Deep layer oscillatory segregation and relaxation of substitutionally disordered Mo$_x$Re$_{1-x}$(100) surfaces

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Abstract

The surface structure and stoichiometry of the substitutionally disordered alloy Mo$_x$Re$_{1-x}$(100) were determined by quantitative LEED I(\(E\)) analyses for bulk concentrations of \(x\) = 0.75, 0.85 and 0.95. Diffraction intensities were measured and analysed for electron energies up to 600 eV in order to also access values of the physical parameters of deeper layers. An excellent theory–experiment agreement, together with a large data base for each bulk stoichiometry, allow the accurate detection of rather strong oscillatory interlayer relaxations. They extend unusually deep into the bulk, i.e. down to the sixth layer. Additionally, a “sandwich segregation” with Mo termination of the surface and Re enrichment in the second layer is found, which is held responsible for the deeper interlayer relaxations. © 1997 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is commonly accepted that alloy surfaces show multilayer relaxations similar to pure metals. For substitutionally disordered alloys there is an additional “chemical relaxation”, i.e. a layer-dependent segregation in the surface region with one of the constituents enriched or depleted. This has been found for a number of alloys (for reviews, see Refs. [1,2]), but in many cases the geometrical and compositional relaxations were investigated for the first few layers only. For deeper layers, bulk parameters were assumed because the relaxations found for the upper layers were already small, or they could not be determined precisely enough. However, for a quantitative understanding of the structure and chemistry of disordered alloy surfaces, and in particular for the testing and further development of corresponding theories, the reliable investigation of a surface region with both deep-layer geometric and compositional relaxations is highly desirable. The present paper presents such a case by application of quantitative low-energy electron diffraction (LEED) to the surfaces of Mo$_x$Re$_{1-x}$(100) for bulk stoichiometries \(x\) = 0.75, 0.85 and 0.95. The choice of Mo$_x$Re$_{1-x}$ is due to the fact that the underlying crystal symmetry is bcc rather than fcc, for which many more investigations exist. Moreover, the atomic radii of Mo and Re are nearly the same. Therefore, little lattice strain or distortion is to be expected, even for...
strong local segregations of one constituent, i.e. possible segregation will not be driven by size and strain effects. This promises an easier implementation of ab initio calculations to describe the structure and chemistry of the surface. Additionally, single crystals of very good quality were available, providing optimum conditions for a precise LEED analysis. Last but not least, the alloy is of some technical interest: Mo as well as Re exhibits catalytic properties, for example in hydrodesulphurization processes [3]. Therefore, the alloy might show improved reactivity or selectivity for specific reactions, e.g. in the process to remove sulphur from oil feed.

Quantitative LEED is the most frequently applied method for the structural and chemical analysis of alloy surfaces. While ordered alloys can be treated using standard LEED program codes [4], substitutionally disordered alloys in principle suffer from the loss of lateral symmetry. Fortunately, the use of layer-dependent average atom scattering matrices has been shown to reproduce measured intensities correctly. Therefore, this average i-matrix approximation (ATA) [5,6] allows for layer-resolved determination of surface composition. However, compared to structural parameters, the surface stoichiometry usually is of less influence with respect to intensities, in particular when the different atomic constituents of the alloy are similar in their scattering characteristics. Therefore, only an excellent theory–experiment agreement allows for the necessary sensitivity to determine the concentration profile in the surface region reliably. This is a demanding task in view of the structural complexity involved, i.e. with composition added to the usual structural parameters.

The present paper reports on detailed LEED analyses of the (100) faces of three substitutionally disordered Mo–Re alloys with Re bulk concentrations of 5, 15 and 25%. This is the range where this alloy crystallizes in a body-centered cubic structure with a random distribution of the constituents [7]. Emphasis of the present paper is on the methodology and depth resolution of the layer-dependent determination of the structure and composition. Also, the results obtained for different bulk concentrations will be compared and the relaxations found will be contrasted to those known for pure bcc metals [8–10]. Additionally, a possible correlation between compositional and structural properties will be discussed. So, the present paper goes beyond earlier papers which contain only part of the present results [11–13].

The paper is organized as follows: Section 2 describes the experimental set-up and the sample preparation. The LEED data acquisition method and the procedure of the intensity analysis are presented in Sections 3 and 4, respectively. In view of the high accuracy desired, more details than usual are given in Sections 2–4. The results are presented in Section 5 and discussed in Section 6.

