Quantification of substitutional disorder and atomic vibrations by LEED – the role of parameter correlations

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Abstract

The composition of substitutionally disordered surfaces, including the layer and site dependent distribution of the chemical elements involved, has frequently been a target of quantitative low-energy electron diffraction. In the present paper, we demonstrate that, at a certain precision level of the intensity analysis, the structural search for these chemical parameters suffers from their correlations with statistical atomic displacements from the ideal lattice sites. The latter can be due to thermal vibrations and/or induced by the random substitution of atoms. Using the example of two (100)-oriented Fe$_{1-x}$Al$_x$ alloy surfaces ($x = 0.15$ and 0.47), we show that unusually large error limits for chemical parameters result when such atomic displacements must be determined simultaneously. Even small systematic errors in the intensity analysis can considerably shift the best-fit chemical structure. In order to avoid incorrect conclusions, the parameter correlations should be taken into account explicitly. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

As well known, quantitative low-energy electron diffraction (LEED) ranges among the primary tools of surface crystallography [1]. One of its applications is the study of multicomponent surfaces that display some substitutional disorder, using the framework of the average $t$-matrix approximation (ATA) [2,3]. Mostly, such investigations address surfaces of metal alloys in which segregation and related deviations from bulk stoichiometry can extend over several atomic layers [4–6]. Accuracies of the order of $\pm 10$ at.\% for lattice site occupation probabilities are claimed in many cases, based on standard error estimates (e.g., Refs. [7,8]). Of course, the sensitivity of LEED towards chemical parameters is system dependent. It relies on the difference between the atomic scattering factors of the elements involved which, roughly speaking, grows with their separation in the periodic system of elements. However, standard error estimates have been further questioned for two reasons in the past. First, the analysis of LEED intensity vs energy spectra, $I(E)$, is a multiparameter problem in which all quantities of interest are determined in a simultaneous fit.
Usually, parameter correlations are neglected when estimating error limits, although the latter may increase considerably when correlations are taken into account. On the other hand, cases in which a surface's composition is known from other sources indicate that the true accuracy reached by LEED may be underestimated substantially [9–11].

In view of the growing importance of multicomponent surfaces in technology, a deeper understanding of the “chemical” resolution reachable by LEED seems to be worthwhile. Of course, this is relevant only for analyses which achieve a sufficiently close fit between experimental and calculated data, so that this accuracy really becomes an issue. However, such cases occur increasingly often due to enhanced computer power and general refinement of theoretical techniques. The present work tries to contribute to this issue. Its focus is on the impact of (isotropic) root mean-square displacements (always referred to as thermal vibrational amplitudes in the following) on the sensitivity of LEED with respect to stoichiometry. In order to conduct a realistic study, structural analyses of experimental \( I(E) \) spectra from two \( \text{Fe}_{1-x}\text{Al}_x(100) \) alloy surfaces \( (x = 0.15 \text{ and } x = 0.47) \) are used as examples. With atomic numbers \( Z = 13 \) and 26 for Al and Fe, respectively, the two elements are separated to the extent demonstrated in Fig. 1 for the modulus and phase of their scattering factors. The differences are moderate, i.e. elemental combinations with both larger and smaller differences exist, so that the present choice of Fe–Al might be a kind of average case. An additional reason for our choice is that, for \( \text{Fe}_{0.55}\text{Al}_{0.47}(100) \), previous studies in our group [12–14] found an unexpected concentration of 20% Al in the second atomic layer. Since the top layer consists of Al only, this is in contrast to the alternating purely elemental layers expected from the bulk (for \( x = 0.5 \)). So, this finding might be caused by some unsuspected (and therefore unconsidered) parameter correlation. Of course, whether or not such correlations really mislead the structural search can only be checked if the stoichiometry is known.

To that end, we focus on the LEED analysis of a \( \text{Fe}_{0.85}\text{Al}_{0.15}(100) \) surface as a second example. Its top layer composition is precisely known from
both low-energy ion scattering (LEIS) and chemically resolved scanning tunneling microscopy (STM) [15], so this surface provides an excellent test case to illustrate the effect of parameter correlations.

The next section contains some basics of the LEED calculations and the physics of thermal vibrations. We then revisit the case of Fe$_{0.53}$Al$_{0.47}$ (1 0 0), showing that the simultaneous variation of chemical and vibrational parameters leads to a considerable uncertainty with respect to the precise stoichiometry of the second atomic layer. Then, we concentrate on Fe$_{0.85}$Al$_{0.15}$ (1 0 0) for which we know the top layer stoichiometry and so can quantify the impact of parameter correlations. A discussion completes the paper, and a mathematically more rigorous treatment of the observed phenomena is appended.

2. Basic considerations

As mentioned, we use experimental $I(E)$ data from two clean and well-annealed (1 0 0)-oriented Fe$_{1-x}$Al$_x$ surfaces ($x = 0.15$ and 0.47), for which the surface preparation and structural analyses have been described earlier [12,13,15–17]. The intensity calculations below make use of the TensErLEED program package [18]. This employs the tensor LEED perturbation method [19,20] to determine the geometrical, chemical [21,22] and vibrational [23] surface properties in an automated structural search procedure [24]. Care was taken not to leave the tensor LEED validity range. In order to obtain true all-parameter fits, bulk properties inaccessible to the perturbational approach (e.g., the lattice parameter $a$, bulk vibrational amplitudes $v_b$) were optimized full dynamically. Inelastic damping was simulated by a constant imaginary part of the inner potential, $V_0$. Its real part $V_0$ was taken to be energy-dependent, whereby a formula provided for the Fe bulk was employed for Fe$_{0.85}$Al$_{0.15}$ [15,25]. For compatibility with earlier work [12,13], a linear energy dependence of $V_0$ was assumed for Fe$_{0.53}$Al$_{0.47}$. Its slope was determined consistent with the well known room temperature lattice parameter $a$ [12]. With that slope kept fixed, the lattice parameter at low temperature was determined, so avoiding a recently reported correlation between both [26].

The structural search is guided by the Pendry $R$-factor $R_P$ [27] as a measure for the fit quality. Originally designed to deal with geometrical parameters, its sensitivity to elemental concentrations is well established [9,28]. Also, it allows to estimate the limits of statistical errors for any parameter by means of its variance, $\text{var}(R_P) = R_{\text{min}}(8V_0/\Delta E)^{1/2}$, with $\Delta E$ the energy width of the data base. Any model structure yielding an $R$-factor below $R_{\text{min}} + \text{var}(R_P)$ is considered to lie within the limits of error [27]. Although, in principle, the full parameter coupling must be considered, error limits are usually determined by varying only one parameter with all others fixed at their best-fit values. Most error bars reported here were determined this way, too. However, when parameter correlations became important, the full coupling was taken into account.

As usual, atomic $t$-matrices were used to describe the atomic scattering in angular-momentum space. For spherical scatterers, they are constructed from phase shifts $\delta_l$ ($l$, angular-momentum quantum number) which were calculated relativistically and spin-averaged up to $l_{\text{max}} = 12$. The matrix $t$ is diagonal for spherical scatterers, with elements $t_l = \sin\delta_l \exp i\delta_l$. Its connection to the usual atomic scattering factor $f$ reads

$$f(\cos \theta) = \frac{-2\pi}{k} \sum_l (2l+1)t_l P_l(\cos \theta)$$

with $k$ the electron wave number (related to the energy by $E = \frac{1}{2}k^2$ in atomic units) and $\theta$ the scattering angle. For each lattice site $i$ both $t$ and $f$ are modified to describe root mean-square statistic displacements $v_i$ by way of a Debye–Waller factor $w_i$. For isotropic displacements, $w_i$ is determined only by $v_i$ and the momentum transfer, $\Delta \mathbf{k}$, i.e. by

$$w_i = \exp \left(-\frac{1}{6} \cdot |\Delta \mathbf{k}|^2 \cdot v_i^2 \right).$$

The total scattering factor for a lattice site $i$, randomly occupied by Al with a probability $c_i$, and by Fe with $(1 - c_i)$, is calculated within the ATA [2,3]. Then, $f_i$ reads
\[ f_{i}^{ve} = c_{i}w_{i}^{Al}f^{Al} + (1 - c_{i})w_{i}^{Fe}f^{Fe}. \] (3)

Eq. (3) can be generalized even further to allow for element-dependent positional displacements on a randomly occupied lattice site. This leads to a non-spherical scattering factor which can easily be treated within tensor LEED [29]. Note that such displacements are different from truly random static disorder. We will denote non-statistical positional differences between the elements by \( b \) since they lead to an effective buckling of the layer involved.

In Eq. (3), the concentration \( c_{i} \) as well as the Debye–Waller factors \( w_{i} \) act as weight factors for the elemental scattering factors. Technically, they can be distinguished through the momentum transfer \( \Delta \mathbf{k} \), as \( w_{i} \) depends on the scattering angle \( \theta \) and energy \( E \) whereas \( c_{i} \) does not. However, if these a priori unknown quantities are optimized in a simultaneous fit, at least a partial correlation could occur, reducing the accuracy for either parameter. So, the quantities \( w_{i} \) deserve some attention when stoichiometric parameters are determined. Since their independent determination is usually not the primary goal of LEED, the simplest way around a suspected correlation would be to use knowledge on the different values of \( v_{i} \) from other sources. Yet, usually this is not available, and simple thermodynamics is also of little help when multicomponent systems are considered. This is in spite of the simple approximation describing the thermal vibrations for the bulk of an elemental solid by means of the Debye model [30],

\[ m\nu_{b}^{2} = \frac{9\hbar^{2}}{k_{B}\theta_{D}^{2}} \left[ \phi \left( \frac{\theta_{D}}{T} \right) + \frac{1}{4} \frac{\theta_{D}}{T} \right] \]

with \( \phi(x) = \frac{1}{x} \int_{0}^{x} \frac{y}{e^{y} - 1} \, dy \) (4)

with atomic mass \( m \), temperature \( T \), and Debye temperature \( \theta_{D} \). A similar equation for our case would be quite desirable, but it would have to hold for (only partially ordered) compounds and vibrations near the surface where the bulk Debye temperature does not apply.

A direct extension of Eq. (4) for a diatomic bulk crystal is only possible for the mass-weighted sum of \( v^{Al} \) and \( v^{Fe} \), \( m_{Al}(v^{Al})^{2} + m_{Fe}(v^{Fe})^{2} \) [30]. The individual amplitudes are still determined by the site-dependent phonon polarization vectors in a non-trivial way, rendering any simple model prediction difficult. In fact, a compilation of experimental results for binary ionic crystals indicates that the ratio of elemental vibrations can vary considerably [31]. While we are unaware of any bulk studies of \( v^{Al} \) and \( v^{Fe} \) in FeAl, their qualitative similarity to NiAl might be of help. Here, \( v^{Al} \) and \( v^{Ni} \) are approximately equal over a wide range of temperatures [32,33]. Interestingly, the theoretical work of Ref. [33] also shows the dependence of \( v^{Al} \) and \( v^{Ni} \) on \( T \) to be different in detail: while \( v^{Al} > v^{Ni} \) as \( T \to 0 \), this trend reverses above 140 K. This behaviour can only be understood from the different contributions of Al and Ni to the acoustic and optic phonon branches. In our case, the situation is yet more complicated as we are additionally dealing with random substitutional disorder. In this case, the elemental mean-square displacements will depend strongly on their average local environment, i.e. also on the a priori unknown degree of short-range order. In addition to thermal vibrations there may be also statistical static displacements leading to considerably enhanced site-dependent Debye–Waller factors [34]. In fact, such displacements have been observed in a Fe_{0.80}Al_{0.20} random alloy [35].

