Hydrogen on Mo\textsubscript{x}Re\textsubscript{1−x}(100) – the impact of alloying on the adsorption structure

L. Hammer \textsuperscript{a,∗}, M. Kottcke \textsuperscript{a}, W. Weiß \textsuperscript{a}, A. Wimmer \textsuperscript{a}, D.M. Zehner \textsuperscript{b}, K. Heinz \textsuperscript{a}

\textsuperscript{a} Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstr. 7, D-91058 Erlangen, Germany
\textsuperscript{b} Solid State Division, ORNL, P.O. Box 2008, Oak Ridge, TN 37831-6057, USA

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Abstract

Hydrogen adsorption at the (100) surfaces of the substitutionally disordered alloy Mo\textsubscript{x}Re\textsubscript{1−x} was studied for three values of the bulk stoichiometry (x=0.75, 0.85 and 0.95) by high resolution electron energy loss spectroscopy (HREELS) and quantitative low energy electron diffraction (LEED). The minority constituent Re is found to be completely depleted in the topmost layer and thus the local adsorption complex with hydrogen bridge-bonded to two substrate atoms is very similar to that retrieved on pure Mo(100). Nevertheless, the Re accumulation found for the second layer inhibits (x=0.75, 0.85) or strongly modifies (x=0.95) the development of ordered adsorption phases known from pure Mo(100) at submonolayer coverages. This behaviour might be due to the considerable substitutional disorder in the second layer. At maximum coverage, \( \theta_\text{H}=2 \), LEED intensity analyses reveal a strong derelaxation of the uppermost two layer spacings. Surprisingly, however, the relaxations of deeper interlayer spacings remain practically unchanged with respect to those of the clean surfaces. This is interpreted to be caused by the frozen-in oscillatory concentration profile and thus reveals a further mechanism to drive surface relaxations.

Keywords: Alloys, Chemisorption, Electron energy loss spectroscopy, Electron–solid interaction, scattering, diffraction, Hydrogen, Low energy electron diffraction (LEED), Low index single crystal surfaces, Surface relaxation and reconstruction

1. Introduction

Hydrogen adsorption on pure metal single crystal surfaces usually leads to modified atomic positions within the topmost substrate layers [1–3]. In particular, the first interlayer distance, which normally is contracted to an extent which depends on the openness of the surface, becomes more and more derelaxed with increasing hydrogen coverage. Of course, deeper layer relaxations, if present, decrease in parallel. Eventually a rather bulk-like terminated surface results at full hydrogen coverage. Additionally, in the case of ordered superstructures at intermediate coverages, the dominantly local bonding of hydrogen leads to a periodic lattice distortion, i.e. a displacive reconstruction of the substrate surface. There are also some cases where the energetic balance of the surface is so heavily disturbed by the presence of hydrogen that severe bond breaking reconstructions can occur with subsets of surface atoms even removed from their local site when the system is allowed to pass a certain activation barrier as e.g. observed for H/Fe(211) [4]. Vice versa, reconstructions already present at the clean surfaces may vanish or switch to another type of reconstruc-
tion upon hydrogen adsorption. For the latter process the case of H/W(100) is a well-known example [5,6].

For hydrogen adsorption on intermetallic systems principally the same behaviour is expected. However, detailed predictions can hardly be made, since the random alloy or ordered intermetallic compound has to be considered as a new material, whose properties can differ substantially from those of the parent materials or from their mere superpositions. Certainly, the elemental distribution within the surface layers will influence the adsorption structure and energetics and so, by corresponding studies, a local picture of the impact of the different constituents might be derived. Moreover, there is a further complication in particular with random alloy surfaces compared to those of elemental metals. Hydrogen adsorption takes place at comparatively low temperatures only leaving interdiffusion of substrate atoms negligible. Consequently, different to stronger bound adsorbates like e.g. oxygen or carbon, which still stick at the surface at elevated temperatures, adsorbate induced segregation or depletion cannot be observed for hydrogen adsorption systems [7]. Instead, the concentration profile established in the clean surface is always preserved. As a consequence, the adsorbate system is not in stoichiometric equilibrium and implications on properties as e.g. structure and ordering at the surface might be expected. The present paper is focusing on this topic. In particular, we present investigations by quantitative low energy electron diffraction (LEED) and high resolution electron energy loss spectroscopy (HREELS) resolving the adsorption site and geometry of hydrogen on the alloy surfaces Mo\(_x\)Re\(_{1-x}\)(100) for three different bulk stoichiometries (\(x = 0.75, 0.85, 0.95\)). Also, we retrieve the adsorbate induced modification of the clean surfaces’ multilayer relaxation. The results are compared to those known from literature for the pure metal surface Mo(100). In this way we can deduce information about the impact of surface alloying on hydrogen adsorption.