2. Sample preparation

The experiments were carried out in a homemade stainless-steel ultra-high vacuum chamber equipped with a four-grid rear-view LEED optics, a 150° hemispherical analyzer (VG, CLAM100) in combination with a 5 keV electron gun used for Auger electron spectroscopy (AES), a cold cathode-source ion gun for sputter etching, and various leak-valve sealed gas-inlet systems. A base pressure below 5 × 10⁻¹¹ mbar was achieved by a combination of ion, titanium sublimation and turbomolecular pumps. During the experiments the pressure was ~1 × 10⁻¹⁰ mbar. The sample holder allowed for x, y and z translations as well as unlimited z-axis rotation and a ±10° tilt of the sample. Only one sample could be mounted at a time; it was fixed on a 0.1 mm thick W sheet by small Ta strips. This assembly could be heated to the melting point of ~2800 K by electron bombardment from the rear. Cooling to below 100 K was achieved by direct contact to a liquid-nitrogen reservoir. A highly efficient heater (~100 W) as well as excellent thermal contacts permitted flashing to ~2000 K in a few seconds and subsequent cooling to 100 K within 1 min. (It turned out that this was of importance in order to obtain reliable intensity data as discussed below.) The temperature was measured with a WRe3%/WRe25% thermocouple directly attached to the sample.

The random Mo₁ₓRe₁₋ₓ single crystals, with x = 0.75, 0.85 and 0.95, were grown in the Solid State
Division of the Oak Ridge National Laboratory. Round samples approximately 6 mm in diameter and 1.5 mm in thickness were cut by spark erosion and mechanically polished to within 0.25° of the (100) orientation, as determined by X-ray Laue back diffraction. In-situ preparation consisted of a few cycles of neon sputtering and annealing above 2000 K to remove, in particular, sulphur contaminations. Carbon, which is known from mass spectrographic analysis to be the major bulk impurity (~15 ppm [14]), was removed from the surface region by extended annealing at temperatures between 1300 and 1800 K in an oxygen ambient atmosphere of 1 × 10⁻⁷ mbar until no carbon could be found by AES, even after annealing at medium temperatures. Remaining oxygen as well as residual gas contaminations could easily be desorbed by a short flash to or above 1900 K, leading to an Auger electron spectrum exhibiting only Mo or Re signals as shown in Fig. 1. The complex peak structure is due to the overlapping low-energy multiplet transitions of Mo and Re. Unfortunately, the complete overlap of lines prevents an estimation of surface segregation by quantitative Auger electron analysis. Only the high energetic lines around 2000 eV may be used for this purpose, but they exhibit poor surface sensitivity. Nevertheless, an earlier investigation of a Mo₀.₉₅Re₀.₀₅(100) sample revealed some Re accumulation in the surface region [14] while for a Mo₀.₇₅Re₀.₂₅(100) sample only minor Re segregation (if any) was found [15].

In the accessible temperature range, a sharp (1 × 1) LEED pattern with very low background was observed for all samples, as displayed in Fig. 2. In agreement with the literature [14], no indication of a surface reconstruction as known for Mo(100) [16,17] was found. The observed (1 × 1) symmetry also rules out any long-range chemical ordering at the surface. Also, clustering of a certain constituent seems to be rather unlikely since this should produce some structure in the diffuse background of the LEED patterns which was not observed.

3. Data acquisition

The integrated intensities of the LEED spots were obtained as a function of electron energy by means of a computer-controlled video technique [18–20], whereby the luminescent screen is viewed by a video camera whose electronic signal output is passed to specially designed hardware equipment. Within a selected window around a specific

![](image1.png)

Fig. 1. Auger electron spectrum from the clean Mo₀.₆₅Re₀.₃₅(100) sample. The positions of carbon, nitrogen and oxygen transitions are indicated by small arrows.

![](image2.png)

Fig. 2. (1 × 1) LEED pattern from the clean Mo₀.₆₅Re₀.₃₅(100) sample at 240 eV and 90 K.
spot, the signal is digitized, background-corrected and integrated under computer control, yielding a single point of the $I(E)$ spectrum. The primary electron beam current is measured as the total loss current of the electron-gun control unit. Also measured automatically, it is digitized and stored for subsequent normalisation of beam intensities. With sweeping energy, the system tracks the moving spot, resulting in $I(E)$ spectra which develop rapidly with a maximum rate of 20 ms per energy. Repetitive measurements allow for improvement of the signal-to-noise ratio. Normal incidence of the primary beam was chosen so that spectra of symmetrically equivalent spots could be used for precise sample alignment. Their eventual averaging was carried out to reduce the influence of some residual misalignment.

It was determined that the spectra were very sensitive to residual gas adsorption. Significant intensity changes were detected after less than 5 min, even at a pressure of $1 \times 10^{-10}$ mbar. Fig. 3a displays a series of spectra taken at different times, i.e. for different residual gas exposures after an initial short flash to 2000 K. The spectrum at 1 min, which was taken as soon as the sample temperature had reached 100 K, is used as a reference spectrum for the quasi-clean surface. The changes in the spectra as function of the residual gas exposure can also be quantified by means of an $R$-factor comparison, as shown in Fig. 3b for the (1,0) beam as an example. Within a quarter of an hour, the spectra change markedly, as reflected by a Pendry $R$-factor [21] of $R_p = 0.35$. This value is much worse than that achievable nowadays for theory–experiment best-fit values, which are well below 0.2 for clean and unreconstructed metal surfaces. Therefore, the time for reliable $I(E)$ measurements was restricted to the first 5 min after a flash, resulting in only small deviations from the spectra of the nominally clean surface ($R_p < 0.05$).

To meet these requirements, the following experimental procedure was chosen. All spectra were taken at normal incidence of the primary electron beam. The accuracy of this alignment was checked by $R_p$-factor comparison of symmetrically equivalent beams which were not allowed to deviate from each other by more than $R_p = 0.05$. All symmetrically equivalent beams were subsequently averaged in order to reduce errors caused by residual misalignment and also to improve the signal-to-noise ratio. The energy range of the spectra extended from the first appearance of the respective beam on the fluorescent screen up to 600 eV. A total of eight symmetrically non-equivalent beams was measured. The data were taken in groups of the four symmetrically equivalent beams, which were recorded simultaneously with the maximum acquisition speed and an energy step width of 0.5 eV. This led to a total measuring time of 2–4 min for each group, depending on the extent of the spectra. Prior to each measurement, the sample was flashed to ~2000 K and measurement.

**Fig. 3.** Influence of residual gas adsorption on $I(E)$ spectra from Mo$_{0.35}$Re$_{0.15}$(100). (a) Spectrum of the (1,0) beam as function of residual gas exposure. (b) Pendry $R$-factor between spectra of the (1,0) beam taken after different residual gas exposures, and a “reference” spectrum which was recorded immediately after a flash to 2000 K and subsequent cooling to 100 K within 1 min.
was started as soon as the sample had reached 100 K. Further cooling to around 85 K during measurement changed the absolute intensities by less than 1%. Finally, the spectra were normalized with respect to the energy-dependent primary electron beam current, as well as corrected for the varying light emission angle from the luminescent screen (cosine law). Moderate smoothing was applied to remove residual noise. The entire data set was measured independently several times with excellent reproducibility, as expressed by \( R_F \)-factors between different data sets of typically around 0.02. Eventually, an average over at least three independent data sets was used as input for the intensity analysis.

### 4. Intensity analysis

Compared to earlier results of preliminary analyses of Mo,Re\(_{1-x}\)\(\text{(100)}\) [11,12], the maximum energy of the spectra was extended to 600 eV in order to achieve reliable information for deeper layers. Energies below 100 eV were not included to avoid influences from residual magnetic fields. The intensities were calculated in steps of 3 eV using slightly modified standard full dynamical program codes [4]. Relativistically calculated and spin-averaged phase shifts of Mo and Re for angular momenta up to \( l_{\text{max}} = 14 \) were used to describe the atomic scattering. They were corrected for thermal diffuse scattering assuming isotropic vibrations according to Debye temperatures \( \Theta_D(Mo) = 380 \text{ K} \) and \( \Theta_D(Re) = 420 \text{ K} \) [22] for subsurface atoms. For surface atoms, the Debye temperature was fitted independently, resulting in a value of about 300 K for both Mo and Re for all three concentrations. The scattering from chemically substitutionally disordered layers was treated by the average \( t \)-matrix approximation \( t_{\text{eff}} = c_{Mo}t_{Mo} + c_{Re}t_{Re} \), where \( c_{Mo} \) and \( c_{Re} \) are the relative concentrations in a certain layer. (Since possible vacancies were not considered due to a very poor sensitivity for them, the two concentrations depend on each other as \( c_{Re} = 1 - c_{Mo} \), resulting in only one fit parameter per layer.) Layer-diffraction matrices were produced by the matrix inversion method. The layers were stacked by the layer-doubling scheme using up to 23 symmetrically inequivalent beams. The electron attenuation was simulated by an energy-independent optical potential \( V_{01} \), which, fitted for the Mo\(_{0.75}\)Re\(_{0.25}\)(100) surface, yielded \( V_{01} = 5 \text{ eV} \). This value was used for all concentrations. An often-applied energy dependence \( \sim E^{1/8} \) [4] was also tested, but did not improve the fit. The real part of the inner potential, however, appeared to be energy-dependent. In the analysis of the Mo\(_{0.75}\)Re\(_{0.25}\)(100) sample, it was separately determined in energy intervals of 50 eV leading to a hyperbolic dependence \( V_{01} = -4.5 \text{ eV} + 140/(E - 85 \text{ eV})^2 \), which fits well to theoretical predictions [23]. The same energy dependence was used for all concentrations; only the constant part of \( V_{01} \) was adjusted as usual during the theory–experiment comparison. In each case, however, it led to the same result to within 0.5 eV. It should be mentioned that the values of \( V_{01} \) determined correspond to the difference of the Fermi energies of the sample and the cathode.

Theoretical and experimental data were compared numerically by means of \( R \)-factors in the energy range 100–600 eV, corresponding to a total data base of about 3000 eV for each surface. Some efforts were made to choose the \( R \)-factor with the highest sensitivity with respect to the layer stoichiometry. As shown in Fig. 4 for a model calculation, the variation of layer concentrations mainly influences the relative peak heights in the spectra. Of course, in regions of very dense (i.e. overlapping) peaks, this additionally leads to shifts of minima and maxima positions. Therefore, we checked

![Fig. 4. Modification of the (1,0) spectrum with changing top-layer concentration.](image-url)
whether the relative mean-square deviation of intensities mirrored by the \( R \)-factor \( R_2 \) [4] or the Pendry \( R \)-factor \( R_p \) [21] was more useful. Since \( R_2 \) does not include derivatives, it is sensitive to relative intensity values, while \( R_p \), being proportional to logarithmic derivatives of the spectra, is mainly sensitive to the positions of minima and maxima. Fig. 5 displays values of both \( R \)-factors which compare experimental and theoretical spectra as a function of Mo concentrations in the first (upper frame) and the second layer (lower frame) with all other parameters fixed at the best-fit values described in Section 5. The scales of the two \( R \)-factors are chosen so that the best-fit values are at the same graphical level. The results in the graphs prove that the sensitivities of both \( R \)-factors are roughly the same. Even more importantly, both \( R \)-factors lead to practically the same best-fit layer concentrations. Therefore, we decided to use \( R_p \) exclusively because it allows an easy error estimation by the variance \( \delta R_p = R_{p, \text{min}} (8V_0/\Delta E)^{1/2} \) with \( \Delta E \) being the energy width of the data base [21]. The level \( (R_{p, \text{min}} + \delta R_p) \) is marked as a dotted horizontal line in Fig. 5.

It is well known that intensity spectra are less sensitive to concentrations than to geometrical parameters, in particular when the latter are displacements normal to the surface. However, as is evident from the above formula for the \( R \)-factor variance, the error limits achieved are lower the smaller the minimum \( R \)-factor. Therefore, for a small enough \( R \)-factor, a significant precision can be achieved for compositional parameters. Hence, every effort was undertaken to yield the optimum \( R \)-factor. With as much as 12 parameters to be varied (six interlayer spacings, four concentrations and two Debye temperatures), the simultaneous optimization of all parameters is rather demanding in the trial-and-error procedure applied. Therefore, a step-like strategy was applied: first, with a reasonable assumption of non-structural parameters and bulk concentrations for all layers, a rough variation of layer relaxations was performed. Then, using these first best-fit relaxations, the non-structural parameters (i.e. the necessary number of phase shifts and plane waves describing the electron wavefield, the surface Debye temperature and the inner potential) were optimized. In the next step, the surface interlayer spacings were readjusted using the improved non-structural parameters. They turned out to differ significantly from the bulk values. In the following step, the chemical composition of the four topmost layers were optimized, now with fixed relaxations. Deviations from bulk concentration in deeper layers were not considered due to both very limited sensitivity and comparably small deviations even in the third and fourth layers. The last two steps were repeated iteratively until convergence was achieved. A final check of the validity of the non-structural parameter values did not lead to significant changes.

The separate optimization of layer spacings and layer concentrations as described is reasonable due to some decoupling of their influences on the spectra. This phenomenon, which is also known from other investigations of alloys [2, 24], is demonstrated in Fig. 6a for the first-layer parameters. It is obvious that for each value of the first-
5. Results

The structure analyses for all three concentrations were performed in an identical manner as outlined above. Best-fit parameter values, together with the error limits as derived from the variance of the Pendry $R$-factors obtained, are summarized in Table 1. First of all, there is an excellent level of theory–experiment agreement, as mirrored by $R_p$-factor values in the range 0.11–0.14. The quality of agreement also becomes obvious from the visual comparison of experimental and theoretical best-fit spectra as displayed in Fig. 7 for the Mo$_{0.75}$Re$_{0.25}$(100) surface as an example.

In general, the parameter values resulting for three concentrations are rather similar, as expected both from the similarity of the experimental spectra and from basic physical considerations. With regard to the interlayer spacings, we find a strong contraction of the top-layer spacing, which is typical for bcc (100) surfaces, as can be seen from Table 2. More striking, however, is the phenomenon of an extended, oscillatory layer relaxation deep into the bulk (i.e. down to the sixth layer), which can clearly be resolved due to the small error limits. Of course, the latter increase with increasing depth as a result of electron attenuation. In principle, alternating contractions and expansions of consecutive interlayer spacings with decreasing amplitudes are well known for open metal surfaces, and are understood on the basis of electrostatic models [25–30]. Nevertheless, such a significant deep-layer relaxation has not been observed before for any other clean metal surface, in particular not for any other bcc (100) surface (Table 2). Regarding the compositional depth profiles, we find an oscillatory behaviour for all samples, but the error limits are in most cases too large for a definite exclusion of the bulk stoichiometry, in particular for deeper layers and small Re concentrations. On the other hand, the chemical composition of the first two layers of the Mo$_{0.75}$Re$_{0.25}$(100) surface has been determined independently by low-energy ion scattering (LEIS) [31]. The results differ from ours by no more than 3 at%. This indicates that the LEED determination of the surface composition is more accurate than

layer distance, the same best-fit value for the Mo concentration is obtained, and vice versa. Also, there is no pronounced coupling between concentration and vibrational amplitude in a layer, as demonstrated by Fig. 6b. This is reasonable because thermal diffuse scattering causes a smooth decrease of intensities with increasing vibrational amplitudes for all beams, while a change of concentrations affects inequivalent beams differently because of the anisotropy of the atomic scattering factor.
Table 1
Structural and compositional best-fit parameter values for all three (100) surfaces of Mo₂Re₁₋ₓ

<table>
<thead>
<tr>
<th>Interlayer relaxations</th>
<th>Mo₀.₇₅Re₀.₂₅</th>
<th>Mo₀.₆₈Re₀.₁₅</th>
<th>Mo₀.₅₂Re₀.₄₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δd₁₂/d₆ (%)</td>
<td>-11.9 (± 0.6)</td>
<td>-11.5 (± 0.6)</td>
<td>-11.1 (± 0.8)</td>
</tr>
<tr>
<td>Δd₂₃/d₆ (%)</td>
<td>+5.1 (± 0.6)</td>
<td>+4.7 (± 0.7)</td>
<td>+4.4 (± 0.9)</td>
</tr>
<tr>
<td>Δd₄₅/d₆ (%)</td>
<td>-3.7 (± 0.9)</td>
<td>-3.3 (± 0.8)</td>
<td>-3.0 (± 1.0)</td>
</tr>
<tr>
<td>Δd₅₆/d₆ (%)</td>
<td>+3.9 (± 0.8)</td>
<td>+3.2 (± 0.8)</td>
<td>+2.3 (± 1.0)</td>
</tr>
<tr>
<td>Δd₆₇/d₆ (%)</td>
<td>-2.5 (± 1.1)</td>
<td>-2.1 (± 1.0)</td>
<td>-1.8 (± 1.1)</td>
</tr>
<tr>
<td>Δd₇₈/d₆ (%)</td>
<td>+1.1 (± 1.3)</td>
<td>+1.4 (± 1.4)</td>
<td>+0.9 (± 1.5)</td>
</tr>
<tr>
<td>d₆ (Å)</td>
<td>1.5635</td>
<td>1.5665</td>
<td>1.5695</td>
</tr>
<tr>
<td>Mo concentrations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c₁(Mo) (%)</td>
<td>99 (± 13)</td>
<td>100 (± 15)</td>
<td>91 (± 13)</td>
</tr>
<tr>
<td>c₂(Mo) (%)</td>
<td>51 (± 14)</td>
<td>72 (± 13)</td>
<td>85 (± 16)</td>
</tr>
<tr>
<td>c₃(Mo) (%)</td>
<td>84 (± 13)</td>
<td>90 (± 13)</td>
<td>89 (± 14)</td>
</tr>
<tr>
<td>c₄(Mo) (%)</td>
<td>72 (± 15)</td>
<td>88 (± 16)</td>
<td>98 (± 20)</td>
</tr>
<tr>
<td>c₅(Mo) (%)</td>
<td>75</td>
<td>85</td>
<td>95</td>
</tr>
<tr>
<td>Width of data basis (eV)</td>
<td>3032</td>
<td>3160</td>
<td>2694</td>
</tr>
<tr>
<td>Pendry R-factor</td>
<td>0.11</td>
<td>0.12</td>
<td>0.14</td>
</tr>
</tbody>
</table>

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6. Discussion and conclusion

All Mo₂Re₁₋ₓ(100) surfaces under investigation (x = 0.75, 0.85 and 0.95) showed sharp and low-background (1×1) LEED patterns without any indications for a temperature-dependent superstructure as observed in the case of Mo(100) [16,17]. However, it could be possible that by alloying with Re the surface order–disorder phase transition, which for Mo(100) takes place at around 220 K [32], is shifted to lower temperatures not accessible in our experiment. In this case, a disordered top layer should be expected with surface atoms statistically displaced from their hollow-site position along the [011] and [0T1] directions according to local reconstructions, similar to the case of W(100) [33]. In a simple hard-sphere model, such lateral displacements should be accompanied by an increase of the first interlayer spacing. However, this is in contrast to the strong 11% contraction found, which is much higher than the value of 6% determined for the disordered Mo(100) surface [34]. Also, the excellent theory–experiment agreement reached for these alloy surfaces without consideration of pos-
Table 2
Comparison of layer relaxation values for different bcc (100) surfaces

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta d_{12}/d_0$ (%)</th>
<th>$\Delta d_{23}/d_0$ (%)</th>
<th>$\Delta d_{34}/d_0$ (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta(100)-(1×1)</td>
<td>-11</td>
<td>+1</td>
<td>Not varied</td>
<td>[10]</td>
</tr>
<tr>
<td>Fe(100)-(1×1)</td>
<td>-5</td>
<td>+5</td>
<td>Not varied</td>
<td>[9]</td>
</tr>
<tr>
<td>V(100)-(1×1)</td>
<td>-7</td>
<td>+1</td>
<td>Not varied</td>
<td>[8]</td>
</tr>
<tr>
<td>Mo(100)<em>1×1</em> disorder. (high T)</td>
<td>-6</td>
<td>+2</td>
<td>+0.5</td>
<td>[34]</td>
</tr>
<tr>
<td>W(100)<em>1×1</em> disorder. (high T)</td>
<td>-8</td>
<td>±0</td>
<td>Not varied</td>
<td>[33]</td>
</tr>
<tr>
<td>Mo$<em>2$Re$</em>{0.95}$O$_{0.05}$ (1×1)</td>
<td>$\sim -11.5$</td>
<td>$\sim +4.5$</td>
<td>$\sim -3.5$</td>
<td>This work</td>
</tr>
</tbody>
</table>

sible local reconstructions is strongly in favour of an ideal (1×1) phase, which is also in agreement with earlier work [13]. Consequently, it can be concluded that bulk concentrations of Re as small as 5% inhibit the development of a charge density wave, which is supposed to be responsible for the reconstruction of the Mo(100) surface [16,17].

The alloys investigated exhibit substantial multi-layer relaxation extending deep into the surface. A strong first-layer contraction and a rather large second-layer expansion do not appear unusual compared to elemental bcc (100) metal surfaces (see Table 2). Our results (extrapolated to $c_{Re} \rightarrow 0$) are also in excellent agreement with results of an ab-initio calculation of the layer relaxation of a hypothetical, unreconstructed Mo(100) surface [29], in which the first and second interlayer relaxations were found to be $-10.7$ and $+2.7\%$, respectively. For deeper layers, however, this calculation did not find any significant deviation from bulk conditions. Also, to our knowledge, the phenomenon of significant layer relaxations down to the sixth layer has not been found for any other bcc (100) metal surface.

The deep-layer relaxation is obviously related to the chemical composition profile within the surface region. This is already evident from the fact that there is a continuous (though only slight) increase of the contraction/expansion amplitudes with increasing bulk Re concentration (see Table 1). However, it is surprising that a concentration of only 5% of Re should cause such a dramatic change compared with the pure metal (including the lifting of the reconstruction). However, inspection of Table 1 shows that for the Mo$_{0.95}$Re$_{0.05}$ sample (compared to the bulk concentration) Re is drastically enriched in the surface, resulting in an average of about 9% in the first four layers. Obviously, considerable diffusion from the bulk into the surface region has taken place. This accumulation is also deduced from quantitative X-ray photoelectron spectroscopy (XPS) and AES analyses [14]. Regarding the layer-dependent concentration of Re for this Mo$_{0.95}$Re$_{0.05}$ sample, resulting from the LEED analysis we find (though oscillating) an overall enrichment of Re. This feature is different from the other samples under investigation (see below). Such a segregation behaviour appears quite unusual, and cannot be understood on the basis of standard models, but requires a fully microscopic theory of segregation under simultaneous consideration of the geometrical surface relaxations involved [35–37]. However, we wish to emphasize that the comparably large error limits for the relative layer concentrations (cf. Table 1), together with the small Re bulk concentration of Mo$_{0.95}$Re$_{0.05}$, does not allow for an unambiguous characterization of the underlying segregation mechanism. For a real proof, more accurate data are required. For the Mo$_{0.85}$Re$_{0.15}$ and Mo$_{0.75}$Re$_{0.25}$ samples, however, the situation appears to be quite clear. On average they exhibit practically bulk-like concentrations; however, a considerable atomic redistribution is observed with a strong and almost complete segregation of Mo to the top layer and a depletion (enrichment of Re) in the second layer (“sandwich segregation”). This kind of oscillatory segregation is frequently observed [1,2], and seems to be more or less the rule for bimetallic systems.

For the case of constituent atoms of different sizes, any variation of the layer-concentration profile should modify the interlayer distances, as is obvious from simple geometrical considerations.
This has been shown recently for the system Nio.50Pd0.50(100) [38]. In the present case, however, the atomic radii of both constituents, as derived from pure elemental lattice constants, differ by only ~1%, which limits geometrically caused relaxations to 0.1% of the layer distance. Therefore, steric reasons can be ruled out, and instead electronic interactions must be responsible for the cause of oscillating interlayer spacings.

The termination of the two samples with higher Re bulk concentrations by a practically complete Mo top layer is in excellent agreement with results from both LEIS [31] and XPS [39] investigations, which also find only negligible amounts of Re in the topmost layer of Mo0.75Re0.25(100). The first-layer segregation of Mo is also predicted theoretically [40] on the basis that the Mo–Mo bond is the weakest bond in the system. Our finding that for all three concentrations the second layer is Mo-depleted (Re-enriched), agrees with the oscillating concentration profile predicted for alloys with a small negative enthalpy of mixing [41]. Although there are no measurements of the latter quantity available, such negative values have been estimated from general theories [31]. In essence, it means that the Mo first layer causes the second layer to be Re-enriched in order to maximize the number of energetically favourable Mo–Re bonds. The oscillation should also extend to deeper layers, consistent with our results. Again, and in addition to the similar results from LEIS cited above, this indicates that our results are more precise than is suggested by the limits of error deduced from the variance of the R-factor.

In conclusion, we have shown by careful quantitative LEED that the (100) surface of the random alloy Mo1-xRe1-x for x = 0.75, 0.85 and 0.95 exhibits a strong layer-dependent and oscillatory segregation and relaxation, whereby at least the latter extends unusually deep into the surface. There are strong indications that the deeper interlayer relaxations are caused by the sandwich segregation. This may be the input to future theoretical investigations.

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