Near a surface, both the number of bonds per atom and the crystal symmetry are reduced, leading to enhanced and layer-dependent vibrational amplitudes. In elemental solids, they can be described through an ad hoc “surface Debye temperature” [36]. Yet, as its precise value is normally unknown, the independent fitting of surface vibrations is demanded. Of course, this additional surface problem also applies to diatomic solids. So, all we can safely assume is that \( v^{Al} \) and \( v^{Fe} \) on near-surface sites \( i \) should be enhanced compared to the bulk, though they might not deviate excessively from each other within the same layer. Ideally, we should treat all inequivalent vibrational amplitudes as independent parameters within these approximate bounds. However, such an amount of low-weight fit quantities would clearly extend our parameter space unreasonably. Instead, we will restrict the number of independently determined
vibrational amplitudes in our fits, but carefully investigate the effect of relaxing this restriction on lattice sites of particular interest.

3. Fe$_{0.53}$Al$_{0.47}$ (1 0 0) revisited

The Fe–Al alloy near 1:1 composition crystallizes in the bcc based, ordered B2-structure (CsCl) [37]. A bulk-terminated (1 0 0) surface would exhibit alternating, nearly pure Al and Fe layers. Yet, the preparation of a surface usually involves sputtering, leaving a certain surface region depleted in Al (“preferential sputtering”). Subsequent annealing at high enough temperatures (here at 900 K or above) activates processes to restore the compositional equilibrium between the bulk and surface region [12,16,17,38]. As reported earlier [12], the analysis of the $I(E)$ spectra (measured at room temperature) confirmed the layer stacking sequence and relaxation pattern originally reported by Wang et al. [38]. The surface is terminated by a pure Al layer with $d_{12}$ considerably contracted. Yet, as already mentioned, the best fit indicated an unexpected 20% Al concentration in the second layer, i.e. the latter seemed to exhibit antisite Al atoms. This result appeared to be significant in view of the limits of errors even with parameter correlations considered. As the formation of Al antisite defects in the bulk is known to be energetically unfavourable in Fe-rich Fe$_x$Al$_{1-x}$ [39], it had to be concluded that conditions special to a near-surface layer (e.g., the strong top layer relaxation) were responsible for the second layer Al enrichment.

Yet, the result was so unusual that it prompted us to take some additional steps in order to verify its validity. In particular, as Eq. (3) shows, vibrational and chemical parameters both modify the scattering factor, even though their influence is different in detail. Possibly, some as yet neglected correlation between displacements and composition in the second layer, i.e. between $v_2$ and $c_2$, might lead to an incorrect conclusion. Therefore, in order to reduce the influence of thermal vibrations, an additional $I(E)$ data set was measured at low temperature ($T \approx 120$ K) using otherwise the same sample preparation. The new data set contains spectra of eight inequivalent beams with a total energy width $\Delta E = 1886$ eV. Variation of the same parameters as earlier, i.e. choosing bulk-like atomic vibrations in the second layer ($v_2 = v_b$), precisely confirms the structural and chemical results obtained with the room temperature data. Again the best-fit structure contains about 20% Al in the second layer. Also again, the enrichment appeared to be significant due to the rather low $R$-factor ($R_p = 0.091$) and the corresponding small error limits. The best-fit values for this set of parameters are summarized in the left column of Table 1 (“Fit 1”).

Next, in order to estimate the influence of $v_2$ on the fit, the analysis of the 120 K data set was repeated, assuming, however, a chemically fully ordered surface (alternating pure Al and Fe layers) and allowing $v_2$ to be varied as an independent parameter in addition to $v_1$ and $v_b$. This best fit is summarized in the right column of Table 1 (“Fit 2”). The mere introduction of the variable $v_2$ produces an overall fit corresponding to $R_p = 0.087$, similar to the value achieved before but clearly improved over that obtained for a fully

<table>
<thead>
<tr>
<th></th>
<th>Fit 1</th>
<th>Fit 2</th>
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<tbody>
<tr>
<td>$a = 2d_0$ (Å)</td>
<td></td>
<td>(2.894)</td>
</tr>
<tr>
<td>$\Delta d_{12}/d_0$ (%)</td>
<td>-14.7 ± 1.0</td>
<td>-14.5 ± 1.2</td>
</tr>
<tr>
<td>$\Delta d_{23}/d_0$ (%)</td>
<td>+3.0 ± 0.7</td>
<td>+2.8 ± 0.9</td>
</tr>
<tr>
<td>$\Delta d_{34}/d_0$ (%)</td>
<td>+1.6 ± 0.7</td>
<td>+1.7 ± 0.7</td>
</tr>
<tr>
<td>$\Delta d_{45}/d_0$ (%)</td>
<td>0.0 ± 1.2</td>
<td>0.0 ± 1.2</td>
</tr>
<tr>
<td>$c_1$ (at.% Al)</td>
<td>100 ± 7</td>
<td>(Al)</td>
</tr>
<tr>
<td>$c_2$ (at.% Al)</td>
<td>20 ± 8</td>
<td>(Fe)</td>
</tr>
<tr>
<td>$c_3$ (at.% Al)</td>
<td>100 ± 5</td>
<td>(Al)</td>
</tr>
<tr>
<td>$c_4$ (at.% Al)</td>
<td>5 ± 9</td>
<td>(Fe)</td>
</tr>
<tr>
<td>$v_1$ (Å)</td>
<td>0.11 ± 0.02</td>
<td>0.11 ± 0.02</td>
</tr>
<tr>
<td>$v_2$ (Å)</td>
<td>(as $v_b$)</td>
<td>0.11 ± 0.02</td>
</tr>
<tr>
<td>$v_x^A$ (Å)</td>
<td>0.12 ± 0.02</td>
<td>0.10 ± 0.02</td>
</tr>
<tr>
<td>$v_y^A$ (Å)</td>
<td>0.09 ± 0.02</td>
<td>0.08 ± 0.02</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.091</td>
<td>0.087</td>
</tr>
</tbody>
</table>

“Fit 1” allowed for substitutional disorder but assumed equal vibrational amplitudes in the second layer and in the bulk. In “Fit 2”, perfect chemical order was enforced but vibrational amplitudes in the second atomic layer were allowed to be independent from the bulk. The error limits given result from single-parameter scans. Values in brackets were kept fixed.
ordered surface with $v_2$ fixed at the bulk value ($R_p = 0.109$). However, the fit quality due to either substitutional disorder in the second layer or an enhanced $v_2$ is quite similar. In other words: The substitution of 20% of second layer Fe atoms by Al is equivalent to an increase of the amplitude of the Fe atoms from the bulk value ($v_b = 0.08$ Å) to the same value as for top layer Al atoms, $v_2 = v_1 = 0.11$ Å. Certainly, neither modification can be favoured over the other. With respect to all other quantities (particularly geometry), both results are very close to each other.

Of course, these findings do not yet prove a real correlation between second layer vibrations and stoichiometry: The impact of both degrees of freedom on details of the spectra could still be dissimilar even at the present $R$-factor level. However, the $R$-factor between the $I(E)$ curves calculated for the two model structures amounts to only $R_p = 0.028$, clearly much lower than that between theory and experiment. Consistently, it is also very hard to detect any visual differences between the respective calculated spectra, as exemplified for the (1,1) beam in Fig. 2 ($R_p = 0.018$ for this single beam). So, the calculated curves show that atomic vibrations and substitutional disorder in the second layer are really correlated quantities. Strictly, both effects cannot be distinguished from one another at their present, small extent with any certainty. The only safe conclusion is that there is no substitutional disorder in the Fe$_{0.53}$Al$_{0.47}$ \((1\,0\,0)\) surface within the limits of error of the LEED analysis. From physical considerations, the most likely surface structure is a fully ordered structure with enhanced atomic vibrations of the second layer Fe atoms (right column of Table 1). The known bulk nearest neighbour interactions in the Fe–Al system [40,41] are consistent with this type of surface order, while a considerable amount of Al antisite defects would inevitably require the respective energetics to be different from the bulk.

The example of Fe$_{0.53}$Al$_{0.47}$ \((1\,0\,0)\) shows that the correlation between chemical and other surface properties deserves attention as it can obviously lead to incorrect conclusions on surface segregation at a certain quality level of the theory–experiment fit. However, Fe$_{0.53}$Al$_{0.47}$ \((1\,0\,0)\) is not ideal to investigate this phenomenon in greater detail. The second layer is difficult to access by other methods, so that an independent measurement of its composition is unavailable, and there are no indications of substitutional disorder anywhere else in the surface. Therefore, the next section focuses on the well-annealed Fe$_{0.85}$Al$_{0.15}$ \((1\,0\,0)\) surface for a closer examination. Here, disorder extends up to the topmost layer [15] which is accessible to other techniques such as STM or LEIS. This promises safer conclusions on the quality and extent of parameter correlations.

4. Fe$_{0.85}$Al$_{0.15}$ \((1\,0\,0)\)

In the bulk, Fe$_{0.85}$Al$_{0.15}$ falls into the A2 random alloy region of the phase diagram [37], i.e., Fe and Al are statistically distributed on a bcc lattice. The preparation of the well-annealed Fe$_{0.85}$Al$_{0.15}$ \((1\,0\,0)\)-\((1\times1)\) surface has been described earlier [15,17,42] as well as the analysis [15] of its $I(E)$ data used...
here (measured at \(\approx 100\) K after ion sputtering and annealing at 1200 K). We use these results to review the determination of the top layer composition, \(c_1\), and the effects of its correlation with other quantities.

### 4.1. LEED, STM and LEIS

The topmost layer of Fe\(_{0.85}\)Al\(_{0.15}\)(100)-(1 x 1) was found to contain \(c_1 = 75\%\) Al using chemically resolved STM and LEIS. Since both methods are well-established independent tools that allow to determine \(c_1\) with high accuracy [11,43], this value was included in the LEED analysis as a fixed condition. The remaining parameters comprised the topmost four interlayer spacings, the composition of the second, third, and fourth atomic layer, vibrational amplitudes different for both elements in the top layer, and joint amplitudes in the second layer and bulk. Furthermore, element-dependent atomic positions in the topmost layer, i.e. the buckling amplitude \(b_1\) of the latter, as well as the lattice parameter for the temperature given were determined. This set of model parameters yields a consistent and convincing picture of the surface structure, repeated from Ref. [15] in Table 2. The geometrical relaxation mainly involves the topmost spacing \((\Delta d_{12}/d_0 = -7.1 \pm 1.5\%)\). As expected for a random alloy with ordering interactions between different elements, the composition profile is oscillatory and damped into the crystal. The vibrational amplitudes decrease towards the bulk. In contrast to Fe\(_{0.53}\)Al\(_{0.47}\), equal bulk vibrational amplitudes \(v_b\) were assumed for Fe and Al as the Al concentration, \(x = 0.15\), is too small for a reliable independent determination of \(v^A_0\). The optimized \(v_b\) is consistent in magnitude with results from \(\gamma\)-ray and neutron diffraction [35]. The lattice parameter is reassuringly close to that expected from extrapolation of the known room temperature value [15]. Although not well outside the limits of error, the top layer buckling shows the same trend as that known from an ordered Fe\(_{0.97}\)Al\(_{0.03}\)(100)-(2 x 2) surface [15]. The best-fit models the surface structure extremely well \((R_p = 0.069)\). So, we can now proceed to investigate parameter correlations that influence the best-fit value of the top layer composition, were it determined by LEED.

### 4.2. The impact of parameter correlations on \(c_1\)

As stated in Section 2, the conventional way to estimate a single parameter’s accuracy in a LEED analysis is to calculate the \(R\)-factor as a function of this parameter while keeping all other quantities fixed at their best-fit values (single-parameter scan). The result of this approach for the top layer concentration \(c_1\) is shown in Fig. 3a: \(R_p(c_1)\) is then of quasi-parabolic shape with a clear minimum at 75% Al. Reassuringly, this is just the value at which \(c_1\) was fixed throughout the fit anyway. The error margin determined from this curve and \(\text{var}(R_p)\) amounts to \(\pm 12\%\), comparable in magnitude to other LEED analyses. Of course, the respective degree of sensitivity shows up also in a visual comparison of \(I(E)\) curves. They are displayed in Fig. 4 for the (1,0) beam with \(c_1\) varying from 55% via 75% to 95% Al. Consistent with the \(R\)-factor behaviour (Fig. 3a) the impact of \(c_1\) is not drastic, but distinct as, e.g., the shape changes between 100 and 200 eV demonstrate.

| Parameter | Value
|-----------|--------
| \(a = 2d_b\) (Å) | 2.887 ± 0.013
| \(\Delta d_{12}/d_0\) (%) | -7.1 ± 1.5
| \(\Delta d_{13}/d_0\) (%) | 0.0 ± 0.7
| \(\Delta d_{14}/d_0\) (%) | +1.4 ± 0.7
| \(\Delta d_{15}/d_0\) (%) | -0.7 ± 0.7
| \(b_1\) (Å) | 0.05 ± 0.04 (Al out)
| \(c_1\) (at.% Al) | 75 (fixed)
| \(c_2\) (at.% Al) | 5 ± 7
| \(c_3\) (at.% Al) | 20 ± 5
| \(c_4\) (at.% Al) | 15 ± 5
| \(v^A_0\) (Å) | 0.17 ± 0.03
| \(v^A_1\) (Å) | 0.16 ± 0.04
| \(v_2\) (Å) | 0.13 ± 0.01
| \(v_b\) (Å) | 0.10 ± 0.02
| \(R_p\) | 0.069

*The top layer composition was determined by LEIS and chemically resolved STM and kept fixed in the LEED analysis.*
However, the single-parameter approach to the error estimate neglects any possible correlation between $c_1$ and other parameters. In order to quantify the true sensitivity of the fit with respect to $c_1$, these remaining parameters should be allowed to readjust for each $c_1$ value. Using this approach, the corresponding section of the $R$-factor hypersurface (full line in Fig. 3b) looks stunningly different from the single-parameter scan of Fig. 3a: Between 55% and 95% Al, $R_p(c_1)$ varies only by 0.005, i.e. the fit seems almost completely indifferent to $c_1$. This observation is confirmed by a look at the $I(E)$ spectra which correspond to Fig. 3b, depicted for $c_1 = 55\%$, 75\% and 95\% Al in Fig. 5. In contrast to the curves shown in Fig. 4 with only $c_1$ varied, it is now much harder to discern any differences between the theoretical curves. Consequently, it is impossible to judge which set of theoretical spectra fits the experimental data best. Technically, the minimum of $R_p(c_1)$ occurs at 80\% Al, quite close to the STM and LEIS result. Yet, despite the excellent fit quality and the corresponding extremely low value of the variance, $\text{var}(R_p) = 0.010$, the only top layer stoichiometry on the Al-rich side ruled out by the variance criterion is a complete Al layer. So, the $R$-factor alone only allows the conclusion that there is some iron in the topmost layer, but no safe statement as to its amount.

The simplest means to discern the reason for the insensitivity towards $c_1$ is to inspect the behaviour of the other, reoptimized fit quantities. As expected from Eq. (3), the main change develops for
the (element-dependent) top layer atomic vibrations \( v_1 \). Fig. 6 shows that the reoptimized value of \( v_1^{\text{Al}} \) rises from 0.12 to 0.20 Å between \( c_1 = 50\% \) and 100% Al whereas \( v_1^{\text{Fe}} \) drops from 0.24 to 0.04 Å. So, an increased elemental concentration is accompanied by increased vibrations of that element since the corresponding decrease of \( v_1 \) again lowers its weight in the overall scattering factor. While a partial compensation of the influence of atomic vibrations and stoichiometry in the LEED fit is thus perfectly plausible, the degree to which it works is quite surprising — and worrying. Fig. 6 also shows that the reoptimized parameters \( v_1^{\text{Al}} \) and \( v_1^{\text{Fe}} \) take on a large range of values as a function of \( c_1 \). In some instances, these combinations are clearly unphysical, thus offering an auxiliary criterion to rule out certain top layer stoichiometries independent of the \( R \)-factor. For example, at \( c_1 = 90\% \), \( v_1^{\text{Al}} \) amounts to 0.20 Å, twice as much as in the bulk, whereas \( v_1^{\text{Fe}} \) is found at only 0.07 Å. There is no obvious physical reason for such a strong difference in vibrational amplitudes for both elements on the same atomic site, rendering \( c_1 = 90\% \) a highly suspicious value. In contrast, \( v_1^{\text{Al}} \) and \( v_1^{\text{Fe}} \) are almost equal at \( c_1 = 75\% \), which seems much more reasonable in view of their common origin (mainly from acoustic phonons and/or static atomic displacements induced by short-range order). Still, this criterion is not rigorous as there is no strict rule for the relationship between elemental displacements, and less so even in the surface layer of a crystal.

Of course, the question arises whether any parameters aside from \( v_1^{\text{Al}} \) and \( v_1^{\text{Fe}} \) contribute to the fit’s insensitivity towards \( c_1 \). Among these remaining quantities, only the best-fit positions of the elements in the top layer of the model surface show a clear trend. While both are approximately equal between \( c_1 = 50\% \) and 65%, a difference of \( b_1 \approx 0.06 \) Å develops for higher \( c_1 \) (consistent with the best fit of Table 2). In fact, a contribution from \( b_1 \) is not entirely unexpected since a correlation between stoichiometry, atomic statistical displacements and elemental positions on the same lattice site was already found for the case of CoAl(1 1 0) [29]. In order to estimate the magnitude of this contribution, we repeated the \( R \)-factor scan of Fig. 3b, this time allowing only \( v_1^{\text{Al}} \) and \( v_1^{\text{Fe}} \) to readjust while keeping all other quantities fixed at their best-fit values (broken curve in Fig. 3b). Already then, \( R_p(c_1) \) is remarkably flat, yielding \( R \)-factors.
below the variance level for all $c_1$ values between 55% and 95% Al. The additional correlation with $b_1$ lowers $R_P(c_1)$ by a much smaller amount, and mainly in the region $c_1 \leq 65\%$. So, the main effect is indeed the correlation between element-dependent vibrations and stoichiometry.