The (100) surface of the substitutionally disordered alloy Mo\(_x\)Re\(_{1-x}\) is a good candidate for such investigations. In the alloy’s bulk up to about 25% of the former Mo bcc lattice sites can be randomly occupied by Re without any significant lattice strain or expansion (cf. bulk layer distances \(d_b\) for the different samples in Table 1, Section 5). This allows us to study the influence of a gradual increase of the concentration of the minority component Re (5%\(\rightarrow\)15%\(\rightarrow\)25%) without interference by stoichiometry dependent size effects. From a previous study the clean (100) surfaces detailed characterizations with respect to their multilayer relaxation and layer dependent composition are available for the concentrations in question [8]. Independent of the Re concentration, the surfaces are unreconstructed. This is different to elemental Mo(100), which exhibits a considerable displacive reconstruction which is either incommensurate [9] or possibly higher order commensurate [10,11].

The outermost layer of each of the alloy surfaces is always found to consist almost exclusively of Mo atoms whilst Re accumulates in the second layer to an extent which depends on the bulk concentration. As common for bcc(100) metal surfaces, a substantial contraction of the first interlayer distance (\(\approx 1\%\)) is found. Yet, in contrast to pure metals, an oscillatory relaxation profile extending unusually deep into the surface was detected. It is one of the basic questions of the present paper, to what extent hydrogen affects this surface relaxation.

Another important subject of the present study is the ordering behaviour of hydrogen and the adsorption sites occupied. From the elemental Mo(100) surface, which can be viewed as the zero Re concentration limit, a variety of ordered phases as functions of coverage and temperature are reported with strong surface reconstructions involved in the submonolayer regime [12]. By means of HREELS measurements the reconstructions were shown to create new bond sites for hydrogen adatoms different to the bridge position on an unreconstructed substrate found at saturation coverage [13]. It is therefore interesting to see whether and how the increasing alloying of the surface with another metal like Re affects the adsorption site and ordering of hydrogen, even more as Re only appears in the second and deeper layers and thus most likely is not directly interacting with hydrogen.

The paper is organized as follows. The next
section describes briefly the experimental and computational basics, i.e. the sample preparation procedure and the essentials of the dynamical LEED analyses. The ordering behaviour of hydrogen as a function of increasing Re bulk concentration is demonstrated in Section 3. The retrieval of the hydrogen adsorption site from HREELS measurements is described in Section 4, while Section 5 presents the results of the quantitative LEED structure determination for the three samples. Finally there is a discussion of the described impact of alloying on hydrogen adsorption together with a summary of the results.

2. Experimental procedure and dynamical LEED intensity analysis

The experiments were performed in a homemade two-level apparatus at a pressure of around $1 \times 10^{-10}$ mbar. The upper level was equipped with a back-view LEED optics, a hemispherical electron energy analyser with separate electron gun for Auger electron spectroscopy (AES) and the usual facilities for sample preparation. The lower level hosted a single-pass HREELS spectrometer with rotatable analyser (LEELS400, Vacuum Generators) with separate magnetic shielding. The sample holder allowed for $x$, $y$ and $z$ translations as well as a rotation and tilt of the samples. The samples could be heated by electron bombardment from the rear up to any required temperature. Quick cooling to below 100 K was realized by direct contact to a liquid nitrogen reservoir. The temperature was measured using a WRe$_3$%–WRe$_{25}$% thermocouple directly attached to the sample.

The random Mo$_x$Re$_{1-x}$ single crystals with $x = 0.75$, 0.85 and 0.95, were grown, cut and polished to within 0.25° of the (100) orientation at the Oak Ridge National Laboratory. In situ preparation was performed first by some cycles of sputtering followed by extended annealing in an oxygen ambient and subsequent flashes to above 2000 K. This procedure, which has been described in more detail in a previous paper [8], finally resulted in a clean surface in each case as characterized by Auger spectra with all impurity signals below the detection limit. Clear and low background $1 \times 1$ LEED patterns were observed. Once the samples were clean, short flashes to above 2000 K turned out to be sufficient to completely remove residual gas contaminations. High purity hydrogen or deuterium were dosed simply through a leak valve right after a flash, as soon as the samples reached the temperature of 100 K. Saturation coverage of hydrogen was achieved for about 1 L exposure (according to a sensitivity factor of 2.4 for hydrogen to correct the reading of the Bayard–Alpert gauge). The saturation was indicated by HREELS and LEED $I(E)$ spectra staying constant upon further exposure.

All experimental data presented in this paper refer to a sample temperature of around 90 K. Data acquisition was performed completely under computer control. Integrated intensities of the LEED spots as a function of electron energy or exposure were obtained using the Erlangen type video LEED system (AUTOLEED) described in detail elsewhere [14,15]. LEED $I(E)$ spectra of the hydrogen saturated surfaces were taken at normal incidence of the primary beam in order to ensure proper alignment and to improve the quality of the data by averaging over symmetrically equivalent beams. The whole data acquisition and evaluation procedure was the same as for the clean surfaces described in detail earlier [8]. HREELS and AES spectra were controlled and monitored using the AUTOLEED system through its built-in D/A and A/D channels. In the case of HREELS, additional noise created by the computer system led to a deterioration of the spectrometer’s resolution from 6 meV to above 10 meV (determined as the FWHM of the specular beam). Low count rates, in particular in the o-V-specular regime, prohibited extended acquisition times and so required repeated measurements and subsequent averaging. Typically, the spectra presented in this paper are averages over five preparations in order to reduce the noise.

LEED intensity spectra $I(E)$ of the hydrogen saturated surfaces were calculated in analogy to the clean surfaces [8]. Slightly modified standard full dynamical program codes [16] were used to calculate spectra in the energy range 100–600 eV.
The chemical composition of the layers was modeled with the average-r matrix approximation (ATA) [17,18]. The hydrogen adlayer and the top substrate layer were treated as a composite layer. The layers were stacked by the layer doubling scheme. Electron attenuation was simulated by a constant optical potential, while for the real part of the inner potential a hyperbolic energy dependence as determined for the clean surface was applied. The surface Debye temperatures of Mo and Re were also taken from the analyses of the clean surfaces (300 K for both elements), while for the H adatoms it was assumed that they adopt the vibrational amplitudes of the underlying substrate atoms. The symmetry of the adsorption site and the hydrogen coverage were taken from HREELS and nuclear reaction analysis (NRA), respectively (see below). They were not varied during the analysis. In the latter, a total of 11 structural parameters, i.e. the height of the adsorbate, six substrate interlayer spacings as well as the stoichiometries of the four topmost metal layers, were iteratively fitted for each substrate. Quantitative comparison of experimental and theoretical spectra was made by the Pendry R-factor \( R_P \) [19]. Error limits for the parameters determined were estimated from its variance.

3. Ordered phases of hydrogen

The clean Mo\(_{0.95}\)Re\(_{0.05}\)(100) surfaces for all investigated bulk stoichiometries showed clear \( 1 \times 1 \) LEED patterns without any hint of a surface reconstruction typical for the elemental Mo(100) surface. Moreover, the possibility of a locally reconstructed but long range disordered surface like the high temperature phase of pure Mo(100) or W(100) can easily be ruled out on the basis of the excellent agreement between experimental and theoretical best fit LEED spectra calculated under the assumption of perfect order.

For saturation coverage of hydrogen, which is achieved for exposures exceeding 1 L, also sharp \( 1 \times 1 \) LEED patterns with very low background were observed. The corresponding coverage \( \theta_H \) was absolutely determined for the Mo\(_{0.95}\)Re\(_{0.05}\)(100) sample by means of NRA resulting in \( \theta_H = 2.0 \pm 0.1 \) [20]. Since the same value was reported for pure Mo(100) at saturation [13], it is justified to assume this maximum hydrogen coverage for all samples in the present investigation.

In the intermediate coverage regime a variety of different ordered phases are reported for pure Mo(100) [12,21]. Developing as a function of coverage and temperature. In contrast, for the alloy samples with higher Re bulk concentration (Mo\(_{0.85}\)Re\(_{0.15}\) and Mo\(_{0.75}\)Re\(_{0.25}\)) no ordered superstructures at all could be found in the accessible temperature range. For the sample with lowest Re concentration (Mo\(_{0.95}\)Re\(_{0.05}\)) however, a single ordered phase, namely a superstructure of \( c(4 \times 2) \) symmetry with quite intense superstructure spots visible even at higher electron energies was observed (Fig. 1a). A characteristic feature of this \( c(4 \times 2) \) structure is the systematic extinction of all half order spots [i.e. \((m, n + 1/2)\) and \((m + 1/2, n)\) spots] at normal incidence of the primary electron beam, while the quarter order spots inside the substrate unit meshes remain rather bright (Fig. 1b). Only at angles of incidence far off normal can the whole set of \( c(4 \times 2) \) superstructure spots be observed.

On another sample of the same ingot we could prepare the \( c(4 \times 2) \) structure as well, however with much lower overall superstructure spot intensities. Thus, our present finding is in some contradiction to an earlier investigation of this alloy system [22], where for nominally the same Re bulk concentration a quartet of extra spots in the centre of the unit mesh was observed with relative positions varying with coverage. The latter structure is also known from pure Mo(100) at low adsorption temperatures [12]. For higher temperatures that phase is reported to undergo an order-order transition into a \( c(4 \times 2) \) structure with quarter order spots also being systematically more intense than half order ones [12]. However, the author explicitly claims that no extinctions could be observed in the LEED pattern, in contrast to our findings in the present case. We therefore conclude that our \( c(4 \times 2) \) structure cannot be identified with the high temperature phase observed on Mo(100), though there might be some structural relation between both phases. Obviously, small Re additives to Mo(100) have a strong influence on...
the ordering and reconstruction behaviour of the surface. Hence, the varying results of different investigations might be attributed to some fluctuations in the local Re concentration, which are reasonable to occur for different samples and, probably, also upon different surface preparations.

The formation of the \( \text{c}(4 \times 2) \) structure with increasing hydrogen exposure is monitored by the corresponding behaviour of the integral intensities of superstructure and integer order spots as displayed in Fig. 2 for selected electron energies. The rather linear increase of the intensity of superstructure spots (Fig. 2a) from the very beginning of exposure is a strong indication for island growth. At a first glance this might appear rather unlikely, since the substrate-mediated H–H interaction is usually found to be repulsive leading to sequences of more and more densely packed superstructures with increasing coverage. However, island growth was also reported for the most dilute H phase on Mo(100) [21] and also for other systems like e.g. Rh(110)-1 \( \times \) 3H [2, 23]. Parallel to the growth of superstructure spots there are strong variations of integer order spot intensities (Fig. 2b) revealing a substantial modification of the substrate (relaxation of layer spacings or reconstruction) accompanying the development of the \( \text{c}(4 \times 2) \) structure. A pronounced reconstruction is indicated by the comparably intense superstructure spots observed, in particular at higher electron energies, which cannot by far be generated by mere hydrogen scattering. In contrast, for samples with higher Re concentration, where no superstructures are observed, the integer order spot intensities develop rather continuously with exposure (Fig. 2c) reflecting the usual hydrogen induced modification of the surface relaxation. There are no indications for any features typical of the \( \text{c}(4 \times 2) \) structure as shown in Fig. 2b, which we would expect to some extent even in case of lacking long range ordered reconstruction. Consequently, we conclude that for higher Re bulk concentrations the exposure is a strong indication for island growth. At a first glance this might appear rather unlikely, since the substrate-mediated H–H interaction is usually found to be repulsive leading to sequences of more and more densely packed superstructures with increasing coverage. However, island growth was also reported for the most dilute H phase on Mo(100) [21] and also for other systems like e.g. Rh(110)-1 \( \times \) 3H [2, 23]. Parallel to the growth of superstructure spots there are strong variations of integer order spot intensities (Fig. 2b) revealing a substantial modification of the substrate (relaxation of layer spacings or reconstruction) accompanying the development of the \( \text{c}(4 \times 2) \) structure. A pronounced reconstruction is indicated by the comparably intense superstructure spots observed, in particular at higher electron energies, which cannot by far be generated by mere hydrogen scattering. In contrast, for samples with higher Re concentration, where no superstructures are observed, the integer order spot intensities develop rather continuously with exposure (Fig. 2c) reflecting the usual hydrogen induced modification of the surface relaxation. There are no indications for any features typical of the \( \text{c}(4 \times 2) \) structure as shown in Fig. 2b, which we would expect to some extent even in case of lacking long range ordered reconstruction. Consequently, we conclude that for higher Re bulk concentrations the exposure is a strong indication for island growth.

Usually, there is no way to extract the geometric structure of a surface from a mere inspection of the LEED pattern. However, the observation of systematic extinctions of certain spots as in the \( \text{c}(4 \times 2) \) pattern of the present case allows us to draw certain conclusions with respect to the distribution of scatterers within the superstructure cell. So, e.g. when superstructure spots along the unit mesh axis are systematically extinguished this is indicative of the presence of one (or more) glide symmetry planes, a circumstance which largely restricts the number of possible structural models. In the present case all half order spots along all
Fig. 3. (a) Schematic distribution of scattering elements within the c(4×2) structure. (b) