.3, $u^1_{\text{Al}}$ and $b^2$ were not determined as $x^2$ proved too low.

Stoichiometry. Of course, the near-surface concentration profile should return to the bulk composition below a certain depth. However, this depth depends sensitively on the particular system. Interatomic interactions, elemental surface strain, the proximity of an order-disorder transition, etc. all influence the composition profile formed. Unfortunately, these quantities are usually unknown. Their investigation is the very focus of this work, so that we cannot restrict the parameter space here.

Atomic positions. Multilayer relaxation is a well-known phenomenon for many surfaces, and the deviation of four average interlayer spacings from the bulk value must be allowed for by all means. In the bulk, the symmetry of the bcc lattice restricts different elements on equivalent, randomly occupied sites to the same average position. However, these may be different in the direct vicinity of a surface, where the local symmetry is reduced. One may assume only the NN and 2NN environment of a lattice site to be important in this respect. So, only the top two layers of a bcc (100) surface should be affected, since only these lack any NN / 2NN at all (Sect. 2.2). Yet, it should be noted that the number of element-dependent positions to be tested for also depends on the fit itself. First, if the overall segregation profile near the surface creates a strongly asymmetric environment of certain deeper layers, element-dependent positions should strictly be tested there, too. Second, an independent elemental position has too little influence on the fit if only a small fraction of the lattice sites in question are occupied by that element. Then, the extra positional parameter would likely reflect statistical noise, and we shall assume equal elemental positions for want of a better approximation.

Vibrational amplitudes. The above list of a priori unknown parameters contains a total of ten different vibrational amplitudes. In principle, these are all quantities of little overall influence on a LEED fit, and not the chief object of investigation here. So, it is desirable to restrict the number
of these parameters drastically by physical arguments. On the other hand, Eq. (3.20) contains vibrational amplitudes and chemical concentrations in a very similar context. As will be seen in Sect. 4.3, this means that any physically motivated restriction referring to thermal vibrations must be rigorously justified, in order to avoid any accidental systematic errors in the fit. In an elemental, cubic bulk solid, the Debye model [Wil75] allows to predict vibrational amplitudes with sufficient accuracy for the purposes of LEED. This yields
\[ M(u^b)^2 = \frac{9h^2 T}{k_B \theta_D^2} \left[ \phi\left(\frac{\theta_D}{T}\right) + \frac{1}{4} \frac{\theta_D}{T} \right] \]
with \( \phi(x) = \frac{1}{x} \int_0^x \frac{y}{e^y - 1} dy \) (3.25)
with atomic mass \( M \), temperature \( T \), and Debye temperature \( \theta_D \). Of course, it would be very useful to have a similar equation for binary materials, preferably accounting for the possibility of substitutional disorder, and the proximity of a surface — but alas, the situation is not so simple. Already for a stoichiometric, cubic binary compound AB, a direct extension of Eq. (3.25) is only possible for the mass-weighted sum \( [M_A (u^b_A)^2 + M_B (u^b_B)^2] \), but not for \( u^b_A \) and \( u^b_B \) individually. Furthermore, the proper description of acoustic and optic phonon branches by the simple Debye model is at least questionable. The lack of a rigorous equivalent to Eq. (3.25) can be understood intuitively: Thermal vibrations depend on the flexibility of local bonds, and the properties of these bonds are specifically determined by the vibrating element. In the phonon picture, this is expressed through non-trivial, site-dependent phonon polarisation vectors [Wil75]. Consistently, no general criterion for atomic vibrational amplitudes in binary compounds exists to the author’s knowledge. A compilation of experimental results for binary ionic solids shows the ratio of elemental \( u^b \) to vary considerably [But93]. On the other hand, in bulk B2 NiAl, \( u^b_{\text{Al}} \) and \( u^b_{\text{Ni}} \) are approximately equal over a wide range of temperatures [Geo77, Gum96, Nue98]. In our case, the surface presents an additional complication due to the reduced crystal symmetry and number of local bonds, and the possibility of a random site occupation allows for statistical static disorder on top of all this. What we may expect are elemental vibrational amplitudes which do not deviate excessively from one another, and their general enhancement on near-surface lattice sites, but these are no rigorous conditions. Yet, there are two restrictions which we can apply. First, the local coordination of sites below the second layer is approximately bulk-like in a bcc(100) surface, so this should also hold for vibrational amplitudes. Second, fitting a separate vibrational amplitude makes no sense for an element which occupies only a small fraction of a lattice site, so that we shall assume equal elemental vibrations in that case.

Strictly, these considerations only eliminate 6 quantities (element-dependent positions, and independent vibrational amplitudes in layers three and four) from the above hypothetical parameter space. Of the remaining ones, none can be ignored a priori. As will be seen in Sect. 4.3, \( x^1 \) may be fixed by other methods, and \( u^2_{\text{Al}}, u^2_{\text{Ni}}, \) and \( h^2_{\text{Al}} \) prove irrelevant in the actual fit. However, each of these restrictions must be individually justified to avoid biasing the remaining parameters. In total, we still face a complex many-parameter problem even for this simple alloy surface. In order to judge the true accuracy of fit quantities of special interest, we must necessarily address the question of parameter correlations explicitly.

So far, we have assumed the model surface to be laterally homogeneous, and to retain the symmetry of the underlying bulk. For a “simple” random alloy surface such as Fe\(_{0.85}\)Al\(_{0.15}\)\((100)\), both surmises are usually straightforward, and strong experimental evidence would be required to abandon either
one. However, these preconditions are not always obvious in complex systems. First, a surface may break its bulk-prescribed symmetry, e.g. because of a strong influence of individual chemical bonds [Sta98]. Due to the formation of equivalent, rotated domains, such behaviour will not be obvious from the LEED pattern. Second, the surface may consist of a set of relatively large, structurally different domains. For instance, this behaviour is a natural consequence of the preparation of epitaxial thin films [Blu99]. In the case of ordered compound materials (which includes ordered alloys), the possibility of coexisting structural domains also deserves some additional attention. For instance, two or more different truncations each are compatible with full bulk order up to the selvedge of (100) and (111) oriented D0$_3$ and B2 crystals (see Sect. 2.2). Generally, one would expect one of these terminations to be energetically most favourable and cover the entire surface, but there is no a priori guarantee for a unique termination to occur. In fact, reports of ordered surface terminations by two domains exist, e.g. for NiAl(111) [Noo87, Noo88] (Sect. 2.3), or oxide surfaces [Bic89, Wlt00, Hov00].

Both modifications, the relaxation of a symmetry constraint as well as the addition of an independent structural unit, simultaneously introduce a whole set of new fit parameters. Obviously, it is problematic to prove or disprove the reality of such extensions to the model by means of a best fit alone. In this situation, the availability of auxiliary information from other methods is of great value to restrict the multitude of potential model extensions. Among the systems studied in the present work, Fe$_{0.70}$Al$_{0.30}$(100), Fe$_{0.53}$Al$_{0.47}$(100), CoAl(100), and CoAl(111) fall into the group of materials with two possible terminations. Fortunately, additional experimental information from STM and LEIS renders anything but a unique surface termination of the former three surfaces quite unlikely. However, for CoAl(111) in Sect. 5.4, the suspicion of a coexistence of two structural domains arises from the related case of NiAl(111), and cannot be dismissed from auxiliary experiments as clearly as in the former cases. Indeed, we shall see that an additional structural domain improves the overall fit quality for CoAl(111), but it is not immediately clear whether this reflects physical reality, or rather the improved fitting of some statistical (or systematic) error in the structural model by too many additional parameters at once. Furthermore, this model competes against a homogeneous, but substitutionally disordered surface model in Sect. 5.4.

From the point of view of a LEED fit, an extra structural domain adds spectral features to $I_g(E)$ which originate from different geometric scattering path lengths, and from atoms situated on different positions of the same basic lattice. At a first glance, very similar effects can be achieved by allowing for substitutional disorder near the surface, through site-dependent elemental concentrations $x^i$, positions $h^i_{\text{Al,TM}}$, and vibrations $v^i_{\text{Al,TM}}$. So, one might suspect the effects of both phenomena to "mask" one another – an unconsidered structural domain to result in the appearance of substitutional disorder in a practical LEED fit, and vice versa – in other words, a correlation between both sets of possible parameters. Yet, we have already established that the effects of incoherent domains and substitutional disorder on LEED $I_g(E)$ are really quite well distinguishable (Sect. 3.2.3): If a correlation yet existed between both, it would have to be weak. We shall return to this issue in Sect. 5.4, showing that a safe conclusion can only be reached by carefully weighing all evidence at hand.
3.3.2 Data fitting: Pendry’s R-factor

Soon after the first surface structural analyses by quantitative LEED in the mid-1970’s, it became clear that the available model parameter space was too large for structure optimisation by visually comparing theoretical and experimental $I_g(E)$ alone. In this situation, mathematical statistics comes to the crystallographer’s aid. Assume we had $N$ discrete experimental data points $D_i$, and statistical errors of measurement following independent Gaussian probability distributions (PD) with variance $\sigma_i^2$. Assume further that a model function $M_i(x)$ (with $x$ a vector of model parameters) had no systematic errors. Then, the combination of model parameters which most likely reflects reality can be found by minimising a sum of squares [Pri82],

$$ S = \sum_{i=1}^{N} \frac{[D_i - M_i(x)]^2}{\sigma_i^2}. \quad (3.26) $$

Unfortunately, it so happens that this noble piece of mathematics does not directly apply to LEED. $I_g(E)$ spectra are not a set of independent data points $D_i$, but rather continuous functions of energy, leading to a strong correlation of neighbouring data points. Also, certain systematic errors of $I_g(E)$ are difficult to avoid: E.g., as seen in Sect. 3.1, the absolute intensity level within an $I_g(E)$ curve may be difficult to model exactly due to details of the data collection technique.

An elegant solution to these issues is provided by the Pendry R-factor (reliability factor) $R_P$ [Pen80], which has become a de facto standard in quantitative LEED. Pendry reasons that intensity peaks and minima are the primary information provided by a diffraction technique. Due to the complexity of multiple scattering, they may be viewed as independent pieces of experimental information in the spirit of Eq. (3.26). Peak positions can be measured with high precision, and their statistical uncertainty is a tractable quantity which may well follow a Gaussian PD of constant variance $\sigma_i^2$ over the entire range of measurement, So, the task is to devise a numerical treatment of continuous functions of energy which, in the limit of well-separated diffraction peaks, yields a least-squares sum of peak position differences $\Delta_i$.

By definition, $R_P$ compares experimental and theoretical Pendry Y-functions $Y_g(E)$, instead of $I_g(E)$ spectra. So,

$$ R_P = \frac{\sum_g \int dE (Y_{g,th} - Y_{g,exp})^2}{\sum_g \int dE (Y_{g,th}^2 + Y_{g,exp}^2)} \quad (3.27) $$

where (dropping the index $g$ for the moment) $Y(E)$ is defined as

$$ Y(E) = \frac{L(E)^{-1}}{L(E)^{-2} + V_{0i}^2}, \quad \text{with} \quad L(E) = I(E)^{-1} \cdot \frac{dI(E)}{dE}. \quad (3.28) $$

Here, any (approximately) constant factors to $I(E)$, which might be due to systematic errors, cancel out in the logarithmic derivative $L(E)$. By using $Y(E)$ instead of $L(E)$, possible numerical problems for $I(E) \approx 0$ are avoided. As can easily be verified, $0 \leq R_P \leq 2$ for any input data $I_g(E)$, with $R_P \rightarrow 0$ for a perfect fit, $R_P \approx 1$ for uncorrelated data (because then, $Y_{th} \cdot Y_{exp}$ becomes zero on average), and $R_P \rightarrow 2$ for “anticorrelated” $I(E)$. $R_P \lesssim 0.2$ on average over a reasonably sized $I_g(E)$ data set is nowadays typical for a satisfactory surface model by experience. The attainable
minimum value depends somewhat on the particular system, and values well below 0.1 may be reached for relatively close-packed surfaces. Comparisons to other R-factors have shown that $R_P$ is well suited to determine also stoichiometric [Ktk97c, Spo98] or vibrational [Loe95b] parameters in addition to geometry.

As hinted above, the real value of $R_P$ for statistical estimates can be assessed by applying it to an $I(E)$ spectrum which consists of a series of well-separated Lorentzian peaks, $I_j(E)$,\(^\text{15}\) positioned at peak energies $E_j$. In the kinematic approximation, the width of LEED peaks is solely determined by inelastic damping, and amounts to $2V_{0i}$ (full width at half maximum, FWHM) [Hov86], so that

$$ I_j(E) = \frac{a_j}{(E - E_j)^2 + V_{0i}^2}. \quad (3.29) $$

Assuming a statistical error of measurement $\Delta_j$ for each peak position $E_j$, but otherwise identical spectra, Pendry establishes a central property of $Y(E)$:

$$ \int_{-\infty}^{\infty} dE (Y_{j,\text{th}} - Y_{j,\text{exp}})^2 \approx \alpha \Delta_j^2. \quad (3.30) $$

Since all peaks are of equal shape, the integral depends only on $\Delta_j$. For the same reason, the normalising integral over $(Y_{j,\text{th}}^2 + Y_{j,\text{exp}}^2)$ is constant:

$$ \int_{-\infty}^{\infty} dE (Y_{j,\text{th}}^2 + Y_{j,\text{exp}}^2) =: \beta. \quad (3.31) $$

For a series of $N$ such well-separated peaks, $I(E) = \sum_{i=1}^{N} I_j(E)$, this directly implies

$$ R_P \approx \frac{\alpha}{N\beta} \sum_{i=1}^{N} \Delta_i^2. \quad (3.32) $$

If $\sigma_i = \sigma$, $R_P$ is obviously proportional to a sum of squares of peak position errors, very similar to Eq. (3.26). In other words, the independent peak positions $E_j$ now play the role of independent data points, just as desired above. Of course, several crude assumptions have been made to obtain this result, and the case for real $I(E)$ spectra must be much more complex. Nevertheless, Eq. (3.32) provides an excellent guideline to apply statistical theory to the LEED problem.

### 3.3.3 Estimating statistical errors in LEED

Assume for the moment that we knew the "ideal" structural model for a given surface, i.e. the model which contains all relevant parameters and only those, free of any systematic errors. A look at Eq. (3.32) shows that, even then, we must not expect $R_P = 0$ for the best fit as long as there are finite random errors of measurement. Rather, the R-factor’s statistical expectation value in an ideal fit is

$$ \overline{R_P} = \frac{\alpha}{\beta} \sigma^2. \quad (3.33) $$

\(^\text{15}\)Note that the index $j$ here refers to the position of an individual intensity peak in a spectrum corresponding to a single beam $g$, and does not denote a particular LEED beam $g$ as in the remainder of this work. For writing convenience, the latter index is still dropped.
from (3.32). In fact, $R_P = 0$ would be highly suspicious, indicating an overfit rather than physically accurate results.

In a practical LEED analysis, it would be useful to have some measure for $R_P$ associated with the available experimental $I_g(E)$ data base. Apart from being an indicator of the data quality as such, this would allow to identify both a clear overfit (if the best-fit R-factor between model and experiment, $R_{\text{min}}$, resulted at $R_{\text{min}} < R_P$), or some missing feature in the model description (if $R_{\text{min}} \gg R_P$). Of course, the straightforward way to obtain information on $R_P$ is simply to remeasure the data once or more under the same nominal experimental conditions, and calculate $R_P$ between independently measured spectra. As this value should characterise the $I_g(E)$ data actually used in the LEED analysis, it is important to compare spectra which underwent the full “processing” prior to the analysis, i.e. including background subtraction, current normalisation, symmetry-averaging, the smoothing of high-frequency noise, etc. (see Sect. 3.1). For instance, the deviation between the (1,0) beam used in the structural analysis of Fe$_{0.85}$Al$_{0.15}$(100) and the control measurement shown in Fig. 3.3b is characterised by $R_P \approx 0.01 (\%)$. Although the statistics produced by two sample measurements is rather crude, this exceptionally low value indicates a very small influence of statistical errors.

Unfortunately, producing and processing a full reproduction measurement of $I_g(E)$ data is usually rather time-consuming, and also requires some care to avoid accidental systematic errors resulting from small differences in the experimental setup. Luckily, for symmetric incidence (as always used in the present work), an upper limit for $R_P$ may also be established from a single LEED data set only, by comparing individual, nominally symmetry-equivalent $I_g(E)$ curves to one another. For the average R-factor between processed (i.e., background-corrected, smoothed, etc.) symmetry-equivalent $I_g(E)$ curves, $\overline{R}_s$, one would generally expect $\overline{R}_s > R_P$: In principle, $\overline{R}_s$ reflects the same statistical error as $R_P$, only the statistics of the final, symmetry-averaged curve is certainly improved compared to the individual ones. In addition, $\overline{R}_s$ will also reflect any residual misalignment of the incident electron beam. For instance, after background-correcting, normalising and smoothing the three curves shown in Fig. 3.3a, $\overline{R}_s$ still amounts to 0.04 between all three, i.e. results clearly higher than the R-factor between the independently measured, averaged curves in Fig. 3.3b.

In Chapters 4 and 5 (Tables 4.1 and 5.1), we shall use $\overline{R}_s$ to characterise the statistical errors of each experimental $I_g(E)$ data set qualitatively. Its quantitative connection to $R_P$ is difficult to establish precisely in general, but it should be remembered that

- a low value of $\overline{R}_s$ will generally mean a good experimental data quality, with $R_P$ even below,
- a best-fit R-factor $R_{\text{min}} \gtrsim \overline{R}_s$ should be clearly on the safe side from an overfit, and
- $R_{\text{min}} \gg \overline{R}_s$ may be taken as a hint for a missing structural feature in the model surface, or even an incorrect model surface as such.

Of course, since $R_P$ is really a statistical quantity, one may also calculate its standard deviation, i.e. the width of the “window” in which an experiment-theory R-factor is expected. By definition,

$$\text{var}(R_P) = (\overline{R}_P - R_P)^2.$$ (3.34)
Assuming a Gaussian probability distribution of peak position errors, some algebraic manipulation suffices to show that the R-factor’s standard deviation is actually proportional to its expectation value [Pen80]:

\[
\text{std}(R_P) := \sqrt{\text{var}(R_P)} = \frac{R_P}{\sqrt{N}}. \tag{3.35}
\]

Interestingly, this result paves the way to estimate any fit parameter’s statistical precision in a practical LEED analysis. The best fit R-factor \( R_{\min} \) is what elementary statistics calls an unbiased estimator [Pri82] of the true R-factor expectation value, \( \overline{R_P} \). The fit is achieved from \( N \) independent data points, i.e. diffraction peaks, in \( I_g(E) \). Assuming an average peak FWHM of \( 2V_{0i} \), [Pen80]

\[
N \approx \frac{\Delta E}{4V_{0i}}, \tag{3.36}
\]

for well-separated peaks, where \( \Delta E \) denotes the integrated energy width of the entire \( I_g(E) \) data base. So, by analogy to Eq. (3.35), one may hope that the quantity

\[
R_{\min} \cdot RR := R_{\min} \cdot \frac{8V_{0i}}{\Delta E} \tag{3.37}
\]

represents a good experimental estimate of \( \text{std}(R_P) \).\(^{16}\)

In fact, this line of argument is not quite statistically sound. \( R_{\min} \cdot RR \) is certainly an estimator of \( \text{std}(R_P) \), but not an unbiased one. Roughly speaking, the problem is that fitting a given set of LEED \( I(E) \) data provides only one “measurement” of \( R_{\min} \), but it is generally impossible to estimate a probability distribution’s standard deviation by a single sample. Nevertheless, \( R_{\min} \cdot RR \) is usually the best available estimate for \( \text{std}(R_P) \). So, any combination of model parameters with \( R_P \leq R_{\min}(1 + RR) \) could, to our knowledge, still reflect experimental reality, not being the exact minimum simply by bad luck (statistical fluctuations of the data base).

Put in a nutshell, \( R_{\min} \cdot RR \) provides a measure for the experimental uncertainty of each parameter of the ideal model quantitatively from the fit itself [Pen80]. By convention, statistical error limits in LEED are determined by calculating \( R_P \) for several values of a parameter, keeping all others fixed at their best fit – a single parameter R-factor scan. The range with \( R_P \leq R_{\min}(1 + RR) \) then defines the parameter’s error bounds, a procedure used throughout most of this work. In Fig. 3.10, it is illustrated for two parameters of Fe\(_{0.85}\)Al\(_{0.15}\)(100) (referring to the best fit described in Sect. 4.3). Obviously, the fit is quite sensitive to \( a^{12} \), with an error bar of \( \pm 0.02 \) Å only. According to the single-parameter scan, it also allows a reliable determination of \( x^1 \), here with an error bar of \( \pm 12 \) %. In fact, the sensitivity of the fit to both quantities is even somewhat reduced in these cases due to enhanced top layer vibrational amplitudes. Even smaller errors are encountered in deeper layers, where vibrations are closer to \( u^b \).

Even assuming the availability of an ideal model, we are still faced with a many-parameter problem, and the realistic possibility of correlations between some of them. In that case, the use of single-parameter R-factor scans for error estimates (as above) has an unfortunate drawback. It provides

\(^{16}\) We have chosen to follow the terminology of Ref. [Hov86] and name \( RR \) the “reliability of the Pendry R-factor”. In the literature, it is customary to call \( R_{\min} \cdot RR \) the “variance of the Pendry R-factor”, \( \text{var}(R_P) \). Unfortunately, \( \text{var}(R_P) \) is highly misleading since \( R_{\min} \cdot RR \) really aims to estimate the R-factor’s standard deviation.
3.3. The multi-parameter problem

no way of knowing whether the effect of a particular parameter on $I_g(E)$ can be partially undone by others. This, of course, would clearly decrease its precision, even if its single-parameter error limits looked nice and small. In a realistic analysis (i.e. one with systematic errors in the model), this problem is enhanced, because a less sensitive parameter may much easier be shifted by a systematic effect than an influential parameter.

As for the statistical error, the clean solution would be to use all-parameter R-factor scans instead of single-parameter ones – i.e., to vary the parameter in question stepwise as in Fig. 3.10, but reoptimising all other parameters at each step. In fact, error analyses based on all-parameter estimates have revealed a reduced effective sensitivity of LEED to particular parameters (see, e.g., Refs. [Spo98, Pla99, Pla99b]). Sect. 4.3 addresses a similar observation for $x^1$ of Fe$_{0.85}$Al$_{0.15}(100)$ in greater depth. Unfortunately, the computational effort associated with the determination of all-parameter error bars is considerable, so that we shall only use these in crucial cases below.

Often, the important question is whether a certain type of a structural modification of the surface (e.g., the occurrence of disorder in a certain layer, the existence of an additional structural domain, etc.) plays a role at all, placing its exact magnitude only in the second rank. Then, all-parameter scans can be circumvented by testing only two different configurations in full: One for a model including the effect in question, and one for a restricted model, assuming some default behaviour of the surface. Heuristically, both cases may again be distinguished through $R_{\text{min}} \cdot RR$. However, the fact that $R_{\text{min}} \cdot RR$ is not an unbiased estimator of the statistical significance of an effect then becomes important: It takes no notice of the number of fit parameters which distinguish the restricted and the unrestricted model. In such cases, a more rigorous approach to statistics would be desirable. Indeed, this exists in the form of the so-called $F$-ratio test [Pri82], which was introduced to bulk crystallography (and recently to LEED [Wlt00, Hov00]) as Hamilton’s R-factor ratio criterion [Ham65]. Unfortunately, the definition used in Ref. [Wlt00] is inconsistent with the statistical properties of $R_P$. A more appropriate adoption would represent a project of its own, and exceeds the scope of this work. For the time being, we shall use $R_{\text{min}} \cdot RR$ to compare restricted and
unrestricted models to one another, with due caution exercised where many parameters are involved at once.

3.4 “Tensor LEED” and the structural search

The previous sections provide all necessary means to perform a successful LEED structural analysis. Yet, one practical problem remains: The simultaneous optimisation of many fit parameters is a time-consuming task, which scales exponentially with their number – the more refined a structural model, the larger the practical effort to find the best fit. As seen in Sect. 3.3.1, the inclusion of chemical degrees of freedom aggravates this problem somewhat even for a “simple” alloy surface, compared to a “simple” elemental one. So, a fast means to calculate LEED spectra and optimise them with respect to the experimental ones is a prime necessity to keep a structural analysis feasible.

The Tensor LEED approximation [Rou86, Rou89, Rou92] to full dynamical LEED theory speeds up individual \( I(E) \) computations drastically, and thus also the structural refinement procedure on the whole. Standard program packages [Hov93, Blu01] nowadays allow Tensor LEED calculations for almost any conceivable surface. In particular, the structural analyses presented below were all performed using the TensErLEED package [Blu01] or its predecessors. Since a separate, detailed technical introduction exists [Blu01], we shall here summarise only the underlying principles, focusing on the range of physics which it covers.

3.4.1 The principle

The most time-consuming drawback of full dynamical LEED theory is that each computation of \( I_g(E) \) must necessarily account for multiple scattering in full. For complex surfaces, the time for such a calculation additionally scales roughly as \( N_a^3 \), with \( N_a \) the number of atoms per 2D unit mesh. Tensor LEED is based on the idea that any small structural deviation from a given reference surface will only cause a small change in the overall LEED wave field diffracted by this surface. If this deviation could be treated by a perturbational approach, any calculations subsequent to the reference surface’s \( I_g(E) \) should only scale linearly in \( N_a \), allowing fast access to \( I_g(E) \) for a large portion of the required parameter space.

Eq. (3.15), the condensed version of full dynamical LEED, provides the seed for Tensor LEED. In principle, any structural modification which is localised at one particular lattice site \( i \) may be written as \( t^i \rightarrow \tilde{t}^i = t^i + \delta t^i \). Inserting this into Eq. (3.15) leads to the Green function of the modified surface,

\[
\tilde{G}^+ = G_0^+ \sum_i G_0^+(t^i + \delta t^i)G_0^+ + \sum_i \sum_{j,j \neq i} G_0^+(t^i + \delta t^i)G_0^+(t^j + \delta t^j)G_0^+ \ldots \tag{3.38}
\]

Assuming its absolute convergence, Eq. (3.38) can be rearranged as a power series in \( \delta t^i \),

\[
\tilde{G}^+ = G^+ + \sum_i C_{\text{start}}^i \cdot \delta t^i \cdot C_{\text{end}}^i + O[(\delta t^i)^2] \tag{3.39}
\]
3.4. “Tensor LEED” and the structural search

Figure 3.11: Visualisation of the Tensor LEED approximation to the full dynamical scattering path formalism (Eq. 3.39). Each scattering path contains the perturbation once at maximum. The perturbed part is further split into the paths which touch the reference structure only, and the modification $\delta t^i$.

Fig. 3.11 illustrates this central result graphically in the picture of scattering paths. In a series expansion, the zeroth order of $\tilde{G}^+$ must naturally equal the reference Green function $G^+$. The first order term in $\delta t^i$ contains the same paths again, but with exactly one scattering event at $t^i$ replaced by scattering only at its variation $\delta t^i$. So, the quantities $G_{\text{end}}^i$ and $G_{\text{start}}^i$ simply sum up all scattering paths ending at (coming from) lattice site $i$:

$$G_{\text{end}}^i = G^+ - G_0^+ t^i G_0^+ - \sum_{j \neq i} G_0^+ t^j G_0^+ t^i G_0^+ - \ldots \quad \text{and} \quad (3.40)$$

$$G_{\text{start}}^i = G_{\text{end}}^{i^*}$$

Both are formally almost identical due to the reciprocity of Green functions [Bil64]. Note that, by construction of Eq. (3.39), scattering events at $t^i$ and then $\delta t^i$ cannot immediately follow one another. The Tensor LEED approximation itself, in the order presented here, is obtained by neglecting all second and higher order terms in Eq. (3.39).\(^{17}\)

The LEED amplitudes diffracted from the modified surface, $\tilde{A}_{g'}^-$, arise from the equivalent of Eq. (3.21), which implies

$$\tilde{A}_{g'}^- = \langle k_{g'}^- | \phi^+ (k_\parallel) \rangle = \langle k_{g'}^- | \tilde{G}^+ | e (k_\parallel) \rangle \quad . \quad (3.41)$$

Note that the set of reciprocal lattice vectors of the modified surface, $\{g'\}$, may differ from that of the reference surface, $\{g\}$, e.g. due to a reconstruction not yet present in the latter. If we now insert the Tensor LEED approximation to $\tilde{G}^+$ into Eq. (3.41), we obtain

$$\tilde{A}_{g'}^- = A_{g'}^- + \sum_i \delta A_{g'}^i \quad (3.42)$$

\(^{17}\)In the original derivation of Tensor LEED [Rou86], this order is termed the “second level of sophistication” of the theory. On the “first level”, some additional approximations are made for $\delta t^i$, while the “third level” would additionally retain the second order terms in $\delta t^i$ in Eq. (3.39).
with
\[ \delta A_{g'}^{i} = \langle k_{g'} | G_{\text{end}}^{i,t} \cdot \delta t^{i} \cdot G_{\text{end}}^{i} | e(k_{||}) \rangle . \] (3.43)

In other words, the amplitude emerging from the modified surface is a simple sum of that from the original surface and a contribution \( \delta A_{g'}^{i} \) which is linear in \( \delta t^{i} \) from each modified lattice site \( i \), and otherwise depends on the reference structure only. As desired, we now have an expression which scales linearly in \( N_{s} \).

### 3.4.2 The application

In a LEED calculation, \( t \)-matrices are best written in angular momentum representation centred about the atomic position \( R_{0} \). As we shall see, \( \delta t^{i} \) must not be restricted to spherical symmetry in general, so that Eq. (3.43) becomes
\[ \delta A_{g'}^{i} = \sum_{l,m,l',m'} T_{g',l,m,l'}^{i} \cdot \langle R_{i}^{i}; l, m | \delta t^{i} | R_{i}^{i}; l', m' \rangle , \] (3.44)
with
\[ T_{g',l,m,l'}^{i} = \langle k_{g'} | G_{\text{end}}^{i,t} | R_{i}^{i}; l, m \rangle \cdot \langle R_{i}^{i}; l', m' | G_{\text{end}}^{i} | e(k_{||}) \rangle . \]

Interestingly, \( \delta A_{g'}^{i} \) depends on the modified surface only through \( \delta t^{i} \), while the Tensor \( T_{g',l,m,l'}^{i} \) can be obtained directly from the reference calculation. The strategy for parameter optimisation using Tensor LEED is illustrated in the flowchart of Fig. 3.12. The necessary steps are:

1. to perform a full dynamical reference calculation, storing the outgoing amplitudes \( A_{g}^{i} \) (as opposed to intensities only), and the components of the Tensor \( T_{g',l,m,l'}^{i} \),
2. to calculate and store amplitude changes \( \delta A_{g'}^{i} \) for each desired change in scattering behaviour \( \delta t^{i} \) within the parameter space to be tested,
3. to perform a structural search beginning with Eq. (3.42), using the previously stored \( A_{g}^{i} \) and \( \delta A_{g'}^{i} \). This procedure allows for both a fast grid search as well as more sophisticated search algorithms.

It should be emphasised that the use of Tensor LEED in the derivation of structural results has no consequences for their final accuracy. A practical Tensor LEED analysis usually employs several successive loops of reference calculation and structural search, with the final reference structure ideally identical to the best fit. Of course, structurally different model classes require separate initial reference structure calculations.

As for the first point, the amplitudes \( A_{g}^{i} \) are the normal targets of any full dynamical calculation. In contrast, deriving the Tensor seems to add a completely new dimension to this task. Fortunately, this is not the case. As visualised in Fig. 3.11, the Tensor components \( \langle R_{i}^{i}; l, m' | G_{\text{end}}^{i} | e(k_{||}) \rangle \) and \( \langle k_{g'} | G_{\text{end}}^{i,t} | R_{i}^{i}; l, m \rangle \) can be identified with those parts of a LEED wave function which are \textit{incident on but not yet scattered by atom \( i \)}. For \( \langle R_{i}^{i}; l, m' | G_{\text{end}}^{i} | e(k_{||}) \rangle \), this is immediately clear from the definition of \( G_{\text{end}}^{i} \). Eq. (3.40). For \( \langle k_{g'} | G_{\text{end}}^{i,t} | R_{i}^{i}; l, m \rangle \), it suffices that
\[ \langle k_{g'} | G_{\text{end}}^{i,t} | R_{i}^{i}; l, m \rangle \propto \langle R_{i}^{i}; l', m' | G_{\text{end}}^{i} | e(-k_{||} - g') \rangle . \] (3.45)
3.4. "Tensor LEED" and the structural search

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**Reference Calculation**

- Choose suitable model structure
- Perform full dynamic I(E) calculation
- Store:
  - Outgoing LEED amplitudes $A_{g'}$
  - Wave field components $A_{i\ell,m}(k\parallel), A_{i\ell,m}(-(k\parallel + g'))$
  for each atom $i$; for each beam $g'$

---

**Calculation of Amplitude Changes**

For each atomic site $i$:

- Choose suitable variational steps:
  - chemical element
  - position
  - thermal displacement
- Calculate and store $\delta \tilde{A}_{i,g'}(\ell_1, \delta \mathbf{r}_i, a_{\text{vib},i})$

---

**Superposition and Search Procedure**

- Choose a combination of model parameters
- Calculate model I(E) spectra from $A_{g'}$ and $\delta \tilde{A}_{i,g'}$
- Compute R-factor between measured and model I(E) spectra
  until global R-factor minimum within chosen portion of parameter space is identified

---

Is best fit close enough to reference structure?

No

Yes

Structural Analysis accomplished.

---

Figure 3.12: Flowchart of a complete structural analysis for one model class, using the TensErLEED program package.
The right hand side can be understood as parts of a time-reversed LEED state, but for a primary beam incident from the direction of the actual diffracted beam $k_{0\gamma}$. While the explicit calculation of $|\Phi^+(k_{0\gamma})|$ within the crystal is usually avoided in the full dynamical scheme of Sect. 3.2.4, the additional computational effort here is relatively small. Proper utilisation of the scattering operators already obtained in the construction of layer diffraction matrices $M_{g_0h_2}^{\pm\pm}$ (either for Bravais or for composite layers), and in the course of layer stacking, does the trick (see Ref. [Blu01] and references therein).

In the versatility of the second step, i.e. the flexibility of $\delta t_i$ to embody different possible structural modifications of the surface, lies the true power of Tensor LEED.

- **Geometrical Tensor LEED.**
  The most frequent application of LEED is the determination of surface geometry. The trick to apply Tensor LEED here is to realize that the atomic scattering potential $v_i(r - R')$, when spatially shifted by an amount $\delta r^i$, is still represented by the same $t$-matrix elements, but now in a basis $\{|R^i + \delta r^i; l, m\}$ instead of $\{|R^i; l, m\}$ as before. Denoting the shifted $t$-matrix by $\tilde{t}$, this can be expressed using quantum mechanical translation operators $\tau(\delta r^i)$ of the general form $\langle \delta r^i; l', m'|0; l, m \rangle$:
  \[
  \delta t^i = \tilde{t}^i - \tilde{t}^i = \tau(\delta r^i) \cdot t^i \cdot \tau(-\delta r^i) - t^i. \quad (3.46)
  \]
  Refs. [Rou89, Rou89b, Rou89c] should be consulted for further numerical details. The validity range of geometrical Tensor LEED extends up to $|\delta r^i| \lesssim 0.4 \text{ Å}$ [Rou92], but naturally depends on the strength of the scatterer in question (heavy elements may show a reduced validity), and the number of simultaneously displaced atoms.

- **Thermal Tensor LEED.**
  Through Eqs. (3.17) and (3.18), thermal vibrations in LEED are most conveniently accounted for in the atomic $t$-matrix [Loe94]. So, when changing a thermal vibrational amplitude from $u^i$ to $\tilde{u}^i$, the corresponding change in $t$-matrix reads simply
  \[
  \delta t^i = \tilde{t}^i(u^i) - t^i(u^i). \quad (3.47)
  \]
  The validity range of thermal Tensor LEED is large, and probably limited by the maximum angular momentum quantum number used in the inversion of Eq. (3.17), rather than the Tensor LEED approximation itself.

- **Chemical Tensor LEED.**
  The representation of chemical properties in LEED also directly affects the atomic $t$-matrix. For instance, consider a lattice site $i$ which is randomly occupied by two elements A and B. If the occupation probability by A is changed from $x^i$ in the reference structure to $\tilde{x}^i = x^i + \delta x^i$ in the modified structure, the ATA (Eq. (3.16) prescribes [Doe93, Hnz96]
  \[
  \delta t^i = \tilde{x}^i t_A + (1 - \tilde{x}^i)t_B - t^i = \delta x^i (t_A - t_B). \quad (3.48)
  \]
  The validity range of chemical Tensor LEED depends strongly on the elements in question. For combinations such as Fe-Al and Co-Al, its reliability is proven, and reaches up to the “exchange” of entire atoms in the model surface’s 2D unit mesh [Ktk97b].
3.4. “Tensor LEED” and the structural search

- Further applications.
  In principle, the Tensor LEED formalism allows to incorporate any change of scattering properties which can be expressed by the modification of an isolated $t$-matrix $t^i$. For instance, the method was used to model anharmonic and anisotropic temperature factors [Loe95, Loe95b], and asphericities of the MT potential $v^i$ itself [Rub95].

In practice, the calculation of amplitude changes must be done simultaneously for all modification of the same scatterer $i$. The straightforward combination of the above applications thus includes substitutional disorder with element-dependent positions and vibrational amplitudes on the same lattice site:

$$
\delta t^i = \tilde{x}^i \tau(\delta r_A^i) \cdot t_A(\tilde{v}_A^i) \cdot \tau(-\delta r_A^i) - (1 - \tilde{x}^i) \tau(\delta r_B^i) \cdot t_B(\tilde{v}_B^i) \cdot \tau(-\delta r_B^i) - t^i.
$$ (3.49)

For binary alloy surfaces, it is particularly convenient to have a formalism at hand which allows for independent positions of different elements on equivalent, randomly occupied lattice sites. This possibility was already mentioned in Sect. 3.3.1, but would require to handle aspherical $t$-matrices in a full dynamical calculation. In contrast, Tensor LEED grants direct access to this type of structural modification. So, apart from speeding up calculations, Tensor LEED also offers an inherent advantage for the study of alloy surfaces [Blu96].

3.4.3 The search strategy

What remains to be addressed is the structural search methodology, employed once the reference amplitudes $A_g^-$ and all possible amplitude changes $\delta A_g^-$ have been calculated. With this input data at hand, the straightforward strategy might seem to be a grid search, i.e. to calculate $I_g(E)$ for all possible geometric, vibrational, chemical, etc. parameter step combinations, and compare them to experiment. However, as outlined in Sect. 3.3.1, the number of free parameters $p$ may easily exceed ten even for simple structures. Assuming ten grid steps per parameter, already the necessary $10^p$ R-factor evaluations are computationally unacceptable, and a more sophisticated approach must be envisioned. Many “classic” optimisation algorithms employ local search schemes [Cow87, Kle89, Kle90, Rou90, Ovr92], typically following the R-factor gradient from a certain start structure into the nearest local minimum. A drawback of this method is that the R-factor hypersurface may be quite complex due to multiple scattering and the sheer number of free parameters, allowing for several local minima apart from the truly global one.

The main reason to use local search schemes is that they usually require relatively few iterations to converge, i.e. need few time-consuming individual $I_g(E)$ calculations. With Tensor LEED at hand, this problem is obsolete, and an altogether different, statistical search strategy is employed within the TensErLEED package. This algorithm, developed by Kottcke and Heinz [Ktk97], begins by randomly choosing a set of trial structures from the allotted parameter space. Each trial structure then develops towards the R-factor minimum individually in the following way. A new set of parameter values is chosen randomly, using a Gaussian probability distribution (PD) centred about the original trial structure. If the R-factor associated with the new structure is lower than the previous one, this structure is accepted, and the search continues from there. Otherwise, the former structure is
Chapter 3. Surface crystallography by LEED

This step-wise procedure is executed simultaneously for each independent trial structure until a certain number of them (e.g., 20 %) have converged into the same structural minimum. Within this scheme, the main trick is to handle the Gaussian PD for each fit parameter and each trial structure properly. Its width scales both with the sensitivity of an individual fit parameter, and with the average R-factor reached. Thus, the search procedure can act relatively “globally” while far away from the true minimum, i.e. for high $R_P$. On the other hand, it becomes an “almost local” search scheme at low $R_P$, when convergence is almost reached.

The numerical intricacies associated with this search strategy are important for its functioning [Ktk97], but do not play any large role in the present thesis – essentially, “it worked”. However, a few practical remarks seem in order. First, with $p^{2.5}$, the scaling found by Kottcke and Heinz is worse than that reported for local search schemes, $p^2$, but clearly better than $p^6$ of the truly global simulated annealing algorithm [Rou93]. Second, with several trial structures developing towards the minimum simultaneously, the algorithm provides some insights into the parameter space beyond the mere global minimum itself. For instance, if there were several local minima in addition to the global one, some trial structures would end up in local minima in addition to those in the global one, thus revealing an important property of the scattering problem at hand. Third, it must be noted that the convergence properties of the method depend on the number and nature of the free parameters investigated. As a rule of thumb, convergence is fast for $p \lesssim 10$. Above, convergence can usually still be attained, but may take much longer if parameters with widely different sensitivities are involved. Finally, proper convergence can not always be expected for $p \gtrsim 15$ – the overall number of grid points simply becomes too large. Nevertheless, convergence can be attained approximately in these latter cases, i.e. clearly within the limits of error of the true best fit: A number of trial structures will always end up very near one another, and hence very close to the global minimum (well within the limits set by $R_{\text{min}} \cdot RR$). Due to the complexity of the parameter space at hand, even getting this close to the “true” best fit within a finite stretch of time must be considered a great achievement.

3.5 Summary

In summary, the present chapter provides the necessary technical means to perform LEED $I_g(E)$ analyses successfully. Today’s sophisticated experimental procedures and the full dynamical theory of LEED form the foundation for an accurate comparison of experimental and calculated intensities. Established statistical tools such as Pendry’s R-factor $R_P$ and its “reliability” $RR$ are available for structure optimisation by a many-parameter fit. By allowing to access $I_g(E)$ extremely fast for many different structures in the vicinity of one reference structure, the Tensor LEED approximation greatly facilitates the practical determination of the best fit, enabling a fast and reliable R-factor minimum search. With these utilities at hand, we can turn towards the actual LEED structural analyses envisioned in this work. As mentioned above, we shall also encounter questions of methodological relevance to LEED on this path, particularly with respect to the intricacies of many-parameter problems. Sects. 4.3 on Fe$_{0.85}$Al$_{0.15}$(100) and 5.4 on CoAl(111) deserve the particular attention of the reader interested in such aspects.
Chapter 4

The structure of Fe$_{1-x}$Al$_x$(100) surfaces

As already mentioned in Sect. 2.3, the segregation of Al to bcc based Fe$_{1-x}$Al$_x$ surfaces is an established fact for many surface orientations [Ham98], and particularly for (100) oriented faces. Generally, the latter class of systems seems quite well-behaved, i.e. shows no large-scale or incommensurate reconstructions, or general surface instabilities, as other orientations. Thus, it offers an ideal opportunity to study the interrelation of order and segregation on a bcc-based lattice in greater detail.