In view of the flatness of $R_P(c_1)$, it is remarkable that its minimum in Fig. 3b is at $c_1 = 80\%$, surprisingly close to the true value of 75% as ascertained by STM and LEIS. Seemingly, even the present strong parameter correlation does not reduce the accuracy of the best fit very much. This finding coincides with similar observations of Sporn et al. [9] and Platzgummer et al. [10,11], who consequently suspected error estimates by var($R_P$) to be too pessimistic when based on the full correlation. Of course, it is difficult to say whether the coincidence of $c_1$ from LEED, STM and LEIS reflects a physical effect or sheer luck. Still, even if the LEED result was ideally more precise than all-parameter error limits make believe, one should bear in mind that the minimum of a flat $R$-factor hypersurface can easily be shifted by a rather small systematic error without strongly affecting the overall fit quality expressed by the $R$-factor. This is illustrated in Fig. 7, which shows $R$-factor curves analogous to those of Fig. 3. Only, the LEED analysis was now restricted by disallowing both the independent top layer element-dependent position (i.e., $b_1 = 0$) and the second layer vibrational amplitude (i.e., $v_2 = v_0$). Both restrictions are usually considered to be of minor importance. Indeed, the achievable fit quality, $R_P = 0.085$, is still excellent. Yet, the all-parameter minimum with regard to $c_1$ shifts down to 60% Al (full curve in Fig. 7). Its single-parameter error, ±10% (see broken curve in Fig. 7), even excludes the value determined by STM and LEIS. Due to the still formidable fit quality, this result could easily be taken seriously in a LEED analysis without any additional information from other methods. Although the best-fit values of the restricted parameter set (listed in Table 3) show some unusual features (a large difference between $v_1^\text{Fe}$ and $v_1^\text{Al}$ and no oscillatory concentration profile below the surface), we emphasize that there is no rigorous argument to dismiss this model as unphysical. In fact, the seemingly enhanced top layer vibrational ampli-

Fig. 7. Dependence of the Pendry $R$-factor $R_P$ on the top layer Al content $c_1$ for Fe$_{0.85}$Al$_{0.15}(100)$ using a modified parameter set for the fit: Elemental positions in the top layer and atomic vibrations in the second layer were not adjusted independently. The solid curve shows $R_P(c_1)$ with all other parameters fixed at their optimum values (see Table 3), while, for the broken curve, all other parameters were reoptimized at each $c_1$ grid value.

| $\Delta d_{12}/d_{12}$ (%) | $-5.5 \pm 1.6$ |
| $\Delta d_{22}/d_{22}$ (%) | $0.0 \pm 0.8$ |
| $\Delta d_{34}/d_{34}$ (%) | $1.4 \pm 1.2$ |
| $\Delta d_{45}/d_{45}$ (%) | $-0.7 \pm 1.0$ |
| $b_1$ (Å) | 0.0 (fixed) |
| $c_1$ (at.% Al) | $60 \pm 10$ |
| $c_2$ (at.% Al) | $15 \pm 8$ |
| $c_3$ (at.% Al) | $15 \pm 7$ |
| $c_4$ (at.% Al) | $15 \pm 7$ |
| $v_1^\text{Fe}$ (Å) | $0.11 \pm 0.04$ |
| $v_1^\text{Al}$ (Å) | $0.20 \pm 0.04$ |
| $v_2$ (Å) | 0.10 (fixed) |
| $R_P$ | 0.085 |

tude of Fe might simply reflect the actual, element-dependent static displacement of the statistically distributed Fe atoms of the full best fit. In conclusion, we believe that caution must be exercised
when estimating the attained fit accuracy in the presence of strongly correlated parameters. At least, care must be taken to check for possible, minor systematic errors even at the present low R-factor level.

5. Discussion and conclusion

For both investigated surfaces, \( \text{Fe}_{0.53}\text{Al}_{0.47}(1\,0\,0) \) and \( \text{Fe}_{0.85}\text{Al}_{0.15}(1\,0\,0) \), statistical atomic displacements \( v_i \) and elemental concentrations \( c_i \) on the same atomic site \( i \) are found to be clearly correlated when simultaneously optimized in quantitative LEED. Of course, the mere existence of this correlation is not surprising in view of Eq. (3). However, the extent to which the fit’s sensitivity towards either quantity is reduced is unexpectedly large, considering their different influence on the angular shape of the effective scattering factor. In the case of \( \text{Fe}_{0.53}\text{Al}_{0.47}(1\,0\,0) \), our investigation shows that a second layer vibrational amplitude enhanced over that in the bulk can be mimicked by a seeming enrichment of Al in that layer. When the former is taken into account, a fully ordered, bulk-like stacking sequence of Fe and Al layers suffices to describe the measured \( I(E) \) spectra, and substitutional disorder no longer leads to a significant improvement. Of course, this also does not disprove any substitutional disorder in the surface but merely enlarges the fit’s error limits. Still, the original physical dilemma is resolved as no inter-atomic interactions special to the surface are needed to explain the LEED result.

The correlation between \( c_2 \) and \( v_2 \) as observed for \( \text{Fe}_{0.53}\text{Al}_{0.47}(1\,0\,0) \) occurs because increased values of both lower the effective scattering strength of second layer atoms. This situation is assessed with greater clarity for \( \text{Fe}_{0.85}\text{Al}_{0.15}(1\,0\,0) \). The topmost atomic layer of this surface is really substitutionally disordered, as confirmed by STM and LEIS results, and its composition is accurately known. Indeed, the element-dependent statistical displacements and the composition of the topmost layer display the behaviour expected from Eq. (3), i.e. an increased \( v_i \) can compensate the influence of an increased \( c_i \) and vice versa. This simple mechanism plays the largest part in reducing LEED’s sensitivity towards either quantity, but the contributions from other fit parameters aggravate the problem. In particular, the adjustment of element-dependent positions on the lattice site in question further flattens out the R-factor hypersurface.

The extent to which the influences of \( c_i \) and \( v_i \) on the LEED spectra can cancel seems surprising in view of the different actions they take. Whilst the Debye–Waller factor, by which \( v_i \) enters the scenario, modifies the angular and energy dependence of the atomic scattering factor, \( c_i \) does not. Yet, this view is too simplistic for at least two reasons:

- The atomic scattering factors of both elements differ in their angular and energetic shape. Their difference (which is the really important quantity in the ATA) will certainly depend on energy. So, the ATA does allow to modify the dependence of the resulting effective scattering factor on the scattering energy and angle, with a characteristics not necessarily all that different from a Debye–Waller factor.

- While scattering factor itself is only defined for a single scattering event, one must remember that the electron wave in LEED is really shaped by multiple scattering processes within the surface. This leads to a relatively isotropic wave field incident onto each scattering atom, instead of a simple plane wave. Thus, a scattered wave does not correspond to only one scattering angle but instead to an average over many different ones. This weakens the dependence of the outgoing wave on the particular angular characteristics of the elemental scattering factors.

In effect, this means that a skillful choice of the three free parameters in the effective scattering factor \( f_i^{\text{av}}(v_i^{\text{Al}}, v_i^{\text{Fe}} \text{ and } c_i) \) does allow to minimize their different energetic and angular impacts quite well. The detailed characteristics of \( f_i^{\text{av}} \) are then averaged even further in the \( I(E) \) spectra, which are eventually subject to a LEED analysis. Of course, both statements remain somewhat qualitative here. For the interested reader, a mathematically more rigorous discussion is provided in Appendix A.
Although, strictly, our findings refer to the Fe–Al system only, they show that atomic vibrations must be taken into account carefully when investigating the stoichiometry of any surface by quantitative LEED. Still, it would be desirable to obtain higher accuracy by somehow circumventing the correlation that originates from Eq. (3):

- In the example of Fe_{0.85}Al_{0.15}(100), top layer stoichiometries far away from 75% Al lead to very different, and, ultimately, unphysical best-fit atomic vibrations for Fe and Al. So, in a straightforward approach to reduce the observed error limits, one could simply discard “unreasonable” amplitudes in a LEED analysis. However, the difficulty lies in determining safely which combinations of elemental vibrations are credible, and which are not (see Section 2). For Fe_{0.85}Al_{0.15}(100), an “educated guess”, e.g. by imposing the fixed condition $v^{\text{Al}}_\parallel = v^{\text{Fe}}_\parallel$, might have sufficed to obtain a fit result close to the true top layer stoichiometry with seemingly higher accuracy. In contrast, the example of Fe_{0.53}Al_{0.47}(100) shows that an educated guess can also cause problems. There, the assumption of atomic vibrations in the second layer equal to those in the bulk leads to a physically problematic best-fit stoichiometry.

- Obviously, where available, the use of complementary techniques, such as STM and LEIS in the case of Fe_{0.85}Al_{0.15}(100), can solve part of the problem. However, there are cases where the quantity in question is difficult to measure independently, e.g. the stoichiometry of the second layer of Fe_{0.53}Al_{0.47}(100).

- Finally, there might also be the chance of improvements to the LEED method in order to deal better with chemical parameters. Aside from a general further refinement of experimental and theoretical techniques, Eq. (3) suggests a straightforward approach, i.e. to try and choose a regime where atomic vibrations are of smaller influence. Due to zero-point motion and possible static displaceable disorder, simply lowering the temperature of measurement does not suffice to achieve this ends. However, it might be possible to enhance the forward scattering contribution manifest in $I(E)$ spectra by performing LEED measurements at grazing incidence. Then, Debye–Waller factors should lose some importance due to the strongly reduced momentum transfer. This possibility remains to be confirmed experimentally.

More generally, our examples show that care must be taken to avoid any conceivable systematic error in the analysis when investigating a relatively small effect – regardless of whether or not this error bears an obvious connection to the quantity of interest. Were it possible to rule out all systematic errors and establish a definitive set of structural parameters for a surface, the reliability of a structural analysis might well be better than a statistical error estimate involving the full parameter correlation makes believe [9–11]. Yet, the difficulty of restricting an analysis to the “correct” parameter set remains, without independent information from other techniques.

To put things into proper perspective, it should be noted that the above LEED analyses still provide highly accurate structure determinations regardless of the described parameter correlations. They compare favourably to related work with respect to atomic positions [38], vibrational amplitudes [35] and lattice parameters [15]. The level of precision achieved for both surfaces is reflected by an excellent fit between experimental and model spectra. This must be due to both high quality experimental data and the efforts undertaken to rule out as many uncertainties of the fits as possible. Often, such detailed refinement may not be absolutely necessary to elucidate the relevant features of a surface, e.g. when determining the nature of an adsorption site. However, when the influence of the physical quantities of interest is more subtle, as is the case when hunting for the exact chemical composition of an alloy surface, precision becomes a crucial issue.

**Appendix A. Cancellation of vibrational and stoichiometric changes**

In this appendix we offer some quantitative reasoning for the mutual cancellation of the influences of stoichiometric and vibrational parameters. In the simplest case, i.e. for $v^{\text{Al}} = v^{\text{Fe}} = v$, the effective scattering factor of Eq. (3) reduces to
\[ f^{av} = \left[ cf^{Al} + (1-c)f^{Fe} \right] w. \tag{A.1} \]

Any variation of \((c, v)\) by amounts \((\delta c, \delta v)\) produces a variation \(\delta f^{av}\) in the effective scattering factor which we may linearize so that
\[ \delta f^{av} = \delta c \frac{\partial f^{av}}{\partial c} + \delta v \frac{\partial f^{av}}{\partial v}. \tag{A.2} \]

Using Eq. (2) for the Debye–Waller factor \(w\), the derivatives amount to
\[ \frac{\partial f^{av}}{\partial c} = (f^{Al} - f^{Fe}) w, \tag{A.3} \]
\[ \frac{\partial f^{av}}{\partial v} = \left[ cf^{Al} + (1-c)f^{Fe} \right] \frac{\partial w}{\partial v} = -\frac{|\Delta k|^2}{3} v f^{av}. \tag{A.4} \]

For an ideal correlation, the effects of \(\delta c\) and \(\delta v\) must cancel, i.e.
\[ \delta f^{av} = \delta c (f^{Al} - f^{Fe}) w - \delta v |\Delta k|^2 \frac{v f^{av}}{3} = 0, \tag{A.5} \]
leading to
\[ \frac{\delta c}{\partial c} = \frac{|\Delta k|^2}{3} v \left( c + \frac{f^{Fe}}{f^{Al} - f^{Fe}} \right). \tag{A.6} \]

Eq. (A.6) cannot hold exactly since its right-hand side (r.h.s.) depends on both \(E\) and \(\theta\) while its left-hand side does not. Yet, it might be sufficient that it holds for the angular and energetic average of the r.h.s. Moreover, if for some reason \(|f^{Fe}/(f^{Al} - f^{Fe})| \propto 1/E\), the \(E\) dependence in Eq. (A.6) cancels for small concentrations \(c \ll |f^{Fe}/(f^{Al} - f^{Fe})|\), since \(|\Delta k|^2 \propto E\).

When allowing for independent amplitudes \((v^{Al}, v^{Fe})\), Eq. (A.6) transforms to
\[ \delta c = \left[ \delta v^{Al} v^{Al} \tilde{f}^{Al} + \delta v^{Fe} (1-c) v^{Fe} \tilde{f}^{Fe} \right] \frac{|\Delta k|^2}{3} v \tag{A.7} \]

with \(\tilde{f}^{Al} := \frac{w^{Al} f^{Al}}{w^{Al} f^{Al} - w^{Fe} f^{Fe}}\)
and \(\tilde{f}^{Fe} := \frac{w^{Fe} f^{Fe}}{w^{Al} f^{Al} - w^{Fe} f^{Fe}}. \tag{A.8} \]

Again, Eq. (A.7) cannot hold exactly but on \(E\) and \(\theta\) average only. However, it can be fulfilled to a much better extent than Eq. (A.6) since \(\delta v^{Al}\) and \(\delta v^{Fe}\) can now be chosen directly to further reduce the \(E\) and \(\theta\) dependence of the r.h.s. For instance, by noticing that \(\tilde{f}^{Al} - \tilde{f}^{Fe} = 1\), we may even fully remove the \(E\) dependence of their weighted sum in Eq. (A.7) if we set
\[ \delta v^{Al} \tilde{v}^{Al} = -\delta v^{Fe} (1-c) v^{Fe}, \tag{A.9} \]
i.e.
\[ \frac{\delta v^{Fe}}{\delta v^{Al}} = -\frac{c}{1-c} \frac{v^{Al}}{v^{Fe}}. \tag{A.10} \]

Then, the only \(E\) and \(\theta\) dependence which remains in Eq. (A.7) is that of \(|\Delta k|^2\), which is relatively simple. Estimating \(|\langle |\Delta k|^2 |^2 \rangle| \approx 2k^2\) (i.e., \(\theta = 90^\circ\) on average), Eq. (A.7) then determines the optimum choice of \(\delta c\) to be
\[ \frac{\delta c}{\delta v^{Al}} \approx \frac{2k^2}{3} \frac{\tilde{v}^{Al}}{v^{Al}} = \frac{4m\langle E \rangle}{3\hbar^2} \tilde{v}^{Al}, \tag{A.11} \]
where \(\langle E \rangle\) denotes some the average energy of the LEED fit.

We can compare Eqs. (A.10) and (A.11) with our results of Section 4. While Fig. 6 contains the true optimized combinations \((\delta c, \delta v^{Al}, \delta v^{Fe})\) as determined by a LEED fit, Eqs. (A.10) and (A.11) directly suggest functional dependencies \(\delta v^{Al}(\delta c)\) and \(\delta v^{Fe}(\delta c)\) based on the best-fit values \((c, v^{Al}, v^{Fe})\) of Table 2. If Eq. (A.10) were fulfilled exactly, we would expect \(\delta v^{Fe}/\delta v^{Al} \approx -3.2\) from Table 2. Actually, linear approximations to the data of Fig. 6 yield \(\delta v^{Al} \propto 0.19 A \delta c\) and \(\delta v^{Fe} \propto -0.46 A \delta c\). So, our “experimental” ratio \(\delta v^{Fe}/\delta v^{Al}\) from Fig. 6 amounts to \(-2.4\). Furthermore, inserting \(\delta v^{Al}(\delta c) \propto 0.19 A \delta c\) into Eq. (A.11) yields \(\langle E \rangle \approx 240 \text{ eV}\), which in fact represents a kind of average energy of the data set used.

In total, the example of Eqs. (A.10) and (A.11) shows that independent parameters \(\delta v^{Al}\) and \(\delta v^{Fe}\) provide a mechanism to manipulate the \(E\) and \(\theta\) dependence of the r.h.s. of Eq. (A.7), enhancing the correlation between \(\delta c\) and \(\delta v^{Al}\). Naturally, our experimental results of Fig. 6 do not quantitatively follow this prescription, since Eqs. (A.10) and (A.11) neglect the \(|\Delta k|^2\) dependence in Eq. (A.7) entirely. The optimum choice of \(\delta v^{Al}(\delta c)\) and \(\delta v^{Fe}(\delta c)\) in a true fit must be more complicated, depending on the shape of the elemental scattering
factors, the peculiarities of the total scattering problem and the fit procedure itself. Moreover, by focusing our discussion on $f^{\text{av}}$ so far, we really only considered a single scattering event with a well defined scattering angle between an incident plane wave and a scattered outgoing plane wave. However, the dominating multiple scattering of electrons renders the effective wave field incident onto a scatterer rather complex, so that some averaging with respect to the $\theta$ dependence of $\delta f^{\text{av}}$ results. Certainly, this enhances the correlation between $c$ and $v$. In fact, for the Debye–Waller-factor it means that $\Delta k^2$ is replaced by an average value $\langle \Delta k^2 \rangle$, and that only its energy dependence $\langle \Delta k^2 \rangle \propto E$ enters Eqs. (A.6) and (A.7) directly. The quantitative formulation of the effects of multiple scattering in a single scattering event is precisely what the well-known tensor LEED approximation is based upon [19,20].

References