Of course, the central prerequisite for this task is a comprehensive crystallographic analysis of the near-surface elemental distribution across the entire bcc based range of compositions. This, it turns out, is as yet lacking. For $x = 0.02$ [Rue86] and 0.15 [Elt97] in the A2 random alloy region, only qualitative studies by AES and LEED were reported so far. In contrast, a quantitative LEED analysis exists for a metastable, D0$_3$-ordered near-surface phase [Ktk96], but not yet for a bulk D0$_3$ sample. Clearly, the B2 phase is best investigated, with quantitative LEED studies for $x = 0.46$ [Wan93] and 0.47 [Ktk96, Ktk97b]. Yet, while the overall findings of both groups agree quite closely, they differ just with respect to near-surface order, which is crucial to the present work.

This chapter aims to provide a complete picture of surface stoichiometry and order in bcc based Fe$_{1-x}$Al$_x$(100). To that end, it features structural analyses of well-equilibrated samples for $x = 0.03$, 0.15, 0.30, and 0.47. For $x = 0.03$ and $x = 0.15$, these studies are the first of their kind. In the D0$_3$ range ($x = 0.30$), one may hope to confirm the stoichiometry of the metastable phase [Ktk96, Ktk97b] also for a bulk crystal. Finally, the reanalysis of $x = 0.47$ should shed some additional light on the question of near-surface antisite defects in B2 Fe-Al(100). In all this work, we must of course grant a central place to the question of the “chemical” accuracy which can be achieved. In the following, we shall first summarise the experimental evidence on which our structural analyses are based, and describe their technical implementation. Of the individual samples, Fe$_{0.86}$Al$_{0.15}$(100) is singled out in Sect. 4.3, employing this surface also as a model system to discuss the factors which affect the chemical accuracy of LEED, in particular the impact of parameter correlations. Equipped with this background, Sect. 4.4 presents results for $x = 0.03$, 0.30, and 0.47. Finally, Sect. 4.5 identifies structural trends across the range of investigated samples. It should be noted that many of the results presented below are also described in Refs. [Blu01b, Blu01c].
Chapter 4. The structure of Fe$_{1-x}$Al$_x$(100) surfaces

4.1 Experimental characterisation

The preparation and equilibration of Fe$_{1-x}$Al$_x$(100) surfaces already served as a showpiece for the general annealing behaviour expected for TM-Al surfaces in Sect. 2.4. In brief, each sample investigated here was initially sputtered, preferentially removing Al from the surface. Compositional equilibrium with the bulk is then re-established by heating to high $T_{\text{anneal}}$. Finally, quenching to the LEED measurement temperature $T_{\text{meas}} \approx 100\,K$ freezes the near-surface stoichiometry and order at some effective equilibration temperature $T_{\text{eq}}$. As we would like to place our findings in the context of equilibrium thermodynamics later, all structural analyses were performed after annealing in the high-temperature plateau ranges of Fig. 2.8. This region indicates that the near-surface composition has largely stabilised, so that the results should reflect the equilibrium behaviour of the bulk samples at $T_{\text{eq}}$. In the following, the available experimental pre-information is summarised for each sample. As stated in the introduction, this experimental work constitutes part of the thesis work of others, specifically Dipl. Phys. W. Meier.

$\text{Fe}_{0.97}\text{Al}_{0.03}(100)$-c$(2 \times 2)^1$.

Of the investigated samples, this was the only one to show a persistent tendency towards impurity segregation (carbon and sulfur) apart from that expected for Al. Upon annealing a weakly sputtered surface, C begins to segregate around $T_{\text{anneal}} \approx 600\,K$. According to AES, its surface concentration reaches a maximum for $T_{\text{anneal}} \approx 700\,K$, before it is displaced entirely, and irreversibly, by segregating Al at $T_{\text{anneal}} \approx 850\,K$. Between 850 K and 1100 K, Al is the only segregant detectable by AES, before S appears in the near-surface region from about 1150 K on. All three elements form c$(2 \times 2)$ superstructures, i.e. cannot be distinguished by the LEED pattern itself. However, their respective spot intensities are strikingly different, allowing to correlate each ordered phase with one segregant only. The structural development during the cosegregation of C, Al and S to the (nominal) Fe$_{0.97}$Al$_{0.03}$(100) surface was only recently analysed by quantitative LEED [Smi01, Smi01b], and further details should be sought there. Here, the emphasis rests with Fe$_{0.97}$Al$_{0.03}$(100)-c$(2 \times 2)^1$, induced by Al segregation, which can be studied in its pure form for 850 K $\lesssim T_{\text{anneal}} \lesssim 1100\,K$. Moreover, it proved possible to fully remove the C contamination by prolonged initial sputtering. Following this procedure, C only returns to the surface region after annealing to above 1150 K. So, the AES plot of Fig. 2.8 and the LEED $I_g(E)$ data sets analysed below are unencumbered by the cosegregation of any other element.

According to Fig. 2.8, Fe$_{0.97}$Al$_{0.03}$(100) reaches its high-temperature plateau for $T_{\text{anneal}} \gtrsim 850\,K$. The superstructure which forms in this range, denoted c$(2 \times 2)^1$ in Ref. [Mei01], was already noted in Ref. [Rue86], and appears best developed for $T_{\text{anneal}} \approx 1000\,K$. No further experimental pre-information exists for this surface phase itself. However, the (metastable) Fe$_{0.85}$Al$_{0.15}$(100)-c$(2 \times 2)^1$ surface must be structurally very similar, according to its LEED $I_g(E)$ spectra [Mei01]. For this structure, STM and LEIS investigations were carried out with the help of Dr. E. Lundgren and Dr. M. Schmid (Vienna).
4.1 Experimental characterisation

Fig. 4.1 shows an atomically resolved STM image of Fe$_{0.85}$Al$_{0.15}$(100)-c(2×2)$_I$, clearly displaying large, nearly perfectly ordered areas of c(2×2) periodicity. The latter can be visually distinguished from a (1×1) arrangement by an antiphase boundary, which is associated with the (untypically large) defect near the centre of the image. The surface’s average apparent corrugation, between 0.15 and 0.20 Å, is relatively small, and only one “atomic” protrusion appears per c(2×2) unit mesh. LEIS measurements of the surface stoichiometry (carried out in the [011] azimuth) clearly indicate the presence of both Fe and Al at the very surface. Together with the proven segregation tendency of Al, these results are compatible with two different structural models. The surface might either consist of a mixed, almost perfectly checkboard-like Fe-Al layer, or of a well-ordered array of Al adatoms and vacancies on a Fe layer (in that case, LEIS would “see” the second layer Fe atoms). Transferring this result to Fe$_{0.97}$Al$_{0.03}$(100)-c(2×2)$_I$, the decision between both models rests with the LEED analysis below.

Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{II}$.

In Fig. 2.8, the high-temperature AES plateau for Fe$_{0.85}$Al$_{0.15}$(100) is less well defined than that for Fe$_{0.97}$Al$_{0.03}$(100). Nevertheless, $r_{AES}$ definitely appears stabilised for $T_{\text{anneal}} \geq 900$ K, the region associated with the (1×1)$_{II}$ superstructure in LEED. While the integer order LEED spots of this arrangement appear bright and sharp, it is noteworthy that this surface also displays some noticeable, diffuse intensity around the half-order spot positions of a c(2×2) arrangement. Attempts to measure the I($E$) characteristics for the (1/2,1/2) spot area showed this to be relatively similar to that of the ordered (1/2,1/2) spot of Fe$_{0.97}$Al$_{0.03}$(100)-c(2×2)$_I$ [Mei01], despite the integer order I($E$) spectra of both surfaces being distinctly different (compare, for instance, Figs. 4.5 and 4.9 below). As mentioned in Sect. 3.1, diffuse intensity from alloy surfaces may be related to short-range order. Thus, we may conclude that the SRO in Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{II}$ bears some resemblance to the LRO of Fe$_{0.97}$Al$_{0.03}$(100)-c(2×2)$_I$.

Additional STM and LEIS measurements for this surface (also performed with help of the Vienna group) shed further light on the properties of Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{II}$. The atomically resolved STM image in Fig. 4.2b clearly shows two different chemical species in the top layer lattice, the minority as protrusions, and the majority as dark indentations, with an average apparent height difference of only 0.21 Å. Evaluating several STM images quantitatively yields an average occupation of the top layer by 76 % “indentations” and 24 % “protrusions”. The distribution of both is not truly random: “protrusions” hardly ever reside immediately next to one another, but rather form small patches of local c(2×2) symmetry. As guessed above, this SRO indeed resembles the c(2×2)$_I$-
Chapter 4. The structure of Fe$_{1-x}$Al$_x$(100) surfaces

LRO qualitatively. It is also noteworthy that STM images of Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{II}$ show some additional corrugation on the scale of a few nm. Although speculative, it is possible that local fluctuations of the subsurface composition manifest themselves in this way. Finally, LEIS definitely clarifies the top layer stoichiometry of Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{II}$. Assuming the top layer of the c(2×2)$_I$ phase to consist of both atomic species (as plausible from comparing the STM images of both surfaces, and definitely proven in the structural analysis below), one may use the surface stoichiometry of Fe$_{0.85}$Al$_{0.15}$(100)-c(2×2)$_I$, exactly 50 % Al and 50 % Fe in STM, to calibrate the sensitivity of LEIS. From LEIS spectra from Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{II}$ (see Fig. 4.2a for a typical example) with this calibration, around 75 % of the surface should consist of Al, with the other 25 % occupied by Fe. The agreement between atom counting in STM and the LEIS result is remarkable, lending additional credibility to both results.

In total, we may conclude that Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{II}$ features a mixed top layer, composed of 75 % Al and 25 % Fe. Additionally, both species form a short-range ordered arrangement, indicating an effective repulsion of Fe atoms on immediately adjacent sites. This rather detailed pre-information serves as a fixed condition in the LEED analysis below. Furthermore, it provides an important benchmark against which to test the attainable chemical accuracy in LEED.

$Fe_{0.70}Al_{0.30}(100)$-c(2×2)$_{II}$.

The high-temperature AES plateau for this sample begins at $T_{\text{anneal}} \gtrsim 700$ K, although its onset is even less well defined than for $x = 0.15$ in Fig. 2.8. The c(2×2)$_{II}$ superstructure resembles c(2×2)$_I$ only periodicity-wise; clear differences of their $I_g(E)$ characteristics reveal that they must be of different structural origin (compare, for instance, Figs. 4.9 and 4.12). In contrast, $I_g(E)$ for Fe$_{0.70}$Al$_{0.30}$(100)-c(2×2)$_{II}$ are very close to the intermediate Fe$_{0.53}$Al$_{0.47}$(100)-c(2×2)$_{II}$ phase [Ktk96, Mei01]. As mentioned, a LEED analysis already exists for the latter phase [Ktk96, Ktk97b],

Figure 4.2: (a) Room temperature STM image of Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{II}$ (100 × 83 Å², sample voltage -6 mV, tunneling current 0.46 nA). Clear chemical contrast between Fe (protrusions) and Al (indentations) is achieved, indicating $x^I = 75$ % Al. (b) LEIS spectrum from Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{II}$, taken in the [011] azimuth, indicating $x^I = 76$ % Al if calibrated against Fe$_{0.85}$Al$_{0.15}$(100)-c(2×2)$_I$. 

Fe$_{0.70}Al_{0.30}$(100)-c(2×2)$_{II}$.
4.2 Technical remarks

finding an Al-capped D0\textsubscript{3} film thicker than the “information depth” of LEED, with the top layer composition additionally supported by LEIS [Ove95]. So, only this structural model is tested for our case below. It should be noted that the annealed Fe\textsubscript{0.70}Al\textsubscript{0.30}(100) surface shows a reversible phase transition c(2×2) ↔ (1×1) at \(T \approx 700\,\text{K}\), consistent with the bulk D0\textsubscript{3} ↔ B2 transition for \(x \approx 0.30\) (Sect. 2.1). However, even quench times of 2 min down to \(T_{\text{meas}} \approx 100\,\text{K}\) are still too long to prevent ordering. An important implication of this finding is that \(T_{\text{eq}}\), the temperature to which the near-surface order and segregation of this surface correspond, must lie clearly below 700 K.

\(\text{Fe}_{0.53}\text{Al}_{0.47}(100)-(1×1)^{\text{III}}\).

The preparation conditions to achieve a stable and reproducible Fe\textsubscript{0.53}Al\textsubscript{0.47}(100)-(1×1)^{\text{III}} surface have been described several times before in the literature [Wan93, Gra95, Mei01]. Essentially, Fig. 2.8 shows the onset of the high-temperature plateau of this sample at \(T_{\text{anneal}} \gtrsim 750\,\text{K}\); it is somewhat better defined than for Fe\textsubscript{0.70}Al\textsubscript{0.30}(100). It should be noted that LEIS experiments performed by Overbury [Ove95] clearly show the top layer of Fe\textsubscript{0.53}Al\textsubscript{0.47}(100)-(1×1)^{\text{III}} to consist of Al only, so that this assumption could enter the LEED analyses below as a fixed condition.

4.2 Technical remarks

With the preceding knowledge established, it remains to perform the LEED analyses necessary for the detailed structural understanding of Fe\textsubscript{1−x}Al\textsubscript{x}(100) surfaces. Table 4.1 summarises some important characteristics of the \(I_g(E)\) data sets analysed below. All measurements were performed with the sample at liquid nitrogen temperature (\(T_{\text{meas}} \approx 100\,\text{K}\), after annealing the surface in the high-temperature plateau range of Fig. 2.8 for several minutes. In each case, the data base covers incident energies between 20 and 500 eV. The resulting total experimental energy widths \(\Delta E_{\text{int}} \approx 2000\,\text{eV}\) for eight inequivalent integer beams, and (where available) \(\Delta E_{\text{frac}} \approx 1000\,\text{eV}\) for three inequivalent half-order beams should guarantee very low statistical limits of error in view of Eq. (3.37).

Table 4.1 also lists \(\overline{R_s}\), the set-averaged R-factor between \(I_g(E)\) for nominally symmetry-equivalent \(g\), which was already discussed in Sect. 3.3.3. Two important conclusions may be drawn from the very low \(\overline{R_s}\) values in Table 4.1. First, we may safely conclude that deviations from normal incidence can hardly introduce any significant systematic errors into the analyses below, especially since this error is again reduced drastically by symmetry-averaging [Lin83]. Second, the statistical noise level in the measurements must also be extremely low, so that even very fine structural details of each surface should be accessible by the LEED analyses. In fact, the experimental reproducibility of the final \(I_g(E)\) was directly tested for \(x = 0.03, 0.15, \text{and } 0.30\), and yielded Pendry R-factors well below 0.05 for the symmetry-averaged spectra in each case.

Due to the contamination issue mentioned above, the \(x = 0.03\) sample received some extra attention. In addition to the data listed in Table 4.1, a second data set for this sample was measured after annealing to 1120 K, i.e. just below the expected onset of S segregation. The \(I_g(E)\) curves themselves, which originate only from the long-range ordered parts of the surface, agree quite closely between both sets \((R_P = 0.06)\). Correspondingly, the full structural analysis of the 1120 K
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<table>
<thead>
<tr>
<th>$x$</th>
<th>LEED pattern</th>
<th>$T_{\text{anneal}}$</th>
<th>int. beams</th>
<th>frac. beams</th>
<th>$\Delta E_{\text{int}}$</th>
<th>$\Delta E_{\text{frac}}$</th>
<th>$R_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>c(2×2)$^I$</td>
<td>960 K</td>
<td>8</td>
<td>3</td>
<td>2012 eV</td>
<td>846 eV</td>
<td>0.079</td>
</tr>
<tr>
<td>0.15</td>
<td>(1×1)$^{II}$</td>
<td>1200 K</td>
<td>8</td>
<td>—</td>
<td>2019 eV</td>
<td>—</td>
<td>0.055</td>
</tr>
<tr>
<td>0.30</td>
<td>c(2×2)$^{II}$</td>
<td>1000 K</td>
<td>8</td>
<td>3</td>
<td>2058 eV</td>
<td>1047 eV</td>
<td>0.092</td>
</tr>
<tr>
<td>0.47</td>
<td>(1×1)$^{III}$</td>
<td>970 K</td>
<td>8</td>
<td>—</td>
<td>1887 eV</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 4.1: Characteristics of the experimental $I_g(E)$ data sets used in the structural analyses of Fe$_{1-x}$Al$_x$(100) in Sects. 4.3 and 4.4. For consistency with Ref. [Ktk97b], the set for $x = 0.47$ is the same as used there ($T_{\text{meas}} \approx 120$ K). Unfortunately, information on $R_s$ is not available any more.

data shows little difference to the eventual results of Fig. 4.10 – all best fit parameters fall into their mutual statistical error limits. Nevertheless, the experiment-theory agreement reached for the fractional-order beams at 1120 K is systematically worse than for the 960 K data set. Moreover, the former is characterised by a significantly lower energy- and beam-averaged ratio of fractional-order and integer-order intensities ($I_{\text{frac}}/I_{\text{int}} = 0.28$ instead of 0.53 for $T_{\text{anneal}} = 960$ K), indicating an already reduced quality of surface order. Since, in principle, this could be related to a beginning S contamination (not yet measurable in AES), the discussion below focuses on the 960 K data only, for which such systematic errors can be ruled out.

Since the objective for $x = 0.47$ is to clarify an issue raised in earlier work [Ktk96, Ktk97b], the data set listed in Table 4.1 is the same as used previously (“120 K” data of Kottcke [Ktk97b]). Nevertheless, another set was measured by W. Meier under formally identical conditions, but in a different vacuum chamber with different instrument types. The agreement between both is extremely close, and a complete structural analysis of the new data set yielded exactly the same results as obtained with the previous one (see later, Table 4.4).

On the numerical side, all LEED analyses below were performed by the means described in Chapter 3. In particular, this includes the TensErLEED program package [Blu01] (Sect. 3.4), and the established, Erlangen-based phase shift package [Lib65, Koe69, Grn77]. The fully relativistic and spin-averaged phase shifts for Al and Fe were calculated for a B2-ordered bulk crystal (the same phase shifts were already used in earlier work [Ktk96, Ktk97b]). For the $x = 0.03$, 0.15, and 0.30 samples, $V_{0r}(E)$ was used as determined by Rundgren [Run01] for bulk bcc Fe,

$$V_{0r}^{Fe}(E) = V_{00} + \max \left( -10.3, 0.39 - \frac{76.63}{(E/\text{eV}) + 9.68} \right) \text{eV} \quad (4.1)$$

This expression turns out to be extremely close to that for a B2 FeAl bulk, i.e. indeed reflects the entire bcc-based concentration range of Fe-Al alloys accurately. For $x = 0.47$, a different approach to $V_{0r}(E)$ was chosen to maintain consistency with Refs. [Ktk96, Ktk97b]. As mentioned in Sect. 3.2.1, a systematic error for the lattice parameter $a$ arises if the average slope of $V_{0r}(E)$ is neglected [Wal00]. Vice versa, using a linear approximation to $V_{0r}(E)$ should avoid this particular problem. With an XRD room temperature lattice parameter as a fixed input condition, Kottcke [Ktk97b] determined $V_{0r}(E) = V_{00} + E/150$ for a room temperature $I_g(E)$ data set. This formula
4.3 The question of chemical accuracy: Fe$_{0.85}$Al$_{0.15}$(100)-(1$\times$1)$^{II}$

then allowed to determine $\alpha$ for the data set of Table 4.1, was also used in the present work. It should be emphasised again that the overall impact of the energy dependence of the MT potential is a small effect in quantitative LEED, and that the above procedure should be sufficient to account for its salient features. Consistently, explicit test calculations for Fe$_{0.85}$Al$_{0.15}$(100)-(1$\times$1)$^{I}$ and Fe$_{0.53}$Al$_{0.47}$(100)-(1$\times$1)$^{I}$ with a fully consistent MT potential (i.e. with energy-dependent exchange-correlation also considered in the phase shifts) after Rundgren [Run01] showed no differences in the optimised parameters, although the best-fit R-factor levels improved slightly.

In the multiple scattering calculations, $l_{\text{max}} = 10$ sufficed to guarantee well converged $I_g(E)$. Nevertheless, $l_{\text{max}} = 12$ was mostly used, e.g. to ensure an enhanced Tensor LEED validity in the single- and all-parameter R-factor scans for Fe$_{0.85}$Al$_{0.15}$(100)-(1$\times$1)$^{I}$ in Sect. 4.3. All analyses included an energy-independent damping constant $V_{0i}$, which reflects its known behaviour quite accurately at least above $\approx 50$ eV. For $x = 0.03$ and 0.15, $V_{0i}$ was kept fixed at 5 eV, and the validity of this assumption checked by test calculations only. For $x = 0.30$ and 0.47, best fit values of $V_{0i} = 5.5$ and 6.5 eV resulted, respectively. In line with Sect. 3.2.4, the full dynamical parts of all calculations were performed using the reliable layer-stacking scheme. For parameter optimisation, Tensor LEED was used wherever possible – only bulk quantities inaccessible to the method ($\alpha$, $V_{0i}$, $u^b$) were varied by separate iterations. All best-fit results are structurally close enough to the initially chosen, truncated-bulk-like Tensor LEED reference structures to fully guarantee the validity of the method. Of course, several successive Tensor LEED reference calculations were performed in each case, until the reference structure and the best fit did not deviate from one another any more.

In total, the applied experimental and calculational procedures should guarantee for highly precise structural analyses in principle. Nevertheless, there remains the question of structural accuracy in a many-parameter problem, to be exemplified once for Fe$_{0.85}$Al$_{0.15}$(100)-(1$\times$1)$^{II}$ in the following section.

4.3 The question of chemical accuracy: Fe$_{0.85}$Al$_{0.15}$(100)-(1$\times$1)$^{II}$

The intricacies of a many-parameter problem have already been alluded to in Sect. 3.3, highlighting especially the problem of possible parameter correlations. Of course, this issue might influence all structural analyses presented in this work, and we require a clear understanding of its implications – particularly for the “chemical” accuracy attainable in LEED, since it directly touches the objective of this work. Some studies to that extent already exist by the Vienna group [Spo98, Pla99, Pla99b] for Pt-based alloy systems. Essentially, these studies noticed significantly larger statistical error bars when using all-parameter R-factor scans together with $RR$ instead of single-parameter error limits. On the other hand, their model experiments seem to imply a much better precision of LEED results in comparisons to other composition-sensitive techniques than all-parameter estimates would warrant. In short, these results hint to a possible impact of parameter correlations on concentration parameters determined by LEED. It is therefore of central importance to check whether such correlations exist for the systems of interest here, and unravel their physical origin, if possible.
For an in-depth study of “chemical accuracy” in LEED, we shall single out the Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{\text{II}}$ surface, which we have already encountered in Chapter 3. As seen in Sect. 4.1, the statistical reliability of the available $I_g(E)$ data is high. Moreover, its top layer stoichiometry $x^1$ is accurately known from STM and LEIS, rendering this quantity an ideal “benchmark” for LEED. The next section summarises the structural best fit for Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{\text{II}}$ when all reasonable constraints are taken into account, and discusses its reliability. On this basis, we then investigate the role of parameter correlations for its top layer stoichiometry, discuss their physical origin, and demonstrate a possible impact of systematic errors of the model on $x^1$. Of course, all structural analyses presented in this work benefit from the lessons drawn from Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{\text{II}}$.

4.3.1 The best fit

The extent of the parameter space which should be considered for Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{\text{II}}$ was already outlined in Sect 3.3.1. In brief, it comprises the composition of the topmost four layers, $x^1$–$x^4$, element-dependent positions $h^1_{\text{Al}}$–$h^2_{\text{Fe}}$ and vibrations $u^1_{\text{Al}}$–$u^2_{\text{Fe}}$ in the topmost two layers, and the average positions of the third and fourth layer. Bulk vibrational amplitudes $u^i_{\text{Al}}$ and $u^i_{\text{Fe}}$, the lattice parameter $a$, a possible constant shift of the muffin-tin zero $V_{00}$, and constant $V_{0i}$ complete the picture. As mentioned before, this would leave us with a theoretical total of 19 free parameters in the analysis.

Fortunately, $x^1 = 0.75$ can directly be taken over from STM and LEIS (Sect. 4.1), since the excellent accuracy of both methods in this respect is well established [Pla99, Pla99b]. Moreover, already the fit results achieved from the initial Tensor LEED reference calculation indicates only Al concentrations $x^i \leq 0.2$ for layers $i > 2$ (below the topmost one). Since Al is the weaker scatterer anyway, the determination of element-dependent vibrational amplitudes can hardly be expected to yield meaningful results in these layers, and the additional restrictions $u^b_{\text{Al}} = u^b_{\text{Fe}} =: u^b$ and $u^2_{\text{Al}} = u^2_{\text{Fe}} =: u^2$ were imposed for want of a better approximation.$^1$ The same applies to $h^2_{\text{Al}}$ and $h^2_{\text{Fe}}$, i.e. $h^2_{\text{Al}} = h^2_{\text{Fe}}$ was assumed.

The best-fit result for the remaining 15 free parameters is visualised in Fig. 4.3, and summarised in the accompanying table, together with single-parameter error limits as defined in Sect. 3.3.3. For the notation of geometry parameters, interlayer distances $d^i$ and intralayer “buckling” amplitudes $b^i$ are used according to the convention defined in Sect. 2.2.

First and foremost, the agreement between experimental and calculated $I_g(E)$ is excellent, monitored by a best fit Pendry R-factor $R_{\text{min}} = 0.069$, and $R_{\text{min}} \cdot RR = 0.010$ indicates a high statistical reliability of the fit results. In fact, $R_{\text{min}}$ lies only little above $\overline{R_s} = 0.055$ from Table 4.1. In view of

$^1$It should be noted that the parameter correlations of Sect. 4.3.3 certainly have their analogon in the second layer and below. So, if $u^2_{\text{Al}}$ and $u^2_{\text{Fe}}$, or $u^1_{\text{Al}}$ and $u^1_{\text{Fe}}$, really were very different for some reason, they might yet induce some systematic error in the fit. Nevertheless, the assumptions made are at least consistent with all known related findings. The eventual best fit shows $u^1_{\text{Al}} \approx u^1_{\text{Fe}}$; $u^b_{\text{Al}}$ and $u^b_{\text{Fe}}$ take on similar values when determined explicitly for $x = 0.30$ and $x = 0.47$ in Sect. 4.4; theoretical and experimental studies for ordered B2 NiAl indicate $u^b_{\text{Al}} \approx u^b_{\text{Ni}}$ there [Geo77, Gum96, Nue98]; and a detailed study of atomic mean-square displacements in bulk Fe$_{0.80}$Al$_{0.20}$ by neutron and $\gamma$ ray diffraction produced reasonable results when assuming $u^b_{\text{Al}} = u^b_{\text{Fe}}$ [Pie89].
4.3. The question of chemical accuracy: Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{II}$

The question of chemical accuracy: Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{II}$

- **Fe**
- **Al**

Figure 4.3: Illustration of the best fit structural model for Fe$_{0.85}$Al$_{0.15}$(10×1)$_{II}$ as described in the text. All best-fit parameters are listed in the accompanying table.

- **Remarks of Sect. 3.3.3**, this result is reassuring: $R_{\text{min}}$ reflects the expected, residual statistical noise of the measurement approximately correctly, and there is no reason to fear an overfit by too many free parameters. Physically, all best fit parameters appear quite plausible. The optimised lattice constant $a = 2.887$ Å is slightly contracted, compared to the known room-temperature value, 2.892 Å [Lih61]. Only the topmost interlayer spacing $d^{12}$ is significantly reduced with respect to the bulk spacing $d^b$ ($\Delta d^{12} / d^b = -7.1\%$), and no strong relaxation is found below. The positional difference between Al and Fe in the top layer is small, with Al displaced outwards by 0.05 ± 0.04 Å.

Note that this value must not be compared to atomic height differences observed in STM, as in Fig. 4.2. Roughly speaking, STM images the local electronic density of states, whereas LEED refers to the average positions of atomic nuclei.

As mentioned in Sect. 3.3.3, the statistical significance of individual effects may also be checked for

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<table>
<thead>
<tr>
<th>$x^i$</th>
<th>$\Delta d^{ij}/d^b$</th>
<th>$b^i/d^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 %</td>
<td>-7.1 %</td>
<td>3.5 %</td>
</tr>
<tr>
<td>5 %</td>
<td>0.0 %</td>
<td></td>
</tr>
<tr>
<td>20 %</td>
<td>+1.4 %</td>
<td></td>
</tr>
<tr>
<td>15 %</td>
<td>-0.7 %</td>
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</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a = 2d^b$ [Å]</td>
<td>2.887 ± 0.013</td>
</tr>
<tr>
<td>$d^{12} - d^b$ [Å]</td>
<td>-0.10 ± 0.02</td>
</tr>
<tr>
<td>$d^{33} - d^b$ [Å]</td>
<td>0.00 ± 0.01</td>
</tr>
<tr>
<td>$d^{34} - d^b$ [Å]</td>
<td>+0.02 ± 0.01</td>
</tr>
<tr>
<td>$d^{15} - d^b$ [Å]</td>
<td>-0.01 ± 0.01</td>
</tr>
<tr>
<td>$h^i_A{\text{Al}} - h^i_F{\text{e}}$ [Å]</td>
<td>+0.05 ± 0.04</td>
</tr>
<tr>
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<td>75 (fixed)</td>
</tr>
<tr>
<td>$x^2$ [%]</td>
<td>5 ± 7</td>
</tr>
<tr>
<td>$x^3$ [%]</td>
<td>20 ± 5</td>
</tr>
<tr>
<td>$x^4$ [%]</td>
<td>15 ± 5</td>
</tr>
<tr>
<td>$u^1_A{\text{Al}}$ [Å]</td>
<td>0.17 ± 0.03</td>
</tr>
<tr>
<td>$u^1_F{\text{e}}$ [Å]</td>
<td>0.16 $^{+0.09}_{-0.04}$</td>
</tr>
<tr>
<td>$u^2$ [Å]</td>
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</tr>
<tr>
<td>$u^b$ [Å]</td>
<td>0.10 ± 0.02</td>
</tr>
<tr>
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</tr>
<tr>
<td>$V_{\text{01}}$ [eV]</td>
<td>-5.0 (tested only)</td>
</tr>
<tr>
<td>$R_{\text{min}}$</td>
<td>0.069</td>
</tr>
<tr>
<td>$R_{\text{min}} \cdot RR$</td>
<td>0.010</td>
</tr>
</tbody>
</table>

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2Note that this value must not be compared to atomic height differences observed in STM, as in Fig. 4.2. Roughly speaking, STM images the local electronic density of states, whereas LEED refers to the average positions of atomic nuclei.
their stability against parameter correlations by performing specific, constrained fits for comparison. In the present case, fits enforcing \( u^2 = u^b \) or \( x^i = 0.15 \ (i \geq 2) \) yield constrained best-fit R-factors \( R_c = 0.084 \) and 0.081, respectively. So, in view of \( R_{\text{min}} \cdot RR = 0.010 \), it is obvious that both the enhanced \( u^2 \), and the oscillatory concentration profile below the topmost layer are formally just significant, regardless of any parameter correlations within the present model. In contrast, a similar constrained fit, setting \( b^1 = 0 \), yields \( R_c = 0.072 \) only. So, although the small positional difference observed between top layer Al and Fe seems plausible (it shows the same trend and magnitude as found for \( \text{Fe}_{0.97}\text{Al}_{0.03}(100)-c(2 \times 2) \) in Sect. 4.4.1), it cannot strictly be proven for the present surface. Finally, a test of the fifth layer’s position and composition did not show any significant differences to the bulk, validating the restriction of fit parameters to those of the topmost four layers.

### 4.3.2 The precision of \( x^1 \) in LEED

Obviously, the best fit of the previous section demonstrates a remarkable quality of agreement between experimental and calculated \( I_g(E) \), promising a high level of both precision and accuracy of all fit quantities. The quantity \( x^1 \) was not varied independently, but introduced as a fixed condition. Nevertheless, had it been determined in the fit, one would certainly have expected an accurate result also for this quantity. Reassuringly, the single-parameter R-factor scan for \( x^1 \) (denoted \( R_s(x^1) \) in the following), shown already in Fig. 3.10b, indeed finds the minimum of \( R_s(x^1) \) at \( x^1 = 75 \% \) Al, with an error of \( \pm 12 \% \) estimated by way of \( RR \).

All in all, the agreement between the LEED result, and the true value \( x^1 = 75 \% \) as ascertained by LEIS and STM might thus seem convincingly established. However, a single-parameter error scan neglects the possible influence of parameter correlations on the precision with which \( x^1 \) can be estimated in LEED. As already mentioned in Sect. 3.3.3, the proper approach would be an all-parameter R-factor scan \( R_a(x^1) \), i.e. adjust all other parameters for each grid step value of \( x^1 \). The result, shown in Fig. 4.4, looks remarkably different from \( R_s(x^1) \) of Fig. 3.10b: \( R_a(x^1) \) is by no means quasi-parabolic any more, but practically flat instead: Between \( x^1 = 55 \% \) Al and 95 \% Al, the variation of the R-factor hypersurface amounts to only 0.005. Its technical minimum still lies at 80 \% Al, i.e. very close to the result affirmed by STM and LEIS. Nevertheless, using

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\(^3\)To keep \( R_a(x^1) \) computationally feasible, only fit parameters accessible to the Tensor LEED approximation (i.e., excluding \( u^b \) and \( a \)) were readjusted for each \( x^1 \) value.
the $RR$ criterion, the only Al-rich top layer stoichiometry outside the error limits is now a full Al
layer, i.e. $x^1 = 100\%$.

Of course, this observation is of central importance in the present work: At first sight, it seems
to shatter all our hopes to determine reasonable chemical information by quantitative LEED. Of
course, this can not truly be the case – too many successful LEED analyses of alloy surfaces already
exist. Rather, we must suspect some way to trigger the observed correlation “by accident”, which
is often avoided. Here, we have a chance to understand this mechanism more fully, and obtain a
conclusive picture of the factors which influence the chemical accuracy of LEED. To that end, two
questions should be addressed:

1. Is the insensitivity of $R_a$ towards $x^1$ a true property of $I_g(E)$, or possibly an artifact of the
fitting procedure itself?

2. Which specific quantities are correlated with $x^1$?

The simplest answer to the first question is a look at the $I_g(E)$ spectra behind $R_s(x^1)$ and $R_a(x^1)$.
If, for some reason, only the fitting procedure (e.g., the Pendry R-factor itself) was responsible for
the flatness of $R_a$, this should be immediately obvious from $I_g(E)$. Fig. 4.5 confronts different
intensity curves for the $(1,0)$ beam which correspond to $R_s$ (left) and $R_a$ (right), using those for
$x^1 = 55\%, 75\%,$ and $95\%$. Of course, the best fit curve for $x^1 = 75\%$ is the same in both
cases, and fits quite closely to the experimental one. And, as expected from $R_s(x^1)$ in Fig. 3.10,
the impact of $x^1$ on the single-parameter spectra is not drastic, but distinct – see, e.g., the shape
changes between $100\ eV$ and $200\ eV$. In contrast, such differences are hardly discernible at all in the
curves corresponding to $R_a(x^1)$. Obviously, the combined influence of other parameters suffices to
revert most of the changes due to modifying $x^1$ already in $I_g(E)$, and the indifference of the fitting
procedure is a perfectly accurate response to this situation.

To answer the second question, we must look at the development of all other fit quantities with
$R_a(x^1)$, depicted in Fig. 4.6. Obviously, the parameters which display the strongest trend are those
associated with the topmost layer in some way. Mainly, this concerns the top layer vibrations: $u_{Al}^1$
risers from $0.12\ \AA$ to $0.20\ \AA$ between $x^1 = 50\%$ and $100\%$, while $u_{Fe}^1$ drops from $0.24\ \AA$ down to
$0.04\ \AA$ over the same range. However, also the difference in top layer elemental positions, $b^1$, shows
a small change from $-0.01\ \AA$ to $0.05\ \AA$, and the average top layer distance $d_{12}^1$ shifts a bit inward.
To demonstrate that the dominant effect is really the correlated change of $u_{Al}^1$ and $u_{Fe}^1$ with $x^1$, Fig.
4.4 also shows the development of the best fit R-factor with $x^1$ when only $u_{Al}^1$ and $u_{Fe}^1$ are allowed
to readjust. Already then, the curve is remarkably flat – the additional contribution from $b^1$ and $d_{12}^1$
lowers the curve by a much smaller amount, and mainly in the region $x^1 \lesssim 65\%$.

We have thus established the phenomenology of a parameter correlation which reduces the net
influence of $x^1$ in the LEED fit dramatically. Since the extent to which it works is quite worrying, we
shall investigate its physical origin in more detail in the next section, before addressing its significance
in a practical fit in Sect. 4.3.4.
4.3.3 The correlation between vibrations and stoichiometry

According to Sect. 3.2.3, $x^1$, $u^1_{Al}$, and $u^1_{Fe}$ all affect the same fundamental quantity in LEED: the $t$-matrix $t^1_{av}$, or scattering factor $f^1_{av}$, of the top layer lattice site. In Eq. (3.20), $x^1$ and the temperature factor $w^1_{Al}$ act as simultaneous weight factors for $f^1_{Al}$, while $(1 - x^1)$ and $w^1_{Fe}$ play the same role for $f^1_{Fe}$. Hence, raising $x^1$ may be compensated by lowering the average of $w^1_{Al}$ which, according to Eq. (3.18), means increasing $u^1_{Al}$, and vice versa for $u^1_{Fe}$. Indeed, $u^1_{Al}$ rises noticeably with $x^1$ in Fig. 4.6, while $u^1_{Fe}$ decreases strongly at the same time. So, the observed correlation is quite plausible in principle. Moreover, the Tensor LEED extension of Eq. (3.20), Eq. (3.49), reveals that $h^1_{Al}$ and $h^1_{Fe}$ also directly affect $t^1$, i.e. their participation is not that surprising, either. In fact, a correlation between the site-dependent quantities of Eq. 3.49 was already noticed for the case of CoAl(110) [Blu96].

On the other hand, the physical roles of $x^1$, $u^1_{Al}$, $u^1_{Fe}$, $h^1_{Al}$, and $h^1_{Fe}$ in $f^1_{av}$ are all well distinguishable. The top layer concentration $x^1$ acts as a constant weight factor only, while the temperature factors associated with $u^1_{Al}$ and $u^1_{Fe}$ depend on the scattering angle $\theta$ and energy $E$. Both $h^1_{Al}$ and $h^1_{Fe}$ create asphericities which cannot be modelled by any of the other quantities. Given that the elemental scattering factors $f^1_{Al}$ and $f^1_{Fe}$ are quite different by themselves (see Fig. 3.5), one should expect a fit to retain a sufficient sensitivity to each individual parameter, as long as the data base consists of sufficiently many beams over a large energy range. To understand the drastically reduced impact of $x^1$ on $I_g(E)$ in Figs. 4.4 and 4.5, we must scrutinise the scattering problem at hand more closely, subdivide into two different steps which address...
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Figure 4.6: Reoptimised values of geometrical, chemical, and vibrational parameters of Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$^{II}$ corresponding to $R_a(x^1)$ in Fig. 4.4. Quantities which show a systematic trend are highlighted by filled black circles.
1. the mutual influence of all quantities on $f_{av}$ through Eqs. (3.20) and (3.49), and

2. the role of $f_{av}^1$ itself in the multiple scattering inherent in LEED.

For simplicity, we shall first focus on the role of $u_{Al}^1$ and $u_{Fe}^1$ only, employing Eq. (3.20). Later, $h_{Al}^1$ and $h_{Fe}^1$ can be understood as a natural but weaker extension of this picture in the context of multiple scattering. Also, the layer-index 1 is dropped for the sake of legibility below.

1. The mutual compensation of $x$, $v_{Al}$, and $v_{Fe}$ in $f_{av}$.

For a rigorous approach, assume the “true” best fit value of $f_{av}$ to correspond to a combination of parameters $(x, v_{Al}, v_{Fe})$. Any variation $x \rightarrow x + \delta x$ must then produce a change $f_{av} \rightarrow f_{av} + \delta f$. In a practical fit, $\delta f$ is only fully determined through auxiliary variations $v_{Al} \rightarrow v_{Al} + \delta v_{Al}$, and $v_{Fe} \rightarrow v_{Fe} + \delta v_{Fe}$, where $\delta v_{Al}$ and $\delta v_{Fe}$ are chosen to minimise $R_P$, yielding $R_{av}(\delta x)$. Of course, this is a complex operation, influenced by multiple scattering as well as Pendry’s R-factor itself. However, we know that an ideal parameter correlation would require $\delta f(\delta x) = 0$ for all $\delta x$, $E$, and $\theta$, and we can use this to formulate the necessary constraints on $\delta v_{Al}(\delta x)$ and $\delta v_{Fe}(\delta x)$. In a linear approximation,

$$\delta f = \delta x \cdot \frac{\partial f}{\partial x} + \delta v_{Al} \cdot \frac{\partial f}{\partial v_{Al}} + \delta v_{Fe} \cdot \frac{\partial f}{\partial v_{Fe}} = 0.$$ \hspace{1cm} (4.2)

Inserting Eqs. (3.20) and (3.18) for the scattering factor $f$ and the temperature factors $w_{Al}$ and $w_{Fe}$, we can calculate the required partial derivatives,

$$\frac{\partial f}{\partial x} = w_{Al}f_{Al} - w_{Fe}f_{Fe},$$ \hspace{1cm} (4.3)

$$\frac{\partial f}{\partial v_{Al}} = -\frac{q^2}{3} \cdot x \cdot v_{Al} \cdot w_{Al} \cdot f_{Al},$$

$$\frac{\partial f}{\partial v_{Fe}} = -\frac{q^2}{3} \cdot (1 - x) \cdot v_{Fe} \cdot w_{Fe} \cdot f_{Fe}.$$ \hspace{1cm} (4.4)

By inserting these into Eq. (4.2), it is straightforward to derive a condition for $\delta v_{Al}(\delta x)$ and $\delta v_{Fe}(\delta x)$, i.e.

$$\delta x = \frac{q^2}{3} \left[ \delta v_{Al} \cdot x \cdot v_{Al} \cdot f_{Al} + \delta v_{Fe} \cdot (1 - x) \cdot v_{Fe} \cdot f_{Fe} \right],$$ \hspace{1cm} (4.5)

where $f_{Al} := \frac{w_{Al}f_{Al}}{w_{Al}f_{Al} - w_{Fe}f_{Fe}}$ and $f_{Fe} := \frac{w_{Fe}f_{Fe}}{w_{Al}f_{Al} - w_{Fe}f_{Fe}}$. \hspace{1cm} (4.6)

Of course, Eq. (4.5) cannot be fulfilled exactly with only two free parameters $\delta v_{Al}$ and $\delta v_{Fe}$ – its right hand side (r.h.s) depends on $E$ and $\theta$ in a complex way through $q^2$, $f_{Al}$, and $f_{Fe}$, whereas $\delta x$ on the left hand side does not. Instead, Eq. (4.5) is merely a rewrite of the original optimisation problem, which we must attempt to satisfy approximately.

To begin with, $v_{Al}$ and $v_{Fe}$ may be chosen to set the angular and energetic average of the r.h.s. of Eq. 4.5 equal to $\delta x$. Interestingly, this already works for equal vibrational amplitudes $v_{Al} = v_{Fe} =: v$, whence Eq. (4.5) collapses to

$$\delta x = \frac{q^2}{3} \cdot v \cdot \left( x + \frac{f_{Fe}}{f_{Al} - f_{Fe}} \right).$$ \hspace{1cm} (4.7)
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We will always face some correlation between $\delta x$ and $\delta v$ already due to this mechanism, but at least, its extent depends on the elements involved through $f^F_e/(f^A_l - f^F_e)$.

The correlation becomes even stronger for independent vibrational amplitudes $\delta v_{Al}$ and $\delta v_{Fe}$. The additional degree of freedom allows to diminish also the $E$ and $\theta$ dependence of the r.h.s. of Eq. (4.5) itself, instead of only its average. For instance, the property $\tilde{f}_{Al} - \tilde{f}_{Fe} = 1$ can be exploited to remove the influence of the scattering factors $f_{Al}$ and $f_{Fe}$ entirely, by choosing

$$\delta v_{Al} \cdot x \cdot v_{Al} = -\delta v_{Fe} \cdot (1 - x) \cdot v_{Fe},$$

i.e.

$$\delta v_{Fe} = -\frac{x}{1 - x} \frac{v_{Al}}{v_{Fe}} \cdot \delta v_{Al}.$$  \hspace{1cm} (4.9)

Of course, this is done at the expense of retaining the full proportionality of Eq. (4.5) to $q^2$. Yet, although this is not exactly a weak function of $E$ and $\theta$, it is at least very well controlled. Estimating $\theta \approx 90^\circ$, i.e. $q^2 \approx 2k^2$, the average of Eq. (4.5) now prescribes

$$\delta v_{Al}(\delta x) = \frac{3}{2(k^2)xv_{Al}} \cdot \delta x = \frac{3\hbar^2}{4m(E)xv_{Al}} \cdot \delta x,$$  \hspace{1cm} (4.10)

where $\langle E \rangle = \frac{\hbar^2}{2m} \langle k^2 \rangle$ denotes some energy average of the LEED fit.

Naturally, the preceding example cannot be expected to describe the observed correlation in full. It may well be advantageous to choose $\delta v_{Al}(\delta x)$ and $\delta v_{Fe}(\delta x)$ somewhat differently in order to diminish the remaining influence of $q^2$ by exploiting the $E$ and $\theta$ dependence of $\tilde{f}_{Al}$ and $\tilde{f}_{Fe}$. This, however, depends on the specifics of the full scattering problem and fitting procedure, and a more general expression than Eq. (4.5) would be hard to derive. The exact result for the top layer of Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{II}$ is that seen in Fig. 4.6, or, reduced to the form $\delta v_{Al}(\delta x)$ and $\delta v_{Fe}(\delta x)$, in Fig. 4.7.

We may certainly attempt to compare Fig. 4.7 to the expressions derived above, Eqs. (4.9) and (4.10). Fig. 4.7 also shows linear approximations to the data, $\delta v_{Al} \approx 0.19 \AA \cdot \delta x$ and $\delta v_{Fe} \approx -0.46 \AA \cdot \delta x$. Inserting $\delta v_{Al}(\delta x)$ into Eq. (4.10) yields $\langle E \rangle \approx 240$ eV, which is really a kind of average energy of $I_g(E)$ used in the fit. Furthermore, the slopes in Fig.4.7 give $\delta v_{Al}/\delta v_{Fe} \approx -2.4$. By comparison, inserting the best fit parameters of Fig. 4.3 directly into Eq. (4.9) yields $\delta v_{Al}/\delta v_{Fe} \approx -3.2$. Obviously, the mechanism of Eqs. (4.9) and (4.10) is reasonably close to our true observations from $R_{a}(x)$. In total, although we cannot expect to derive the exact fit results from first principles, our
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considerations certainly motivate why the correlation between \(x\), \(v_{\text{Al}}\), and \(v_{\text{Fe}}\) is so much stronger than one might have expected at first sight.

2. The role of multiple scattering.

By focusing on the effective atomic scattering factor \(f_{\text{av}}\), the preceding considerations were restricted to a single scattering event only. Yet, the prescription which determines \(R_{a}(\delta x)\), and hence \(\delta v_{\text{Al}}(\delta x)\) and \(\delta v_{\text{Fe}}(\delta x)\), really requires to minimise the LEED amplitude changes \(\delta A_{g}^{-}\), and not \(\delta f\) itself. Both conditions would be identical only for kinematic scattering from a well-defined incident plane wave into an outgoing one. This, however, is not the situation encountered in LEED. Due to strong multiple scattering, the wave field incident on any particular scatterer in a surface is much more isotropic than a plane wave, so that any outgoing wave always reflects some angular average of \(f_{\text{av}}\). This blurs the impact of the \(\theta\) dependence of \(w_{\text{Al}}\) and \(w_{\text{Fe}}\) on \(\delta A_{g}^{-}\). Moreover, it also limits the influence of asphericities introduced by small elemental positional deviations \(h_{\text{Al}}\) and \(h_{\text{Fe}}\), which were neglected in the previous step.

To put this more quantitatively, it is useful to remember the Tensor LEED approximation (Sect. 3.4). Since Eq. (3.17) establishes a direct correspondence \(f_{\text{av}} \leftrightarrow t_{\text{av}}\), it also implies \(\delta f \leftrightarrow \delta t\). The effect of modified single-site scattering properties on the outgoing LEED amplitudes is the given according to Eq. (3.44),

\[
\delta A_{g}^{-} = \sum_{l,m,l',m'} T_{g,l,m,l',m'} \cdot \delta t_{l,m,l',m'}. \tag{4.11}
\]

Here, the Tensor \(T\) reflects the interaction of both the incident and outgoing LEED waves with the scatterer in question, i.e. just the multiple scattering wave fields which were referred to above. Since these wave fields are both dominated by multiple scattering effects, the mixing of the angular momentum components of \(\delta t\) by the sum in Eq. (4.11) is the direct equivalent of the angular averaging of \(\delta f\) mentioned above. Note that this conclusion does not depend on the Tensor LEED approximation, the use of which is rather a matter of convenient writing here; similar insights arise from Eq. (3.39) to all orders of \(\delta t\).

The strength of the correlation between \(\delta x\), \(\delta v_{\text{Al}}\) and \(\delta v_{\text{Fe}}\) is also partly due to the fact that each quantity affects only the spherical parts of \(t\), i.e. the small subset of its diagonal elements \(t_{l}\). Yet, as Eq. (4.5) shows, this correlation is never exact. In this situation, geometric modifications \(\delta h_{\text{Al}}\) and \(\delta h_{\text{Fe}}\), which affect both diagonal and off-diagonal \(t\)-matrix elements, may still enhance the observed correlation through improved averaging in Eq. (4.11). This expected behaviour fits perfectly well with Figs. 4.4 and 4.6. Only little influence of \(h_{\text{Al}}\) and \(h_{\text{Fe}}\) on \(R_{a}(x^{-1})\) arises for \(x\) close to 75 \% Al, where the correlation of Eq. (4.5) (represented by the broken line in Fig. 4.4) works best on its own. However, in the region \(x^{-1} \lesssim 65 \%\) Al, this is no longer the case, and it is here where the effect of \(\delta h_{\text{Al}}\) and \(\delta h_{\text{Fe}}\) comes into play.
4.3.4  The correlation’s practical impact: Stoichiometric accuracy in LEED

So far, we have shown that the parameter correlation which blurs the LEED fit’s sensitivity to $x$ can be understood quite well from general considerations. In fact, throughout the preceding section, we never made use of the elemental properties of Fe and Al, so that the described effect should occur for other materials as well. The similar role of $x$, $v_{\text{Al}}$, and $v_{\text{Fe}}$ in the scattering factor $f_{\text{av}}$ forms the basis of the effect, which is then enhanced further by the multiple scattering wavefield. Nevertheless, the most important question is unanswered as yet: How well can this parameter correlation be circumvented in a practical fit?

Already from its phenomenology alone, it is clear that the full correlation described above arises since quite extreme combinations of $u_{1\text{Al}}$ and $u_{1\text{Fe}}$ were allowed in the fit. For instance, the optimum vibrational amplitudes for $x^1 = 0.9$ amount to 0.20 Å (Al) and 0.07 Å (Fe) in Fig. 4.6. The first is twice as high as $u^b$, while the second lies actually below. No obvious physical reason for this behaviour exists, and the combination would appear highly suspicious in a practical analysis. In contrast, nearly equal vibrations result for $x^1 = 0.75$, which is much more credible. So, the simplest way to avoid the strong correlation due to Eq. (4.5) would be to restrict the allowed range of $u_{1\text{Al}}$ and $u_{1\text{Fe}}$ by some physically plausible scheme. Unfortunately, as already discussed in Sect. 3.3.1, there exists no rigorous general law for elemental vibrational amplitudes near binary alloy surfaces. So, whenever such a criterion is imposed, one also runs the risk of introducing a hidden systematic error into the fit of $x^1$, which one must weigh against the benefit of having fewer insensitive parameters.

Another puzzling observation is that the actual minimum of the all-parameter scan $R_{a}(x^1)$ in Fig. 4.4 lies at $x^1 = 80$ % Al. Since $RRI$ would allow for $x^1$ between 50 % and 95 % Al, the minimum’s proximity to the true $x^1$ value, 75 % Al as determined by STM and LEIS, is surprising. In fact, other combined LEED/STM/LEIS studies [Spo98, Pla99, Pla99b] also observed that the true accuracy of LEED fits was much better in practice than suggested by all-parameter error bars. Of course, it is possible that this conclusion is correct, and that LEED results are really much more stable against statistical errors than estimated by Pendry [Pen80]. However, even in that case, one must remember that a LEED fit is also subject to systematic errors of the structural model. Normally, the risk associated with small glitches in the model is limited. However, if the R-factor hypersurface for a certain quantity is already shallow, even a small omission could shift its best fit value considerably – without much impact on the fit quality otherwise. To demonstrate that this danger is real for

![Figure 4.8: All-parameter R-factor scan $R_{a}(x^1)$ for Fe$_{0.85}$Al$_{0.15}$(100)-(1×1)$_{\text{II}}$ as in Fig. 4.4, but with the constraints $h_{1\text{Al}} = h_{1\text{Fe}}$ and $u^2 = u^b$ (full line), and single-parameter R-factor scan for the shifted best-fit (broken line).](image-url)
Chapter 4. The structure of Fe_{1-x}Al_{x}(100) surfaces

Table 4.2: The parameter set associated with the minimum of the restricted fit shown in Fig. 4.8 (left column). For comparison, the “full” fit result of Sect. 4.3.1 is repeated from Fig. 4.3 (right column).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Restricted fit</th>
<th>Full fit (Fig. 4.3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^{12} - d^b$ [Å]</td>
<td>$-0.08 \pm 0.025$</td>
<td>$-0.10$</td>
</tr>
<tr>
<td>$d^{23} - d^b$ [Å]</td>
<td>$0.00 \pm 0.01$</td>
<td>$0.00$</td>
</tr>
<tr>
<td>$d^{34} - d^b$ [Å]</td>
<td>$+0.02 \pm 0.02$</td>
<td>$+0.02$</td>
</tr>
<tr>
<td>$d^{45} - d^b$ [Å]</td>
<td>$-0.01 \pm 0.02$</td>
<td>$-0.01$</td>
</tr>
<tr>
<td>$h^1_{\text{Al}} - h^1_{\text{Fe}}$ [Å]</td>
<td>$0.00$ (fix)</td>
<td>$+0.05$</td>
</tr>
<tr>
<td>$x^1$ [%]</td>
<td>$60 \pm 10$</td>
<td>$75$</td>
</tr>
<tr>
<td>$x^2$ [%]</td>
<td>$15 \pm 8$</td>
<td>$5$</td>
</tr>
<tr>
<td>$x^3$ [%]</td>
<td>$15 \pm 7$</td>
<td>$20$</td>
</tr>
<tr>
<td>$x^4$ [%]</td>
<td>$15 \pm 7$</td>
<td>$15$</td>
</tr>
<tr>
<td>$u^1_{\text{Al}}$ [Å]</td>
<td>$0.11 \pm 0.04$</td>
<td>$0.17$</td>
</tr>
<tr>
<td>$u^1_{\text{Fe}}$ [Å]</td>
<td>$0.20$^{+0.07}_{-0.04}</td>
<td>$0.16$</td>
</tr>
<tr>
<td>$u^2$ [Å]</td>
<td>$0.10$ (fix)</td>
<td>$0.13$</td>
</tr>
<tr>
<td>$V_{00}$ [eV]</td>
<td>$-0.5$</td>
<td>$-1.0$</td>
</tr>
<tr>
<td>$R_{\text{min}}$</td>
<td>$0.085$</td>
<td>$0.069$</td>
</tr>
<tr>
<td>$R_{\text{min}} \cdot RR$</td>
<td>$0.012$</td>
<td>$0.010$</td>
</tr>
</tbody>
</table>

Table 4.2: The parameter set associated with the minimum of the restricted fit shown in Fig. 4.8 (left column). For comparison, the “full” fit result of Sect. 4.3.1 is repeated from Fig. 4.3 (right column).

Fe_{0.85}Al_{0.15}(100)-(1\times1)^\text{II}, we reperformed the structural analysis of Sect. 4.3.1. This time, however, we treated $x^1$ as a normal fit parameter, and introduced a \textit{deliberate} systematic error into the model by enforcing two constraints: $h^1_{\text{Al}} = h^1_{\text{Fe}}$, i.e. no element-dependent positions, and $u^2 = u^b$, i.e. no independent vibrational amplitude for second layer atoms. Both are frequent assumptions for binary alloy surfaces, and at least the second one has no direct connection to $x^1$ in the light of Sect. 4.3.3. The all-parameter hypersurface $R_a(x^1)$ associated with this parameter space is shown in Fig. 4.8 (full line). Predictably, it is similarly flat as that of the full fit in Fig. 4.4, only shifted upwards by $\Delta R \approx 0.02$. However, the R-factor \textit{minimum} is now found at 60 % Al, i.e. clearly away from the true value of 75 %. Even worse, the single-parameter error bars for this result would amount to $\pm 10 \%$ (broken curve in Fig. 4.8), excluding the true top layer composition. Still, $R_{\text{min}} = 0.085$ stands for a formidable fit quality, so that this result could easily have been taken seriously if no additional information on $x^1$ had been available.

Table 4.2 lists all optimised parameter values of the restricted fit. For the most part, these appear quite plausible. Certainly, the absence of an oscillatory composition profile (due to the restriction of $u^2$) and the relatively large difference between $u^1_{\text{Al}}$ and $u^1_{\text{Fe}}$ should incur the scepticism of a wary crystallographer. Yet, neither aspect provides a rigorous argument to dismiss the entire result of Table 4.2 as unphysical. In this example, the optimal conclusion would have been to treat the precise result for $x^1$ with some caution due to the associated inconsistencies of other parameters, and take
4.3. The question of chemical accuracy: Fe0.85Al0.15(100)-(1×1)II

the all-parameter error bars seriously despite their extent. On the other hand, from the behaviour of \( u^{1}_{Al} \) and \( u^{1}_{Fe} \) (which is similar to that displayed in Fig. 4.6), one would probably have deemed values \( x^1 > 60 \% \) Al more reasonable than otherwise.

In total, the case study of Fe0.85Al0.15(100)-(1×1)II shows that the determination of chemical parameters in LEED is indeed affected by correlations. However, this does not mean that their study is futile altogether. Rather, we may draw a few valuable lessons from the above considerations:

- From statistical errors alone, the results of a LEED fit might generally be somewhat more precise than RR prescribes when the full correlation is taken into account – at least, several investigations suggest this, and we have no evidence to the contrary.

- The true danger of the observed correlation stems from hidden systematic errors. It is therefore important to question even small effects when striving for high accuracy of correlated quantities.

- Some systematic errors will be inherent in any model, so that parameter correlations must be tested for any crucial statement – e.g., by simply assuming the counter-hypothesis, as done for \( u^{2}, b^{1} \), and the concentration profile in Sect. 4.3.1.

- The behaviour of vibrational amplitudes may contain valuable information on the chemical accuracy of a fit. Seemingly strange best fit vibrations may hint to an inaccurate stoichiometry.

- Trivially, if the suspicion arises that a particularly important fit result is somehow biased, information from dedicated complementary techniques (such as STM and LEIS for \( x^1 \) above) should be sought. At least, this reduces the uncertainty’s impact on the remaining fit. Unfortunately, such alternative methods are unavailable in many cases.

We shall often draw upon these insights in the remaining investigations in this work. In some instances, we must yet accept model constraints which are fixed by physical intuition, even at the risk of introducing a small bias into the fit. Nevertheless, crucial findings will always be weighed carefully against the possibility of parameter correlations.

Before concluding this section, some final remarks on Fe0.85Al0.15(100)-(1×1)II are in order. Obviously, \( R_P = 0.069 \) between measured and calculated \( I_g(E) \) indicates an outstanding fit quality. So, the general accuracy of the best-fit model is still extremely good, regardless of the parameter correlations described. In particular, it is reassuring that the LEED all-parameter best fit yields \( u^{1}_{Al} \approx u^{1}_{Fe} \), as qualitatively expected from Sect. 3.3.1, and \( x^1 \) quite close to the known STM/LEIS result. So, there is reason to believe that the constraints \( h^{2}_{Al} = h^{2}_{Fe}, u^{2}_{Al} = u^{2}_{Fe}, \) and \( u^{b}_{Al} = u^{b}_{Fe} \), imposed due to the relatively low Al concentration in these layers, are good approximations to physical reality, and that the concentration profile found reflects this. We can now proceed to place these results in the context of other Fe1−\( x \)Al\( x \)(100) surfaces.
4.4 Concentration-dependent structure of Fe\textsubscript{1-x}Al\textsubscript{x}(100)

In analogy to Fe\textsubscript{0.85}Al\textsubscript{0.15}(100)-(1×1)\textsuperscript{II}, the quantitative LEED studies of the remaining Fe\textsubscript{1-x}Al\textsubscript{x}(100) surfaces in this work (x = 0.03, 0.15, and 0.30) determined the structural parameters of the topmost four layers. In each case, the consistency of the fifth layer with a bulk-like position and stoichiometry was explicitly tested. Of course, the sublattices responsible for c(2×2) superstructure formation were treated individually for x = 0.03 and 0.30, excluding only symmetry-breaking stacking sequences. In each case, some preliminary structural information is available, allowing to constrain the tested model classes.

4.4.1 Fe\textsubscript{0.97}Al\textsubscript{0.03}(100)-c(2×2)\textsuperscript{I}

As mentioned in Sect. 4.1, an important prerequisite in the structural analysis of Fe\textsubscript{0.97}Al\textsubscript{0.03}(100)-c(2×2)\textsuperscript{I} is the nearly perfect c(2×2) order inferred from STM results for Fe\textsubscript{0.85}Al\textsubscript{0.15}(100)-c(2×2)\textsuperscript{I}. On this basis, two structural models were tested against the experimental I\textsubscript{g}(E): first, an ordered overlayer consisting of Fe and Al in a checkboard pattern, and second, a primitive c(2×2) overlayer of Al atoms only. Already the initial Tensor LEED reference calculation (bulk-like atomic positions assumed) and following optimisation clearly rule out the primitive Al overlayer, which yields a minimum R-factor above 0.35 – the checkboard arrangement yields \( R_p = 0.10 \) in the same step. Obviously, this finding is also consistent with the mixed top layer established for Fe\textsubscript{0.85}Al\textsubscript{0.15}(100)-(1×1)\textsubscript{II} above.

After further refinement, the average experiment-theory agreement reached with a fully ordered “checkboard” top layer corresponds to \( R_{\text{min}} = 0.083 \), describing integer (\( R_{\text{int}} = 0.075 \)) and fractional (\( R_{\text{frac}} = 0.106 \)) order beams similarly well. As for x = 0.15, \( R_{\text{min}} \) fits well with \( R_s = 0.079 \) from Table 4.1, and \( R_{\text{min}} : R_R = 0.010 \) again suggests a high statistical reliability of the best fit. Fig. 4.9 demonstrates the favourable comparison of experimental and model spectra for the (1,0) and (1/2,1/2) beams. An illustration of the converged best-fit is shown in Fig. 4.10, together with a table of all optimised parameters. For consistency with later results, the denomination of layer sublattices is that of a B/D-terminated D\textsubscript{0}\textsubscript{3} stacking sequence (Fig. 2.3), i.e. sublattices 1B and 1D are occupied by Fe and Al, respectively, sublattice 3D is situated directly below 1B, and vice versa.

Except for the ordered arrangement of segregated Al in the topmost layer, the overall surface structure is surprisingly close to the truncated bulk. The best-fit lattice parameter amounts to \( a = 2.865 \pm 0.013 \) Å, again slightly contracted compared to the known room temperature value, and equivalent to a bulk interlayer spacing \( d^b = 1.433 \) Å. The deviations of the averaged near-surface interlayer distances from this value are extremely small, but credible since they produce an oscillatory relaxation pattern which is just outside the limits of error. Interestingly, the top layer Fe position (sublattice 1B) with respect to the second layer is almost the same as for elemental Fe(100) [Wan87]. The Al atoms reside 0.06 ± 0.04 Å above, consistent with Fe\textsubscript{0.85}Al\textsubscript{0.15}(100)-(1×1)\textsubscript{II} in sign and magnitude. Below the topmost layer, the only noticeable deviation from the average bulk stoichiometry occurs on sublattice 3D, which appears slightly enriched in Al. However, a constrained
4.4. Concentration-dependent structure of Fe$_{1-x}$Al$_x$(100)

Figure 4.9: Best fit $I_g(E)$ for Fe$_{0.97}$Al$_{0.03}$(100)-c(2×2)$^1$ vs. experimental ones. The (1,0) and (1/2,1/2) beams demonstrate the excellent level of agreement achieved for both integer and fractional order beams.

<table>
<thead>
<tr>
<th>$x^{(B)}$</th>
<th>$x^{(D)}$</th>
<th>$\Delta d_{ij}/d^b$</th>
<th>$b_i/d^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 %</td>
<td>100 %</td>
<td>-1.4 %</td>
<td>4.2 %</td>
</tr>
<tr>
<td>0 %</td>
<td></td>
<td>+1.7 %</td>
<td>0.7 %</td>
</tr>
<tr>
<td>5 %</td>
<td>15 %</td>
<td>-0.4 %</td>
<td></td>
</tr>
<tr>
<td>5 %</td>
<td></td>
<td>+0.7 %</td>
<td></td>
</tr>
</tbody>
</table>

Fe Al

bulk

Figure 4.10: Illustration of the best fit structure obtained for Fe$_{0.97}$Al$_{0.03}$-c(2×2)$^1$. The full set of best fit parameters is listed in the accompanying table.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a = 2d^b$ [Å]</td>
<td>2.865 ± 0.012</td>
</tr>
<tr>
<td>$d^{12} - d^b$ [Å]</td>
<td>-0.02 ± 0.02</td>
</tr>
<tr>
<td>$d^{23} - d^b$ [Å]</td>
<td>+0.025 ± 0.015</td>
</tr>
<tr>
<td>$d^{34} - d^b$ [Å]</td>
<td>-0.005 ± 0.015</td>
</tr>
<tr>
<td>$d^{45} - d^b$ [Å]</td>
<td>+0.01 ± 0.015</td>
</tr>
<tr>
<td>$h^{1D} - h^{1B}$ [Å]</td>
<td>+0.06 ± 0.04</td>
</tr>
<tr>
<td>$h^{3D} - h^{3B}$ [Å]</td>
<td>-0.01 ± 0.01</td>
</tr>
<tr>
<td>$x^{1B}/x^{1D}$ [%]</td>
<td>Fe / Al (fixed)</td>
</tr>
<tr>
<td>$x^2$ [%]</td>
<td>0 ± 12</td>
</tr>
<tr>
<td>$x^{3B}/x^{3D}$ [%]</td>
<td>5 ± 8 / 15 ± 12</td>
</tr>
<tr>
<td>$x^4$ [%]</td>
<td>5 ± 10</td>
</tr>
<tr>
<td>$u^1_{Al}$ [Å]</td>
<td>0.12 ± 0.04</td>
</tr>
<tr>
<td>$u^1_{Fe}$ [Å]</td>
<td>0.12 ± 0.03</td>
</tr>
<tr>
<td>$u^2$ [Å]</td>
<td>0.10 ± 0.02</td>
</tr>
<tr>
<td>$u^b$ [Å]</td>
<td>0.06 ± 0.03</td>
</tr>
<tr>
<td>$V_{00}$ [eV]</td>
<td>-1.0</td>
</tr>
<tr>
<td>$V_{0i}$ [eV]</td>
<td>-5.0 (tested only)</td>
</tr>
<tr>
<td>$R_{min}$</td>
<td>0.083</td>
</tr>
<tr>
<td>$R_{int}/R_{frac}$</td>
<td>0.075 / 0.106</td>
</tr>
<tr>
<td>$R_{min} \cdot RR$</td>
<td>0.010</td>
</tr>
</tbody>
</table>
fit with \( x^i = x^b \) for all sublattices in layers \( i > 1 \) yields \( R_c = 0.091 \), i.e. within the bounds of statistical error defined by \( R_{\text{min}} \cdot RR \). So, any possible deviations from the bulk-like stoichiometry are not outside of the error limits. Finally, the fitted vibrational amplitudes again show a consistent trend, with \( u_{\text{Al}}^1 \approx u_{\text{Fe}}^1 > u^2 > u^b \).

In the LEED analysis summarised in Fig. 4.10, the assumption of a fully ordered top layer was never questioned. The main argument for this restriction is the STM image of \( \text{Fe}_{0.85}\text{Al}_{0.15}(100)-c(2\times2) \), Fig. 4.1, which proves this surmise for that system. Yet, \( \text{Fe}_{0.97}\text{Al}_{0.03}(100)-c(2\times2) \) is another surface, and small deviations of its top layer order might occur. In fact, a revised fit which adds \( x^{1\text{B}} \) and \( x^{1\text{D}} \) to the free parameters of Fig. 4.10 finds approximately 10% of the 1B sites occupied by Al instead of Fe. Unfortunately, with \( R_P = 0.081 \), the fit quality reached with this modification is practically the same as for the fully ordered model, and an exact statement cannot be expected. However, due to the nature of the superstructure formed, there is another way of estimating the amount of disorder present in the surface. Each atom on the “wrong” top layer sublattice constitutes a defect in the \( c(2\times2) \) periodicity, reducing the total intensity scattered into the superstructure LEED spots. In fact, since the superstructure is practically restricted to the topmost layer, the reduction corresponds almost exactly to the contribution from one surface unit cell. On the other hand, by way of the ATA, that unit cell still contributes to the integer order spots as before. Hence, the ratio of energy- and beam-averaged intensities within fractional and integer order beams, \( r = I_{\text{frac}}/I_{\text{int}} \) may be used to estimate the maximum level of disorder within the topmost layer.

Assuming a small defect concentration \( x^{\text{defect}} \), the averaged intensities leaving the surface are

\[
I_{\text{frac}} \approx \sum_{\text{frac},g} \int dE \left[ A_g^- \cdot \frac{n}{2} (1 - x^{\text{defect}}) \right]^2 \tag{4.12}
\]

\[
I_{\text{int}} \approx \sum_{\text{int},g} \int dE \left[ A_g^- \cdot \frac{n}{2} \right]^2 \tag{4.13}
\]

with \( n \) atoms in the top layer (i.e., \( n/2 \) unit cells), and \( A_g^- \) the amplitude diffracted per unit cell from an ideally ordered surface. With \( r_{\text{exp}} = 0.53 \), the actual intensity ratio of the 960 K \( I_g(E) \) data set is not far from \( r_{\text{th}} = 0.63 \), which would be expected for the fully ordered best fit model (Fig. 4.10). Estimating \( r_{\text{exp}} \approx (1 - x^{\text{defect}})^2 \cdot r_{\text{th}} \), the number of defects per unit cell of the experimental surface should indeed not have exceeded \( \approx 10\% \). In fact, this result is almost frighteningly close to that of the extended fit above; even more so, as the intensity ratio \( r_{\text{disord}} \) associated with the fit result including disorder really amounts to \( r_{\text{disord}} = 0.52 \). In short, the assumption of almost ideal chemical order in the top layer is fully consistent with quantitative LEED, and the deviations from this arrangement on both surface sublattices should not exceed 10%.

### 4.4.2 \( \text{Fe}_{0.70}\text{Al}_{0.30}(100)-c(2\times2)^{\Pi} \)

As mentioned, the \( I_g(E) \) spectra of \( \text{Fe}_{0.70}\text{Al}_{0.30}(100)-c(2\times2)^{\Pi} \) are very similar to those of the intermediate \( \text{Fe}_{0.53}\text{Al}_{0.47}(100)-c(2\times2)^{\Pi} \) phase, which was already subject to a quantitative LEED
study by Kottcke et al. [Ktk96]. These authors tested a variety of structural models, of which only a D0\textsubscript{3} ordered surface slab, capped by a full layer of Al, fit the experimental spectra well. Based on this evidence, no other model was tested in the present case.

The best fit model for Fe\textsubscript{0.70}Al\textsubscript{0.30}(100)-c(\text{2}\times\text{2})\textsuperscript{I1} after refinement of all necessary geometrical, chemical and vibrational parameters is shown in Fig. 4.11. The accompanying table lists all relevant parameters, and contrasts them with the structure of Fe\textsubscript{0.53}Al\textsubscript{0.47}(100)-c(\text{2}\times\text{2})\textsuperscript{I1} as determined by Kottcke et al. [Ktk96]. The structural agreement between both results is surprisingly good despite the different underlying bulk crystals, also proving that the structure found by Kottcke et al. was really a surface slab with the full properties of a D0\textsubscript{3} bulk crystal. Quite obviously, with \( R_{\text{min}} = 0.078 \), the experiment-theory agreement reached in the present analysis is again excellent, and also equally good for integer (\( R_{\text{int}} = 0.071 \)) and fractional (\( R_{\text{frac}} = 0.094 \)) beams. The visual comparison of measured and calculated \( I_g(E) \) is exemplified for the (1,0) and (1/2,1/2) beams in Fig. 4.12. In this case, \( R_{\text{min}} \) is even slightly lower than \( R_{\text{s}} = 0.092 \) as given in Table 4.1. Yet, as discussed in Sect. 3.3.3, this is not problematic: \( R_{\text{s}} \) reflects the statistical uncertainty of the LEED experiment prior to averaging symmetry-equivalent beams, whereas \( R_{\text{min}} \) itself corresponds to experimental \( I_g(E) \) after averaging. Thus, the result is still on the safe side of an overfit, and rather reflects an almost ideal description of the experimental data base by the model spectra.

The geometrical relaxation found for this surface is more pronounced than for \( x = 0.03 \) and \( x = 0.15 \) before, with a marked inward contraction \( \Delta d_{12} = -0.18 \text{ Å} \) of the top layer, and a somewhat enhanced average second interlayer distance, \( \Delta d_{23} = 0.045 \text{ Å} \). Apparently, the asymmetric 2NN environment of Al atoms in the third layer induces a small buckling of 0.05 Å there, compared to the nominal Fe sublattice 3B, the Al sublattice 3D is drawn towards the surface.\textsuperscript{4} It is interesting that no such effect occurs in the top layer, which is practically flat. The fit proved insensitive to element-dependent positions in both the top and third layer. Regarding stoichiometry, the topmost layer consists indeed almost fully of Al, but with about 10 % Fe still homogeneously distributed therein. In the lower layers, the sublattice occupation obviously deviates somewhat from an ideal Fe\textsubscript{3}Al arrangement. As for the seeming Al enrichment in sublayer 3B, it should be remembered that, for \( x = 0.30 \), the bulk D sublattice is completely filled, and the bulk B sublattice must hold the excess Al, leading to 20 % Al antisite defects there. So, \( x_{\text{3B}} \) is actually perfectly bulk-like within error limits, and the difference to the result of Kottcke et al. probably due to a different average stoichiometry of their D0\textsubscript{3} surface slab. Nevertheless, we also find some near-surface disorder beyond that expected in the bulk, most prominently in the second layer (\( x_{\text{2}} = 15 \% \) Al), and on sublattice 3D. Finally, it should be noted that, again, the layer-dependent vibrational amplitudes determined certainly show a plausible trend. In particular, almost equal values are obtained for Fe and Al in the bulk.

In the context of near-surface order and segregation, the exact top layer composition (which, from its single-parameter error bars, still appears to contain some Fe) and the possibility of some disorder

\textsuperscript{4}In Refs. [Ktk96, Ktk97b], the third layer buckling is assigned the opposite direction – i.e., Fe relaxes outward instead of Al. In Fig. 4.11, the listed value has the same sign as in the original reference. However, from the original computer programs of M. Kottcke, it seems possible that the tabulated buckling should really bear the opposite sign, consistent with that found in the present study.
Chapter 4. The structure of Fe$_{1-x}$Al$_x$(100) surfaces

<table>
<thead>
<tr>
<th>$x^{(B)}$</th>
<th>$x^{(D)}$</th>
<th>$\Delta d^{ii}/d^{ib}$</th>
<th>$b^{i}/d^{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 %</td>
<td>90 %</td>
<td>-12.3 %</td>
<td>0.7 %</td>
</tr>
<tr>
<td>15 %</td>
<td>90 %</td>
<td>+3.2 %</td>
<td>3.5 %</td>
</tr>
<tr>
<td>25 %</td>
<td>90 %</td>
<td>-0.6 %</td>
<td>0.6 %</td>
</tr>
<tr>
<td>5 %</td>
<td>90 %</td>
<td>-0.7 %</td>
<td>0.7 %</td>
</tr>
</tbody>
</table>

Figure 4.11: Best fit structural model of Fe$_{0.70}$Al$_{0.30}$(100)-c(2×2)$_{II}$. The accompanying table lists all structural parameters determined in the fit, and contrasts them with those found by Kottcke et al. [Ktk96] for Fe$_{0.53}$Al$_{0.47}$(100)-c(2×2)$_{II}$.
below are certainly the most interesting points noted above. Both phenomena must therefore be reinvestigated more carefully to check their stability against parameter correlations.\(^5\)

- Naturally, the sensitivity of our fit would probably not suffice to prove either point, were the full correlation with site- and element-dependent vibrational amplitudes and positions taken into account (Sect. 4.3.3). Of course, this procedure would also exaggerate the error bars somewhat, since the assumptions made below (\(u_{\text{Al}} = u_{\text{Fe}}\) for sites with a small minority fraction only, and equal average elemental positions per site) are quite consistent with observations for \(x = 0.15\) and \(x = 0.03\).

- One may still test for the impact of parameter correlations even within the assumptions made for the best fit above. To that end, a restricted structural analysis was performed, constraining the top layer composition to Al only, and enforcing the idealised bulk-like stoichiometry below. Technically, the optimum agreement achievable with these conditions ends up outside the statistical limits set by \(R_{\text{min}} \cdot RR\), yielding \(R_P = 0.092\). Still, this also demonstrates that the fit is not extremely sensitive to the restriction of six concentration parameters at once.

In total, one should be careful to take the small deviations of the best fit from an idealised, D0\(_3\)-ordered and fully Al-capped model too literally. Our analysis clearly indicates this possibility, but the deviations are certainly not excessive.

\(^5\)Unlike in the case of Fe\(_{0.97}\)Al\(_{0.03}\)-(100)-c(2×2)\(^\Pi\), \(I_{\text{frac}}/I_{\text{int}}\) does not provide a criterion to estimate the degree of chemical disorder here. \(r_{\text{exp}} = 0.23\) in experiment is somewhat smaller than \(r_{\text{th}} = 0.35\) for the fit in Fig. 4.11, but this time the theoretical model already contains disorder. Moreover, the c(2×2)\(^\Pi\) superstructure is not restricted to a single layer only, forbidding the simple interpretation of the previous section.
Chapter 4. The structure of Fe$_{1-x}$Al$_x$(100) surfaces

Table 4.3: Previous structural results for B2 Fe$_{1-x}$Al$_x$(100), all obtained by quantitative LEED. The right column is based on the data set which is reanalysed in the present section.

<table>
<thead>
<tr>
<th></th>
<th>Fe$<em>{0.54}$Al$</em>{0.46}$</th>
<th>Fe$<em>{0.53}$Al$</em>{0.47}$</th>
<th>Fe$<em>{0.53}$Al$</em>{0.47}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{\text{meas}} = 293$ K</td>
<td>$T_{\text{meas}} = 293$ K</td>
<td>$T_{\text{meas}} = 123$ K</td>
</tr>
<tr>
<td>$a = 2d^b$ [Å]</td>
<td>(2.904)</td>
<td>(2.903)</td>
<td>2.894</td>
</tr>
<tr>
<td>$d^{12} - d^b$ [Å]</td>
<td>-0.21 ± 0.03</td>
<td>-0.23 ± 0.02</td>
<td>-0.21 ± 0.02</td>
</tr>
<tr>
<td>$d^{23} - d^b$ [Å]</td>
<td>+0.06 ± 0.03</td>
<td>+0.04 ± 0.02</td>
<td>+0.04 ± 0.02</td>
</tr>
<tr>
<td>$d^{34} - d^b$ [Å]</td>
<td>(0)</td>
<td>+0.02 ± 0.02</td>
<td>+0.03 ± 0.02</td>
</tr>
<tr>
<td>$d^{45} - d^b$ [Å]</td>
<td>(0)</td>
<td>-0.01 ± 0.03</td>
<td>0.00 ± 0.03</td>
</tr>
<tr>
<td>$x^1$ [%]</td>
<td>(100)</td>
<td>95 ± 8</td>
<td>100 ± 8</td>
</tr>
<tr>
<td>$x^2$ [%]</td>
<td>(0)</td>
<td>22 ± 11</td>
<td>17 ± 10</td>
</tr>
<tr>
<td>$x^3$ [%]</td>
<td>(100)</td>
<td>100 ± 14</td>
<td>100 ± 10</td>
</tr>
<tr>
<td>$x^4$ [%]</td>
<td>(0)</td>
<td>0 ± 13</td>
<td>0 ± 11</td>
</tr>
<tr>
<td>$u^1$ [Å]</td>
<td>(0.11)</td>
<td>0.14 ± 0.025</td>
<td>0.12 ± 0.03</td>
</tr>
<tr>
<td>$u^{\ell}_A$ [Å]</td>
<td>(0.11)</td>
<td>0.12 ± 0.02</td>
<td>0.115 ± 0.02</td>
</tr>
<tr>
<td>$u^{\ell}_F$ [Å]</td>
<td>(0.11)</td>
<td>0.115 ± 0.02</td>
<td>0.095 ± 0.02</td>
</tr>
</tbody>
</table>

4.4.3 Fe$_{0.53}$Al$_{0.47}$(100)-(1×1)$^{\text{III}}$

The analysis of B2 Fe$_{0.53}$Al$_{0.47}$(100), near the Al-rich edge of the bcc based phase area (see Fig. 2.1), completes the picture of the structural development of Fe$_{1-x}$Al$_x$(100) surfaces painted in this work. Unlike for the preceding surfaces, at least three different crystallographic analyses of the equilibrated (1×1)$^{\text{III}}$ structure already exist, all by quantitative LEED. The geometric, chemical, and vibrational results of these studies, as given in Refs. [Wan93, Ktk96, Ktk97b], are summarised in Table 4.3. With respect to geometry and the overall termination, there is close agreement between all three – the surface is terminated by Al, adheres to B2-like stacking sequence, the topmost interlayer spacing is considerably contracted, and a small expansion results for $d^{23}$. As mentioned, a full Al top layer is also the result of LEIS work by Overbury [Ove95]. Nevertheless, there is one feature which distinguishes the work of Wang et al. [Wan93] (first column) from that of Kottcke et al. [Ktk96, Ktk97b] (second and third column): In the latter case, small compositional deviations from the ideal B2 stacking sequence were explicitly tested for. Indeed, such a deviation occurs with statistical significance, due to 20 % Al antisite defects found in the second layer. Although small, this kind of enrichment is quite unexpected, given the system’s known trend to form heterogeneous NN bonds (Chapter 2.1). If true, it would require these bond properties to change dramatically around the second layer.

The present work’s motif is the interplay of ordering forces and surface segregation. A population
4.4. Concentration-dependent structure of Fe$_{1-x}$Al$_x$(100)

<table>
<thead>
<tr>
<th>Constraint</th>
<th>$u^2 = u^b$</th>
<th>full order</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a = 2d^b$ [Å]</td>
<td>(2.894)</td>
<td></td>
</tr>
<tr>
<td>$d^{12} - d^b$ [Å]</td>
<td>$-0.21 \pm 0.015$</td>
<td>$-0.21 \pm 0.02$</td>
</tr>
<tr>
<td>$d^{23} - d^b$ [Å]</td>
<td>$+0.04 \pm 0.01$</td>
<td>$+0.04 \pm 0.015$</td>
</tr>
<tr>
<td>$d^{34} - d^b$ [Å]</td>
<td>$+0.02 \pm 0.01$</td>
<td>$+0.025 \pm 0.01$</td>
</tr>
<tr>
<td>$d^{45} - d^b$ [Å]</td>
<td>$0.00 \pm 0.02$</td>
<td>$0.00 \pm 0.02$</td>
</tr>
<tr>
<td>$x^1$ [%]</td>
<td>$100 \pm 7$</td>
<td>(Al)</td>
</tr>
<tr>
<td>$x^2$ [%]</td>
<td>$20 \pm 8$</td>
<td>(Fe)</td>
</tr>
<tr>
<td>$x^3$ [%]</td>
<td>$100 \pm 5$</td>
<td>(Al)</td>
</tr>
<tr>
<td>$x^4$ [%]</td>
<td>$5 \pm 9$</td>
<td>(Fe)</td>
</tr>
<tr>
<td>$u^1$ [Å]</td>
<td>$0.11 \pm 0.02$</td>
<td>$0.11 \pm 0.02$</td>
</tr>
<tr>
<td>$u^2$ [Å]</td>
<td>(as $u^b$)</td>
<td>$0.11 \pm 0.02$</td>
</tr>
<tr>
<td>$u^b_{Al}$ [Å]</td>
<td>$0.12 \pm 0.02$</td>
<td>$0.10 \pm 0.02$</td>
</tr>
<tr>
<td>$u^b_{Fe}$ [Å]</td>
<td>$0.09 \pm 0.02$</td>
<td>$0.08 \pm 0.02$</td>
</tr>
<tr>
<td>$V_{00}$ [eV]</td>
<td>$-10.0$</td>
<td>$-9.5$</td>
</tr>
<tr>
<td>$V_{0i}$ [eV]</td>
<td>$-6.0$</td>
<td>$6.5$</td>
</tr>
<tr>
<td>$R_{\text{min}}$</td>
<td>$0.091$</td>
<td>$0.087$</td>
</tr>
<tr>
<td>$R_{\text{min}} \cdot RR$</td>
<td>$0.015$</td>
<td>$0.014$</td>
</tr>
</tbody>
</table>

Table 4.4: Best fit results for Fe$_{0.53}$Al$_{0.47}$(100)-(1×1)$^{III}$ when keeping $u^2 = u^b$, but allowing for substitutional disorder (left) vs. a model allowing for independent $u^2$, but assuming full B2 order. See Sect. 4.2 for the different meaning of $V_{00}$ here, compared to $x = 0.03$, 0.15, and 0.30.

of Al antisite defects in a near-surface layer would add a whole new facet to this picture, and therefore deserves careful attention. The result of Kottcke et al. was certainly proven with statistical significance within the tested parameter space. However, prominently absent from the latter is the possibility of a second layer vibrational amplitude $u^2$ enhanced over that in the bulk. Such an enhancement was found for all three preceding samples $x = 0.03$, 0.15, and 0.30, and a correlation of $u^2$ with $x^2$ seems well possible in view of Eq. (4.7) in Sect. 4.3.3.

Table 4.4 lists the results of two comparative analyses to clarify the influence of $u^2$ on $x^2$ in Fe$_{0.53}$Al$_{0.47}$(100)-(1×1)$^{III}$. The same $I_g(E)$ data as analysed by Kottcke et al. were used, selecting the set measured at $T_{\text{meas}} = 123$ K to minimise the overall influence of thermal vibrations. Since there still exist some minor technical differences between the present analysis and the former one, the left column lists the results with the same parameter set as used in Ref. [Ktk97], ensuring the direct comparability of old and new results. Indeed, the structural and chemical results are practically identical to the original analysis (right column of Table 4.3) [Ktk97]. $R_{\text{min}} = 0.091$ moreover indicates a satisfactory reproduction of experimental $I_g(E)$ curves by the model spectra. Again,
substitutional disorder proves significant in view of $R_{\text{min}} \cdot RR$ – the same parameter set (i.e., still $u^2 = u^b$), but constrained to a fully ordered model, yields only $R_P = 0.107$. Next, the influence of an independent $u^2$ was tested for, this time not allowing for any substitutional disorder in the fit (right column of Table 4.4). Strikingly, the resulting experiment-theory agreement, $R_{\text{min}} = 0.087$, is even slightly better than for the former analysis, with the enhanced second layer vibrations fully compensating for the missing Al antisites. Otherwise, the parameters of both analyses are extremely similar, and consistent with the older results of Wang et al. [Wan93].

From a strict, statistical viewpoint, Table 4.4 also does not rule out the possibility of substitutional disorder at the level claimed by Refs. [Ktk96, Ktk97b], since $R_{\text{min}}$ for both parameter sets lie within the limits set by $R_{\text{min}} \cdot RR$. The indistinguishability of both models can also be visualised directly from $I_g(E)$. As an example, Fig. 4.13 compares the calculated curves of the (1,1) and (2,0) beams to experiment. Quite obviously, both models reproduce the experimental features equally well. However, the mutual difference between the theoretical spectra (monitored by $R_P = 0.018$ for the (1,0) beam, $R_P = 0.026$ for the (2,0) beam, and $R_P = 0.028$ on average over all beams) is much smaller than the discrepancy remaining to experiment, proving the correlation of the model parameters $x^2$ and $u^2$ beyond doubt. Accordingly, introducing substitutional disorder in addition to $u^2$ now produces only a negligible improvement of the fit quality compared to the fully ordered model in the right column of Table 4.4, far below the statistical limit set by $R_{\text{min}} \cdot RR$.

In total, while we cannot rule out the occurrence of small amounts of antisites in this surface, the safe conclusion to be drawn is that Fe$_{0.53}$Al$_{0.47}$(100)-(1×1)$^{\text{III}}$ appears fully ordered within the present statistical resolution. This finding (depicted schematically in Fig. 4.14) appears physically...
4.5 Structural trends

The preceding structural analyses provide a comprehensive overview of bcc-based Fe$_{1-x}$Al$_x$(100) surfaces. It now remains to place these in a common picture, identifying similarities and composition-induced differences across the phase diagram.

Segregation and Order.
Certainly, the most obvious feature of Fe$_{1-x}$Al$_x$(100) is the strong tendency of Al to segregate to the topmost layer, and to eventually terminate the surface in full. However, $x^1$ is not as smooth a function of $x$ as one might naively expect. Rather, half the top layer sites are already occupied by Al at $x$ as low as 0.03. The other half is filled much more gradually – at $x = 0.15$, there are still 25 % Fe atoms left in the top layer. A (nearly) completely filled Al top layer is only reached in the D0$_3$ region of the bulk phase diagram ($x = 0.30$). Obviously, Al segregation in Fe$_{1-x}$Al$_x$(100) is a two-step process, although the development of the initial step (below $x = 0.03$) is not observed by us. The key to understand this are in the order properties of the surface plane: Obviously, there is a pronounced tendency for the formation of lateral LRO ($x = 0.03$) or SRO ($x = 0.15$), based on the avoidance of in-plane Fe-Fe or Al-Al pairs as far as possible. This suggests the following, qualitative scenario. In the first step, Al segregation is unencumbered by 2NN opposition$^6$ – many top layer sites can be found which do not yet have an Al 2NN. However, as $x^1$ approaches 0.5, this becomes increasingly difficult, forcing the surface into a c(2×2) arrangement, in order to maximise the number of heterogeneous bonds. After that, filling the remaining sites with Al faces a much

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$^6$Note that this refers to 2NN in *bulk* terminology, which are the closest neighbours found in a bcc(100) plane (Chapter 2).
tougher opposition – each additional Al atom must now work against four Al 2NN. This second step apparently lasts across the whole A2 random alloy phase.

Obviously, the two-step scenario is consistent with the known role of 2NN interactions in the bulk. However, it should be noted that it also requires a delicate balance between the initial Al segregation driving force, and the strength of 2NN interactions. If the latter were too weak, segregation would proceed smoothly up to \( x^1 = 100\% \) Al. On the other hand, if the latter were too strong, no second step of segregation could occur – \( x^1 \) would simply stop at 50\% Al. In this sense, we may state that order shapes the segregation process in \( \text{Fe}_{1-x}\text{Al}_x(100) \). We shall explore the conditions for this to occur more quantitatively in Chapter 6.

As \( x \) rises, the formation of first SRO and then LRO also progresses perpendicularly to the surface. Only, bulk-like NN interactions dominate this scene. In the A2 region, the top layer Al enrichment first induces a strongly damped, oscillatory composition profile (\( x = 0.15 \)), as observed for many other ordering systems [Vas97, Pol00, Der01]. In the ordered regions of the phase diagram, the Al top layer also leaves its imprint, by “pinning” the stacking sequence of the layers below – the initial oscillatory composition profile extends to become LRO.

Next, one might also suspect a vertical action of 2NN forces. In particular, any lateral order in the topmost layer should induce this order in the third layer, and vice versa. The fit for \( \text{Fe}_{0.97}\text{Al}_{0.03}(100) \) indicates such third-layer ordering, but unfortunately, the effect is too small to be proven with statistical certainty. On the other hand, if the topmost layer of \( \text{Fe}_{0.70}\text{Al}_{0.30}(100) \) really contained 10\% Fe (as given by the best fit in Fig. 4.11), one would at least expect some lateral LRO due to the interaction with the ordered third layer, as found by Kottcke et al. [Ktk96]. If so, this would again be below the detection limit of our analysis – at least, an even spread of Fe on both top layer sublattices is found here. However, it must be remembered that, in a \( \text{D}_0^3(100) \) plane, lateral LRO is primarily due to four in-plane 2NN bonds, and only the registry between adjacent planes is mediated by their perpendicular interaction. For dilute concentrations of one element, the former mechanism breaks down. Possibly, the single 2NN bond between the topmost and third layer is too weak to enforce top layer LRO on its own.

The last question which should be asked concerns the observed near-surface order of \( \text{Fe}_{0.70}\text{Al}_{0.30}(100) \). Taking the fit result seriously, a certain degree of near-surface disorder is found both in the top and in the second layer. If they were real, they would certainly imply some modification of bulk-like ordering interactions near the surface. However, as stated above, the impact of these effects on the fit is relatively small, and a more precise measurement would be required before risking a definite statement to that extent.

Geometrical relaxation.

At first sight, the relaxation pattern observed for \( \text{Fe}_{1-x}\text{Al}_x(100) \) is not unusual. Any strong deviations from a bulk-like arrangement are well restricted to the very surface region, with only \( d^{12} \) and \( d^{23} \) deviating appreciably from \( d^b \), and only small ordered and/or element-dependent buckling amplitudes are detected. This simple picture could be consistently explained by a purely local view of relaxation. The immediate NN/2NN environment of atoms in the third layer and below hardly deviates from that in the bulk, and they are electronically well screened from the selvedge. So, it is understandable
4.5. Structural trends

Figure 4.15: Development of $\Delta d^{12}/d^b$ (left) and $a$ (right) as a function of Al content $x$ in $\text{Fe}_{1-x}\text{Al}_x(100)$ surfaces. Some literature values are shown for comparison, including the top layer relaxation of Fe(100) [Wan87], and the bulk lattice parameter of $\text{Fe}_{1-x}\text{Al}_x$ [Lih61], extrapolated to $T_{\text{meas}} = 100$ K using the thermal expansion coefficient of pure Fe [Cor61]. Also shown is the lattice parameter of $\text{Fe}_{0.53}\text{Al}_{0.47}(100)$ as determined by Kottcke [Ktk97b], which was used in the present study.

that their positions adhere closely to bulk-like values.\textsuperscript{7} In fact, a quick glance at related systems seems to confirm this “local” picture – including the systems listed in Table 5.7 (Chapter 5.5), in the “Surface Science Database” [Wat99], or the (100) surfaces of other B2-ordered materials – CoAl(100) (Chapter 5.3), NiAl(100) [Dav88, Tak99] and FeRh(100) [Kim99]. In contrast, a much deeper-reaching multilayer relaxation is reported for the A2 random alloy system $\text{Mo}_{1-x}\text{Re}_x(100)$ [Ktk97c, Ham99], and could again be correlated to local factors through a deep-reaching oscillatory segregation profile.

However, the most striking geometrical aspect of $\text{Fe}_{1-x}\text{Al}_x(100)$ points beyond the above reasoning. As seen in Fig. 4.15 (left), $d^{12}$ contracts continuously with growing $x$, starting with $\Delta d^{12}/d^b = -1.4 \%$ at $x = 0.03$,\textsuperscript{8} but ending with as much as $\Delta d^{12}/d^b = -14.5 \%$ for $x = 0.47$ – this is the largest value reported for bcc(100)-based systems as yet, and also exceeds other B2(100) surfaces by far. During this development, the top layer composition grows from $x^1 = 0.5$ to $x^1 = 1.0$, while the second layer always remains (practically) pure Fe. Of course, one might try to hold $x^1$ responsible for the development of $d^{12}$, using the change of bond partners or the overall top layer charge density to explain the observed relaxation in a local picture. However, it would then be hard

\textsuperscript{7}Of course, some influence of the surface is still felt in the third layer. For $\text{Fe}_{0.70}\text{Al}_{0.30}(100)$ the Al-enrichment of the top layer manifests itself in $b^3 = 0.05$ Å. And, the slight but significant expansion of $d^{14}$ in $\text{Fe}_{0.53}\text{Al}_{0.47}(100)$ may be correlated to the unusual contraction of $d^{12}$ in this case. However, the extent of both third layer effects is clearly small.

\textsuperscript{8}Pure Fe(100) forms no exception to this rule. $\Delta d^{12}/d^b = -5 \%$ [Wan87] must be compared to the top layer Fe position in $\text{Fe}_{0.97}\text{Al}_{0.03}(100)$. Here, Fe resides below Al in the top layer, at $\Delta h^1_{\text{Fe}}/d^b = -4.2 \%$ – the same as for pure Fe within error limits.
to understand why $d^{12}$ should continue to contract even after an almost full top Al layer has been reached at $x = 0.30$. Whatever the true reason for the development of $d^{12}$, it seems that a simple picture based on local bonds can not account for it in full. Instead, one might envision a slightly less "local" relaxation driving force – for instance, electronic changes in the second layer. Possible reasons for this could be the continuously changing charge density in the third layer, where the Al concentration $x^3$ increases from practically zero to 100 %, or even a decreasing magnetic moment of second layer atoms with rising $x$. (The latter is expected as the overall magnetisation of $Fe_{1-x}Al_x$ decreases in the bulk as well, indicated by the behaviour of its ferromagnetic $T_c$ – until only the paramagnetic phase remains above $x = 0.30$ [Lan91]). Of course, any such explanation must remain speculative here. In the literature, many much more sophisticated approaches to surface relaxation exist, beginning with the classic "point-ion" model, originally due to Finnis and Heine [Fin74], and reaching up to state-of-the-art $ab$ initio treatments. The investigation of the $d^{12}$ development in $Fe_{1-x}Al_x(100)$ by such a more quantitative scheme might turn up some interesting insights, e.g. the activity of yet another mechanism, overlooked above. However, the present work is not a suitable platform for this task.

**Bulk properties.**

Actually, quantitative LEED is not designed to determine the bulk properties of any material. Quantities such as the lattice parameter or thermal vibrations can be determined with much higher accuracy by generic bulk diffraction techniques, such as XRD or neutron scattering. In this light, it is remarkable that some values determined above agree very well with bulk literature data, where these are available.

First, consider the lattice parameter $a$ of all four samples as determined by quantitative LEED. Here, literature data only exist for RT or above, but not for $T_{\text{meas}} \approx 100$ K, which was the main reason to explicitly include $a$ as a fit parameter here. Of course, one may now compare these results to the available literature. To that end, the room temperature data of Lihl et al. [Lih61] were extrapolated to $T_{\text{meas}} = 100$ K by applying the known thermal expansion coefficient of bulk Fe [Cor61]. Fig. 4.15 (right) shows these values together with the LEED results above. The agreement achieved is truly surprising – both groups lie much closer together than one would have expected even from our single-parameter error bars only. In retrospect, this observation also validates the approach to $V_0(E)$ taken in the present work, and by Kottcke in Ref. [Ktk97b]. Obviously, the $ab$ initio energy-dependent inner potential by Rundgren suffices to fully avoid its correlation with $a$ [Wal00], but also the attempt to fit the average slope of $V_0(E)$ for known $a$ and then use that slope to determine $a$ at another temperature provides a consistent description.

Second, a brief look may be taken at the vibrational amplitudes determined above. It was said before that their values are relatively uncertain, not least due to the correlation with chemical quantities. On the other hand, since $u^b$ were always determined for bulk-ordered crystals below the fourth layer, one should not expect this correlation to be too extreme for well-annealed samples. In fact, it turns out that the elemental bulk vibrational amplitude for Fe gives a consistent picture across all investigated samples – it varies between $0.06 \text{ Å} \leq u^b_{Fe} \leq 0.08 \text{ Å}$ for $x = 0.03, 0.30, \text{ and } 0.47$, and fits perfectly with the magnitude expected from the Debye model, Eq. (3.25), for bulk Fe at 100 K, $u^b = 0.07$ Å ($\theta_D = 465$ K [Gry72]). For $x = 0.30$ and 0.47, where an independent vibrational amplitude $u^b_{Al}$
can be determined, it seems that $u_{Al}^b$ and $u_{Fe}^b$ are approximately equal within error limits, consistent with the experimental and theoretical finding for bulk NiAl [Geo77, Gum96, Nue98].

The only $u^b$ value that slightly (though not outside its error limits) deviates from this trend is $u^b = 0.10 \text{ Å}$, determined for $x = 0.15$. In fact, all vibrational amplitudes determined for this sample appear systematically enhanced over those of the other samples. The most likely explanation for this behaviour is a contribution of static displacive disorder, which here adds to the usual thermal disorder. In fact, a bulk $\gamma$-ray and neutron diffraction study of Fe$_{0.80}$Al$_{0.20}$ [Pie89] suggests an enhanced average root mean-square displacement of 0.092 Å, with 0.074 Å due to thermal vibrations and 0.055 Å due to static displacements. Remarkably, using the parametrisation of Ref. [Pie89], exactly $u^b = 0.10 \text{ Å}$ would be expected for $T_{meas} = 100 \text{ K}$, identical to the result obtained here. Hence, one may speculate that such static displacive disorder really only develops well within the A2 phase region, where different local bonding environments must be expected, but not in the long-range ordered regions of the phase diagram, where the local coordination is always the same for each site.

4.6 Summary

The impact of the present chapter’s quantitative LEED studies, completed by results from the proven combination of STM and LEIS [Pla99, Pla99b], is twofold.

On the methodological side, the factors which affect the “chemical” precision of quantitative LEED are now unravelled: The example of Fe$_{0.85}$Al$_{0.15}$(100) reveals a correlation of occupation probabilities with other parameters, particularly element-dependent thermal vibrations on the lattice site in question. These insights allow to formulate some guidelines, which hopefully enable an optimal judgement of chemical accuracy in the remaining structure determinations of this work. Most importantly, it is now clear that all aspects which affect the effective site-dependent scattering factor deserve our attention, and that the elimination of even small systematic errors from the entire structural model is worth the effort.

Regarding the physics of alloy surfaces, we now possess a detailed picture of the structural and stoichiometric development of Fe$_{1-x}$Al$_x$(100) across all bcc-based phases ($0 \leq x \leq 0.50$). Most importantly, the rise of $x^1$ with $x$ happens mainly below the D0$_3$ phase region, and proceeds in two distinct steps. This splitting can be qualitatively understood from the activity of bulk-like 2NN interactions within the surface plane, but requires their delicate balance with the segregation driving force: “Order shapes the segregation process”. Nevertheless, even with these insights, our understanding of Al segregation in Fe$_{1-x}$Al$_x$(100) remains at a qualitative level only: There is no guarantee that the listed effects suffice to explain our results in full. Thus, we shall scrutinise their interplay more quantitatively in Chapter 6.
Chapter 5

The structure of CoAl surfaces

Having established a clear picture of the surface physics of Fe$_{1-x}$Al$_x$(100), a study of CoAl surfaces is ideally suited to broaden this view in two directions. First, modifying the chemical identity of the transition metal allows to study the behaviour of an isostructural system with a different set of interatomic interactions in play. Second, the influence of different surface orientations of the same fundamental bcc lattice may here be studied. For B2 FeAl, this path is blocked by nature, since orientations other than (100) show a tendency to form large-scale reconstructions, or even to facet (see Sect. 2.3). No such restriction applies to CoAl, and in fact, a quantitative LEED study of the close-packed CoAl(110) surface already exists [Blu96]. Here, we shall focus on the physics of (100) oriented samples first, and then study the much more open (111) orientation for comparison.

In a way, the Co-Al system also furnishes a missing link in the existing knowledge on TM-Al surfaces in general. Both neighbouring combinations Fe-Al and Ni-Al have been extensively studied in the past, not least in the preceding chapter. While the latter confirms a simple, bulk-like termination for B2 Fe$_{1-x}$Al$_x$(100), the situation is much more confusing for NiAl(100) — at any rate, the minimum conclusion from Sect. 2.3 must be that FeAl(100) and NiAl(100) are not directly equivalent. The same seems to hold for the (111) orientation — for FeAl, the surface with this orientation reconstructs, whereas a bulk-like unit mesh prevails for NiAl(111) in principle, albeit with contradictory structure models from different sources. Earlier, CoAl(110) was shown to behave much more similar to NiAl(110) than to FeAl(110). The following sections clarify whether this also holds for CoAl(100) and (111), and, for CoAl, answer the question which as yet haunts the NiAl system: Which bulk-like ordered termination forms, or does a bulk-like termination form at all?

We will subsequently summarise the available experimental evidence for CoAl(100) and (111), and outline some technical aspects of the following LEED structural analyses. Their results are described in Sect. 5.3 for CoAl(100), and in Sect. 5.4 for CoAl(111). In Sect. 5.5, we shall finally attempt to establish common trends, and link these to related work.
5.1 Experimental characterisation

In certain aspects of their behaviour, CoAl(100) and (111) are relatively similar. The available experimental information for both is therefore discussed together in the following, split into results from different techniques: AES, LEED (drawing on the work of Ch. Rath, Ch. Müller, W. Meier and Ch. Schmidt), and STM (performed in collaboration with Dipl.-Phys. M. Wiets and Dr. M. Weinelt, Erlangen). The overall preparation method for Co-Al surfaces used here is the same as that described for Fe-Al(100) in Sect. 2.4: An initial ion sputtering treatment depletes the near-surface region of Al, high-temperature annealing brings Al back from the faraway bulk, and quick quenching to low $T$ ($\approx 100$ K) precedes any quantitative measurements. On this basis, the present section aims to define the surface conditions which correspond to a state of "compositional equilibrium" most closely.

**AES observations**

As for $\text{Fe}^{1-x}\text{Al}_x(100)$ in Sect. 2.4, the ratio of Auger peak-to-peak intensities for Al (68 eV) and Co (53 eV), $r_{\text{AES}}$, is a useful measure to characterise the dependence of the overall surface composition of CoAl(100) and (111) on $T_{\text{anneal}}$. Fig. 5.1 shows the development of $r_{\text{AES}}$ for both (annealing time: $\Delta t = 5$ min per step) [Smt99], and also for the (110) surface in comparison (Ref. [Blu96]). At each step, it proved impossible to change $r_{\text{AES}}$ significantly by prolonged annealing — at least, not within the limits set by beginning surface contamination. Different initial sputtering conditions (1 keV $\text{Ne}^+$ ions instead of 2 keV $\text{Ar}^+$ ions for $\text{Fe}^{1-x}\text{Al}_x(100)$) and a different spectrometer type preclude a quantitative comparison of the CoAl(100) and (111) results to both CoAl(110) and $\text{Fe}^{1-x}\text{Al}_x(100)$. However, already their qualitative appearance reveals striking differences to the Fe-Al curves of Fig. 2.8: For CoAl(100) and (111), $r_{\text{AES}}$ increases continuously with $T_{\text{anneal}}$, displaying neither a low-temperature nor a high-temperature plateau. The absence of the former may be understood by comparison to CoAl(110) — here, the onset of near-surface mobility lies just below the lowest annealing temperature used for (100) and (111), $T_{\text{anneal}} \approx 500\,K$. However, the lack of a high-temperature region of stationary $r_{\text{AES}}$ leaves more room for questions.

For $\text{Fe}^{1-x}\text{Al}_x(100)$, the plateaus of approximately constant $r_{\text{AES}}$ at high $T_{\text{anneal}}$ in Fig. 2.8 were taken as an indicator that here, compositional equilibrium with the faraway bulk was established well enough to guarantee a stationary surface structure — i.e., the segregation profile which corresponds to thermal equilibrium of the bulk crystal at $T_{\text{eq}}$. Due to the lack of similar plateaus for CoAl(100) and (111), such "globally" stable surface conditions cannot be guaranteed from AES. This holds even at the highest possible $T_{\text{anneal}}$, just below the onset of Al evaporation. We must conclude that forming the "global" thermal equilibrium surface structure of CoAl(100) and (111) requires annealing temperatures at least 400-500 K higher than for FeAl(100), possibly even above. Two factors could be responsible for such behaviour:

- **Distinctly slower self-diffusion in CoAl than in FeAl:** Indeed, a tracer diffusion measurement shows the Co self-diffusion coefficient in B2 CoAl [Nix51] to be more than an order of magnitude smaller than for Fe in FeAl [Lar75, Hel99]. These results suggest a shift of the diffusion temperature scale by about 400 K between both systems.
Figure 5.1: Near-surface stoichiometry of CoAl(100) and (111), monitored by $r_{AES}$, as a function of annealing temperature after sputtering [Smt99]. For comparison, older data for CoAl(110) [Blu96] are also shown. Due to the use of different spectrometer types and sputter conditions, the data for (111) and (100) can only be compared qualitatively to CoAl(110), and to Fe$_{1-x}$Al$_x$(100) in Fig. 2.8.
Greater sensitivity of the surface concentration profile to the near-surface Al concentration:
As outlined in Sect. 2.4, partial annealing upon preferential sputtering brings an entire near-surface region (of thickness $\gtrsim 1$ nm) to some average Al concentration $x^{\text{av}}$. However, $r_{\text{AES}}$ is not a simple measure of $x^{\text{av}}$ – rather, it depends strongly on the actual contribution from the topmost layers, i.e. the composition profile at the selvedge (for a detailed discussion of $r_{\text{AES}}$, see Ref. [Gra95b]). For instance, if $x^1$ or $x^2$ depended markedly on $x^{\text{av}}$ as $x^{\text{av}} \lesssim 0.5$, $r_{\text{AES}}$ would "magnify" even small changes in this range, delaying the development of a plateau with $T_{\text{anneal}}$.

In principle, the first point suffices to explain the present differences between Fe-Al and Co-Al within the error limits of Figs. 5.1 and 2.8. Indeed, the CoAl(110) surface retains a small, residual near-surface Co enrichment even after annealing at around 1300 K, showing the near-surface stoichiometry to be not yet completely restored. Nevertheless, the second point should be borne in mind.

Qualitative LEED observations
As for Fe$_{1-x}$Al$_x$(100), distinct changes of the LEED patterns with increasing $T_{\text{anneal}}$ develop also for CoAl(100) and (111). The freshly sputtered CoAl(100) surface is characterised by a high-background (1×1) pattern. At and above $T_{\text{anneal}} = 650$ K, the integer order spots sharpen. However, Fig. 5.2a shows that some distinct diffuse intensity remains, centred about the half-order positions of a hypothetical c(2×2) structure (compare Fig. 3.2). Its brightness increases up to $T_{\text{anneal}} \approx 900$ K, and then weakens again, but remains visible even at $T_{\text{anneal}} \approx 1300$ K, as seen in Fig. 5.2b. In parallel, the ordered $I_g(E)$ spectra undergo strong structural changes around $T_{\text{anneal}} \approx 600$ K, and then some weaker ones between 1100 and 1200 K [Smt99]. As mentioned in Sect. 3.1, diffuse intensity can be an indicator for the existence of lateral short-range order in alloy systems. In view of
both FeAl(100) and NiAl(100), the occurrence of intermediate ordered structures during annealing is no surprise as such. However, it is remarkable that

1. an ordered superstructure does not form for CoAl(100), indicating that a possible order-disorder transition temperature lies below the temperature of local equilibrium formation, \( T_{eq} \), and

2. the lateral SRO persists over the entire range of \( T_{anneal} \), although any substitutional disorder is incompatible with a bulk-like, ordered B2 (100) arrangement – if so, one would have to expect CoAl(100) to deviate from a fully ordered structure in some way.

It is tempting to interpret the diffuse intensity distribution found in Fig. 5.2 as the broadened superstructure spots of an (ideally) long-range ordered c(2\( \times \)2) structure – this type of SRO would be perfectly well consistent with the behaviour of Fe\(_{1-x}\)Al\(_x\)(100) surfaces, again hinting to the activity of 2NN interactions. However, the broad intensity “clouds” around half-order spots could also hide a yet more complex arrangement. For instance, the LEED pattern of a c(\( \sqrt{2} \times \sqrt{2} \))\( R45^\circ \) superstructure (known from NiAl(100), Fig. 2.7) has four superstructure spots at third-order positions, as depicted in Fig. 5.3, resulting from two different, rotationally equivalent domains. Comparing this to Fig. 5.2, it proves hard to distinguish between both possibilities by plain eye – the “half-order” diffuse intensity is broad enough to be a conglomerate of four broadened third-order spots. Clearly, more quantitative investigations would be needed to decide on the precise nature of SRO near this surface.

In contrast, the LEED development of CoAl(111) is less spectacular. The LEED spots sharpen above \( T_{anneal} \approx 625 \text{ K} \), with two faint superstructures of (\( \sqrt{3} \times \sqrt{3} \))\( R30^\circ \) and (2\( \times \)2) periodicity developing below \( T_{anneal} \approx 850 \text{ K} \). Above this point, a sharp and low-background (1\( \times \)1) pattern persists, and the \( I_g(E) \) characteristics suggest only little structural changes up to the onset of Al evaporation.

**STM observations**

According to Sect. 2.2, the B2 structure consists of alternating Al and Co planes both in the (100) and (111) orientation. Hence, the corresponding surfaces may terminate either by the Al or by the Co sublattice – or, possibly, both [Noo87, Noo88, Dav88]. Obviously, important evidence for either possibility can already be gained from the mere surface morphology in STM. If the termination is unique (i.e., if one structural domain characterises the entire surface), only double steps can form. In contrast, large amounts of single steps would hint to a mixed termination by both sublattices of the B2 structure. Note that these points hold irrespective of the actual surface composition – they are enforced by the order of the underlying B2 bulk.

1Note that the pattern in Fig. 5.3 is rotated by \( \approx 45^\circ \) relative to the experimental one in Fig. 5.2.
Chapter 5. The structure of CoAl surfaces

Fig. 5.4 (a) and (b) shows room temperature STM images obtained from CoAl(100) and (111), both annealed at $T_{\text{anneal}} = 1273$ K. In general, CoAl(100) consists of terraces with widths of several $100 \, \text{Å}$. As the line scan in Fig. 5.4a shows, these terraces are always separated by double steps (remembering the bulk interlayer distance of CoAl(100), $d_b^{100} = 1.43 \, \text{Å}$). So, we already possess a valuable piece of information: Most likely, the CoAl(100) surface is terminated by one sublattice only. The existence of another domain, hiding somewhere outside the view of STM, would be quite surprising. CoAl(111), on the other hand, shows a less clear surface morphology. In general, its terraces are much smaller than for CoAl(100), and it is more difficult to find large-scale flat areas, such as that shown in Fig. 5.4b. Although this could strictly be a preparational artifact, a lower overall surface stability of the (111) orientation would be plausible in view of its openness. At any rate, the worse-defined morphology renders the identification of individual steps more difficult than for CoAl(100): Multiple steps often group together between adjacent “plains”. Nevertheless, the central result is that here, too, the height of the observable individual steps is twice $d_b^{111} = 0.826 \, \text{Å}$. The line scan in Fig. 5.4b demonstrates this clearly for both well-separated steps shown there. So, our findings for CoAl(111) are again consistent with a surface termination by one B2 sublattice only. Unfortunately, the difficulty of assigning multiple step heights precisely in the available images precludes a statement as definitive as for CoAl(100), but a mix of bulk-like, A- and B-terminated domains, proposed for the closely related NiAl(111) system, seems unlikely for CoAl(111) from STM.

For both CoAl(100) and (111), atomic resolution could not be attained in STM. Hence, any direct information on their surface chemical order, or even lateral short-range order, is unavailable from
Table 5.1: Characteristics of the experimental $I_g(E)$ data sets used in the structural analyses of CoAl(100) and (111).

<table>
<thead>
<tr>
<th>Orientation</th>
<th>LEED pattern</th>
<th>$T_{\text{anneal}}$</th>
<th>beams</th>
<th>$\Delta E$</th>
<th>$\overline{R}_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>(1×1)</td>
<td>1230 K</td>
<td>7</td>
<td>1889 eV</td>
<td>0.055</td>
</tr>
<tr>
<td>(111)</td>
<td>(1×1)</td>
<td>1000-1300 K</td>
<td>14</td>
<td>3020 eV</td>
<td>0.11</td>
</tr>
</tbody>
</table>

5.2 Technical remarks

Table 5.1 gives a summary of outward characteristics of the $I_g(E)$ data sets which were used in the structural analyses of CoAl(100) and (111). The range of incidence energies reaches from 20 eV to 500 eV, giving rise to large data bases in either case: seven and fourteen beams, with overall energy widths of 1889 and 3020 eV, respectively. As usual, the data were measured at liquid nitrogen temperature ($T_{\text{meas}} \approx 100$ K).

The data set for CoAl(100) was obtained after annealing the surface to $T_{\text{anneal}} = 1230$ K, i.e. above the second structural transition region mentioned in the preceding section. The average R-factor between symmetry-equivalent $I_g(E)$ curves, $\overline{R}_s$, amounts to 0.055 only, i.e. lies clearly at the lower end of the range already known from Fe$_{1-x}$Al$_x$(100) (Table 4.1). Again, this signifies excellent data quality with respect to both normal incidence and residual statistical errors of measurement. A control data set, measured after annealing to 1300 K, confirms this expectation. The deviation the flat terraces in both Figs. 5.4 (a) and (b) display some nanometre-scale random corrugation, with peak-to-peak amplitudes of around 0.5 Å in either case. It seems that this is not due to experimental noise, but rather due to some physical effect. In the case of Fe$_{0.85}$Al$_{0.15}$(100) above, a similar corrugation was also observed, and tentatively attributed to medium-range lattice relaxations due to fluctuations of the local composition. If so, a similar finding here could be another hint that such disorder also exists in the well-annealed CoAl(100) and (111) surfaces.

Summary

In summary, AES, qualitative LEED and STM suggest the following prerequisites for the LEED analyses below. Obviously, in order to study surfaces close to compositional equilibrium with the bulk, annealing temperatures just below the Al evaporation onset are required. However, AES does not guarantee that a stationary composition profile, corresponding to the equilibrium of the faraway bulk, is reached even then. In analogy to Fe$_{1-x}$Al$_x$(100) (Sect. 2.4), the investigated surfaces would then reflect at least the local thermodynamic equilibrium of a near-surface region which still deviates slightly from a fully B2-ordered bulk. STM certainly points to a homogeneous termination of CoAl(100) and (111) for the present conditions, but the possibility of near-surface substitutional disorder must be tested for. LEED for CoAl(100), and STM for CoAl(100) and (111) would be consistent with its occurrence.
Figure 5.5: Experimental reproducibility of $I_g(E)$ for CoAl(111) for $T_{\text{anneal}} \gtrsim 900$ K, showing the (1,1), (2,0), and (0,3) beams. All spectra are normalised to the same height, but the absolute intensity of the (0,3) beam is lower than for the other two.

between both sets is extremely small (monitored by $R_P = 0.027$), and, not surprisingly, the results of a test analysis are practically identical to those presented in the next section (Table 5.3). In total, the structural analysis of CoAl(100) has a solid experimental foundation.

STM measurements have already shown that the overall surface quality of CoAl(111) is lower than for CoAl(100). Likewise, $R_s = 0.11$ for the (111) data set somewhat exceeds the values seen for (100) surface before, but is not unusually high. However, Table 5.1 also shows that $T_{\text{anneal}}$ is less precise defined here than for the other surfaces investigated in this work, the reason being an inaccurately calibrated thermocouple in experiment. $T_{\text{anneal}}$ definitively ranged above 1000 K, i.e. above any structural changes as judged by the development of $I_g(E)$, and below the Al evaporation onset ($\approx 1300$ K). Hence, it is certainly characteristic of the desired surface conditions. Nevertheless, some additional steps were taken to ensure the reliability of the tested data beyond doubt. Most importantly, two additional $I_g(E)$ data sets were measured after annealing to 900 K and 1300 K, respectively, marking the bounds of the temperature range of interest. Both are quite close to the set listed in Table 5.1, monitored by average Pendry R-factor values $R_P = 0.08$ ($0.10$) for the 900 K (1300 K) data. Thus, the reproducibility of $I_g(E)$ over the desired temperature range is clearly established, but as $R_s$, the respective R-factors are higher than analogous values for (100) oriented surfaces.

To illustrate the probable reason for this observation, Fig. 5.5 compares intensity spectra from all three data sets for the (1,1), (2,0), and (0,3) beams. Visually, the intensity spectra for the feature-rich (1,1) and (2,0) beams are extremely similar, confirming that the data must correspond to structurally identical surfaces. Also shown is the (0,3) beam, which illustrates best an issue with many open surfaces: Their spectra are often dominated by single, “quasi-kinematic” diffraction peaks, and accompanied by long stretches of relatively low intensity. Nevertheless, these regions do contain important diffraction information, and should therefore be included in the structural analysis if possible. Of course, they are more difficult to measure, particularly for higher-index beams, where also the background correction becomes more tedious. The comparison of the (0,3) beam from different data sets illustrates this: Structural features are visually quite close also in the enlarged
5.2. Technical remarks

low-intensity region, but the discrepancies are larger than, e.g., for the (2,0) beam, which is overall much more intense. These areas are responsible for the slightly enhanced $R_P$ values between formally equivalent beams – any systematic discrepancies can be ruled out.\(^2\)

As a definite test that the structural results for CoAl(111), presented in Sect. 5.4, are not influenced by either the uncertain annealing temperature or possible statistical errors, full intensity analyses with the parameter set of the right column of Table 5.6 were also performed for the 900 K and 1300 K control data. Indeed, the results are the same within error limits. In total, the extensive background work done for CoAl(111), which can only be sketched here, proves that the $I_0(E)$ data analysed here are definitely characteristic of the preparation conditions which we are interested in: the high-temperature (1x1) surface for $T_{\text{anneal}}$ between 900 K and 1300 K.

As for Fe\(_{1-x}\)Al\(_x\)(100), all quantitative LEED calculations below were performed using the TensEr-LEED package, including the simultaneous optimisation of all model parameters. The fully relativistic, spin-averaged phase shifts for Co and Al again stem from the package long used in Erlangen [Lib65, Koe69, Grn77], and were calculated for a B2 CoAl bulk crystal. In the multiple scattering calculations, $l_{\text{max}} = 10$ was found sufficient for convergence within the given energy range.

Unfortunately, the calculational restrictions for CoAl(111) (see below) forbid the determination of bulk quantities within a reasonable time frame. To guarantee the consistency between results for all three surfaces, these were therefore fixed at the values obtained in an earlier structural analysis of CoAl(110) [Blu96]. Table 5.2 summarises the parameters concerned. The elemental bulk vibrational amplitudes $u_{\text{Al}}^b$ and $u_{\text{Co}}^b$ both amount to 0.09 Å. As mentioned in Sect. 4.3, fixing these values requires some care, since wrong values would bias any chemical properties of lower layers to be determined. Thus, it is reassuring that they lie in the very range predicted theoretically for NiAl at 100 K ($u_{\text{Al}}^b = u_{\text{Ni}}^b = 0.07$ Å [Gum96]), measured by Nüchter et al. ($u_{\text{Al}}^b = u_{\text{Ni}}^b \approx 0.08$ Å [Nue98]\(^3\), and obtained by extrapolating room temperature results for B2 CoAl to 100 K ($u^b = 0.08$ Å, where $u_{\text{Al}}^b = u_{\text{Co}}^b$ was assumed [Fox83]). Similar to Fe\(_{0.53}\)Al\(_{0.47}\)(100), a linear approximation to $V_{0r}(E)$ was also used for CoAl(110), and is hence carried over to CoAl(100) and (111). Its slope was determined assuming a lattice parameter $a = 2.86$ Å, slightly below the known room temperature value for B2 CoAl, 2.862 Å [Coo63], and actually takes the same value as for Fe\(_{0.53}\)Al\(_{0.47}\)(100) ($V_{0r}(E) = V_{00} + E/150$). While, the exact low-temperature value of $a$ was not fitted itself, this procedure guarantees at least the consistency of $a$ and $V_{0r}$, avoiding the correlation reported in Ref. 2.

Note that the measurement of low-intensity regions in LEED spectra from open surfaces is much simplified by using more modern video equipment, such as a 12-bit camera, mentioned in Sect. 3.1 (see Ref. [Wal01]). However, such equipment was unavailable at the time of measurement of the current spectra.

Note that Refs. [Gum96, Nue98] give to the atomic root mean square displacement in one dimension, while this work refers to the three-dimensional root mean square displacement. The quoted values were therefore multiplied by a factor of $\sqrt{3}$. 

<table>
<thead>
<tr>
<th>Bulk parameter</th>
<th>CoAl(110) [Blu96]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ [Å]</td>
<td>2.86 (fixed)</td>
</tr>
<tr>
<td>$u_{\text{Al}}^b$ [Å]</td>
<td>0.09</td>
</tr>
<tr>
<td>$u_{\text{Co}}^b$ [Å]</td>
<td>0.09</td>
</tr>
<tr>
<td>$V_{0r}(E)$ [eV]</td>
<td>$V_{00} + E/150$</td>
</tr>
<tr>
<td>$V_{0r}$ [eV]</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table 5.2: Bulk parameters used in the structural analyses of CoAl(100) and (111), as originally determined for CoAl(110) [Blu96].
Chapter 5. The structure of CoAl surfaces

[Wal00]. Finally, with \( V_{0i} = 5.5 \) eV, inelastic damping falls into the usual range. For CoAl(100), the bulk interlayer distance \( d_{100} = 1.43 \) Å guarantees the applicability of the layer-stacking scheme (Sect. 3.2.4) in all full dynamical calculations. In contrast, successive (111) planes are spaced much more closely, and \( d_{111} = 0.826 \) Å ranges clearly below the reported validity range of layer stacking. Indeed, tests produced the expected convergence problems with this approach. So, all full dynamical calculations were performed by treating the entire surface slab as one composite layer in angular momentum space. The drawback of this method is its time consumption. To account for all elastic scattering contributions leaving the surface, a slab of 18 layers was required, using about 22 CPU hours even on the most modern-day workstations.\(^4\) Fortunately, the use of the Tensor LEED approximation to optimise all surface structural parameters limits the number of necessary full dynamical calculations quite efficiently. Four successive reference calculations per model were the maximum required, so that the effort associated with a state-of-the-art structure analysis remained at a tractable level. In fact, this technique was already successfully employed for several other open surfaces, including Mo(111) [Arn98], Fe\(_3\)Si(111) [Wei98], Mo\(_{0.75}\)Re\(_{0.25}\)(111) [Ham99], FeSi(111) [Wal01b], and Cu(117) [Wal01], and its application proved straightforward in the present work.

In the structural analysis of CoAl(111) below, many different possible stacking sequences of Al and Co layers had to be tested on equal footing. However, the number of permutations of the topmost \( n \) layers for both possible, B2-terminated domains grows as \( 2 \cdot 2^n \). Even for low \( n \) (say, \( n = 4 \)), this number of full dynamical reference calculations becomes difficult to handle. Fortunately, the problem is simplified by chemical Tensor LEED, which allows to “replace” elements on each lattice site in the perturbational step. So, only two different basic reference calculations were needed to compare all different stacking sequences of the topmost \( n = 8 \) (!) layers. As shown in Fig. 5.6,

\(^4\)22 hours correspond to one Tensor LEED reference calculation for 17 beams between 20 and 500 eV in steps of 3 eV on a state-of-the-art, 667 MHz Alpha-based Compaq XP1000 workstation.
eight “undecided” layers (i.e., 50-50 random in the reference structure) were stacked atop a ten-layer slab of B2 CoAl, terminated by either Al or Co. The maximum parameter space then comprised all possible ordered stacking sequences of the topmost eight layers, in conjunction with geometrical displacements of $\pm 0.3$ Å for layers 1-4 and $\pm 0.2$ Å for layers 5-8. In this approach, the use of random layers in the reference structure has a convenient advantage. If any ordered reference structure were selected, the error due to the use of chemical Tensor LEED would be particularly low for this stacking sequence. In the fit, this would create an inherent imbalance between this and other potential models, and also among the latter. In contrast, the chosen variant avoids biasing the fit by “equalising” any errors due to chemical Tensor LEED as far as possible.

Since it formed the basis of the entire structural analysis, the sufficient generality of this approach must be ascertained carefully. This concerns both the parameter space spanned and the much-stretched validity of the Tensor LEED approximation.

- Relaxations near bcc-based (111) surfaces are generally large (Tables 5.7 and 5.8 in Sect. 5.5), but rarely exceed 0.3 Å. So, even if the true surface structure fell outside the scanned geometry range, one would at least expect a distinct local R-factor minimum at the parameter space’s limits, allowing to identify the true optimum in a refinement step. Fortunately, the search strategy of Sect. 3.4.3 reveals such local minima within the chosen parameter space.

- Taking Sect. 3.4 literally, Tensor LEED can certainly cover the above parameter range, given that Co and Al are both relatively light scatterers. Indeed, the proper identification of the geometric R-factor minimum for a given stacking sequence works reliably in the structural analysis below, justifying the chosen path. However, the matter could be different if several atoms were simultaneously but independently displaced by large distances, since the neglected multiple-scattering terms then gain influence disproportionately. In this respect, the method’s limits are hard to quantify exactly, especially in conjunction with experimental $I_g(E)$ data, which introduce statistical or systematic errors of their own.

To verify the practical resilience of the chosen fit method against both issues, several complete test analyses were performed for explicitly chosen, ordered layer stacking sequences. For instance, this included all ordered permutations of the top two layers on a B2 bulk. Here, the converged geometric best fit always resulted quite close to the structure already found with the initial reference structures of Fig. 5.6. Although incorrect stacking sequences gave rise to more than one geometrical structural minimum in several cases, such artifacts were never due to Tensor LEED itself. In total, these tests further demonstrate the reliability of the actual structural analysis of Sect. 5.4.

### 5.3 Surface structure of CoAl(100)

As already mentioned in the introduction to this chapter, the main question for CoAl(100) is whether it assumes a fully B2-ordered, bulk-like stacking sequence, or deviates from this trend in any way. Of course, we have seen already in Sect. 4.4.3 that B2 Fe$_{0.53}$Al$_{0.47}$(100) adheres to the former, simple
picture, and there is no a priori reason for CoAl(100) to behave otherwise. On the other hand, some of the preinformation collected in Sect. 5.1 suggests otherwise. In particular, the diffuse intensity present in the LEED pattern could be associated with some kind of disorder, the nature of which can only be clarified in a quantitative analysis.

According to Sect. 2.2, even a bulk-terminated B2-ordered (100) surface may assume two different terminations – either by sublattice A (Co) or B (Al). The initial analysis was restricted to these two basic models, allowing the topmost four interlayer spacings and the vibrational amplitudes of the top two layers to deviate from the bulk. The result of this approach is clear, and reproduces that known from FeAl(100): With $R_{\text{min}} = 0.129$, the experiment-theory agreement achieved for the Al-termination is convincing, leaving the Co-terminated version far behind ($R_{\text{min}} = 0.37$). A look at the relaxation pattern associated with this agreement, shown in the left column of Table 5.3, confirms the qualitative similarity to FeAl(100): $d^{12}$ is significantly contracted, $d^{23}$ is slightly expanded, and no measurable relaxation occurs below. On the other hand, the best-fit vibrational amplitudes associated with this structural model appear rather high, at least in comparison to those found for Fe$_{1-x}$Al$_x$(100) surfaces – in particular, $u^1 = 0.23 \pm 0.06$ Å indicates a strangely soft potential for surface atoms in CoAl(100). And, although the experiment-theory agreement reached is good, it still remains somewhat behind the levels reached for Fe$_{1-x}$Al$_x$(100). So, a fully B2-ordered structural model might not reflect experimental reality in all details. Together with the evidence of Sect. 5.1, the enhanced best-fit $u^1$ clearly hint at near-surface substitutional disorder as a possible refinement.

Essentially, CoAl(100) is but a bcc-based (1×1) surface, so that exactly the same parameters as described for Fe$_{0.85}$Al$_{0.15}$(100) in Sect. 3.3.1 can be selected to model near-surface disorder. Hence, possible chemical disorder in the top four layers, the relaxation of these layers including possibly element-dependent positions in the topmost one, a second layer vibrational amplitude, and element-dependent top layer vibrations were optimised below. Indeed, these modifications yield a considerable improvement of the overall fit quality, compared to the ordered model: $R_{\text{min}} = 0.075$ now falls into the very range which is already known from Fe$_{1-x}$Al$_x$(100) surfaces above, and compares similarly well to the experimental data quality as measured by $R_s = 0.055$ (Table 5.1).

As the right column of Table 5.3 and the structural model of Fig. 5.7 show, this change is mainly brought about by about 30 % Co atoms in the topmost layer (the nominal Al sublattice of the B2 structure) – quite unexpected, given the almost universal Al segregation tendency in TM-Al alloys otherwise (Sect. 2.3). Yet, some antisite atoms are also encountered in the second and third layers, and full B2 order commences only in the fourth (in fact, the fifth layer also shows no deviation from the bulk geometry and stoichiometry when explicitly included in the analysis). In itself, the relaxation pattern of the best fit is still plausible: $d^{12}$ is contracted by 0.05 Å (i.e. $-3.7\%$ of $d^b$), spear-heading an oscillatory relaxation which decays over the next two layers. Obviously, $d^{12}$ is now much closer to $d^b$ than for the ordered model above – mainly, this is due to top layer Co, which is 0.08 Å higher than Al, placing the former even slightly outside the truncated-bulk position (by $+0.3\%$ of $d^b$). Nevertheless, top layer Al atoms are now displaced inward of the bulk position by only

\[5\text{In principle, element-dependent positions and vibrations might also have been considered in the second layer. However, as seen in Table 5.3, } x^2 \text{ is too low to allow a meaningful determination of } u^2_{\text{Al}} \text{ and } h^2_{\text{Al}}.\]
5.3. Surface structure of CoAl(100)

<table>
<thead>
<tr>
<th>Model</th>
<th>Ordered B2</th>
<th>Near-surface disorder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al termination</td>
<td>allowed</td>
</tr>
<tr>
<td>$d_b^b$ [Å]</td>
<td>1.43 (fix)</td>
<td></td>
</tr>
<tr>
<td>$d_{12}^b - d_b^b$ [Å]</td>
<td>-0.10 ± 0.04</td>
<td>-0.05 ± 0.02</td>
</tr>
<tr>
<td>$d_{23}^b - d_b^b$ [Å]</td>
<td>+0.02 ± 0.025</td>
<td>+0.03 ± 0.015</td>
</tr>
<tr>
<td>$d_{34}^b - d_b^b$ [Å]</td>
<td>+0.01 ± 0.02</td>
<td>-0.01 ± 0.01</td>
</tr>
<tr>
<td>$d_{45}^b - d_b^b$ [Å]</td>
<td>0.00 ± 0.02</td>
<td>0.00 ± 0.01</td>
</tr>
<tr>
<td>$h_{\text{Al}}^1 - h_{\text{Co}}^1$ [Å]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x^1$ [%]</td>
<td>100 (fix)</td>
<td>70 ± 7</td>
</tr>
<tr>
<td>$x^2$ [%]</td>
<td>0 (fix)</td>
<td>10 ± 8</td>
</tr>
<tr>
<td>$x^3$ [%]</td>
<td>100 (fix)</td>
<td>85 ± 5</td>
</tr>
<tr>
<td>$x^4$ [%]</td>
<td>0 (fix)</td>
<td>0 ± 7</td>
</tr>
<tr>
<td>$u_{\text{Al}}^1$ [Å]</td>
<td>0.23 ± 0.06</td>
<td>0.17 ± 0.02</td>
</tr>
<tr>
<td>$u_{\text{Co}}^1$ [Å]</td>
<td></td>
<td>0.16 ± 0.03</td>
</tr>
<tr>
<td>$u^2$ [Å]</td>
<td>0.14 ± 0.02</td>
<td>0.15 ± 0.02</td>
</tr>
<tr>
<td>$V_{00}$ [eV]</td>
<td>-8.0</td>
<td>-7.5</td>
</tr>
<tr>
<td>$R_{\text{min}}$</td>
<td>0.129</td>
<td>0.075</td>
</tr>
<tr>
<td>$R_{\text{min}} \cdot RR$</td>
<td>0.020</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Table 5.3: Best fit parameters for CoAl(100). The left column shows the result when assuming full B2 order in the near surface region. The right column additionally allows for some substitutional disorder in the topmost four layers.

$X^i$

<table>
<thead>
<tr>
<th>$X^i$</th>
<th>$\Delta d^i/d^b$</th>
<th>$b^i/d^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 %</td>
<td>- 3.7 %</td>
<td>5.6 %</td>
</tr>
<tr>
<td>10 %</td>
<td>+ 2.3 %</td>
<td>- 0.7 %</td>
</tr>
<tr>
<td>85 %</td>
<td></td>
<td>0.0 %</td>
</tr>
<tr>
<td>0 %</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Co
Al

Figure 5.7: Best fit structure of CoAl(100) including substitutional disorder, according to the right column of Table 5.3.
Chapter 5. The structure of CoAl surfaces

-5.4 %, i.e. also less than in the fully ordered model (-7.0 % of $d^\parallel$). So, substitutional disorder is apparently correlated with both top layer elemental positions.

Reassuringly, $u_{\text{Al}}^1$ and $u_{\text{Co}}^1$ are now reduced to 0.17 Å and 0.16 Å, respectively, correcting the weakness of the ordered model there. This again demonstrates the correlation between vibrations and stoichiometry, described in Sect. 4.3, for CoAl(100). So, the single-parameter error bars of Table 5.3 for $x^\parallel$ are probably again much narrower than true all-parameter error bars would be. However, the best-fit values obtained for $u_{\text{Al}}^1$ and $u_{\text{Co}}^1$ here strengthen the credibility of $x^\parallel = 70 %$: According to the brief discussion of Sect. 3.3.1, $u_{\text{Al}}^1 \approx u_{\text{Co}}^1$ seems very reasonable. Both values lie in the range known from Fe$_{1-x}$Al$_x$(100) surfaces, particularly Fe$_{0.85}$Al$_{0.15}$(100), and their remaining enhancement might again be understood as the product of additional statistical static displacements, induced by chemical disorder. In contrast, no such explanation could be found for the much higher $u^1$ of the ordered model of Table 5.3. This, rather, seems to be the artifact of the mentioned correlation.

Nevertheless, to obtain a precise impression of the statistical significance of certain phenomena regardless of correlations, some crucial statements may be tested against constrained fits, and their impact compared to $R_{\text{min}} \cdot RR = 0.011$. This clarifies a number of important points:

1. **There is substitutional disorder in the near-surface region.**
   As already seen, the model enforcing full order in Table 5.3 has a significantly higher $R_{\text{min}}$ than the disordered one. Moreover, it features physically questionable vibrational amplitudes.

2. **There are Co antisite atoms in the topmost layer.**
   A constrained reanalysis with $x^\parallel = 100$ % Al reaches $R_{\text{min}} = 0.108$ only, again significantly worse than the unconstrained fit. Interestingly, the remaining improvement over a fully ordered model is brought about solely by 10 % Co antisites in the third layer of the constrained result. Again, $u^1$ is dubiously enhanced to 0.22 Å.

3. **There is also subsurface disorder in layers two and three.**
   Restricting the fit to $x^\parallel = 0$ %, 100 %, 0 % for $i = 2,3,4$, respectively, also leads to a significantly increased $R_{\text{min}} = 0.107$. In this scenario, the would-be best-fit value of $x^\parallel$ decreases to 60 % Al, accompanied by a drastic increase of $\Delta d_{12}^\parallel = -0.125$ Å, $x^\parallel$ would now amounting to 0.24 Å).

4. **There is a positional difference of Al and Co in the top layer.**
   With the constraint $h_{\text{Al}}^1 = h_{\text{Co}}^1$, the achievable R-factor increases to $R_{\text{min}} = 0.101$. At the same time, the best-fit top layer relaxation decreases to $\Delta d_{12}^\parallel = 0.125$ Å, $x^\parallel$ would now amount to 80 % Al, and again, $u_{\text{Co}}^1 = 0.24$ Å becomes unphysically high. Obviously, the neglect of top layer element-dependent positions is a severe systematic error.

Of course, the superiority of a disordered model surface over a fully ordered one should also show up in the $I_g(E)$ curves. Fig. 5.8 illustrates this for the (1,1) and the (2,2) beams. First, the overall agreement of the model with the experimental data is excellent, i.e. even small features of $I_g(E)$ are reproduced correctly. Yet, since already the ordered model allowed a high-quality reproduction of $I_g(E)$, the influence of substitutional disorder is rather subtle. The latter manifests itself e.g. in
5.4 Surface structure of CoAl(111)

Figure 5.8: Calculated and measured $I_g(E)$ for the (1,1) and (2,2) beams of CoAl(100). Model spectra are shown for both the fully ordered model, and for the best fit including substitutional disorder (left and right columns of Table 5.3).

the small peak shape changes for the (1,1) beam between 150 and 200 eV or at 400 eV, or above 400 eV for the (2,2) beam. Apparently, the main features of the spectra are shaped by the correct overall stacking sequence and relaxation pattern. Substitutional disorder then improves the shapes of many small features, positions of intensity minima, etc. A high-quality experimental data base, as given here, is crucial to address such phenomena.

In total, the present section establishes a clear description of CoAl(100) annealed at high $T$. In view of the excellent experimental reproducibility of $I_g(E)$, the fit result is certainly characteristic for these surface conditions in general. Similar to FeAl(100), the surface terminates with the nominal Al sublattice. However, this top layer contains a remarkably large amount of Co antisite defects, further complemented by antisites also in the second and third layers. In view of the underlying, strongly ordering B2 crystal (fully ordered within error limits from the fourth layer on), these are surprising findings. We shall discuss this issue in greater detail in Sect. 5.5, after enlarging the picture with the structure of CoAl(111).

5.4 Surface structure of CoAl(111)

Through its orientation, CoAl(111) differs qualitatively from all other systems studied in this work – all intra- and interlayer NN and 2NN relationships are changed as described in Sect. 2.2. In particular, an unreconstructed bcc-based (111) surface is much more open than its (100) oriented counterpart, with atoms in the topmost three layers located directly at the selvedge. Nevertheless, one basic question can be directly transferred from the above investigations of B2 Fe$_{0.53}$Al$_{0.47}$ and CoAl (100) systems: Does CoAl(111) retain its bulk-like B2 order near the surface, or do deviations
from this order occur?

Some preliminary hints to the answer might be expected from the adjacent systems FeAl(111) and NiAl(111) (see Sect. 2.3), but as mentioned before, these do not provide a uniform picture. The former surface exhibits large-scale superstructures, and is most likely unrelated to the $(1\times1)$ truncation of CoAl(111). In contrast, NiAl(111) does display a $(1\times1)$ LEED pattern, and only B2-ordered structural models were presented so far. Still, it remains unclear whether this surface is terminated by only one of the two possible B2 sublattices, or whether both coexist in the form of large domains. If the latter model was correct, this possibility must certainly be envisioned for CoAl(111) as well. As mentioned, the absence of single steps on CoAl(111) in STM is a rather strong indicator for a unique termination. Yet, the rather complex morphology of this surface does not allow for a conclusion as clear as for CoAl(100). Moreover, it should be noted that the NiAl(111) dilemma persisted despite the proven predominance of double steps from STM and SPA-LEED – mainly, since no consensus on an alternative explanation for the presence of both Al and Ni in the top layer could be reached. Hence, this class of models also deserves some consideration in the present case.

To deal adequately with these issues, the $I_g(E)$ analysis of CoAl(111) below is split into two parts. The first set of models to be tested are those which retain full B2-order, including the possibility of a domain mix. Deviations from B2 order are considered in the second step. The comparison of both model classes is also an example of a very general, methodological aspect of quantitative LEED, mentioned in Sect. 3.3.1: The introduction of a whole set of additional model parameters, e.g. from an additional structural domain, will always improve a fit to some extent. Care must be taken to test any credible alternatives before accepting such a result as physical reality.

### 5.4.1 B2 ordered model surface termination

According to Sect. 2.2, a (111)-oriented B2 crystal consists of two sublattices A and B, stacked in alternating hexagonal layers. The two possible bulk-ordered model surfaces are natural starting points of the structural analysis, including the geometrical relaxation and vibrational properties of near-surface atoms as free parameters. Due to the openness of bcc-based (111) surfaces and the resulting small interlayer distances, even seemingly deep layers are actually close to the selvedge, and the multilayer relaxation may reach quite deeply. The most extreme reported case is a Mo$_{0.75}$Re$_{0.25}$(111) random alloy surface, where even the eight layer is still affected [Ham99]. Furthermore, a (111) surface changes the NN/2NN environments of all atoms in the topmost three layers, so that significantly changed vibrational amplitudes must be expected there. In short, vertical atomic positions $h^1$-$h^8$ and $u^1$-$u^3$ were all adjusted below.

Already the first step of the analysis, using the general Tensor LEED reference structures depicted in Fig. 5.6, clearly favours the B2-ordered, Al-terminated variant, with $R_P = 0.372$ vs. 0.448 for the Co termination. This trend is confirmed also by the converged results, with $R_{\text{min}} = 0.252$ vs. 0.361, respectively.\(^6\) Also, both initial results (those reached by Tensor LEED from the basic reference

\(^6\) The improvement between the initial and the “converged” result reflects both the Tensor LEED error and the
structures) are geometrically close to their refined versions (after successive reference calculations, and no more deviation between reference and best fit structure). Apparently, the Tensor LEED approximation only causes a more or less systematic increase of the R-factor after the initial step, but identifies the best-fit geometry correctly.

The latter, summarised in Table 5.4, seems quite reasonable at first sight: Any deviations from \( d^b \) remain below 10%. They mainly concern \( d^{23} \) and \( d^{56} \), not unplausible as fifth layer atoms are here NN to those in the second, situated perpendicularly below. On the other hand, the very absence of strong relaxations makes this structural model unusual in the context of other bcc based (111) surfaces – it does not follow their established pattern (see also Sect. 5.5). Moreover, although the fit favours the Al terminated model over the Co terminated one, the difference in fit quality is less clear than for CoAl(100) in the previous section. \( R_{\text{min}} = 0.252 \) as an optimum is high compared to the preceding structural analyses. Although \( R_s = 0.11 \) (Table 5.1) is also higher than in the former cases, its discrepancy to \( R_{\text{min}} \) is still clear. So, the reduced fit quality can hardly be explained by the lower statistical quality of the experimental data alone. Certainly, the model of a unique B2-ordered surface termination cannot be accepted without testing plausible alternatives.

It is worthwhile to compare this situation to the LEED analysis of NiAl(111) as published in the 1980’s [Noo87, Noo88, Dav88]. There, both individual B2-ordered models also lead to similar experiment-theory agreement, which remained worse than for other clean metal surfaces. So, the proposed remedy must at least be tested for CoAl(111): A model surface which contains B2-ordered domains, contributions from which add incoherently in the observed \( I_g(E) \) spectra (Eq. (3.3)). In order to account correctly for parameter correlations, the structure of both must of course be fully reoptimised, including each domain’s top eight interlayer spacings \( d^{12} - d^{89} \) and independent vibrational amplitudes \( u^1 - u^3 \) for a meaningful comparison to Table 5.4. Additionally counting \( V_{00} \), this doubles the number of free parameters from 12 to 24. Technically, the data base is large enough to determine even this amount safely. Nevertheless, one must be wary, as so many additional parameters always allow to improve the fitting of mere noise.

In fact, an assumed coexistence of both domains does enhance the overall fit quality significantly, at least by the standards of \( R_{\text{min}} \cdot R R \). Compared to the single-domain result, the minimum R-factor shrinks by almost 1/3 to \( R_{\text{min}} = 0.174 \), i.e. much more than the estimated influence of statistical experimental errors, \( R_{\text{min}} \cdot R R = 0.021 \). Although the overall fit quality is still not comparable to that reached for (100) surfaces, a domain mix is obviously favoured over both individual B2-ordered terminations. The structural model is depicted in Fig. 5.9 and summarised in Table 5.5. A fraction influence of \( u^1-u^3 \) and \( V_{0\Gamma}(E) \), which were not included in the first approach.
Chapter 5. The structure of CoAl surfaces

<table>
<thead>
<tr>
<th>Model</th>
<th>Domain mix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area fraction $s$ [%]</td>
<td>70 ± 17</td>
</tr>
<tr>
<td>$d^b$ [Å]</td>
<td>0.826 (fix)</td>
</tr>
<tr>
<td>$d^{12} - d^b$ [Å]</td>
<td>-0.04 ± 0.04</td>
</tr>
<tr>
<td>$d^{23} - d^b$ [Å]</td>
<td>-0.05 ± 0.03</td>
</tr>
<tr>
<td>$d^{34} - d^b$ [Å]</td>
<td>-0.01 ± 0.03</td>
</tr>
<tr>
<td>$d^{15} - d^b$ [Å]</td>
<td>-0.01 ± 0.02</td>
</tr>
<tr>
<td>$d^{56} - d^b$ [Å]</td>
<td>-0.06 ± 0.02</td>
</tr>
<tr>
<td>$d^{67} - d^b$ [Å]</td>
<td>+0.03 ± 0.02</td>
</tr>
<tr>
<td>$d^{78} - d^b$ [Å]</td>
<td>0.00 ± 0.03</td>
</tr>
<tr>
<td>$d^{89} - d^b$ [Å]</td>
<td>-0.03 ± 0.04</td>
</tr>
<tr>
<td>$u^1$ [Å]</td>
<td>0.16 ± 0.05</td>
</tr>
<tr>
<td>$u^2$ [Å]</td>
<td>0.14 ± 0.03</td>
</tr>
<tr>
<td>$u^3$ [Å]</td>
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</tr>
<tr>
<td>$V_{00}$ [eV]</td>
<td>-10.5</td>
</tr>
<tr>
<td>$R_{\text{min}}$</td>
<td>0.174</td>
</tr>
<tr>
<td>$R_{\text{min}} \cdot RR$</td>
<td>0.021</td>
</tr>
</tbody>
</table>

Table 5.5: Optimised parameters for CoAl(111), assuming a mix of two B2-ordered domains.

Figure 5.9: Would-be best fit structure of CoAl(111) for the model of two fully B2-ordered domains. The full set of best-fit parameters is listed in Table 5.5.
5.4. Surface structure of CoAl(111)

Figure 5.10: Optimised spectra of the (2,0) beam of CoAl(111). Calculated spectra are shown for a B2-ordered, Al-terminated model surface (Table 5.4), and a mix of both possible, B2-ordered domains (Table 5.5). Compared to experiment, the visual improvement between both models is rather limited on a linear scale (left), and becomes much clearer only when plotted on a logarithmic scale (right).

of 70% of the surface is terminated by Al, and the geometry of this area is only slightly changed by the addition of Co-terminated regions. Similar to what was reported for NiAl(111), the latter are characterised by massive relaxations of up to -41% for $d_{12}$. Since the atoms perpendicularly underneath the top layer are located in the fourth layer only, the full impact of this contraction is lessened by expanded $d_{23}$ and $d_{34}$, with +13% and +23%, respectively. However, with -31%, $d_{45}$ again shows a significant contraction, which is not compensated for but rather enhanced by deeper layer distances. On the whole, the interatomic distance $d_{47}$ is reduced by 0.35 Å, or 14.1%, which is indeed rather much. Obviously, the model of coexistent domains deserves some further scrutiny before being accepted as physical reality.

First, it should be ascertained that the overall drop of $R_{min}$ is convincingly reflected by the best-fit $I_g(E)$ spectra themselves. Since the most drastic change in R-factor between the simple termination and the domain mix occurs for the (2,0) beam, from $R_P = 0.319$ down to $R_P = 0.126$, this is certainly the prime candidate for a closer inspection. In its $I_g(E)$ curve, depicted in Fig. 5.10 (left), some improvements due to the additional domain are indeed visible, concerning certain relative peak heights or peak shapes. However, the overall change is nowhere as pronounced as the R-factor drop suggests. In this beam, as in all others, there are no clear missing spectral features of the single-domain model which the additional domain furnishes – an argument which was successfully invoked in the NiAl(111) case. The reason for the difference in experiment-theory R-factors between both models becomes much clearer when remembering that $R_P$ actually compares $(\frac{d}{dE} \ln(I_g(E)))$, instead of $I_g(E)$ itself. A logarithmic plot of $I_g(E)$, shown again for the (2,0) beam in the right panel of Fig. 5.10, presents a much more convincing view: Here, the shape of the (2,0) beam for the single termination deviates profoundly from that for the mixed termination. Apparently, the domain mix produces a much better balance in the ratio of peak and minimum heights – but adds no crucial spectral features otherwise.
Second, the “making” of the fit result in Table 5.5 deserves some attention. The tabulated structure converged only after several successive Tensor LEED reference calculations, which were accompanied by marked geometry changes of the Co-terminated domain from step to step. In particular, its relaxation also proved sensitive to the handling of non-structural parameters, e.g. $V_0r$, or independent vibrational amplitudes $u_2$ and $u_3$. Finally, the R-factor hypersurface contains at least one more local minimum with respect to the structure of the Co-terminated domain, which yields a best fit R-factor below 0.20. In contrast to the result of Table 5.5, $d_{12}$, $d_{23}$ and $d_{34}$ are here expanded compared to $d^b$. Precise convergence of the best fit proves difficult to achieve in this case, possibly due to multiple, close-spaced minima of the R-factor hypersurface. However, the important message is another one: Even if a domain mix really occurred, the structure of the Co-terminated domain is unusually unstable, and fit artifacts are possible with this model. Obviously, parameter correlations are a dominant factor for this model class.

Although the preceding paragraphs do not disprove a mixed termination of CoAl(111), they certainly cast severe doubts on its existence. Strange interatomic distances, visually unconvincing $I_g(E)$ spectra, and artifacts in the fit procedure all hint towards too many additional fit parameters acting together. However, the improvement still exceeds $R_{\text{min}} \cdot RR$ by far. So, if the Co-terminated domain were an artifact itself, it would have to be due to more than only the residual statistical errors of the data base. Rather, some undetected systematic error of the entire class of B2-ordered models would have to be suspected – a possibility which must be investigated before passing a final judgement on the above results.

### 5.4.2 Deviations from the B2 stacking sequence

Obviously, the class of fully B2-ordered structural models did not yield an entirely satisfactory description of CoAl(111). Since some disorder was already encountered for CoAl(110) [Blu96] and (100) (Sect. 5.3), deviations from B2 order must also be envisioned as a possibility in the present case. In testing these, we shall revert to the assumption of a unique surface termination. After all, a mix of ordered domains was motivated primarily through the NiAl(111) debate, as a means allowing to preserve B2 order. The latter motivation is now irrelevant. On the other hand, one good argument for a unique termination hasn’t changed, and that is the absence of single steps in STM.

CoAl(110) [Blu96] and (100) largely retain their overall lattice arrangement, deviating only by moderate amounts of randomly distributed near-surface antisites. Consequently, the LEED fit quality for a fully B2 ordered model was already satisfactory in either case. In contrast, the best-fit R-factor for B2-stacked CoAl(111), $R_{\text{min}} = 0.252$, leaves more space for improvement, implying that a possible reordering could reach much further. In fact, several plausible scenarios can be envisioned to motivate an altered overall layer stacking sequence near a (111) surface. For instance, an Al segregation tendency might lead to an atop slab of three Al planes, since the top three layers form the selvedge together. *Vice versa*, any near-surface Co enrichment could also affect more than just the top layer. Finally, one might even imagine the precipitation of an entirely different near-surface phase with the selvedge as a nucleus, but affecting also deeper crystal layers. To account for these phenomena in full, the following analysis is split into two steps. Starting from the basic Tensor LEED reference
structures of Fig. 5.6, all possible sequences of pure elemental (1×1) planes within the topmost eight layers are first considered. Based on the result, substitutional disorder is allowed for only in the second step. This procedure avoids the pitfalls of biasing the Tensor LEED fit by starting from a certain ordered elemental arrangement, and of stretching the scanned parameter space too far in the initial search step. For simplicity, this analysis step also did not yet consider independent near-surface vibrations, or an energy-dependent inner potential.

As seen in the last section, the best fit R-factor amounts to $R_P = 0.37$ for the B2-ordered Al-termination, and $R_P = 0.44$ for its Co-terminated counterpart with the initial reference structure. When performing the fit within the same geometric parameter space, but without the constraint of a specified stacking sequence, one might again expect the best fit to be the Al-terminated B2 model. Instead, the optimum $R_P = 0.32$ is achieved for an altered variant: the third layer is replaced by Co, i.e. the preferred vertical order reads AlCo$_3$AlCoAlCo... Consistently, the converged R-factor for this model is $R_{\min} = 0.195$, i.e. also clearly lower than for the two bulk-terminated models, and certainly significant in view of $R_{\min} \cdot RR = 0.024$. The corresponding best-fit parameters are summarised in the left column of Table 5.6. Geometrically, they only deviate from the fully B2-ordered model (Table 5.4) in the position of the third layer: Its outward shift by 0.19 Å leads to a strong contraction of $d_{23}$ (by -32.6 % of $d_b$), and an almost equally strong expansion of $d_{34}$ (by +24.2 %). In fact, this relaxation pattern resembles other bcc (111) systems much more than before.

At first, the observed stacking sequence seems somewhat unexpected. The deviation from a B2 arrangement is certainly induced by the presence of a surface. However, it does not affect the topmost layer, even though this layer is modified most, lacking four NN and three 2NN bonds compared to the bulk. The substituted third layer only lacks one of eight NN, which seems a much weaker effect. On the other hand, the result is not outrightly unphysical, either. Its defining structural element, an AlCo$_3$ slab, is known from the D0$_3$ structure, or the metastable, bcc-based Ni$_2$Al phase (see Sect. 2.1). Neither phase exists in the Co-Al bulk phase diagram, but a residual near-surface Co enrichment as already observed for CoAl(110) and (100) might well induce this type of SRO. Nevertheless, certain alternative stacking sequences were still ruled out through explicit tests. As already mentioned in Sect. 5.2, these comprised all ordered permutations of the top two layers on either an Al- or a Co-terminated B2 substrate, none of which yields a converged best-fit R-factor below 0.35. Also, models extending a D0$_3$- or Ni$_2$Al-like stacking sequence were considered, with either the 7th or the 9th layer also substituted by Co instead of Al, but remained at $R_{\min} > 0.26$. In total, an AlCo$_3$-terminated B2 slab is clearly favoured among the ordered stacking sequences of the top eight layers – in particular, it supersedes the purely Al-terminated B2 arrangement of the previous section.

Comparing the ordered models of Table 5.4 and 5.6, it is striking that $u^3$ is enhanced over $u^2$ in either case. By way of the parameter correlation described in Sect. 4.3, substitutional disorder might well be responsible for this trend. However, its consistent investigation increases the number of free parameters drastically: the composition of each layer, element-dependent positions and vibrations in the top three layers, the relaxation pattern below, plus $V_{00}$, mean a total of 23 fit quantities for the top eight layers. Of course, the search strategy of Sect. 3.4.3 technically allows to optimise all these at once. And indeed, a moderate R-factor improvement to $R_P \approx 0.155$ results,
<table>
<thead>
<tr>
<th>Model</th>
<th>ordered “AlCo$_3$”</th>
<th>disordered “AlCo$_3$”</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.826 (fix)</td>
<td></td>
</tr>
<tr>
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<td>-0.02 ± 0.05</td>
</tr>
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<td>$d_{23}^b - d^b$ [Å]</td>
<td>-0.27</td>
<td>-0.23 ± 0.02</td>
</tr>
<tr>
<td>$d_{34}^b - d^b$ [Å]</td>
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<td>+0.17 ± 0.02</td>
</tr>
<tr>
<td>$d_{45}^b - d^b$ [Å]</td>
<td>-0.02</td>
<td>-0.02 ± 0.02</td>
</tr>
<tr>
<td>$d_{56}^b - d^b$ [Å]</td>
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<td>-0.06 ± 0.02</td>
</tr>
<tr>
<td>$d_{67}^b - d^b$ [Å]</td>
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<td>+0.02 ± 0.02</td>
</tr>
<tr>
<td>$d_{78}^b - d^b$ [Å]</td>
<td>+0.02</td>
<td>+0.02 ± 0.02</td>
</tr>
<tr>
<td>$d_{89}^b - d^b$ [Å]</td>
<td>-0.02</td>
<td>-0.03 ± 0.03</td>
</tr>
<tr>
<td>$h_{Al}^3 - h_{Co}^3$ [Å]</td>
<td>—</td>
<td>-0.10 ± 0.06</td>
</tr>
</tbody>
</table>

Table 5.6: Best fit result for CoAl(111) after testing all ordered stacking sequence of the topmost eight (!) layers. The fully ordered model (left) represents a clear improvement over the B2-ordered, Al-terminated model of Table 5.4. The refined best fit (right) additionally allowed for substitutional disorder in the uppermost three layers.
using the above, AlCo$_3$-terminated geometry as a reference structure. Nevertheless, this brute force approach is decidedly hampered by the sheer number of parameters and their correlation, so that the search procedure fails to converge properly even after an exceptionally long running time. In the preliminary result, some degree of disorder develops in all layers, but is only pronounced in layers 2 and 3, remaining at 5-10% otherwise. In the top three layers, random disorder is associated with unphysical values of the minority elements’ vibrational amplitudes, whereas the positions and vibrational amplitudes of the majority adhere quite closely to the ordered AlCo$_3$ best fit – except for $u^3_{\text{Co}}$, which is now reduced slightly below $u^2_{\text{Co}}$.

As a whole, the full fit indicates that there is some truth to substitutional disorder, but too many insensitive fit parameters appear to prevent a definite result. Also, the overall R-factor still remains relatively high compared to the level known from (100) oriented surfaces, so that one must accept a somewhat lower precision of the conclusions to be drawn here. Possible reasons include the slightly lower statistical quality of the data themselves ($R_s = 0.11$) due to the pathologic shape of some beams (Sect. 5.2), or the overall lower morphological quality of CoAl(111) found in STM (Sect. 5.1), although their impact is hard to quantify. Of course, there might also remain some simpler systematic effect which was overlooked so far. Unfortunately, since the framework of the present model is already quite general, no clear picture of the nature of such a hypothetical effect emerges.

Under these circumstances, the strategy to extract fit results which reflect the average surface structure as accurately as possible must be modified. Instead of further extending the given model, we shall resort to a restricted set of necessary quantities, ruling out any relevance of the remaining ones later. So, the fit was repeated under the following assumptions:

1. Equal elemental vibrational amplitudes: Using the results for (100) surfaces as a guideline, vibrations $u^1$-$u^3$ were assumed to be independent of the element in question.

2. Equal elemental positions in layers 1 and 2: Since the main deviation from B2 order occurs in the third layer, $h_{\text{Al}}^1 = h_{\text{Co}}^1$ and $h_{\text{Al}}^2 = h_{\text{Co}}^2$ were fixed.

3. No substitutional disorder below the third layer: Since no clear trend towards disorder in these layers emerges from the preliminary fit above, they were assumed to be fully B2-ordered in the following.

With these restrictions in place, the converged best fit still yields an optimum R-factor $R_{\text{min}} = 0.172$. Comparing this to the extended result above, it is already clear that neither neglected parameter could have any significant impact on the fit quality in view of $R_{\text{min}} \cdot RR = 0.021$, i.e. the chosen parameter space is justified at least by this formal criterion. Of course, possible correlations of the remaining quantities with excluded ones should be remembered, but the limits of accuracy attainable within the present model are obviously reached.

The restricted best fit is summarised in the right column Table 5.6, and additionally visualised in Fig. 5.11. As expected, the third layer shows some substitutional disorder: While it retains Co as the majority element, it also contains $x^3 = 30 \pm 18$ at.% Al. Some Al is also encountered in the second layer, but this effect can not proven beyond doubt – already the single-parameter error
limits are almost as large as $x^2$ itself. In contrast, the topmost layer consists exclusively of Al, albeit with large error limits, allowing for up to 25 % Co. Interestingly, the relaxation pattern is virtually unchanged compared to the above-described, AlCo$_3$-terminated ordered structural model. The main deviation from $d^b$ still concerns $d^{23}$ and $d^{34}$, changed by -27.9 % and +20.1 %, respectively. The difference to the ordered model is solely due to $h^3_{\text{Al}}$, which lies about 0.10 Å further inward than $h^3_{\text{Co}}$ – the Co position itself remains unchanged. Other than that, the only change of deviation from $d^b$ which is significant in view of its single parameter error bars concerns $d^{56}$, with $\Delta d^{56}/d^b = -7.3$ %. At first sight, this relaxation seems unusually deep, but in fact, the sixth layer atoms are NN to the much more displaced third layer site, which is situated perpendicularly above. Possibly, the third layer just “drags” the sixth layer behind.

Overall, the R-factor improvement between the ordered and the disordered model only just exceeds $R_{\text{min}} \cdot RR$, which indicates a relatively large uncertainty of $x^1$, $x^2$, $x^3$, and $b^3$ individually. Compared to the single-parameter error bars in Table 5.6, their true accuracy is reduced mainly through the correlation with vibrational amplitudes. Nevertheless, the latters’ best fit values strengthen the credibility of substitutional disorder in the third layer: $u^2$ and $u^3$ are still enhanced compared to $u^b$, but $u^3$ no longer exceeds $u^2$. However, $u^2 = 0.12$ Å itself seems relatively low, adding some uncertainty to the observation of Al antisite atoms in the second layer. In contrast, $u^1 = 0.20$ Å is somewhat large compared to $u^b$, and to $u^1$ in Fe$_{1-x}$Al$_x$ and CoAl(100). Although the reduced bonding near a (111) surface and some additional static displacive disorder due to chemical disorder below could explain $u^1$ in principle, the large error bar of $x^1$ should be taken seriously. Finally, the existence of a positional difference $b^3$, certainly cannot be proven from the LEED fit itself. A restricted fit with $b^3 = 0$ still allows for an optimum R-factor $R_P = 0.180$, clearly within the limits set by $R_{\text{min}} \cdot RR$, and correlated with a decrease of $x^3$ to 20 % Al.$^7$ Nevertheless, $b^3 = -0.10$ Å

$^7$With respect to the exact value of $b^3$, some further uncertainty arises from the two additional analyses of the control data sets measured after annealing to 900 K and 1300 K, mentioned in Sect. 5.2. While all other trends of Table 5.6 are well confirmed, a discrepancy results for $b^1$, with best fit values $-0.16 \pm 0.06$ Å and $-0.03 \pm 0.08$ Å, respectively. So, both show the same general tendency as 5.6 (Al is displaced slightly inwards), but the absolute magnitude of $b^3$ is far from certain.
as listed in Table 5.6 is at least not unplausible. In fact, one would have to fear that its neglect introduced an unwanted systematic error into the analysis. In total, the chosen parameter space certainly increases the accuracy of the best-fit compared to the fully ordered model, but its fragility with respect to certain subtleties must be kept in mind when attempting a detailed interpretation in Sect. 6.2.3.

5.4.3 Disorder vs. B2 domains

So far, the overall fit quality achieved was only judged by the R-factor average over the entire $I_g(E)$ data base. Compared to the bulk-like Al-terminated model of Table 5.4, permitting deviations from B2 order does lead to a clear fit improvement. However, $R_{\text{min}} = 0.172$ is still relatively high, preventing a closer investigation of certain subtleties of the AlCo$_3$-terminated, partially disordered model. Moreover, almost exactly the same fit quality is reached for a mix of two fully ordered B2 domains in the surface: the R-factor criterion alone also does not allow to decide between both competing model classes.

In this situation, one should naturally go beyond the mere R-factor criterion, and check whether the observed trends can be verified directly from the spectral features (peaks shapes, positions of minima, etc.) of $I_g(E)$. The first question to be addressed concerns the AlCo$_3$-terminated model Table 5.6 itself: How visible is the imprint of the various structural refinements? Similar to the domain-mix model, the strongest effect is again shown by the (2,0) beam. Fig. 5.12 compares its step-wise development – from the basic, Al-terminated and B2-ordered model (Table 5.4) via the AlCo$_3$-terminated, fully ordered model (Table 5.6, left column) to the best fit of Table 5.6 (right column) – to the experiment. Here, the shape change between the two ordered models is clearly distinguishable, leading to an obvious improvement particularly in the low-intensity region between 100 and 250 eV. In contrast, the further change by allowing for substitutional disorder is less distinct, leading only to some barely visible adjustments (e.g., of the double peak at 150 eV). By and large, similar trends are also observable in the spectra of the remaining beams, although not as pronounced as for the (2,0) beam. On the whole, the visual impression certainly confirms the trend of the average R-factor.
The second question concerns the distinguishability of the B2-ordered domain mix and the model of a unique, but partly disordered termination by way of $I_g(E)$. Obviously, the (2,0) beams of both models (Figs. 5.10 and 5.12) reach approximately the same R-factor level, consistent with the overall trend. However, the spectral shape improves much more visibly for AlCo$_3$ surface termination, without need to resort to a logarithmic plot as in case of the domain mix model (Fig. 5.10). From this observation, it is also clear that the formal indistinguishability between both models is not the product of a true parameter correlation. After all, both impact $I_g(E)$ in different ways, while much more similar spectra would be expected for a true correlation (compare, e.g., the spectra for Fe$_{0.53}$Al$_{0.47}$(100) in Sect. 4.4.3). Again, this trend also holds for other beams. In particular, the AlCo$_3$-terminated model also adds some spectral features which were still missing for the Al-terminated, B2-ordered structure. For instance, the (1,1) beam, shown in Fig. 5.13, contains a triple peak around 100 eV in experiment, but only one peak in both the Al-terminated model and the domain mix. In contrast, the triple shape is obviously present for the “disordered” model, even if its shape still seems somewhat blurred.

These findings are in line with the conclusion already drawn in Sect. 3.2.3: A priori, the impact of incoherent domains on LEED $I_g(E)$ is clearly distinct from that of substitutional disorder. Hence, a full correlation between both sets of parameters could not be expected. If related at all, the observed R-factor equivalence of both approaches for CoAl(111) could only be the product of a relatively weak correlation in the presence of remaining statistical or systematic errors between both models and experiment. However, when going beyond the R-factor, it appears that the AlCo$_3$-terminated model seems to yield a somewhat clearer visually improvement of LEED $I_g(E)$ spectra than its competitor.

In summary, a unique termination with deviations from B2 order certainly yields a more consistent picture than a coexistence of both B2-ordered domains for CoAl(111):

- The single domain model is consistent with STM, while the domain mix is not.
- The single domain model leads to a best-fit description of the surface which is overall plausible. In contrast, the best fit geometry of the domain mix is at least questionable, and structural ambiguities appear during the fit.
- Compared to a B2-ordered, Al-terminated structure, the disordered single domain model adds missing spectral features, while the domain mix does not.

Although both models are still strictly indistinguishable by the R-factor criterion alone, these arguments appear sufficient to discard the fully B2-ordered domain mix model as a likely artifact of too many free parameters. Of course, it is conceivable that both models, the domain mix as well as
the AlCo$_3$-terminated one, are yet part of some larger truth, i.e. a domain mix model including the possibility of substitutional disorder. However, not only does the number of involved parameters increase excessively in such a scenario, the resulting parameter space also becomes increasingly ambiguous. So, such a fit is not attempted at this point. For the time being, the physical foundation of the AlCo$_3$-terminated model seems solid enough to consider this the most likely average surface structure of CoAl(111) by far, even more so as its underlying segregation behaviour and SRO point to the same direction as already observed for CoAl(100). In fact, Chapter 6 explains the AlCo$_3$-like sequence of the top four layers as a natural consequence of a unified picture of order and segregation in all surfaces presented in this work.

5.5 Structural trends

Despite the inherently different geometric properties of (100) and (111) oriented surfaces, their comparison may yet prove fruitful for the understanding of the physics of ordering alloy surfaces as a whole. The following discussion focuses first on aspects of their relaxation in the context of other bcc-based systems, and then addresses a possible scenario to explain their unexpected near-surface composition and ordering.

Geometrical relaxation.

The surface orientation change from (100) to (111) impacts all basic geometric properties drastically, including the bulk interlayer spacing, the size and shape of the 2D unit mesh, and the relative location of NN and 2NN to one another. So, no one could seriously expect any direct comparability of (100) and (111) relaxation patterns, and indeed, the trends found in Table 5.3 and 5.6 are distinctly different from one another. Nevertheless, we may still attempt to place them in the context of similar surfaces, both elemental and alloy ones. If there arose any simple, general trends from the presence of two elements on a (more or less) ordered lattice, these would have to become apparent in the course of that discussion.

Many detailed, comparative studies of the relaxation of different elemental bcc surfaces can be found in the literature (e.g., Refs. [Luo88, Xu94, Che98]), so that a brief summary suffices here. Table 5.7 lists the relaxation patterns of unreconstructed (100) and (111) surfaces of Fe, Ta, Mo, and W. Theoretical data have been inserted where experimental data either do not exist (Ta(111), W(111)), or cannot be obtained due to surface reconstruction (Mo(100), W(100)). Obviously, the trends which arise are quite general. As already mentioned in Sect. 4.5, (100) surfaces feature a simple “$-$+$+” relaxation sequence, with $d_{12}$ contracted rather strongly, and $d_{23}$ expanded moderately. In contrast, (111) surfaces are characterised by a “$-$ $-$ $+$” sequence, i.e. a pronounced double contraction of $d_{12}$ and $d_{23}$, followed by a comparably expanded $d_{34}$. Here, the relative change of $d_{ij}$ is much larger than for (100) surfaces; however, this does not carry over directly to interatomic distances, as perpendicular NN are here located three layers apart (Sect. 2.2), so that successive contractions and expansions may compensate one another.

The compilation of elemental surfaces is contrasted by some results for bcc-based, ordered alloys in Table 5.8. One basic similarity to elemental surfaces is immediately obvious: The depth of their
Chapter 5. The structure of CoAl surfaces

### (100) orientation

<table>
<thead>
<tr>
<th>Material</th>
<th>Fe</th>
<th>Mo</th>
<th>Ta</th>
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<td>—</td>
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### (111) orientation

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<td>[Luo88]</td>
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<td>+0.9</td>
<td>—</td>
<td>—</td>
<td>+2.4</td>
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</tbody>
</table>

Table 5.7: Multilayer relaxation of elemental bcc (100) and (111) surfaces, exemplified for Fe, Mo, Ta, and W. Theoretical data have been inserted in cases where experiments do not exist (Ta(111), W(111)), or are precluded by surface reconstruction (Mo(100), W(100)). In several cases, a choice arose between several works in the literature, particular concerning theoretical studies. In these cases, the \textit{ab initio} studies which seemed best converged with respect to calculational parameters were selected. This suffices for the present, qualitative overview; further details should be sought in the references given.

relaxation profiles is comparable. This may seem trivial, but really is an interesting point as a much deeper-reaching multilayer relaxation was reported for surfaces of the A2 random alloy Mo\(_{0.75}\)Re\(_{0.25}\) [Ktk97c, Ham99]. The latter was tentatively explained by pronounced segregation profiles, creating asymmetric environments also for deep layers. In fact, this reasoning is overall consistent with CoAl(100) and (111): In both cases, we do not find any significant deviations from bulk-like B2 order below the third layer, so that no motivation for much deeper relaxations would exist.\(^8\)

Regarding its average interlayer distances, the trend for CoAl(100) follows that from other elemental surfaces, since \(\Delta d^{12}/d^b = -3.7 \%\) and \(\Delta d^{23}/d^b = +2.3 \%\). \(d^{12}\) is merely a bit less decreased than in the other cases (note the contrast to the strong contraction of \(d^{12}\), in Fe\(_{0.53}\)Al\(_{0.47}\)(100), which is not shared by CoAl(100)). However, the individual atomic positions in the topmost layer do deviate from the general trend. Only Al shows the expected inward contraction \((\Delta d^{12}_{\text{Al}}/d^b = -5.4 \%)\), whereas the Co antisite defects remain practically at the truncated-bulk location \((\Delta d^{12}_{\text{Co}}/d^b =\)

\(^8\)Strictly, \(d^{56}\) in CoAl(111) does change somewhat, but not excessively. Even so, this is probably a consequence of the strong shift of the third layer above.
Table 5.8: Reported multilayer relaxation of some B2- or D0\textsubscript{3}-based (100) and (111) alloy surfaces. In each case, the terminating (nominal) sublattice is also listed. For NiAl(111) the Al-terminated part of the domain mix after Ref. [Dav88] is listed. For FeSi(111), two results are shown. Ref. [Wal01b] is an experimental study of a thin B2 film grown of Si(111), using quantitative LEED. Ref. [Str01] is a very recent \textit{ab initio} study of the system.

<table>
<thead>
<tr>
<th>Material</th>
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<td>Al</td>
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<table>
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</tbody>
</table>

Naturally, such a buckling is a generic degree of freedom of a diatomic surface, known for instance from NiAl(110) [Dav85a, Dav85b, Yal88, Mul88, Tor01], CoAl(110) [Blu96], or the A2 Fe\textsubscript{1-x}Al\textsubscript{x}(100) surfaces studied in Chapter 4. Only, in all these cases, Al is the element displaced outwards. For NiAl(110), this was explained by the greater flexibility of its sp-like charge density [Kan87, Lee87]. One difference between NiAl(110) and CoAl(100) is that we are dealing with Co antisite defects in the latter case. Already in the bulk, these carry a significant magnetic moment of about 1.5 $\mu_B$ [Ste87, Kul99], and this should rather be enhanced in the surface layer. Since spin-polarised atoms are generally larger than their unpolarised counterparts (a consequence of Pauli’s principle), a relative outward displacement of Co atoms might be anticipated. Only, why should this trend not apply to A2 Fe\textsubscript{1-x}Al\textsubscript{x}(100)? On the other hand, a LEED study of D0\textsubscript{3} Fe\textsubscript{3}Si(100) [Wei98] (Table 5.8) finds a similar trend – the transition metal relaxes outward in a mixed top layer. Here, too, magnetism might play a role; or, the similarity might be due to a particular electronic configuration (the combinations Co-Al and Fe-Si differ only by one TM d electron, shifted to the
main group element’s sp orbitals).

The preceding lines show that it is difficult to extract a precise picture of relaxation mechanisms without any in-depth knowledge of the underlying electronic structure. For CoAl(100), we may summarise that its overall relaxation fits with other bcc-based (100) surfaces. The main effect of two different elements’ placement on the same lattice is the observed, disordered top layer buckling. Speculative explanations for the Co outward displacement exist, but their truth can hardly be proven from the present data.

The situation is more complex for CoAl(111): Here, already the qualitative “−−+” trend from elemental surfaces is not reproduced. Rather, its relaxation could be characterised by “0−+”, since \( \Delta d^{12}/d^b = -2.4 \% \) only, whereas \( \Delta d^{23}/d^b = -27.9 \% \) and \( \Delta d^{34}/d^b = +20.1 \% \). Here, too, two observations mentioned for the (100) orientation hold: First, there is some similarity to the Fe-Si system, since a derelaxation of \( d^{12} \) is also observed for B2 FeSi(111) (Table 5.8) – in fact, its entire relaxation pattern seems conspicuously close to CoAl(111). Second, the rather extreme displacement of third layer Co antisites (even slightly further out than the third layer’s average position) might again be connected to a potential magnetic moment of these defects. On the other hand, the uncertainty of the Al position in that layer is very large, and the third layer of FeSi(111) resides at a similar position at least in theory [Str01], although it consists entirely of Si. So, again, definite conclusions can not be drawn here.

Nevertheless, the overall difference between the elemental surfaces of Table 5.7 and CoAl(111) shows that an impact of two distinct chemical species on a mostly ordered lattice definitely exists, regardless of the particular electronic reasons. We may conclude with at least this basic similarity of CoAl(100) and (111).

**Segregation and Order.**

Regarding their near-surface composition and order, CoAl(100) and (111) share several features, including the most surprising one. Both are terminated by their nominal Al-sublattice, with the Co termination clearly ruled out by LEED. Also, no deviations from B2 order below their third layers are detected. However, both contain significant amounts of Co antisite defects at the selvedge – mainly in the first layer for CoAl(100), and in the third layer for CoAl(111). In either case, the observed near-surface SRO is consistent with a D0₃- or bcc-Ni₂Al-like arrangement.

Despite the experimental evidence presented, the structure of both surfaces is still puzzling from a physical point of view.

- In the (100) and (111) orientations, ideal (and exactly stoichiometric) B2-ordered crystals already consist of alternating monoelemental planes. So, even if one element had a tendency to segregate, this segregation could be reconciled with bulk-like order by selecting the appropriate termination – as does Fe₀.₅₃Al₀.₄₇(100), for instance. In contrast, deviations from B2 order are energetically quite unfavourable, since Al-Al or Co-Co NN bonds must be formed. Of course, “normal” segregation could still make a difference for CoAl(111). Here, both B2 sublattices are exposed to the selvedge, so that an enrichment of the top layer element also in the second layer might have been understandable. However, there is no apparent reason
why either surface should choose to terminate by one sublattice (Al), and then have the other element (Co) partially segregate to that sublattice.

- Even if not questioning the existence of near-surface Co antisite defects as such, the orientation-dependence of their location and amount is surprising. For CoAl(100), at least, the effect is strongest in the layer most affected by the surface, and an overall B2-like stacking sequence is retained on average. For CoAl(111), however, the topmost layer contains no Co – the defects rather appear in the third layer, and at a level which switches even the average capping sequence from B2 to AlCo$_3$.

The central argument from the first point can not be dismissed: In stoichiometric, B2-ordered CoAl, the necessary creation of Co antisite defects makes our results seem extremely unlikely. In the bulk, their effective formation enthalpy amounts to 1.29 eV [Bes99]. It would be quite bold to postulate some surface effect which could overcome this barrier. However, a look at Sect. 5.1 shows that this reasoning is based on a central assumption for which there is no proof: the assumption that we are dealing with the equilibrium surfaces of a fully ordered B2 crystal. Since a high-temperature plateau of $r_{AES}$ is lacking in Fig. 5.1, there is no guarantee that the surface composition has yet stabilised at the compositional equilibrium of the faraway bulk. However, if there remained a small, sputter-induced excess of Co in the near-surface region, Sect. 2.4 predicts its structure to be the same as for a Co$_{1-x}$Al$_x$ bulk crystal with $x \leq 0.5$ in full equilibrium. In that case, the main argument against the observed near-surface disorder breaks down: The creation of antisite defects is no longer required, because they already exist – as the normal structural defect in a Co-rich B2 Co-Al crystal.

Fig. 5.14 illustrates the segregation model for CoAl(100) which results if the assumption of compositional equilibrium with a fully B2-ordered underlying bulk is dropped. Essentially, we now have three reservoirs for surface segregation, instead of two. These are Al atoms on the Al sublattice, and Co atoms on the Co sublattice – and, Co atoms which occupy Al sublattice sites. While the Co atoms on the correct sublattice are firmly bound by eight attractive Co-Al NN bonds, the Co antisite defects are in a much less advantageous position – they must form eight repulsive Co-Co bonds. If we assume that a truly stoichiometric B2 CoAl(100) surface preferred a pure Al termination, our slightly Co-enriched surface region should correspond to that depicted in the upper panel of Fig. 5.14. However, we now also face two types of Al sublattice sites: those in the bulk, which are surrounded by eight Co NN, and those in the surface, which have only four Co NN. Obviously, energy may be gained by exchanging a bulk Co antisite defect with a surface Al atom – four unfavourable Co-Co NN bonds are replaced by four favourable Co-Al ones. In this simple model, any slightly off-stoichiometric B2 crystal features antisite segregation!

Of course, this is not yet the full truth. The assumption of an Al termination for stoichiometric CoAl(100) implies Al in the topmost layer should be energetically preferred. So, we really face two opposing forces: bulk NN interactions, driving Co into the topmost layer, and “normal” Al segregation, which by definition favours Al there. Their relative strength determines whether Co antisites are forced out to the surface layer (Fig. 5.14, lower left), or pushed into the crystal (Fig. 5.14, lower right). Obviously, the former case corresponds exactly to our findings for CoAl(100),
Figure 5.14: Section through a B2 (100) surface along (110). In a slightly TM-rich alloy (upper panel), the excess TM atoms (dark atoms) reside on sites of the Al sublattice (lighter atoms). Both Al atoms and TM antisites are directly surrounded by TM nearest neighbours on their normal sublattice (shaded atoms). If the surface terminates by the Al sublattice, the repulsion of TM-TM NN may either be strong enough to drive TM atoms out of the crystal (left), or the usual Al segregation tendency will be stronger, forcing all antisite defects into the crystal (right).

while the latter fits Fe0.53Al0.47(100) (which naturally contains Fe antisite defects). Reassuringly, the bond strength in CoAl (estimated from its formation enthalpy) is roughly more than twice as high as that in FeAl (Sect. 2.1). This fundamental argument is easily extended to CoAl(111): Third layer Al atoms here still lack one NN. So, one unfavourable Co-Co NN bond can be replaced by a Co-Al one if a bulk Co antisite atom switches places with a third layer Al one. If the segregation of excess Co to the topmost Al layer were hindered for some reason, the third layer would be the natural place for it to go.

Another appealing side effect of this scenario is that it explains the apparent difference of the $r_{\text{AES}}$ dependence on $T_{\text{anneal}}$ between Fe-Al and CoAl in the spirit already proposed in Section 5.1. For a dilute solution of Co antisites on the Al sublattice, and with the former segregating, the selvedge composition must depend sensitively on their overall amount. Since it dominates the AES signal, the selvedge acts as a “magnifying glass” for the small remaining deviation from bulk stoichiometry, which would otherwise escape unnoticed both in AES and quantitative LEED. Thus, the near-
5.5. Structural trends

Surface composition profile stabilises at much lower $T_{\text{anneal}}$ for Fe-Al than for CoAl, reflected in the appearance of a plateau in $r_{\text{AES}}$ for the former which cannot be reached for the latter.

It must be noted that the above, qualitative reasoning still contains a number of hidden pitfalls. First, in a nominally Al-terminated $\text{Co}_{1-x}\text{Al}_x$(100) surface, unfavourable Co-Co NN bonds in the bulk could also be removed by a termination switch (a termination by the Co sublattice), instead of the segregation of excess Co to the Al top layer. Second, our argument for CoAl(111) requires that Co antisite segregation to the topmost layer should be somehow unfavourable there – but why, given that top layer atoms lack exactly four NN both for (100) and (111)? And third, why is antisite segregation to the third layer of CoAl(111) more pronounced than to the top layer of CoAl(100)? Obviously, our scenario is as yet speculative, and requires some more quantitative reasoning. Nevertheless, a central insight has been gained already: The physics of structural defects may strongly influence the surface properties of ordering alloys.

The link to NiAl(100) and (111).

Some final words concern the relationship between the structure of CoAl(100) and (111) and that found in previous LEED studies of NiAl(100) and (111) [Dav88] (also listed in Table 5.8).

Relaxation-wise, NiAl(100) and CoAl(100) are reasonably similar, although the possibility of top layer Ni antisites [Mul88, Roo96, Tag98] was ignored in Ref. [Dav88]. In contrast, the structure of NiAl(111) (the Al-terminated part of the domain mix model of Ref. [Dav88]) shows hardly any relaxation, and compares quite badly to our results. Moreover, $d^{34}$ was not optimised, which should constitute a severe deficiency in the light of Table 5.7. However, the truly interesting observation is that both NiAl(100) and NiAl(111) are much closer to our results for CoAl(100) and CoAl(111) in Tables 5.3 (left column) and 5.5, when the same basic structural models were assumed. So, the original LEED studies of NiAl(100) and (111) seem easy prey to our observations. In either case, a segregation of antisite defects was (probably) never considered. Now, if our CoAl(111) surface could produce a domain mix model when ignoring deviations from B2 order, so could NiAl(111).

Concerning stoichiometry, the concept of antisite segregation is easily extended to NiAl(100) and (111). If small amounts of (unnoticed) near-surface structural defects (Ni antisite atoms) had an unexpectedly strong influence at the selvedge, the strange discrepancies between different studies could well be understood: Different workers examined different Al depletion levels, and found the corresponding “local equilibrium” terminations. For NiAl(100), some LEIS results [Mul88, Roo96, Tag98] indicate almost the same top layer concentration as found here for CoAl(100). Furthermore, the mysterious dependence of $x^1$ on the number of successive preparation cycles, reported by Mullins and Overbury [Mul88], would be an immediate consequence of a slowly increasing concentration of residual Ni antisite defects in the near-surface region by repeated preferential sputtering.

Unfortunately, the situation is not quite as simple as the preceding paragraphs might make believe. First, there are credible reports which claim an (almost) bulk-like Ni-termination for NiAl(100) under certain circumstances [Blm96, Sti00]. Why should the same surface prefer the segregation of antisites to an Al top layer for some conditions, and a termination switch for others? Then, the LEED evidence for a domain mix in NiAl(111) is somewhat sounder than in our case, since Noonan and Davis [Noo87, Noo88, Dav88] are actually able to point out individual diffraction peaks which
a single termination cannot reproduce. Finally, there are investigations of NiAl(111) by LEIS which find either a termination by pure Ni [Nie90], or the presence of both Al and Ni in the top layer [Nie88, Ove90]. In contrast, nobody ever reported a full Al termination. LEIS, of course, is a highly sensitive method in this respect, and cannot simply be ignored. So, some discrepancies between our scenario for CoAl(100) and (111), and related findings for NiAl remain. These do not devalidate our proposed basic mechanism of a pronounced influence of structural defects, but a more refined scenario is certainly in order. Any definite conclusions would certainly require a direct reinvestigation of NiAl(100) and (111); still, we will come back to the issue one more time in Chapter 6.3.

5.6 Summary

In total, our analyses of CoAl(100) and CoAl(111) can certainly produce the initially desired “missing link” between Fe-Al and Ni-Al. By nature, both surfaces are certainly much closer to NiAl, as known from many other material properties, and not least the structure of their (110) surfaces. However, both cases add a highly exciting facet to the surface physics of strongly ordering alloys in general. If our interpretation is true, both materials would probably terminate by a pure layer of Al – provided that the underlying crystal was fully B2 ordered. In reality, however, there always remains a slight Co enrichment near the surface, incorporated as structural defects. Of course, the importance of bulk structural defects in B2 TM-Al alloys has often been stressed. However, it is now our understanding that these “bulk” structural defects (Co antisite defects) also dominate the surface properties of CoAl(100) and (111), by segregating on the respective sublattice. Consistently, the observed segregation and ordering behaviour for both surfaces is closely related, despite their nominally different orientation: After all, a “bulk” effect provides the basic driving force. Only the actual segregation profile and the geometrical relaxation retain their usual orientation dependence.

If correct, the seemingly best defined sample composition, an equiatomic crystal, really marks the worst point at which to study surface properties at all. The latter must necessarily change discontinuously here, since the nature of bulk structural defects changes discontinuously as well. This unexpected realization could serve as a starting point to explain the known controversies for NiAl(100) and (111) – the observations of different workers might not contradict each other at all, they might simply have been obtained at slightly different levels of near-surface structural defects.

Obviously, the consequences of this scenario are grave, so that its consistency should be established more rigorously. The following, and final, discussion chapter of this thesis provides some formal groundwork to this effect.
Chapter 6

The interplay of bulk order and surface segregation

The preceding structure determinations of Fe$_{1-x}$Al$_x$(100), CoAl(100) and CoAl(111) provide an accurate picture of their surface stoichiometry and order. However, the underlying physical forces were only discussed on a rather qualitative level. In order to check their completeness and consistency from the available data, a more rigorous description of their nature and origin is required. The present chapter is dedicated to this task.

In principle, surface segregation can be theoretically predicted with high precision. The most accurate treatments are based on a quantum mechanical \textit{ab initio} description of an alloy’s electronic structure [Mon97, Rbn99, Drc99, Tre99]. For instance, total energies may be calculated for a limited number of configurations, which are then mapped onto an effective interaction Hamiltonian to allow the description of disordered systems. However, the effort associated with such a complete theory is considerable, and exceeds the scope of the present work by far.

Fortunately, we do not even require such a theory. After all, instead of predicting our results from scratch, we should rather strive to draw as many conclusions as possible from them. In the following, we will therefore first formulate a “minimal” physical model of our results, based on the previous, qualitative observations. We can then check its consistency by performing some simple quantitative estimates. So, we may hope to identify and verify some dominant mechanisms associated with surface segregation in transition metal aluminides. Of course, this model may later provide a valuable benchmark to test a possible, more sophisticated theoretical description. In the remainder of this chapter, we will first outline some elements of a rigorous description of surface segregation in binary alloys. Based on these, we attempt to formulate the above-mentioned “minimal” model, including the qualitatively obvious features from our structural results. Its application to Fe-Al and Co-Al surfaces tests the model’s ability to quantitatively describe our observations. A consistency check with related systems concludes this chapter.
6.1 Fundamentals of surface segregation

In Chapter 1, we defined "surface segregation" as any deviation from an alloy’s bulk-like composition and order in the vicinity of its surface. This includes layer-dependent elemental concentrations, where these layers may themselves consist of inequivalent sublattices. Normally, surface-induced compositional changes are localised within but a few atomic layers from the selvedge. Still, under special circumstances (e.g., near a phase transition), they may extend considerably into the bulk. In thermodynamic equilibrium, the external variables which determine the "segregation profile" are surface orientation, the composition of the bulk, external strain or pressure\(^1\), and temperature.

Modelling surface segregation basically requires two steps. First, one must express the total energy \(E\) of the system.\(^2\) Since our definition of surface segregation assumes individual lattice sites, we must necessarily account for \(E\) on a microscopic level. Second, the effects of finite temperature must be accounted for by statistical mechanics. The following subsections will briefly introduce a formally correct approach to both aspects. More detailed accounts can be found in the literature [Mon97, Pol00].

6.1.1 Segregation energetics

As outlined above, we require a Hamiltonian which provides a rigorous description of alloy energetics (i.e., which is per se free of any approximations) but can easily be modified to provide a quick, qualitative description of an alloy purely by well-defined approximations. A highly suitable formulation is based on the equivalence of a binary alloy \(A_{1-x}B_x\) and a three-dimensional Ising system [Diu94]. Assuming all atoms to occupy the sites of a specific underlying lattice, spin variables can be defined by \(\sigma_i = 1\) if site no. \(i\) is occupied by atom A, and \(\sigma_i = -1\) if it is occupied by atom B.\(^3\) Of course, the accuracy of an Ising Hamiltonian depends crucially on the chosen interaction model between the different spins. Fortunately, it has been proven that it is possible to account for the exact total energy of the electronic ground state of any predefined lattice configuration \(\sigma = (\sigma_1, \sigma_2, ...)\) for any given binary alloy by means of a suitable, Ising-like Hamiltonian [San84]. The cluster expansion method accounts separately for interactions associated with individual lattice sites \(i\), pairs \((i, j)\),

---

1. In the present work, we may safely assume zero pressure.
2. It should be noted that, at finite pressure, one would really have to express the system’s enthalpy, and not just its energy: Segregation experiments must be conducted at constant pressure, and not at constant volume, as it is (trivially) impossible to prevent a surface’s relaxation from changing when replacing one atom type by another. However, since any observations in the present work were made at zero pressure, there is no factual difference between both quantities, and only energy is referred to below for simplicity. If needed, a generalisation to enthalpy would be straightforward: For instance, the quantity referred to as the segregation energy below is really the segregation enthalpy of many other works.
3. By restricting ourselves to two elements on a predefined, underlying lattice, we have introduced two approximations. First, we neglect the possibility of structural vacancies, as they cannot be accounted for in this scheme. Second, individual atoms cannot leave their lattice sites to form an entirely different arrangement. So, neither a bulk martensitic transformation nor an incommensurate surface layer could be described by a lattice Hamiltonian. Such phenomena can indeed occur for Fe-Al and Co-Al alloys, but we have no evidence for their relevance to the results of the present work.
Figure 6.1: Examples of inequivalent multisite figures (triples and quadruples) on a bcc lattice which might play a role in Eq. (6.1).

Here, the interaction parameters $J$ may be viewed as the energy contribution associated with a particular occupation of the involved lattice sites. They are a priori independent of the overall alloy composition, provided that the underlying lattice stays the same. They may even account for certain local lattice relaxations. The usefulness of this approach originates from the assumption that $J^{ijk...}$ rapidly approach zero with both intersite separation and cluster size. To that end, it can be advantageous to represent certain terms by physically more intuitive descriptions, for instance to separate out long-range strain terms entirely [Lak92].

Eq. (6.1) is a versatile tool for the description of binary alloys. In itself, it makes no assumptions on the nature of the underlying lattice, as all interaction parameters still depend on particular lattice sites $(i, j, k, \ldots)$. The lattice type (fcc, bcc, with or without a surface, \ldots) is only specified when adapting Eq. (6.1) to a particular problem. Then, symmetry considerations may reduce the number of independent parameters $J$ drastically. The simplest case is a three-dimensional, periodic bulk lattice of equivalent sites. Then, all single-site terms $J^i$ are equal, all pair spin parameters $J^{ij}$ will
only depend on the distance of the lattice sites \((i, j)\), etc.:

\[
J^i \equiv J^{\text{bulk}} \quad \text{all sites are equivalent} \\
J^{ij} \equiv \begin{cases} 
J^{\text{NN}} & \text{if } i, j \text{ are nearest neighbours} \\
J^{2\text{NN}} & \text{if } i, j \text{ are second nearest neighbours} \\
\ldots & \text{etc.}
\end{cases}
\] (6.2)

Obviously, bulk short- and long-range order are solely determined by pair- or multisite-terms in Eq. (6.1), as all single-site terms are equal. It is also noteworthy that, even if all bulk lattice sites are treated as formally equivalent, their \(a \ posteriori\) subdivision into inequivalent sublattices of an ordered structure is still possible. Hamiltonians based on Eq. (6.2) have often been used to predict SRO and LRO in bulk alloys [Ozo98, Wol98].

Similar Hamiltonians can also be used to predict order and segregation on a lattice with a surface [Mon97, Drz99, Tre99, Pol00]. In this case, the positional translational symmetry is reduced, and all interaction parameters depend on their location with respect to the selvedge:

\[
J^i \equiv J^l \quad \text{if site } i \text{ is located in layer } l \\
J^{ij} \equiv \begin{cases} 
J^{\text{NN},lm} & \text{for nearest neighbours } i, j \text{ located in layers } l, m \\
J^{2\text{NN},lm} & \text{for second nearest neighbours } i, j \text{ located in layers } l, m \\
\ldots & \text{etc.}
\end{cases}
\] (6.3)

Again, this grouping is straightforward. Since single-site parameters \(J^l\) now depend on the layer number \(l\), placing a specific element in the surface may be energetically favourable regardless of pair (or higher) interactions. This accounts for classic empirical explanations of segregation, such as the size effect [Lea57] or the lower elemental cohesive energy [Ter91]. Actually, the total number of independent parameters may be further reduced since all \(J\) should approach common bulk values below a certain depth.

While Eq. (6.1) suffices for a formally correct description of alloy energetics, the significance of the interaction parameters \(J\) remains somewhat abstract. For a physically more tangible description, it is often useful to be able to simply “count bonds” in a given configuration, i.e. to use the language of bond energy parameters \(\epsilon_{AA}^{ij}, \epsilon_{BB}^{ij}, \text{ and } \epsilon_{AB}^{ij}\). These were already introduced in an informal way in Sect. 2.1, and we shall draw upon them for greater clarity in several instances below.

To translate spin parameters \(J\) into bond parameters \(\epsilon\), we must rewrite Eq. (6.1) up to pair terms
by counting individual "bonds", \(^4\)

\[
H_{\text{pair}}(\sigma) = \epsilon_0 + \sum_i (\epsilon_A^i \delta_A^i + \epsilon_B^i \delta_B^i) + \frac{1}{2} \sum_{ij} (\epsilon_A^{ij} \delta_A^i \delta_A^j + \epsilon_B^{ij} (\delta_A^i \delta_A^j + \delta_B^i \delta_B^j) + \epsilon_{AB}^{ij} \delta_B^i \delta_B^j) .
\] (6.4)

Here, the Kronecker symbols

\[
\delta_A^i = \frac{1 + \sigma_i}{2} \quad \text{and} \quad \delta_B^i = \frac{1 - \sigma_i}{2}
\]

(6.5)
denote the occupation number of each site \(i\), replacing the previous spin variables \(\sigma^i\). Comparing Eqs. (6.1) and (6.4) up to pair terms yields the connection between bond energy variables \(\epsilon\) and spin energy variables \(J\):

\[
\begin{align*}
J_0 &= \epsilon_0 + \sum_i \frac{\epsilon_A^i + \epsilon_B^i}{2} + \frac{1}{2} \sum_{i,j \neq i} \frac{\epsilon_A^{ij} + \epsilon_B^{ij} + 2\epsilon_{AB}^{ij}}{2} \\
J^i &= \frac{\epsilon_A^i - \epsilon_B^i}{2} + \frac{1}{2} \sum_{j \neq i} \frac{\epsilon_A^{ij} - \epsilon_B^{ij}}{2} \\
J^{ij} &= \frac{\epsilon_A^{ij} + \epsilon_B^{ij} - 2\epsilon_{AB}^{ij}}{4}.
\end{align*}
\] (6.6)

Obviously, the bond energy Hamiltonian (6.4) contains many more free parameters than the equivalent part of the "spin" Hamiltonian (6.1). Hence, some of the quantities \(\epsilon\) in (6.4) must be redundant. They can be removed by setting

\[
\begin{align*}
\epsilon_A^i + \epsilon_B^i &= 0 \\
\epsilon_A^{ij} - \epsilon_B^{ij} &= 0 \\
\epsilon_A^{ij} + \epsilon_B^{ij} + 2\epsilon_{AB}^{ij} &= 0
\end{align*}
\]

(6.7)

Inserting these conventions into Eq. (6.6) yields

\[
\begin{align*}
\epsilon_0 &= J_0 \\
\epsilon_A^i &= -\epsilon_B^i = J^i \\
\epsilon_A^{ij} &= \epsilon_B^{ij} = -\epsilon_{AB}^{ij} = J^{ij}.
\end{align*}
\] (6.8)

The connection between "spin" and "bond" parameters is now highly symmetric, and uses the minimal number of independent parameters only. We have exploited the freedom to choose the energy zero of single-site and bond energies to effectively include all average bond energy contributions in the constant offset \(\epsilon_0\). Furthermore, any homogeneous bond energies are properties of one element only, and our choice to equalise them means that their difference is now accounted for by single-site terms.

\(^4\)The single-site parameters \(\epsilon_A^i\) and \(\epsilon_B^i\) are often omitted from pair bond Hamiltonians, as they are not associated with "bonds" in the strict sense. However, the missing single-site contributions then become properties of the homogeneous pair energies \(\epsilon_A^{ij}\) and \(\epsilon_B^{ij}\) (see Eq. (6.6)). For instance, different single-site energies \(J^i\) would lead to site-dependent homogeneous bond energies for no intuitive reason. Including \(\epsilon_A^i\) and \(\epsilon_B^i\) explicitly yields a much more consistent description.
Chapter 6. The interplay of bulk order and surface segregation

A\textsubscript{1-x}B\textsubscript{x} bulk

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6_2}
\caption{Segregation to an A\textsubscript{2} random A\textsubscript{1-x}B\textsubscript{x}(100) surface, effectively amounting to a place exchange of a surface A atom with a bulk B atom. SRO and multilayer segregation are neglected. Within an interaction model of NN interactions $J^{\text{NN}}$ and a single-site energy difference $\tilde{J}^{1}$ between surface and bulk sites, only the highlighted neighbourhood (black bars: NN bonds) contributes to the segregation energy balance.}
\end{figure}

Together with the choices of Eqs. (6.3) and (6.7), the Hamiltonians proposed in Eqs. (6.1) or (6.4) provide us with a complete formalism to describe surface segregation. Of course, even if symmetry is accounted for, their complexity still exceeds the scope of the present work by far. Their true value in the following considerations is that any approximations made are now obvious, i.e. we now possess the desired, rigorous foundation on which to critically review our conclusions below.

In the following, we shall use a simple example to illustrate some basic trends in surface segregation. Consider the (100) oriented surface of a bcc-based, A\textsubscript{2} random binary alloy A\textsubscript{1-x}B\textsubscript{x}, and the following approximations:

- site-independent nearest neighbour interactions $J^{\text{NN}}$, a difference of single-site energies $\tilde{J}^{1} := J^{1} - J^{\text{bulk}}$ between sites in the top layer and those below, but no further non-zero interactions,
- segregation to the topmost layer only (i.e., a bulk-like stoichiometry already in the second
6.1. Fundamentals of surface segregation

layer), and

- an ideal random solution (no SRO) both in the topmost layer, and below.

On a lattice without vacancies, “B” segregation effectively amounts to the process depicted in Fig. 6.2: A “B” atom is taken from the bulk and placed in the surface. There, it replaces an “A” atom, which in turn reappears in the bulk. Of course, “B” segregation will only happen when the segregation energy $\Delta E_{\text{seg}}$ associated with this process is negative. As highlighted in Fig. 6.2, each bulk atom has eight nearest neighbours (of average occupation $A_1 - x B_x$ in the absence of SRO), whereas in the surface, each atom has only four (located in the second layer, i.e. also of composition $A_1 - x B_x$). Using the simple interaction model above, we can now calculate $\Delta E_{\text{seg}}$ by counting the number of bonds per atom:

$$\Delta E_{\text{seg}} = (E_B^1 - E_A^1) - (E_B^{\text{bulk}} - E_A^{\text{bulk}}),$$  

(6.9)

where

$$(E_B^1 - E_A^1) = \epsilon_B^1 - \epsilon_A^1 + 4(1 - x)\epsilon_{AB}^{NN} + 4x\epsilon_{BB}^{NN} - 4(1 - x)\epsilon_{AA}^{NN} - 4x\epsilon_{AB}^{NN}$$  

(6.10)

$$(E_B^{\text{bulk}} - E_A^{\text{bulk}}) = \epsilon_B^{\text{bulk}} - \epsilon_A^{\text{bulk}} + 8(1 - x)\epsilon_{AB}^{NN} + 8x\epsilon_{BB}^{NN} - 8(1 - x)\epsilon_{AA}^{NN} - 8x\epsilon_{AB}^{NN}$$

Summing up the various terms and inserting the conventions chosen in Eq. (6.8) directly yields

$$\Delta E_{\text{seg}} = -2\tilde{J}^1 + 16\left(\frac{1}{2} - x\right)J^{NN}.$$  

(6.11)

It is important to notice that, by definition of $\Delta E_{\text{seg}}$, the origin of the segregating atom is not irrelevant. In order to understand surface segregation, we must account properly for the “reservoir” from which these atoms stem.

In our example, the segregating element is determined by the balance of two different terms. First, there may be inherent segregation tendencies regardless of all bonds through $\tilde{J}^1$: If $\tilde{J}^1 > 0$, “B” will tend to segregate, and vice versa. This classic “single-site” effects may either be enhanced or diminished by “broken-bond” effects. Obviously, the latter depend on the composition of the bulk, and in an ordering alloy, ($J^{NN} > 0$) would induce the majority element (“B”, if $x > 0.5$) to segregate.

The above example contains an important assumption: All atom have some average environment which determines $\Delta E_{\text{seg}}$. It therefore belongs to the class of so-called mean-field models [Diu94]. In a real alloy, $\Delta E_{\text{seg}}$ can not be defined in this way. Its value will not be unique since the energy terms associated with each lattice site depend on its particular environment, and not on its averaged one. Even if we chose to use a mean value for $\Delta E_{\text{seg}}$, this would be determined by the alloy’s particular SRO properties, and rarely correspond to an ideal random solution. So, we must take SRO explicitly into account to describe the energetics of surface segregation properly.
6.1.2 Thermodynamics of segregation

Of course, a description based on the total energy alone is not enough to predict surface segregation. At finite temperature, elementary statistical mechanics [Diu94, Pol00] prescribes to calculate the energy \( E(\sigma) \) for each possible atomic configuration \( \sigma \), and insert these values into the canonical partition function \( Z \):

\[
Z = \sum_\sigma \exp \left( -\frac{E(\sigma)}{k_B T} \right).
\] (6.12)

From the partition function, one can then calculate the free energy \( F \) of the entire system, which must be minimised to determine the thermal equilibrium state. Of course, this straightforward recipe is a computationally forbidding task even for an interaction Hamiltonian such as (6.1) if the lattice becomes reasonably large. Probably the most accurate approximation to this procedure is the Monte Carlo method [Bin93]. It attempts to average a system’s properties only over those \( \sigma \) which contribute non-negligibly to Eq. (6.12). Since individual configurations are selected stochastically, the number of necessary evaluations of (6.1) is restricted. The MC method is generally applicable as long as the underlying Hamiltonian can be evaluated easily enough. However, since it samples the ensemble statistically, any analytical interpretation of the results must still be done separately.

Of course, there is a number of analytical approaches to surface segregation. The "classic" model is that of McLean [Lea57], which is an extension of Langmuir’s adsorption model [Lan18] (hence, the Langmuir-McLean (LL) model). In the LL model, the segregant is distributed on \( N \) “reservoir” sites (normally the bulk) and \( n \) “surface” sites (normally the topmost layer). Both are only distinguished by the segregation energy \( \Delta E_{\text{seg}} = E_{\text{surf}} - E_{\text{res}} \). Most importantly, any further interactions are neglected, either among surface sites or among reservoir sites. So, the total energy of the system depends only on the number of atoms \( p \) which reside on surface sites, but not on their particular distribution. In that case, one can directly write the free energy \( F_{\text{LL}} \) of the system, obtaining the entropy term from elementary statistics:

\[
F_{\text{LL}} = pE_{\text{surf}} + PE_{\text{res}} - kT \ln \left[ \frac{n}{p} \cdot \left( \frac{N}{P} \right) \right]
\] (6.13)

(where \( P \) denotes the number of solute atoms remaining in the reservoir). Minimising this expression as a function of \( p \) eventually yields

\[
\frac{p}{n-p} = \frac{P}{N-P} \exp \left( -\frac{E_{\text{surf}} - E_{\text{res}}}{k_B T} \right)
\] (6.14)

or, translated to surface and “reservoir” concentrations \( x_{\text{surf}} = p/n \) and \( x_{\text{res}} = P/N \),

\[
\frac{x_{\text{surf}}}{1-x_{\text{surf}}} = \frac{x_{\text{res}}}{1-x_{\text{res}}} \exp \left( -\frac{\Delta E_{\text{seg}}}{k_B T} \right).
\] (6.15)

The biggest advantage of the LL model is that it provides an easy way to visualise the essentials of surface segregation. Fig. 6.3 illustrates the behaviour of “surface” composition as a function of both the “reservoir” concentration and temperature. If there is a tendency for segregation (i.e.,
6.1. Fundamentals of surface segregation

Figure 6.3: Equilibrium surface segregation in the Langmuir-McLean model (Eq. (6.15)). The left panel shows the development of $x_{\text{surf}}$ with $T$ at constant $x_{\text{res}} = 0.03$, while the right panel shows the $x_{\text{surf}}$ as a function of $x_{\text{res}}$ at constant $T = 500$ K.

$\Delta E_{\text{seg}} < 0$), $x_{\text{surf}}$ naturally approaches 100 % as $T \to 0$. With rising $T$, it diminishes towards the “reservoir” value as entropy gains the upper hand. Also naturally, the surface concentration must increase together with the “reservoir” value. The main increase of $x_{\text{surf}}$ occurs in a $(T,x_{\text{res}})$ window which depends sensitively on the magnitude of $\Delta E_{\text{seg}}$.

Of course, the shortcomings of the LL model are manifold. It clearly neglects some important microscopic properties of a surface:

- There is only one type of “surface” site – the possible occurrence of inequivalent surface sites is neglected. In particular, there is no room for multilayer segregation in the LL model.

- Any interaction among “surface” atoms is neglected, as is that between atoms located in the “reservoir”. Hence, the total energy depends only on the number of segregated atoms, but not on their particular distribution $\sigma$.

- Only the configurational part of entropy is considered. Although this contribution usually dominates, other effects such as atomic vibrations are not always negligible [Ant93].

The first point could be partially rectified by allowing for more than one “surface” site within the LL model. The problem of interatomic interactions may then still be solved by accounting for each inequivalent near-surface lattice site in the mean-field approximation: $\Delta E_{\text{seg}}$ can be approximated by assuming an average environment for each site. By moreover assuming a random distribution of elements on each site, one still retains an LL-like entropy term. However, the statistical weight of individual microscopic configurations is then not accounted for properly, and mean-field theories must become increasingly inaccurate with growing interatomic interactions. Still, they serve as a starting point for numerous improved approximations. First, the statistical weights of certain short-range correlations can be accounted for explicitly (“generalised mean field” theories, e.g. the cluster variation method [Duc91, San93, Fon94]; the Bethe-Peierls method [Diu94] is a more elementary example of great tutorial value). On the other hand, a mean-field theory can also serve as a basis for a formal series expansion of the partition function which treats short- and long-range correlations on
Chapter 6. The interplay of bulk order and surface segregation

the same footing (e.g., the Kirkwood method [Kir38, Pol00]). However, these remedies for mean-field-based theories in strongly ordering alloys require some considerable analytical and computational overhead. This renders them quite inconvenient for our purposes. Instead, we shall attempt to utilise the original LL model in the discussion of Fe-Al and Co-Al surfaces below. Of course, one should expect this model to be far too simple to describe a true surface correctly, since the strong ordering interactions in TM aluminides render the original LL formula inapplicable. Yet, we shall see that these very ordering properties create the (nearly) non-interacting “reservoir” and “surface” sites which the LL formalism requires.

6.2 Experimental reality: Segregation in Fe-Al and Co-Al alloy surfaces

The preceding considerations allow to formulate a simple model of surface segregation in Fe-Al and Co-Al, which is the goal of the present section. On this basis, the results of Chapters 4 and 5 may be used to obtain some rough quantitative estimates of the underlying energetics. Of course, no such simple model can claim true uniqueness in a theoretical sense, and any parameters obtained should be digested with a grain of salt only. Their great value is of another kind: If the qualitative mechanisms invoked in the discussion of Fe-Al and Co-Al surfaces in Sects. 4.5 and 5.5 were incomplete, a quantitative approach should certainly reveal this. So, we may either prove the quantitative consistency of our surmises with the available results and literature, or reveal the existence of further, hitherto undetected physical mechanisms on our experimental “radar”. After outlining the model’s general framework, we will discuss its validity separately for Fe$_{1-x}$Al$_x$ and CoAl surfaces as investigated in this work.

6.2.1 Order and segregation in bcc-based alloys: The “D0$_3$” model

Regarding the energetics of Fe-Al and Co-Al surfaces, some qualitative trends are immediately evident from the preceding chapters. First, all investigated TM-Al alloy surfaces terminate by a layer composed mainly of Al. So, we must assume a driving force for the surface segregation of Al which is independent of ordering interactions, i.e. depends only on the location of the surface site itself: $(j^1 - j^{bulk}) = j^1 > 0$. Then, the formation of B2-like SRO and LRO requires strong ordering nearest-neighbour interactions. In the language of Eqs. (6.1), (6.3), (6.6) and (6.8), this means $J^{NN} > 0$. Finally, the D0$_3$ phase of the Fe-Al system implies non-negligible second nearest neighbour ordering forces, supported by the observed near-surface short-range order in Fe-Al and Co-Al. So, $J^{2NN} > 0$. So, a minimal description of the energetics which shapes the surfaces investigated in this work should definitely contain these three independent parameters: $j^1$, $J^{NN}$, and $J^{2NN}$. However, there is no apparent need for single-site terms different from the bulk below the topmost layer. So,

---

5In the following, the transition metal (Fe or Co) always takes the role of element A in Eq. (6.8), and Al takes the role of element B. If Al is to be the segregating element, we must have $j^1 = j^1 - j^{bulk} = -(\varepsilon^A_{Al} - \varepsilon^{bulk}_{Al}) > 0$, i.e. placing Al in the surface must be more favourable than placing it in the bulk.
all other single-site terms are assumed to take the bulk value in the following. Furthermore, we have no indication that any pair interactions beyond 2NN, or even multisite interactions, play a role in shaping the observed surface structures, and no indication for near-surface pair interactions which are qualitatively different from those in the bulk. So, we will assume equal pair bond energies for near-surface and bulk sites alike, and no interactions other than NN and 2NN will be considered. Of course, some of these restrictions may later be questioned.

Having defined the basic ingredients to describe segregation in Fe-Al and Co-Al alloys, we still need to determine their quantitative role in surface segregation. The example of Sect. 6.1.1 demonstrates the calculation of $\Delta E_{\text{seg}}$ in a mean-field model (assuming an ideal random solution), and the LL model of Sect. 6.1.2 allows to calculate the appropriate entropy for this situation. Of course, both approaches are inapplicable in our case, since we are by no means dealing with ideal random solutions. So,

- the mean-field segregation energy should be incorrect because the average environment of each lattice site strongly depends on its occupation. For instance, in a TM-rich B2 ordered alloy, each Al atom clearly has 8 TM NN, and not $8x$ TM NN as in a mean-field model.

- the LL entropy should be incorrect since it assigns equal statistical weight to all microscopic configurations. For instance, at finite temperature, ordering interactions drastically reduce the probability of configurations with Al-Al NN pairs in a TM-rich alloy.

Obviously, both shortcomings can be traced back to the incorrect description of SRO and LRO in TM-Al alloys. For an improved description, it is useful to turn towards the canonical partition function $Z$ in Eq. (6.12). If $J^{NN} > 0$ and $J^{2NN} > 0$, the largest contributions to $Z$ come from those configurations $\sigma$ which minimise (maximise) the overall number of homogeneous (heterogeneous) NN and 2NN bonds. The weight of all remaining arrangements diminishes exponentially with the number of “extra” homogeneous bonds. As long as the interatomic interactions are strong compared to $k_B T$, this property eliminates most of the configurations which would have been counted in an ideal random entropy. So, a better description of segregation energetics can be obtained by explicitly disallowing all $\sigma$ with more than the minimal number of homogeneous NN/2NN pairs, i.e. by assuming ideal SRO. Of course, the possibility of a selvedge stoichiometry different from that in the bulk complicates matters. However, one may still treat the SRO in a certain surface region (to be defined below) and the bulk as separate, corresponding to different overall composition.

In order to estimate the segregation energy for an alloy with ideal SRO, we must determine the average environment of the segregating atoms. This task is much simplified by realizing that the average environment is the same for ideal SRO and ideal LRO. Fortunately, we know the LRO type appropriate for bcc-based alloys with strong ordering NN and 2NN interactions: the D$_{03}$ structure. According to Sect. 2.1, there are four different sublattices in the D$_{03}$ structure (denoted A, B, C and D in Fig. 2.3), two of which (A and C) are equivalent. For $x = 25 \%$ Al, the D sublattice of an ideal D$_{03}$ structure is fully occupied by Al, while the remaining ones contain Fe only. Of course, deviations from this exact stoichiometry may occur, which may be incorporated into an ideally long-range ordered D$_{03}$ structure in the following manner: For $0 \leq x \leq 25 \%$ Al, Al atoms
are restricted to sublattice D ($x^D = 4x$), on which they are randomly distributed. This minimises the number of homogeneous bonds by ensuring that no Al-Al NN or 2NN pairs are formed at all. Above 25 % Al, the formation of Al-Al 2NN pairs can no longer be avoided. Sublattice D is now completely occupied by Al, and the remaining Al atoms are randomly distributed on sublattice B ($x^B = 4x - 1$). The resulting arrangement can also be viewed as a B2 structure, with the excess TM atoms situated on the Al sublattice as antisite atoms. Here, D03 order avoids the formation of 2NN TM antisite pairs, again effectively maximising the number of heterogeneous bonds. Finally, at $x = 50 \%$, both sublattices B and D are completely filled with Al, now forming a stoichiometric B2 crystal.

Based on these considerations, Fig. 6.4 illustrates the model by which we shall approximate the segregation processes in the (100) and (111) surfaces studied in this work. In the “D03 model”, the crystal consists of a “selvedge region”, i.e. the outermost primitive D03 unit cell of the crystal, and a “bulk region” which begins immediately below. Any interaction between both regions, which would lead to a kind of generalised multilayer segregation, is neglected. In (100) orientation, the D03 structure consists of an alternating sequence of two layer types, one of which contains the (equivalent) A and C sites, while the other comprises B and D sites in a c(2×2) arrangement. Hence, the outermost D03 unit cell consists of the topmost two layers. In (111) orientation, each layer of the D03 structure consists of a single site type only, forming the stacking sequence ...A-B-C-D... Hence, there are four inequivalent ways to terminate a D03(111) surface, and the outermost D03 unit cell comprises the topmost four layers. In fact, this definition of “selvedge” and “bulk” regions approximates our experimental situation quite well. Moreover, we can now identify the “bulk” lattice site on which Al is weakest bound, and the “selvedge” lattice site on which TM atoms are weakest bound for each combination of bulk and selvedge Al concentration values. Al segregation must proceed between these two site types, i.e. the segregation energy is now much better defined than in a mean-field model. We will use this approximation in the following sections.

Even with an improved segregation energy at hand, we still require a suitable model entropy to account for the effects of finite temperature. Since the temperature of equilibrium is not precisely defined in our experiments anyways, even a simple approach could be accepted for this task. Again, approximating ideal SRO by D03 LRO facilitates this task considerably. As mentioned above, we can
6.2. Experimental reality: Segregation in Fe-Al and Co-Al alloy surfaces

then identify unique “reservoir” and “surface” sublattices. The remaining lattice does not participate in the segregation process, and merely forms an effective field in which the active sublattices are embedded. As our interaction model includes only NN and 2NN interactions, there is obviously no interaction between different sites of each active sublattice, and all microscopic configurations \( \sigma \) on that sublattice have equal statistical weight. Thus, the central condition of the LL model is fulfilled. We can use the LL formula (6.15) to describe the segregation process between “reservoir” and “surface” sublattices by inserting the Al concentration on each as prescribed by the D0\(_3\) structure.

Of course, both Fe-Al and Co-Al alloys are not truly D0\(_3\)-ordered between 0 % and 50 % Al. While, for Fe-Al, this type of order at least exists in the phase diagram, the experimentally observed long-range correlation between different sublattices significantly deviates from our idealised description [Law61]. However, as the SRO around each atom type should be D0\(_3\)-like, any estimated segregation energy will hopefully be accurate. Co-Al is not reported to display a D0\(_3\) type phase at all. Instead, the system is a phase separating one, involving a martensitic transformation of the basic lattice. However, in the concentration range that we are interested in (Co-rich but near the B2 stoichiometry), excess Co atoms are still incorporated into the B2 structure as antisites on the Al sublattice. So, we may again hope that we are describing the relevant short-range order correctly in practice.\(^6\)

While D0\(_3\) LRO should clearly yield a good approximation for \( \Delta E_{\text{seg}} \), its substitution for ideal SRO has more consequences for the accuracy of the LL entropy model. For instance, in a TM-Al alloy with \( x < 0.25 \), the D sublattice of the D0\(_3\) structure forms the reservoir, and \( x_{\text{res}} = x^D = 4x \) must be inserted into the LL formula. In other words, only a quarter of the \( N \) available bulk lattice sites now act as reservoir sites, while all others do not since they might have an Al NN or 2NN. This assumption is certainly valid for \( x \to 0.25 \), but it breaks down as \( x \to 0 \). In the limiting case of only one bulk Al atom, the number of available “reservoir” sites is clearly \( N \) for ideal SRO, and not \( N/4 \) as resulting from D0\(_3\) LRO. So, the true “reservoir” concentration \( x_{\text{res}} \) somehow scales from \( x \) to \( 4x \) between \( x = 0 \) and \( x = 0.25 \). Fortunately, this effect really only matters in the very dilute limit. Obviously, if ideal SRO is assumed, each Al atom effectively “blocks” its 14 NN and 2NN lattice sites for other Al atoms, i.e. the number of available “reservoir” sites is reduced by 15. Only skillful ordering reduces the number of “blocked” lattice sites per Al atom to four in the ideal D0\(_3\) arrangement. So, the required SRO to accommodate all Al atoms should already be quite D0\(_3\)-like around, say, \( x \approx 0.1 \), and the LL formula with D0\(_3\) type reservoir concentrations should be expected to hold. Similar considerations apply to other cases where ideal SRO and D0\(_3\)-like LRO no longer coincide, e.g. for \( x \to 0.5 \).

A quick qualitative check against the discussions in Sects. 4.5 and 5.5 reveals that the assumption of D0\(_3\)-type LRO explains the segregation profiles observed much better than the original LL model:

- D0\(_3\)-like order terminated by the 1B/1D sublattices explains the observed two-step segregation process for Fe\(_{1-x}\)Al\(_x\)(100) satisfactorily. The 1D sublattice is filled first (as in the bulk). This step is already complete at \( x = 3 \% \) Al in the bulk. The 1B sublattice is energetically less

\(^6\)In contrast, the structural defect for Al-rich Co-Al alloys is a different one, and a description of this regime by assumed D0\(_3\) type long-range order must necessarily fail completely.
favourable since Al-Al 2NN bonds must now be formed, distinctly slowing down the second step of segregation.

- For CoAl(111), the terminating layer would be the 1D sublattice, with the 1B sublattice site in the third layer only partially filled by Al (as already assigned in Fig. 6.4).

- Obviously, our model assumes an ideal D0₃-like arrangement on the remaining selvedge sites. Indeed, this is approximately the case for Fe₁₋ₓAlₓ(100), CoAl(100), and CoAl(111) in experiment, i.e. multilayer segregation effects appear to be small. This is a direct consequence of strong ordering forces.

We will test this model more quantitatively in the following section.

6.2.2 Fe₁₋ₓAlₓ(100): Order shaping segregation

We shall first review the properties of Fe₁₋ₓAlₓ(100) surfaces in the context of the “D0₃” model. As mentioned, we must now identify one specific “reservoir” site in the bulk from which segregating atoms stem, and one specific “surface” site to which segregation proceeds. Since the termination of Fe-rich Fe₁₋ₓAlₓ(100) surfaces is always Al-rich, the top layer corresponds to the 1B/1D sublattices, while the second layer can be associated with the 1A/1C sublattice as defined by Fig. 6.4 (left).

With this prerequisite, we need only consider four cases to calculate \( \Delta E_{\text{seg}} \). The bulk may contain less or more than 25 % Al, determining if the Al “reservoir” is the D or the B sublattice. Likewise, the topmost layer may contain less or more than 50 % Al, whereby the destination of segregating Al is either the 1D or 1B sublattice. In each case, \( \Delta E_{\text{seg}} \) can be calculated from simple broken-bond arguments. Of course, the kinetic path between the initial and final configuration is irrelevant to equilibrium segregation.

In the following, the procedure is exemplified for \( x < 25 \% \text{ Al} \) and \( x^1 < 50 \% \text{ Al} \). As illustrated in Fig. 6.5a, the only sublattices to contain Al in this case are the bulk D sublattice \( (x^D = 4x^1) \) and the surface 1D sublattice \( (x^{1D} = 2x^1) \). So, Al segregation must proceed by interchanging a bulk D Al atom and a surface 1D Fe atom, as illustrated in Fig. 6.5b. From the location of both atoms and their local NN/2NN environments (highlighted), it is straightforward to calculate \( \Delta E_{\text{seg}} \). Obviously, the exchange yields the difference of single-site energies, \( (\epsilon^1_{\text{Al}} - \epsilon^1_{\text{TM}}) - (\epsilon^\text{bulk}_{\text{Al}} - \epsilon^\text{bulk}_{\text{TM}}) = -2J^1 \). Then, each bulk D site has eight Fe NN, but each surface D site has only four (located in the second layer). Finally, the bulk D sublattice has six Fe 2NN, while a surface D site has only five (four within the topmost layer and one in the third). So, we are breaking eight Fe-Al NN bonds in the bulk, but only four are recreated in the surface. Of course, we are also creating eight Fe-Fe bonds in the bulk, whereas we are breaking only four in the surface – i.e., in effect, we swap four Fe-Al for four Fe-Fe NN bonds. Of the six broken Fe-Al 2NN bonds, only five are recreated in the surface, and vice versa for Fe-Fe, i.e. we have effectively replaced one Fe-Al 2NN bond by Fe-Fe. In total, the segregation energy reads

\[
\Delta E_{\text{seg}}^{D \rightarrow 1D} = (\epsilon^1_{\text{Al}} - \epsilon^1_{\text{TM}}) - (\epsilon^\text{bulk}_{\text{Al}} - \epsilon^\text{bulk}_{\text{TM}}) + 4(\epsilon^\text{NN}_{\text{TM-TM}} - \epsilon^\text{NN}_{\text{TM-Al}}) + (\epsilon^\text{2NN}_{\text{TM-TM}} - \epsilon^\text{2NN}_{\text{TM-Al}})
\]

\[
= -2J^1 + 8J^{\text{NN}} + 2J^{2\text{NN}} \text{.} 
\]

(6.16)
6.2. Experimental reality: Segregation in Fe-Al and Co-Al alloy surfaces

Figure 6.5: Al Segregation in D0₃ ordered Fe₁₋ₓAlₓ(100) for \( x^1 < 50 \% \) Al and \( x < 25 \% \) Al (Eq. (6.16)). (a) Occupation of sublattices in the bulk (surface) for these conditions. The D (1D) sublattice is the only one to contain Al, all others being occupied by Fe. (b) The same arrangement, showing a place exchange between a bulk Al atom (D sublattice) and a surface Fe atom (1D sublattice). The local NN/2NN environment (3D spheres) of both involved atoms consists exclusively of Fe.

Since the segregation of Al to the top layer creates homogeneous instead of heterogeneous bonds, the process should be energetically unfavourable. From our results, it seems that this is more than compensated for by the single-site energy \( 2J^1 \) which favours Al segregation.

Similar arguments can be constructed for the remaining cases. Note that, for any Fe-rich structure, the single site vs. NN bond energy balance is always the same as above, as the 1A/1C sublattices in the second layer are always (almost) fully occupied by Fe both in the “D0₃” model and in experiment. The observed split of the segregation process into two steps must be due to 2NN terms, as postulated in Sect. 4.5.

- \( x < 0.25, x^1 > 0.5 \): Segregation now proceeds between sublattice D and sublattice 1B. This is less favourable than the previous case, since the segregated Al atom, having had six Fe 2NN
in the bulk, now has four Al in-plane 2NN. The fifth 2NN in the third layer is a bulk D site, also partially occupied by Al.\footnote{Our model explicitly assumes only the topmost D0$_3$ unit cell to differ from the bulk below. This, of course, is an approximation: Due to the interaction between the 1B sublattice and the D sublattice in the third layer, directly below, there should be a weak correlation of the occupation of both sites. However, we expect its quantitative consequences to be small since only one 2NN bond is involved. For simplicity, we use the mean-field approximation, leading to the term proportional to $x$.}

$$\Delta E_{\text{seg}}^{\text{D--1B}} = -2J^1 + 8J^{\text{NN}} + (\epsilon_{\text{TM-TM}}^{2\text{NN}} - \epsilon_{\text{TM-Al}}^{2\text{NN}}) - (4 + 4x)(\epsilon_{\text{TM-Al}}^{2\text{NN}} - \epsilon_{\text{TM-TM}}^{2\text{NN}} - \epsilon_{\text{Al-Al}}^{2\text{NN}})$$

$$= -2J^1 + 8J^{\text{NN}} + (18 + 16x)J^{2\text{NN}} \quad (6.17)$$

- $x > 0.25$, $x^1 < 0.5$: In the bulk, Al is weakest bound on sublattice B, and segregation fills the 1D sublattice. The modified 2NN environment now assists segregation instead of hindering it.

$$\Delta E_{\text{seg}}^{\text{B--1D}} = -2J^1 + 8J^{\text{NN}} + (\epsilon_{\text{TM-Al}}^{2\text{NN}} - \epsilon_{\text{Al-Al}}^{2\text{NN}}) + (6 - 4x)(\epsilon_{\text{TM-Al}}^{2\text{NN}} - \epsilon_{\text{TM-TM}}^{2\text{NN}} - \epsilon_{\text{Al-Al}}^{2\text{NN}})$$

$$= 2J^1 + 8J^{\text{NN}} - (26 - 16x)J^{2\text{NN}} \quad (6.18)$$

- $x > 0.25$, $x^1 > 0.5$: The bulk reservoir site is again sublattice B, and sublattice 1B is being filled. Except for the improved 2NN bond between the top and third layer, segregation is determined exclusively by the balance of the improved single-site energy and the unfavourable NN bond environment change.

$$\Delta E_{\text{seg}}^{\text{B--1B}} = -2J^1 + 8J^{\text{NN}} + (\epsilon_{\text{TM-Al}}^{2\text{NN}} - \epsilon_{\text{Al-Al}}^{2\text{NN}})$$

$$= -2J^1 + 8J^{\text{NN}} - 2J^{2\text{NN}} \quad (6.19)$$

We will use Eqs. (6.16)-(6.19) and the LL formula (6.15) to check the D0$_3$ model’s quantitative consistency against the LEED results of Chapter 4 and the existing literature.

Of course, any segregation energy estimated by way of the LL formula depends on the experimental temperature of thermal equilibrium, $T_{\text{eq}}$, to which near-surface order phenomena correspond. As mentioned in Sect. 2.4, this temperature is not well defined but depends on the point where short-range diffusion processes freeze out during quenching. Fortunately, the experimental quench times ranged around 2 min, identical to the time step $\Delta t$ used in the annealing experiments of Fig. 2.8. So, $T_{\text{eq}}$ should lie somewhere in the vicinity of the transition ranges observed there, for which 400 K $\lesssim T_{\text{eq}} \lesssim$ 800 K (and maybe a bit less for $x = 0.47$) is a conservative estimate. We will set $T_{\text{eq}} \approx 500$ K below, but the reader should remember that any extracted energies vary proportional to the assumed $k_B T_{\text{eq}}$.

The systems best suited for a “quantitative” test of the D0$_3$ model are those where surface segregation is not yet complete: Fe$_{0.97}$Al$_{0.03}$(100) and Fe$_{0.85}$Al$_{0.15}$(100), the structural analyses of which are summarised in Figs. 4.10 and 4.3. Here, the application of Eqs. (6.16)-(6.19) and the LL formula (6.15) leads to the following conclusions:
For $\text{Fe}_{0.97}\text{Al}_{0.03}(100)$, perfect top layer order was a fixed condition of the LEED analysis, inferred from STM evidence for the equivalent $\text{Fe}_{0.85}\text{Al}_{0.15}(100)-c(2\times2)^\|$ case. So, sublattice 1B consists completely of Fe, and sublattice 1D consists completely of Al. Of course, this limiting case is thermodynamically forbidden: it would imply $\Delta_{\text{seg}}E_{\text{D}^\text{1D}} \to -\infty$ and $\Delta_{\text{seg}}E_{\text{D}^\text{1B}} \to +\infty$ when inserted blindly into the LL formula. However, the true segregation energies are hidden somewhere in the experimental error for $\text{Fe}_{0.97}\text{Al}_{0.03}(100)$, and it is this which we must exploit to extract more meaningful results.

As shown in Sect. 4.4.1, it is possible to estimate the overall number of “defects” in the top layer of $\text{Fe}_{0.97}\text{Al}_{0.03}(100)-c(2\times2)^|$ by comparing the averaged intensity ratios of fractional and integer order beams, $r = I_{\text{frac}}/I_{\text{int}}$, between experimental and model spectra. This yields $x_{\text{defect}} \lesssim 10\%$, i.e. the segregation steps D→1D and D→1B are separated rather sharply. We can obtain a bound for the responsible 2NN interaction by exploiting $x_{\text{1B}} \lesssim 10\%$ Al and $x_{\text{1D}} \gtrsim 90\%$ Al, knowing that $x^D = 4x = 12\%$ for the reservoir in the LL formula. Inserting these exact numbers, we arrive at $\Delta_{\text{seg}}E_{\text{D}^\text{1B}} \gtrsim 10\text{ meV}$, but also at $\Delta_{\text{seg}}E_{\text{D}^\text{1D}} \lesssim -180\text{ meV}$. Of course, both limits by themselves are not strictly accurate, since they are derived from an experimental error estimate. However, through Eqs. (6.16) and (6.17), they may be combined to give $\Delta_{\text{seg}}E_{\text{D}^\text{1D}} - \Delta_{\text{seg}}E_{\text{D}^\text{1B}} = -(16 + 16x)J^{2\text{NN}}$. So, the splitting of the surface into two sublattices for the 3\% sample could already be explained by bulk-like 2NN interactions if $J^{2\text{NN}} \gtrsim 11\text{ meV}$.$^5$ Obviously, this value is somewhat larger than $J^{2\text{NN}} = J_{\text{FeAl}} = 7.1\text{ meV}$ as found in the bulk by Sanchez et al. [San95] (Table 2.1). Nevertheless, both results are certainly consistent within experimental error. For instance, assuming less than 20\% top layer defects in $\text{Fe}_{0.97}\text{Al}_{0.03}(100)$, i.e. $x_{\text{1D}} \lesssim 20\%$ Al and $x_{\text{1B}} \lesssim 20\%$ Al (which is well within our error limits), already requires only $J^{2\text{NN}} \gtrsim 7\text{ meV}$, the value given by Sanchez et al.

Remembering the discussion of experimental precision in Sect. 4.4.1, we may take yet another step: a rather daring attempt to locate the above-mentioned top layer defects by way of an extended LEED analysis would have placed them in the 1B sublattice, i.e. $x_{\text{1B}} \approx 10\%$ Al. If this were correct, the limit $\Delta_{\text{seg}}E_{\text{D}^\text{1B}} \gtrsim 10\text{ meV}$ might not be too far from reality. Of course, given the assumptions made, this result is quite speculative; yet, it seems probable that $|\Delta_{\text{seg}}E_{\text{D}^\text{1B}}| \lesssim k_BT_{\text{eq}}$.

Turning towards $\text{Fe}_{0.85}\text{Al}_{0.15}(100)$, we find again that the surface sublattice 1D is already completely filled by Al. $x^1 = 75\%$ is well established from STM and LEIS (and supported by LEED, too), so that $x_{\text{1B}} \approx 50\%$ Al should here hold with quite good precision. From this, we can estimate $\Delta_{\text{seg}}E_{\text{D}^\text{1B}}$ with much better accuracy than in the case of $\text{Fe}_{0.97}\text{Al}_{0.03}(100)$: At $x$

\[\text{This estimate has the additional advantage of being independent of the approximation of ideal SRO in the bulk by ideal LRO. According to the “D0$_i$” model, } x^\text{res} = 12\% \text{ arises if one assumes all Al atoms to reside on one sublattice of an ideal D0$_3$ arrangement. We can estimate the maximum impact of ideal SRO by simply assuming the original, uncorrelated LL entropy for the entire bulk, i.e. by using } x^\text{res} = 3\% \text{ Al. Then, we obtain } \Delta_{\text{seg}}E_{\text{D}^\text{1D}} \lesssim -240\text{ meV for } x_{\text{1D}} \gtrsim 90\% \text{ Al. On the other hand, the opposite boundary case } x_{\text{1B}} \lesssim 10\% \text{ Al now yields } \Delta_{\text{seg}}E_{\text{D}^\text{1B}} \gtrsim -50\text{ meV.}
\]

We again arrive at the estimate $J^{2\text{NN}} \gtrsim 11\text{ meV}$, as for the full “D0$_i$” model. In fact, this is not surprising. Since we estimated $J^{2\text{NN}}$ by comparing two limiting surface configurations for the same underlying bulk, all bulk properties must naturally cancel.
Figure 6.6: Dependence of the top layer Al concentration, $x^1$, on the bulk Al content, $x$, across all bcc-based Fe-Al phases. The dashed line shows $x^{1D} + x^{1B}$ according to the D0$_3$ model, with segregation energies derived to be consistent with Fe$_{0.97}$Al$_{0.03}$(100) and Fe$_{0.85}$Al$_{0.15}$(100). The symbols signify the experimental results for all Fe-Al samples studied in Chapter 4.

= 15 %, the D0$_3$ model yields a “reservoir” Al concentration $x^D = 60 \%$, i.e. very close to $x^{1B}$. In remarkable agreement with Fe$_{0.97}$Al$_{0.03}$(100), this immediately implies $|\Delta E_{\text{seg}}^{D\leftrightarrow1B}| \ll k_B T_{\text{eq}} \approx 40 \text{ meV}$! On the 1B sublattice, there is a close balance between $\tilde{J}^1$, which favours Al segregation, and the opposing NN and 2NN interactions.

- To be precise, $\Delta E_{\text{seg}}^{D\leftrightarrow1B}$ might even slightly oppose Al segregation: It amounts to +20 meV if $x^D$ and $x^{1B}$ are taken as exact and inserted into the LL formula, Eq. (6.15). Using this in conjunction with the bulk interactions of Sanchez et al., we can derive an estimate for the single-site energy term $\tilde{J}^1$. This results at $\tilde{J}^1 \approx 150 \text{ meV}$ – indeed, the single-site driving force for Al segregation is relatively strong in Fe$_{1-x}$Al$_x$(100).

Fig. 6.6 summarises the development of $x^1$ as expected from the D0$_3$ model in the A2 range, and contrasts it with all experimental $x^1$ values derived in Chapter 4. The steep initial rise to $x^1 = 50 \%$ Al is modelled using $\Delta E_{\text{seg}}^{D\leftrightarrow1D} = -180 \text{ meV}$, the upper limit derived from Fe$_{0.97}$Al$_{0.03}$(100), while the following, approximately linear slope up to $x^1 = 100 \%$ Al belongs to $\Delta E_{\text{seg}}^{D\leftrightarrow1B} = 20 \text{ meV}$, extracted for Fe$_{0.85}$Al$_{0.15}$(100). As discussed previously, both parts of the curve are subject to considerable uncertainty. Nevertheless, they show that the D0$_3$ model is clearly capable of describing Al segregation in the A2 random alloy range.

It is also interesting to compare the predictions of the strict D0$_3$ model to experimental reality for the ordered D0$_3$ and B2 phases of Fe$_{1-x}$Al$_x$. According to Fig. 6.6, $x^1$ should reach 100 % Al at $x = 25 \%$. Of course, the sharp edge shown in the curve is an artifact of the model: At 25 %, ideal SRO would enforce a completely filled bulk D sublattice, leading to a full top layer in the simple LL model. In reality, this is not the case – neither will the bulk D sublattice be completely filled...
by Al at $T > 0$, nor are the surface sites 1D and 1B the only target sites for Al in the real crystal. Rather, the bulk B sublattice now enters the scene. As it begins to contain Al around $x \approx 25\%$ Al, it acts as another Al sink which competes with 1B and 1D. At larger $x$, it eventually assumes the role of the only relevant “reservoir” for Al segregation. Hence, the transition expected at $x = 25\%$ Al should be smooth, and a proper description by the D0$_3$ model could only continue to hold well above the transition point, then with the bulk B sublattice as a reservoir.

Our observations for Fe$_{0.70}$Al$_{0.30}$(100) and Fe$_{0.53}$Al$_{0.47}$(100) seem reasonably well consistent with this extended picture. Since the B sublattice is now the Al “reservoir”, repulsive Al-Al 2NN interactions in the bulk actually assist its segregation. In fact, B→1B place exchanges (Eq. (6.19)) are even slightly more favourable than the initial segregation step D→1D (Eq. (6.16)). Thus, nothing short of a full top layer of Al could be expected for Fe$_{0.53}$Al$_{0.47}$(100), and this is certainly true both in LEED and LEIS [Ove95]. Moreover, with a smooth continuation of $x^1$ at $x=25\%$ to the weakly occupied bulk B sublattice, one might indeed predict some residual Fe in the topmost layer of Fe$_{0.70}$Al$_{0.30}$(100), as seen by quantitative LEED (Fig. 4.11).

On the other hand, the amount of Al really found in the topmost layer of Fe$_{0.70}$Al$_{0.30}$(100), $x^1 = 90 \pm 5\%$, is quantitatively still much too low if $\Delta E_{B\rightarrow 1B}^{seg} < \Delta E_{D\rightarrow 1D}^{seg} \leq -180$ meV was the sole responsible segregation energy in this system. Moreover, a moderate level of disorder also appears also below the top layer of this sample, a phenomenon which is not accounted for at all by our simple model. So, while the qualitative aspects of Fe$_{0.70}$Al$_{0.30}$(100) adhere reasonably well to the scheme expected from the D0$_3$ model, the exact LEED fit results do not. For one thing, this might simply indicate the limits of our definition of “equilibrium”, which is really just the product of freezing different diffusion mechanisms during quenching. On the other hand, it might also point to the existence of near-surface interactions beyond those included in the “D0$_3$” model. However, much more importantly, the extent of these effects is on the verge of the sensitivity reached by the fit (Sect. 4.4.2). Much more solid evidence would be required before discussing them in detail.

One last issue which deserves attention is the question of Al antisite defects in the second layer of Fe$_{0.53}$Al$_{0.47}$(100). As outlined in Sect. 4.4.3, the LEED fit indicates their presence if a bulk-like temperature factor in the second layer is assumed. Naively, this could be viewed as the natural continuation of Al segregation within the “D0$_3$” model, after the top layer sublattices are filled. However, bond-breaking arguments similar to those above yield an effective segregation energy of $\Delta E_{seg}^{B\rightarrow 1A} = 32J_{NN}^{2} - 24J_{2NN}^{2}$ to the second layer for $x \leq 0.5$. So, there is an overwhelming resistance of NN bonds against Al in the second layer, which is weakened only insignificantly by their improved 2NN environment. If this continued segregation really occurred, it would require a severe modification of our interaction model, e.g. a second layer single site energy $J^2 \neq J_{bulk}$, or strongly modified interatomic interactions near the surface. Both possibilities seem much less likely than the enhanced second layer vibrational amplitude which was suggested in Sect. 4.4.3.

In total, the “D0$_3$” approximation to the true SRO properties in Fe$_{1-x}$Al$_x$(100) provides a consistent description of the general segregation process, and bulk-like interatomic interactions between NN and 2NN suffice to explain our overall observations. Given the experimental error and the crudeness of our estimate of $T_{eq}$, our findings are in reasonable agreement with the published data of Ref. [San95]. The two most pronounced quantitative conclusions drawn within these models are that (a)
the 2NN interaction required for the observed segregation splitting is in the range $J^{2NN} \gtrsim 11$ meV, and (b) the effective segregation energy for the second step of segregation is probably relatively small, and maybe even slightly positive; at any rate, $|\Delta E_{\text{seg}}^{\text{D}1=1B}| \ll k_B T_{\text{eq}} \approx 40$ meV. It would certainly be interesting to quantitatively check both statements for Fe$_{1-x}$Al$_x$(100) independently, e.g. from first principles.

### 6.2.3 Co$_{1-x}$Al$_x$(100) and (111): Segregation reversal by bulk ordering forces

The previous section showed the “D0$_3$” model to describe Fe$_{1-x}$Al$_x$(100) surfaces consistently within the experimental resolution. In particular, near-stoichiometric B2 Fe$_{1-x}$Al$_x$ displays a bulk-like termination by a full layer of Al. Because both materials are chemically quite close to one another, similar findings might well be predicted for CoAl(100). Yet, the structural analysis of Sect. 5.3 reveals a different, and unexpected picture: The crystal is terminated by a layer which contains a significant amount of Co antisites ($\approx 30 \pm 7\%$) although, from the underlying stacking sequence, it corresponds to the Al sublattice. In an equiatomic, B2-ordered and Al-terminated CoAl crystal, the exchange of a top layer Al atom with a bulk Co atom amounts to the simultaneous creation of two antisites.\footnote{In fact, it is not an Al antisite which would form. Rather, TM antisite defects are created in conjunction with two TM vacancies in the bulk, the so-called triple defect. In our model, the possibility of vacancies is not included, but triple defect formation is as clearly an unfavourable process as the joint formation of two antisites, requiring approximately 1.3 eV in the bulk [Bes99].} From simple bond counting, the segregation energy\footnote{In keeping with the convention of the preceding section, $\Delta E_{\text{seg}}$ is still defined by an Al atom segregating to the “surface” site, replacing a TM atom which moves to the “reservoir”. Hence, $\Delta E_{\text{seg}} > 0$ would favour the segregation of TM antisites.} for this process amounts to

$$\Delta E_{\text{seg}}^{\text{A}1=1B} = -2J^1 - 24J^{\text{NN}} + 22J^{2\text{NN}}.$$  \hspace{1cm} (6.20)

So, Co segregation from its correct lattice site to the top layer Al sublattice is opposed by an exceedingly strong NN term, which can certainly not be compensated for by the somewhat improved 2NN environment. In this scenario, the driving force for TM segregation would have to be an extremely strong single-site preference for Co segregation, in contrast to the tendency observed for Fe-Al. However, even if such a driving force existed, a bulk-like Co-terminated surface should be more favourable since it avoids the creation of unfavourable antisites altogether. As already stated in Sect. 5.5, our model fails to account for the observed near-surface order if an underlying, ideal B2 crystal is assumed.

Sect. 5.5 also suggested a more likely explanation for the surface composition found for CoAl(100). Due to preferential sputtering, the near-surface region may still be slightly Co-enriched even at the highest $T\text{anneal}$. Then, it should display the same order as a Co$_{1-x}$Al$_x$(100) crystal ($x \leq 0.5$) in full thermal and compositional equilibrium at $T_{\text{eq}}$. As the excess Co atoms in Co-enriched B2 Co$_{1-x}$Al$_x$ are incorporated into the B2 lattice as antisite defects, these are now already there, and need not be created to segregate to the surface layer. Hence, the situation corresponds rather to Eq. (6.19), i.e. $0.25 \leq x < 0.5$, and $x^1 > 0.5$, and not to Eq. (6.20). The reservoir for segregating atoms is
now the B sublattice of the Co-enriched near-surface region, which fundamentally changes the role of NN interactions. They assist the segregation of TM atoms instead of opposing it, since their placement in the top layer reduces the number of unfavourable homogeneous bonds. In other words, our results can be understood by antisite segregation on the Al sublattice alone, reducing the role of the regular Co sublattice to that of an effective field.

We can make a quick quantitative check to see whether modified NN interactions in Co-Al could be responsible for Co antisite segregation. The single-site term $\tilde{J}_1$, which favours Al segregation, should be primarily shaped by the chemical nature of the individual elements. So, there is no apparent reason for $\tilde{J}_{\text{CoAl}}^1$ to be very different from $\tilde{J}_{\text{FeAl}}^1 = 150$ meV as estimated above. In Co-Al, the condition for antisite segregation is

$$\Delta E_{\text{seg}}^{\text{B}\rightarrow\text{1B}} = -2\tilde{J}_{\text{CoAl}}^1 + 8J_{\text{CoAl}}^{\text{NN}} - 2J_{\text{CoAl}}^{2\text{NN}} \geq 0.$$  

Assuming $\tilde{J}_{\text{CoAl}}^1 \approx \tilde{J}_{\text{FeAl}}^1$ and simply scaling the interactions reported for bulk Fe-Al, $8J_{\text{FeAl}}^{\text{NN}} - 2J_{\text{FeAl}}^{2\text{NN}} = 180$ meV [San95], this means that pair interactions in Co-Al must be roughly twice as large, consistent with the trends inferred from the formation enthalpy and the melting point (Sect. 2.1). Yet, a much larger enhancement of pair interactions would also be unexpected, so that the segregation energy for Co antisites to the surface should still be relatively small. This would conveniently explain why the 1B sublattice is not completely filled by antisites (i.e., $x^1 > 0.5$), and enable 2NN interactions to prevent Co from occupying the 1D sublattice entirely (Eq. (6.18)).

When estimating $\Delta E_{\text{seg}}$ directly from the LEED best-fit for CoAl(100), there are two important differences compared to Fe$_{1-x}$Al$_x$(100):

- It is more difficult to guess $T_{\text{eq}}$, the “freezing” temperature of local diffusion in the near-surface region to which the observed segregation profile corresponds. Fig. 5.1 does not show the same, clearly defined AES transition ranges which we exploited in the Fe-Al case, but rather a straight increase of $r_{\text{AES}}$ with $T_{\text{anneal}}$. Unfortunately, the remaining evidence of which the author is aware is somewhat contradictory. On one hand, bulk self-diffusion in B2 Co-Al [Nix51] is distinctly slower than in Fe-Al [Lar75, Hel99]. Also, the diffuse superstructure which develops for CoAl(100) never orders, i.e. $T_{\text{eq}}$ could be above a possible order-disorder transition temperature. Assuming similar interactions as those responsible for LRO in Fe$_{0.97}$Al$_{0.03}$(100)-c(2×2), both points speak for a considerably higher $T_{\text{eq}}$ than in the Fe-Al case. On the other hand, Fe-Al also shows that bulk- and near-surface diffusion processes may behave differently (Sect. 2.4), but the latter shape the surfaces discussed here. According to Fig. 5.1, the onset temperatures of near-surface mobility for CoAl(100) and (111) do not range above 500 K, i.e. they are similar to Fe$_{1-x}$Al$_x$(100) (with the exception of $x = 0.47$). Also, the sharp integer-order LEED spots of CoAl(100) and (111), at least above 650 K [Smt99], show that atoms must be mobile near both surfaces in this range. In short, we will assume $T_{\text{eq}} \approx 500$ K for the moment, as we have no clear evidence for a fundamental difference to Fe$_{1-x}$Al$_x$(100) near the surface.

- We have no direct evidence regarding the amount of excess Co in the near-surface region. The LEED analysis indicates the presence of Co antisites in the third layer, but not in the fifth. So, $x^3$ is certainly not representative for the composition of the near-surface region but might rather reflect a surface effect itself. However, LEED allows us to guess an upper limit for
the near-surface Co concentration. If we assume the average Co concentration per nominal Al layer to be 5 % or less, the reservoir concentration within the “D0₃” model becomes \(x^B \geq 90\%\) Al.

In short, our foundation for quantitative estimates within the D0₃ model is much weaker for Co-Al surfaces than it was for Fe-Al surfaces, i.e. any actual numbers derived below should be regarded with yet more caution. However, the purpose here is primarily to test whether the D0₃ model can provide a consistent description of our experiments at all, and not to provide high-precision interatomic interaction values. Also, several crucial conclusions below do not depend on \(T_{eq}\) at all, but merely on the sign of the energy involved.

In the CoAl(100) surface, the observed Al concentration amounts to \(x^{1B} \approx 40\%\), clearly less than \(x^B \geq 90\%\). Inserting these values into the LL formula (6.15) yields \(\Delta E_{seg}^{B-1B} \approx 110\) meV. Returning to the comparison with Fe-Al above, we are now in the position to refine our condition regarding NN and 2NN interactions. Again taking \(J_{CoAl}^1 \approx J_{FeAl}^1 \approx 150\) meV, we only need to scale the effective NN and 2NN bulk interactions for Fe-Al as given by Sanchez et al. [San95] by a factor of 2.5.

Given the crudeness of the underlying assumptions (particularly, \(J_{CoAl}^1 \approx J_{FeAl}^1\)), the “D0₃” model can describe antisite segregation in CoAl(100) consistently.

One of the open questions in Sect. 5.5 concerns the stability of the overall crystal truncation of CoAl(100). If Co has a tendency to segregate, why does the surface not simply display a bulk-like Co termination? For the answer, we must obviously calculate the energy difference between a surface with Co segregated to the B sublattice of an Al top layer, and a bulk-like Co-terminated stacking sequence. Only, the transition between both arrangements is not a mere place exchange of Co and Al atoms. Rather, part of the surface must be rebuilt by either removing or adding a crystal plane. At the same time, the overall number of atoms must remain constant to ensure the comparability of both model surfaces. Indeed, this condition can be met. Fig. 6.7 illustrates a hypothetical path by which a D0₃-terminated surface, capped by a layer which consists of half Al and half Co in a \(c(2x2)\) arrangement, can be transformed into a simple, bulk-like Co-terminated surface. First, the \(c(2x2)\) top layer is “demixed”, leaving half the surface terminated by two successive Co layers, while the other half is bulk-like Al-terminated. By taking the uppermost Co layer of the former domain and placing it atop the latter, the desired, fully Co-terminated B₂-ordered arrangement is reached. Careful book-keeping of atoms removed from and added to the very surface, and bonds broken and formed, then yields the energy difference associated with the termination switch,

\[
\Delta E_{switch} = \frac{n}{2} \left[ (\epsilon_{Co}^1 - \epsilon_{Al}^1) + (\epsilon_{bulk}^{Al} - \epsilon_{bulk}^{Co}) + 4(\epsilon_{Al-Co}^{NN} - 4\epsilon_{Co-Co}^{NN}) \right. \\
+ 2(\epsilon_{Co-Co}^{2NN} + \epsilon_{Al-Al}^{2NN} - 2\epsilon_{Co-Al}^{2NN}) + \left. (\epsilon_{Co-Co}^{2NN} - \epsilon_{Co-Al}^{2NN}) \right] \\
= \frac{n}{2} \left[ 2J_{Co}^1 - 8J_{NN} + 10J_{2NN} \right].
\]  

Comparing this last line to Eq. (6.19) (which describes the segregation of Al from the bulk B sublattice to replace a top layer 1B TM atom, or, vice versa, the segregation of a bulk Co antisite

\[11\text{This choice is in the range of lower-layer error bars in Table 5.3, and also consistent with the B2 phase boundary in the bulk below 1000 K.}\]

\[12\text{Of course, the energy of the single step created in this thought experiment can be neglected if the surface is large enough.}\]
defect to replace a top layer Al atom on the same sublattices), it is striking that

\[ \Delta E_{\text{switch}} = \frac{n}{2} \left[ -\Delta E_{\text{seg}}^{B_{1B}} + 8J^{2NN} \right]. \tag{6.22} \]

The last line reveals a crucial insight: If energy is gained by Co segregation to the topmost layer of an Al-terminated surface (the process which turns a purely Al-terminated CoAl(100) surface into the c(2×2) arrangement on the left side of Fig. 6.7), \textit{the same amount of energy per Co atom can be gained again by switching to a bulk-like, Co terminated surface – opposed only by the unfavourable contribution of four in-plane 2NN bonds!} So, in a system with only NN interactions, the termination in Table 5.3 would be intrinsically unstable. If it could form, a Co-terminated surface would automatically be twice as favourable, containing no homogeneous NN bonds at all any more. But, an Al-terminated surface with Co antisites can be stabilised by switching on 2NN interactions if

\[ 0 \leq \Delta E_{\text{seg}}^{B_{1B}} \leq 8J^{2NN}. \tag{6.23} \]

Inserting the above estimate of \( \Delta E_{\text{seg}}^{B_{1B}} \geq 110 \) meV, this 2NN barrier is sufficient if \( J^{2NN} \geq 14 \) meV. Once more, roughly doubled 2NN interactions compared to Fe-Al are perfectly consistent with our estimate above.

The surface termination of CoAl(111) seems even stranger than that of CoAl(100). Again, it nominally adheres to an Al-terminated stacking sequence, but incorporates a considerable amount of Co antisite defects. This time, however, these are not found in the topmost layer, but seem perfectly well localised in the third. Nevertheless, the explanation of this behaviour follows almost the same lines as CoAl(100). Again, the “D0_3” model cannot predict the observed behaviour if full equilibrium with an equiatomic B2 bulk is assumed, but doubts exist that this presumption is justified in the first place. Rather, small amounts of residual, sputter-induced Co antisite defects in the near-surface region must be suspected. The observed surface structure should thus be the equivalent of slightly Co-enriched \( \text{Co}_1-x\text{Al}_x(111) \) in full equilibrium.

In order to explain the details of the observed arrangement, we must take the structural peculiarities of a bcc based (111) surface into account. As pointed out before, this truncation affects more than just the topmost layer even in a simple interaction model. Compared to the bulk, each top layer atom lacks four NN (which would have been located one and three layers above, respectively), and three 2NN (two layers above). Each second layer atom lacks one NN (three layers above) and three

Figure 6.7: Particle-number conserving transformation path between CoAl(100), terminated with the nominal Al sublattice, but an actual c(2×2) Co-Al-layer on top, and a B2-ordered, Co-terminated surface.
2NN (two layers above). Finally, each third layer atom still lacks one NN atom. The sublattices of a D0$_3$ structure are now arranged in layers of their own, stacked in the sequence ...-A-B-C-D-... Returning to the D0$_3$ model, the denomination of sublattices in Fig. 6.4 (right panel) corresponds directly to our needs. Apparently, antisite atoms segregate to the third layer, which must therefore be the 1B sublattice, while the topmost layer corresponds to 1D sublattice, still completely filled by Al.

Once more, we can apply broken-bond arguments to calculate the segregation energy for this situation. In the “D0$_3$” model, the energy gained by segregation between the bulk B sublattice and the 1C sublattice (i.e., the third layer) amounts to

$$\Delta E_{seg}^{B \rightarrow 1B} = (\epsilon_{TM-TM}^{NN} - \epsilon_{TM-Al}^{NN}) = 2J_{NN}^{NN}.$$  \hspace{1cm} (6.24)

Since we assumed $\tilde{J}_3 = 0$ in the D0$_3$ model, only the single missing NN bond contributes to the effective segregation energy. Qualitatively, it favours the segregation of bulk antisite defects, as this process replaces a Co-Co bond with a Co-Al one.

For a quantitative estimate of $\Delta E_{seg}^{B \rightarrow 1B}$, we face the same difficulties as for CoAl(100). The “freezing” temperature during quenching of the surface is not precisely known, but may again be assumed to be of the same order as in Fe-Al, i.e. $T_{eq} \approx 500$ K. A precise value for the concentration of “reservoir” Co antisites is as difficult to estimate. $x^B \geq 90$ % Al seems reasonable since the annealing process is not fundamentally different from CoAl(100). Note, however, that the experimental precision reached for CoAl(111) is worse than for CoAl(100), i.e. the error limits of the LEED analysis itself would allow for an even larger deviation from stoichiometry. With $x^{1B} \approx 30$ % Al, the LL formula allows to estimate $\Delta E_{seg}^{B \rightarrow 1B} \geq 130$ meV. So, the required NN interaction for Co-Al is $J_{NN}^{NN} \geq 65$ meV. Being 2.7 times as high as the Fe-Al literature value, this value is again in reasonable agreement with our expectations of enhanced NN interactions. It also coincides remarkably well with the estimate derived from CoAl(100) when assuming $\tilde{J}_{CoAl}^1 \approx \tilde{J}_{FeAl}^1$ for that surface orientation.

Of course, the stacking sequence observed by us must also follow from the “D0$_3$” model. In principle, the (111) orientation allows for two alternative terminations.

- First, the surface might terminate with the B sublattice, i.e. antisites might segregate to the topmost layer instead of the third. The corresponding segregation energy reads

$$\Delta E_{seg}^{B \rightarrow 1B} = (\epsilon_{Al} - \epsilon_{TM}^{1}) - (\epsilon_{bulk}^{Al} - \epsilon_{bulk}^{TM})$$

$$+ 4(\epsilon_{TM-TM}^{NN} - \epsilon_{TM-Al}^{NN}) + 3(\epsilon_{TM-Al}^{2NN} - \epsilon_{Al-Al}^{2NN})$$

$$= -2\tilde{J}_1 + 8J_{NN}^{NN} - 6J_{2NN}^{2NN}.$$  \hspace{1cm} (6.25)

Formally, this expression is quite similar to that for the (100) orientation, Eq. (6.19). The segregation of a bulk antisite to the topmost layer is again assisted by ordering NN forces, but hindered by a single-site term, and by 2NN interactions. In fact, the difference to CoAl(100) is an additional barrier of $4J_{2NN}^{2NN}$. However, the single-site term $\tilde{J}_1$ depends on surface orientation by definition. If this term was somewhat stronger in favour of Al segregation for (111) than for (100) (the local environment change for a top layer atom is more severe), the effective
antisite segregation energy might well be unfavourable, at least in comparison to that for the third layer.

- As with CoAl(100), we must again ask why antisites segregate within an otherwise B2-ordered, Al-capped structure, instead of simply reverting the termination. To answer this question, we may use the same formal argument as depicted in Fig. 6.7 for the (100) surface. After filling the topmost layer with 50% TM antisite atoms, we may again rearrange the surface to form a bulk-like stacking sequence, terminated by a Co layer. The main difference to (100) arises because there are now no in-plane 2NN to form a barrier against the switch. It can easily be verified that the energy difference associated with the stacking switch amounts to

\[ \Delta E_{\text{switch}} = \frac{n}{2} \left[ 2j^1 - 8J^{NN} + 6J^{2NN} \right] = -\frac{n}{2} \cdot \Delta E_{\text{seg}}^{B\rightarrow 1B}, \tag{6.26} \]

Per antisite, this is exactly the same energy as required to bring it from the bulk to the surface in the first place. So, one would not expect to encounter top layer antisites from the “D0$_3$” model at all. If energy could be gained by that process, the same amount of energy could again be gained by switching to a Co-terminated sequence. Vice versa, if the latter process is already unfavourable, a stacking switch is even more unfavourable.

So, the “D0$_3$” model can again explain the observed surface termination consistently.

We may summarise our most important “quantitative” estimates for CoAl(100) and CoAl(111) as follows. Within the D0$_3$ model, much larger bond energies lead to a changed segregation pattern compared to Fe$_{1-x}$Al$_x$(100), changing the sign of the involved segregation energies under certain circumstances: \( \Delta E_{\text{seg}}^{B\rightarrow 1B} \gtrsim 110 \text{ meV} \) for CoAl(100) is clearly in favour of Co antisite defect segregation. Moreover, the absence of a stacking switch to a B2-ordered, Co-terminated arrangement allows us to place a bound on 2NN interactions, \( J^{2NN} \gtrsim 14 \text{ meV} \). Similar considerations for CoAl(111) even allow to estimate NN interactions directly, indicating that \( J^{NN} \gtrsim 65 \text{ meV} \). All in all, scaling the bulk interactions for A2 Fe-Al known from the literature by a factor \( \gtrsim 2.5 \) allows to obtain full consistency with the D0$_3$ model.

On the other hand, the uncertainties of our assumptions are much larger than for the Fe-Al case above, mainly from the unknown “reservoir” concentration and the unknown temperature of local equilibrium. Hence, a strong caveat seems in order. It must be stressed that the D0$_3$ model’s ability to explain the observed surface structures depends crucially on the error limits assumed for the “reservoir” concentration, \( x^C \gtrsim 90 \text{ %} \) Al. If, for some reason, the latter were significantly closer to stoichiometric CoAl than anticipated (after all, the annealing temperature used for both surfaces was extremely high), our simple interaction model would break down. A similar consequence would result if \( T_{eq} \) was significantly higher than estimated, e.g. above 1000 K.

A final remark concerns the completeness of the D0$_3$ model for CoAl surfaces. Of course, we have shown that it is possible to explain the prominent features of the (100) and (111) orientation by this means. However, even if the qualitative trends result already from \( J^1, J^{NN} \) and \( J^{2NN} \) alone, some additional interaction could yet exist. There are two indicators which might (or might not) hint to such an interaction. First, quantitative LEED shows the presence of antisites to be statistically
significant also in the second and third layer of CoAl(100). This cannot be an equilibrium feature of
the D0\textsubscript{3} model, since it contains no near-surface effects to favour antisites in these layers. On the
other hand, the equilibrium which forms during quenching is not too well defined, i.e. small levels
of disorder in the second and third layer need not necessarily be true equilibrium features. Second,
the SRO-induced, diffuse LEED intensity observed for CoAl(100) (Fig. 5.2, and Ref. [Smt99])
is ambiguous. While the intensity maxima are centred around half-order spots in agreement with
D0\textsubscript{3}-like, c(2\times2)-based SRO, they do appear somewhat broadened, and the existence of some
substructure within them is possible. In fact, a candidate would be a c(\sqrt{2} \times 3\sqrt{2})R45\degree arrangement,
already known from the closely related NiAl(100) surface. This, it turns out, is also consistent with
the metastable Ni\textsubscript{2}Al phase in the bulk (compare Fig. 2.7a to the top layer of Fig. 2.4!). Moreover,
x\textsuperscript{1} = 70 % Al in CoAl(100) correspond exactly to the value expected for Ni\textsubscript{2}Al-like SRO. In this
scenario, the additional antisites in the third layer could signify the beginning precipitation of this
phase into the bulk, using the topmost layer as a seed. Of course, there are numerous further ways
to extend the basic D0\textsubscript{3} model in a physically plausible fashion. All of them remain speculative
within the accuracy of our results, and additional experiments of yet improved quality would be
needed to establish the SRO properties of Co-Al surfaces more precisely.

6.3 A bigger picture: Some remarks on other alloy surfaces

The preceding sections showed that a useful model for segregation and ordering in Fe\textsubscript{1-x}Al\textsubscript{x}(100),
CoAl(100), and CoAl(111) may be established from some elementary considerations. Its main feature
is to account for the impact of SRO and LRO both in the surface and in the bulk simultaneously.
Although not necessarily exact in a numerical sense, it performs the task defined at the beginning of
this Chapter: To draw as many conclusions as possible from our results, instead of predicting them
afresh.

With this success at hand, only two final tasks remain. The first is the attempt to review other bcc-
based alloy surfaces in the light of the D0\textsubscript{3} model to see how much further it carries. In particular,
this concerns the controversies regarding NiAl(100) and (111) (Sect. 2.3). Second, much related
work has been done particularly for fcc based alloys. At least a brief connection to this field should
be established, although no completeness is aimed, or could be even hoped for.

6.3.1 bcc-based alloy systems

The central assumption of the D0\textsubscript{3} model is that of nearly ideal, NN- and 2NN-based SRO. Of course,
this restricts its application to alloys with such interactions of sufficient strength. For truly random
alloys, some equivalent of Eq. (6.11), i.e. a mean-field based approach, should be more appropriate
to predict segregation. However, it is noted in passing that in alloys with ordering J\textsuperscript{NN} of intermediate
strength, a “B2” restriction of the D0\textsubscript{3} model might be suitable. For instance, this concerns the
well-investigated low-index surfaces of Mo-Re-based alloys [Ktk97c, Ham99]. Nevertheless, for closer
comparability to Fe\textsubscript{1-x}Al\textsubscript{x} and CoAl, the following remarks summarise only those systems which show
B2 or D\text{0}_3 order in the bulk, i.e. where sufficiently strong $J^{NN}$ and $J^{2NN}$ are anticipated.

**CoAl(110) and NiAl(110).**

Since results for CoAl(100) and (111) were discussed above, a comparison should certainly include the closest packed surface of this material, the (110) orientation. Its basic structure is shown in Fig. 6.8, including the relative location of the four D\text{0}_3 sublattices in analogy to Fig. 2.5 (Sect. 2.2). Obviously, all four sublattices are coplanar in this case, rendering the D\text{0}_3 model particularly simple. To extract segregation energies as in the previous section, we note that a top layer atom here lacks only two NN and two 2NN, with four intralayer NN, two intralayer 2NN, and two of each in the second layer. For a slightly TM-enriched near-surface region, any segregation proceeds between sublattice B in the bulk, and sublattice 1B. So, the relevant segregation energy becomes

$$\Delta E_{\text{seg}}^{B\rightarrow1B} = -2\hat{J}^1 + 4J^{NN} - 4J^{2NN}. \quad (6.27)$$

Obviously, this is the direct equivalent of Eq. (6.19), on which our considerations for CoAl(100) were based. Only, the driving force for antisite segregation is weaker for (110) by 4$J^{NN}$. Remembering that $\Delta E_{\text{seg}}^{B\rightarrow1B} \leq -110$ meV from CoAl(100), but 4$J^{NN} \geq 260$ meV from CoAl(111), and assuming $\hat{J}^1$ to be approximately unchanged, one can not seriously expect any antisite segregation to occur for CoAl(110). On the contrary, a pure Al sublattice 1B is energetically favourable, even if some Co enrichment yet remains below. On the other hand, any further Al segregation to a nominal Co top layer site is characterised by

$$\Delta E_{\text{seg}}^{B\rightarrow1C} = -2\hat{J}^1 + 28J^{NN} - 20J^{2NN}. \quad (6.28)$$

even for exactly equiatomic CoAl – the NN barrier to the creation of a top-layer Al antisite is forbidding. Hence, one would expect an ideally B2-ordered topmost plane even for a slight Co enrichment remaining below. In fact, this is precisely the LEED result [Blu96]. The often-reported B2-ordered termination of NiAl(110) [Dav85a, Dav85b, Yal88, Mul88, Tor01], and the absence of controversies similar to NiAl(100) and (111), is perfectly consistent with CoAl(110) – any structural defects simply do not segregate.\(^{13}\)

**NiAl(100).**

The controversy surrounding NiAl(100) was already summarised in Sect. 2.3. One of the conclusions of Chapter 5 was that the concept of antisite segregation presents a plausible mechanism to explain

\(^{13}\)Due to the dominance of in-plane NN terms for the bcc (110) termination, treatments based only on NN interactions can be applied here with some success. For instance, the classic paper of Moran-Lopez and Falicov [Mor78] investigates trends as a function of $\hat{J}^1/J^{NN}$ and $T$ for equiatomic AB alloys. However, the author does not know of any similar work for slightly off-stoichiometric alloys.
the apparent discrepancies in principle. As mentioned there, several workers find a nominal Al termination, containing between 0 % and 30 % antisites [Mul88, Roo96], which fits almost perfectly with our observations for CoAl(100). On the other hand, it seems that a Ni-termination can also be produced somehow – if correct, our preceding considerations for CoAl(100) do not yet cover NiAl(100) fully. Of course, one might speculate that a small energy gain might yet result from a stacking switch of the entire surface (Eq. 6.21). Then, the surface might prefer an Al termination with a moderate amount of segregated Ni (for low antisite concentrations in the near-surface region), but switch over to the Ni-terminated geometry with growing Ni-enrichment in the near-surface region. While a qualitative explanation for both observed terminations seems thus possible, it should be noted that the D0₃ model is nevertheless quantitatively incomplete for NiAl(100): The well-ordered c(\(\sqrt{2} \times \sqrt{2}\))R45° “MP” superstructure clearly requires an ordering interaction beyond \(J_{NN}\) and \(J_{2NN}\), e.g. the same which is responsible for the metastable, bcc-based Ni₂Al phase in the bulk.

**NiAl(111).**

As for NiAl(100), a strong dependence of the selvedge composition on small amounts of near-surface Ni antisites could here motivate apparent contradictions between different workers (Sect. 2.3 and 5.5), but neither of two competing alternatives – either a pure Ni termination [Nie90], or a mix of Al- and Ni-terminated, B2-ordered domains [Dav88, Nie88, Ove90] – resembles CoAl(111). As stated before, it might be tempting to interpret the latter findings as an artifact of a LEED fit, but LEIS results on the top layer stoichiometry of NiAl(111) can hardly be ignored. So, one must accept the fact that a real difference between our findings for CoAl(111) and earlier ones for NiAl(111) probably exist. Nevertheless, one may use our considerations for CoAl(111) to venture yet another tentative scenario for NiAl(111). Even if the most favourable target for Ni antisite segregation was the third layer, it is still possible that a segregation to the topmost layer and a stacking switch was not absolutely unfavourable. In that case, antisite segregation would initially fill third layer sites to form an AlNi₃ termination. However, above a certain Ni concentration, an appreciable amount of top layer sites would also be populated by Ni, and at some point enable a stacking switch in the spirit of Fig. 6.7. The result would be a surface terminated partially by Al (with Ni antisites in the third layer), and partially by Ni (but then, with second layer Ni antisite defects!). The Ni-terminated area would gradually grow with rising Ni concentration, to eventually yield the once reported full Ni termination under certain circumstances. Of course, this scenario is quite speculative, and is mainly included here to show how far the D0₃ model could carry. Nevertheless, it might be instructive to test the predicted structure model experimentally.

**FeAl(110) and (111).**

As mentioned, both FeAl(110) and (111) impede a direct comparison to the above cases by reconstructing. At least for FeAl(110), this involves a switch of the lattice geometry as such – an incommensurate surface layer forms [Gra95, Bad96, Ham98]. Clearly, the limits of the D0₃ model are reached in this case, but it provides some interesting insights nevertheless. On the original bcc lattice, any Al segregation beyond a perfect B2 top layer would certainly be prevented by the overwhelming resistance of NN bonds, as noticed for CoAl(110) above. However, since this surface orientation is quite close-packed, *interlayer* bonding should be relatively weak, so that a completely rearranged top
layer gains more energy by the segregation of additional Al than is lost due to interfacial mismatch. However, annealing a sputter-depleted FeAl(110) surface produces a commensurate (2\times1) phase for low $T_{\text{anneal}}$, followed by the incommensurate arrangement only at higher $T_{\text{anneal}}$ [Gra95]. Similar to FeAl(100) [Ktk96], it is possible that sputtering here allows to reduce the near-surface Al content below 25%. The intermediate (2\times1) structure would then be due to near-surface D0$_3$ ordering in the course of compositional equilibration [Ham98]. The important point is that, within the D0$_3$ model, the Al bulk reservoir changes discontinuously at $x_{av} = 25\%$, from the strongly bound D to the weaker bound B sublattice. Hence, the driving force for Al segregation increases. The development of the LEED pattern according to Graupner [Gra95] might simply reflect this change: The top layer remains commensurate below $x_{av} = 25\%$ Al, and switches to the incommensurate form above. In that case, one might yet use the D0$_3$ model to gain at least an estimate for the energetics behind the incommensurate surface layer, from the bulk 2NN contribution which marks the reservoir switch from sublattice D to B.

CoGa(100)
The clean and well-annealed B2 CoGa(100) surface shows a c(4\times2) reconstruction. A very recent study [Pan01] by means of thermal energy atom scattering (TEAS), LEED and AES shows that the very surface contains around 0.25 ML Co at low temperatures, and undergoes a reversible order-disorder transition around 500 K, before further, reversible Co segregation sets in above 850 K. Although the authors favour an adatom model, they can not rule out a mixed top layer, either. Of course, this latter model would again correspond very well to our findings for CoAl(100), except that yet another interaction is needed to explain the observed LRO quantitatively. In fact, the continued Co segregation at high $T$ could also pictured within this framework: The diminishing top layer SRO removes the 2NN-based energy barrier that prevents the stacking switch of Eq. (6.21). Certainly, the atomic mobility around 850 K is high enough to allow for a corresponding rearrangement.

Fe$_3$Si(100), (110), and (111).
Quantitative LEED studies exist for all three listed surfaces, each showing a low-temperature phase of D0$_3$ symmetry and a high-temperature, B2-based one [Wei98]. The D0$_3$-based (100) and (110) phases deserve particular attention in the present context. The top layer of the former retains its D0$_3$ order in principle, but the D sublattice is fully occupied by Si, while the B sublattice contains 30\% Si and 70\% Fe. Qualitatively, this places the driving force for Si segregation somewhere in the middle between that for Fe$_{1-x}$Al$_x$(100) and CoAl(100) of the present work, but certainly adheres to the “D0$_3$” model. In contrast, the (110) surface features a fully CsCl-ordered topmost layer. Apparently, the mechanism of Eq. (6.27), which was invoked for CoAl(110) and NiAl(110) above, applies here, too: Even though the bulk B sublattice contains significant amounts of Fe, these do not appear in the first layer: The energy gain through improved NN bonding simply cannot overcome the single-site segregation driving force for Si.

In short, the present section’s brief review shows that a D0$_3$-based model could be adapted to describe many systems beyond those of the present work. Most importantly, it provides a guideline to account for both bulk and surface SRO and LRO effects in an intuitive way. Thus, it provides insights even for cases which it does not cover quantitatively – be it the mere absence of additionally important, but system-dependent interatomic interactions, or even the switch to a different surface lattice.
Chapter 6. The interplay of bulk order and surface segregation

Figure 6.9: Possible superstructures of a fcc(111) surface. A $(\sqrt{3} \times \sqrt{3})R30^\circ$ arrangement (left) is encountered for $\text{Cu}_{0.84}\text{Al}_{0.16}(111)$ [Bai86], and for $\text{Pt}_3\text{Sn}(111)$ after sputtering and incomplete annealing [Atr93]. A $p(2\times2)$ superstructure (right) forms on $\text{Ni}_{0.90}\text{Al}_{0.10}(111)$ [Rei00].

6.3.2 The link to fcc-based systems

Certainly, the interrelation between ordering forces and surface segregation has drawn much attention in general throughout the past decades, but much of this was directed at fcc-based systems. So, some final words seem in order, clarifying how some of the above-illustrated concepts carry over to this lattice type. Of course, no detailed review of the abundant literature is attempted — for this, the reader is referred to the dedicated recent review articles, Refs. [Vas97, Pol00]. Likewise, well-founded theoretical treatments exist [Mon97, Drc99, Boz99, Tre99], which should be sought for more quantitative insights. Here, we shall only highlight some qualitative parallels to our own results above.

A fundamental difference between the bcc and fcc lattices regards the location of atomic pairs: the difference between NN and 2NN distances is clearly larger in the latter case than in the former. So, phenomenological treatments of segregation in fcc based systems often neglect any interactions beyond NN altogether [San85, Ter91]. In fact, such an interaction model is sometimes [Mon97, Drc99, Sad99, Tre99] but by no means always [Ozo98, Tre99] justified even qualitatively. Nevertheless, we shall tentatively adopt it in the following cases.

The strongest similarity to work presented here regards the competition of in-plane ordering interactions and surface segregation. In the case of $\text{Fe}_{1-x}\text{Al}_x(100)$, this leads to the formation of a $c(2\times2)$ superstructure at low $x$. For the further segregation of Al, in-plane 2NN interactions approximately balance the initial segregation driving force of $J^1$ and $J^{NN}$. Compare this to the case of fcc based random $\text{Cu}_{0.84}\text{Al}_{0.16}(111)$ [Bai86]. Although disordered in the bulk, it forms an ordered top layer of $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity (left panel, Fig. 6.9), composed of $2/3$ Cu and $1/3$ Al. In fact, this arrangement accommodates the maximum possible amount of Al atoms if Al-Al NN pairs are avoided. Quite obviously, the interplay of lateral ordering forces and an Al segregation tendency defeats entropy, leading to an ordered top layer, as for $\text{Fe}_{0.97}\text{Al}_{0.03}(100)-c(2\times2)$. A quantitative confirmation
of this scenario was given by Teraoka [Ter90]. Furthermore, a fcc(111) \((\sqrt{3} \times \sqrt{3})R30^\circ\) arrangement does not allow to place any Al atoms in the adjacent layer without creating Al-Al NN pairs, and AES indeed indicates second layer composed of purely Cu. So, \(\text{Fe}_{0.97}\text{Al}_{0.03}(100)-c(2\times2)\) and \(\text{Cu}_{0.84}\text{Al}_{0.16}(111)-(\sqrt{3} \times \sqrt{3})R30^\circ\) resemble one another also in this respect. To broaden the picture, a (metastable) \((\sqrt{3} \times \sqrt{3})R30^\circ\) phase of similar origin is also reported for Pt,Sn(111) [Atr93].

Another case which deserves attention is that of fcc Ni,\textsubscript{0.90}Al,\textsubscript{0.10}(111). Al is the segregating element, but this time, the near-surface concentration remains “pinned” at \(25\%\) Al [Sul94a], forming a \(p(2\times2)\) arrangement (right panel, Fig. 6.9) [Rei00] instead of the denser \((\sqrt{3} \times \sqrt{3})R30^\circ\) one. Obviously, repulsive NN interactions again limit the amount of segregated Al, but this time, the resulting structure cannot be based on \(\vec{J}^1\) and in-plane \(\vec{J}^{NN}\) alone. In fact, the \emph{ab initio} work of Schulthess et al. [Sul94b, Mon97] shows an enhanced ordering interaction specifically between top layer 2NN sites, which probably prevents Al segregation beyond \(25\%\).

![Figure 6.10: Bulk unit cell of the fcc based L1\(2\) structure.](image)

Since the competition between lateral ordering forces and surface segregation is so obvious for some fcc based system, one should expect also our other main observation to occur at least in certain cases: The impact of bulk structural defects near an ordered alloy’s ideal composition. Yet, the author knows of no such reports for fcc based systems. Consider, for instance, the “classic” example of Cu,\textsubscript{3}Au(100), which crystallises in the L1\(2\) structure (Fig. 6.10). NN-based estimates along the lines of Sects. 6.2.2 and 6.2.3 would predict either Au defect segregation in the Au-rich case, or Cu defect segregation for the Cu-rich stoichiometry. Yet, both cases are reported to display the same bulk-truncated, mixed Au-Cu termination (Ref. [Riv95] and references therein). Either there is an approximate balance between segregation and ordering forces (as for the 1B sublattice of A2 \(\text{Fe}_{1-x}\text{Al}_x(100)\)), or some further interaction inhibits the simple mechanism of “antisite segregation” from working in this case.\(^{14}\)

In total, we may conclude that at least some of our findings for bcc based alloy surfaces have an equivalent in fcc based materials. However, the author knows of no equivalent to our most striking results: First, the two-step segregation process as a function of \(x\) for \(\text{Fe}_{1-x}\text{Al}_x(100)\), which is the product of a delicate balance between all involved forces, and second, the marked influence of bulk structural defects in strongly ordering alloys. Searching for these effects in fcc-based alloy surfaces might be a fruitful task.

\(^{14}\)Of course, much more work on Cu,\textsubscript{3}Au alloys exists than could here be addressed. It was certainly proven that a model based on bulk-like \(\vec{J}^{NN}\) and \(\vec{J}^1\) only is overly simplistic for this case. For instance, there exists at least one strong bulk multisite interaction in this system [Ozo98]. Further, a quantitative analysis of the (100) surface’s order-disorder transition claims the top layer NN bond to be significantly weaker than the bulk one [San85].
6.4 Summary

The present chapter attempted to place the qualitative surmises of Chapters 4 and 5 with regard to order and segregation in Fe$_{1-x}$Al$_x$ and CoAl surfaces on a foundation as rigorous as possible to remain tractable. Indeed, this aim can be achieved by drawing on the specific properties of ordering materials in the $T$ range where SRO and LRO are relevant. First, the assumption of ideal SRO on separate “bulk” and “surface” lattice sites gives an appropriate description of segregation energetics in these systems. Second, the approximation of ideal SRO by ideal, D0$_3$-based LRO provides the framework to include entropic effects, allowing to use the simple Langmuir-McLean expression. Together, these rough approximations avoid the limitations of conventional, mean-field based approaches, while retaining a conceptual simplicity which more precise but abstract treatments lack.

In brief, the “D0$_3$” model proves that a “minimal” set of parameters for our surfaces indeed requires interactions $\tilde{J}^1$, $J^{NN}$, and $J^{2NN}$. In particular, the latter interaction must not be neglected — neither the two-step segregation in Fe$_{1-x}$Al$_x$(100) nor the absence of a stacking switch for CoAl(100) could be explained by $\tilde{J}^1$ and $J^{NN}$ only. Within the D0$_3$ approximation, one may even venture certain quantitative statements: for instance, the segregation energy above half a monolayer of Al in the two-step segregation process in Fe$_{1-x}$Al$_x$(100) should be clearly smaller than $k_B T_{eq}$, the thermal energy at which local diffusion processes freeze out during the quenching of our samples. It also reveals how enhanced NN interactions in CoAl lead to a fundamentally changed surface physics, as bulk structural defects take charge. The D0$_3$ model is able to account for these trends in detail, including the differences between the CoAl(100), (110), and (111) orientations. The underlying concepts apply qualitatively also to other bcc-based surfaces of ordering alloys, as well as to fcc-based ones. However, the comparison with other systems also draws attention to the model’s limitations: In particular, interatomic interactions beyond NN and 2NN are definitely relevant in many materials. In fact, this possibility must even be considered for CoAl(100) and (111) as studied here.

With this knowledge in mind, a more advanced theoretical treatment does appear desirable. However, such predictions might well reach beyond the accuracy which the present LEED analyses can reach. While the limitation of chemical resolution due to parameter correlations can partially be overcome by carefully eliminating any conceivable systematic errors, another point seems even harder to attain. The concept of thermal equilibrium in low-temperature experiments is a difficult issue, and a better definition of its effective temperature $T_{eq}$ would be most desirable. In this light, the present chapter certainly explores the results of Chapters 4 and 5 to their limits.
Chapter 7

Concluding remarks

The preceding chapters aimed to paint a detailed and feature-rich picture of the structural properties of three system classes: Fe$_{1-x}$Al$_x$(100) ($x = 0.03$, 0.15, 0.30, and 0.47), CoAl(100), and CoAl(111). Of course, already the present work’s title states the link between these different results: The desire to understand the interplay of bulk order properties and surface segregation. Specifically, this includes the four goals listed in the introductory chapter: To investigate the role of the bulk composition $x$ in Fe$_{1-x}$Al$_x$(100), to understand the influence of different elemental interactions by advancing to CoAl(100), to exemplify the impact of the surface orientation by adding CoAl(111), and to tie all these phenomena together within a common framework.

The required information is provided in the form of structural analyses by quantitative LEED. Of course, this method is well established today, and its existing “tools”, particularly Tensor LEED, allow to extract even complex surface structural information in great detail. Nevertheless, in order to ensure high-precision results below, one central aspect of the method had to be addressed in greater detail, namely the intricacies associated with a multi-parameter space. There exists no general method to access individual structural quantities directly in a LEED analysis, so that all features of a surface must rather be addressed by one simultaneous fit, including all vibrational and geometric properties along with order and stoichiometry, which are the main focus of this work. Of course, the accuracy of the chosen overall model and correlations among these parameters all influence the precision of individual findings.

The example of Fe$_{0.85}$Al$_{0.15}$(100) reveals which factors determine the “chemical” precision of quantitative LEED. With respect to site-dependent concentrations, a strong correlation exists with element-dependent vibrational amplitudes on that site, but also – though weaker – with other quantities, e.g. element-dependent positions, where allowed by local symmetry. Although the fit’s sensitivity to stoichiometry alone is good, its effective impact on the fit quality is clearly reduced when the mentioned quantities are co-optimised. Even for low statistical errors, this means that systematic deficiencies of the model structure may shift the structural optimum much more than without the correlation. Of course, one might disable this mechanism directly by imposing physically “reasonable” constraints on thermal vibrations. However, Fe$_{0.53}$Al$_{0.47}$(100) demonstrates that such constraints must be chosen carefully: Here, fixing the second layer vibrational amplitude to the bulk value would lead to a
physically questionable second layer stoichiometry. A qualitatively different pitfall of data fitting is illustrated by a third case, CoAl(111): The simultaneous extension of a structural model by many parameters at once will always improve a fit, but their physical truth can be difficult to prove. Here, a model of coexisting, ordered structural domains had to be weighed against a unique termination with deviations from bulk order, and both models proved equivalent in terms of the fit quality reached.

Where possible, a trivial but sound way around such issues is the use of pre-information from other methods, e.g. STM or LEIS. Yet, fixing isolated quantities can certainly not replace the entire structure determination – in contrast, it may here serve to enhance the accuracy of all remaining fit results. As for the “chemical” accuracy of LEED, understanding the underlying correlation already implies a recipe to avoid it partially. First, seemingly counter-intuitive best-fit vibrational amplitudes may serve as a warning that the surface’s chemical description could as yet be incomplete. Second, in cases where element-dependent vibrational amplitudes are of too low influence in the fit, the most reasonable constraint for the present class of systems is to choose approximately equal vibrations on the same lattice site, inferred by analogy to the remaining analyses performed in this work. Third, a standard way to circumvent correlations is to test an effect as such, i.e. by comparing a “constrained” fit to an “unconstrained” one. Its statistical significance may then be assessed by conventional means, e.g. the R-factor reliability, $RR$. Finally, in cases such as CoAl(111), the fit results, and the $I_g(E)$ spectra themselves, must be closely scrutinised for additional hints as to the trustworthiness of each model.

By taking these points into account carefully, conclusions of high accuracy could be drawn in all three cases, and also in the further analyses performed in this work. As mentioned, each fit also includes all relevant geometric and vibrational properties of the surfaces in question. In short, these parameters reflect the impact of $x$, different elements, and surface orientation quite clearly, and a consistent picture arises in each case, including some trends between different systems. So, one may expect similar consistent findings regarding near-surface order and segregation.

For Fe$_{1-x}$Al$_x$(100), the most striking development with growing $x$ – across the three bcc-based regions, A2, D0$_{3}$, and B2, of the bulk phase diagram – is the “two-step” nature of Al segregation to the topmost layer. The first step is complete already in the very dilute range ($x = 0.03$), with half the topmost layer sites occupied by Al in a c(2$\times$2) arrangement. The second half is then filled only gradually across the A2 random alloy region (e.g. $x = 0.15$), and a (practically) full layer of Al is only reached within the D0$_3$ phase area ($x = 0.30$). Finally, a bulk-ordered, Al-terminated arrangement characterises the B2 regime ($x = 0.47$).

CoAl(100) contrasts this picture with a striking difference. Overall, its layer stacking sequence is the same as for B2 Fe$_{0.53}$Al$_{0.47}$(100), i.e. CoAl(100) terminates with the nominal Al sublattice as well. However, the topmost layer itself shows a large amount ($\approx 30\%$) of Co “antisite” defects, which is quite surprising in view of the general Al segregation/termination trend observed for most TM-Al alloys to date – of course, particularly compared to the Fe-Al case.

CoAl(111) adds yet another facet to the spectrum. As the former cases, it also terminates with the nominal Al sublattice. And, as CoAl(100), it also shows a significant amount of well localised near-surface Co antisite defects. However, these are found in the third instead of the topmost layer.
And, their relative amount is larger than for CoAl(100) – with $\approx 70\%$ third layer Co antisite defects, one must even speak of a modified average elemental stacking sequence away from the B2 structure – rather yielding an approximate AlCo$_3$ sequence.

All these phenomena may be understood within the same unified model, by accounting for ordering forces and Al segregation on the atomic scale. The model is based on an Ising-like lattice Hamiltonian which contains but three basic ingredients: A “single-site” Al segregation driving force to the top layer of each sample $\tilde{J}^1$, a nearest-neighbour pair interaction $J^{NN}$ which strongly favours heterogeneous bonding, and a weaker, but non-negligible second-nearest neighbour interaction $J^{2NN}$.

Of course, both bulk pair interactions depend on the material. Yet, within the precision of our experiments, no need for separate near-surface interactions arises, and no strong dependence of $\tilde{J}^1$ on either the material or surface orientation must be demanded. In conjunction with a model of the corresponding short-range order (equivalent to D0$_3$-type LRO – hence, the “D0$_3$” model), and a model for the preparation process (including preferential sputtering, annealing, and fast quenching to low $T$), our basic observations can be explained as follows:

- In Fe$_{1-x}$Al$_x$, the competition between single-site Al surface segregation and the breaking of four Al-Fe NN bonds is clearly in favour of Al segregation. Four in-plane 2NN bonds further shape this process: Through the formation of first SRO and then c(2×2) LRO, Al segregation is initially unencumbered by 2NN opposition. $J^{2NN}$ is not strong enough to prevent all further Al segregation once the first step is complete. Rather, the second step is clearly slowed down, characterised by an effective segregation energy $\Delta E_{\text{seg}} \ll k_B T_{\text{eq}}$. At $x = 0.25$, the surface should be completely filled by Al; additionally, the bulk “reservoir” changes at this point, toppling the balance to become more friendly to Al segregation. Reassuringly, these surmises are in good qualitative agreement with pair interactions given in the literature.

- The behaviour of CoAl(100) cannot be understood for an ideal, equiatomic B2 crystal, but arises naturally if a residual near-surface Co enrichment from initial sputtering is considered. This leaves Co antisite defects behind, and their segregation to the surface removes four unfavourable Co-Co NN bonds. It is again counteracted by a “single-site” Al preference in that layer, but NN interactions are much stronger in Co-Al than in Fe-Al, so that antisite segregation becomes a favourable process. Again, 2NN interactions play a crucial role in shaping this near-surface order – only 2NN-based in-plane SRO prevents a stacking switch to a bulk-ordered, Co-terminated surface. Quantitatively, an enhancement of interactions by a factor of $\approx 2.5$ over those in Fe-Al would be required by this model, which is again in good agreement with known trends e.g. from the formation enthalpies of both alloys.

- The same mechanisms as inferred for CoAl(100) also describe CoAl(111). However, the changed NN and 2NN environments of selvedge atoms here create a different “target site” for antisite segregation. In fact, if antisite segregation proceeded to the top layer, a stacking switch would be the automatic consequence, since no in-plane 2NN interactions exist to form a barrier. However, top layer antisite segregation is here less favourable than for CoAl(100) just because of the absence of top layer 2NN. In contrast, relatively much energy may be gained by placing antisites in the third layer – there, only one NN bond is broken, but apparently, no
pronounced single-site preference for Al counteracts this process. In short, antisite segregation to the third layer is the most favourable process for CoAl(111), and since it proceeds without any opposition from in-plane 2NN, this layer can be filled almost completely by Co.

The most important insight from these findings cannot be stressed enough: In strongly ordering alloys, segregation is a balance between “classic” single-site driving forces, and a potentially strong opposition from bonds broken in the bulk. So, sufficiently strong bulk ordering interactions will eventually gain the upper hand, causing even small amounts of bulk structural defects to dominate surface stoichiometry and order.

From these basic concepts, the behaviour of related systems may be understood as well. In particular, the structure of CoAl(110) is perfectly consistent with the trends inferred from (100) and (111) above. And, the importance of small amounts of structural defects for surface properties is a natural starting point to explain the seeming literature discrepancies for NiAl(100) and (111). True, our observations cannot be transferred blindly, and quantitatively, at least one ordering interaction is missing from our model for NiAl. Nevertheless, an application of our concepts to this case could prove a fruitful undertaking.

Before concluding, a final look back to the introduction seems in order: As it happens often, its very first paragraphs concern the practical importance of the investigated systems, although this work itself is dedicated to basic science – l’art pour l’art, as it might seem. Thus, the reader may rightfully ask how well the initial motivation is justified at all.

In fact, it is, although a long way remains to be covered to complete this link. TM-Al alloys in practical use as structural materials differ much from the single-crystalline, binary samples studied here. Yet, fundamental aspects of their behaviour, most notably deformation, fatigue and fracture, are primarily determined by their microstructure, i.e. grains, grain boundaries, dislocations, or even isolated structural defects. If ever a quantitative, atomistic modelling of the behaviour of TM-Al-based alloys in practice is to be reached, the properties of these defects must be accounted for on the atomic scale. Surfaces, of course, are easily accessible model systems for complex defect types – mainly for grain boundaries, but more generally for any kind where “bonds” are broken. Particularly when counter-intuitive phenomena play a role (e.g. the antisite segregation in Co-Al surfaces above), direct experimental evidence, such as that presented here, may be hoped to have some stimulating influence even on theories which, ultimately, reach far beyond our momentary “playground”: the surfaces of binary, single-crystalline alloys.
Appendix A

Abbreviations

2NN: second-nearest neighbour
A2: bcc-type long-range order (Fig. 1.1)
AES: Auger electron spectroscopy
ATA: average t-matrix approximation
B2: CsCl-type long range order (Fig. 1.1)
bcc: body-centered cubic
CPA: coherent potential approximation
D0_3: BiF_3-type long-range order (Fig. 1.1)
DLEED diffuse low-energy electron diffraction
fcc: face-centered cubic
hcp: hexagonally close-packed
HP: the surface phase which forms after high-temperature annealing of NiAl(100) (Ref. [Blm96]).
L1_0: CuAu-type long-range order
L1_2: Cu_3Au-type long-range order (Fig. 6.10)
LEED: low-energy electron diffraction
LEIS: low-energy ion scattering
LP: the surface phase which forms after low-temperature annealing of NiAl(100) (Ref. [Blm96]).
LRO: long-range order
MEED: medium-energy electron diffraction
MP: the surface phase which forms after intermediate-temperature annealing of NiAl(100) (Ref. [Blm96]).
MT: muffin-tin
Appendix A. Abbreviations

NN: nearest neighbour
PD: probability distribution
QC: quasicrystalline
$S/N$: signal-to-noise ratio
SPA-LEED: spot-profile analysis LEED
SRO: short-range order
STM: scanning tunneling microscopy
TM: transition metal
UHV: ultra-high vacuum
VLEED: very-low-energy electron diffraction
XRD: X-ray diffraction
Bibliography


Bibliography


Bibliography


[Ove95] S.H. Overbury, private communication in Ref. [Gra95b].


[Paw82] G.S. Pawley, quoted in Ref. [Pri82], p. 122.


[Run01] J. Rundgren, Phase shift package (private communication, 2001, and to be published).


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- Atomic structure of Fe thin films on a Au(100) surface
- Atomic Structure of CoAl(110) and FeAl(110) Alloy Surfaces
- Development of the TensErLEED program package for the computational evaluation of LEED intensity data
- Energy dependence of the scattering potential in LEED
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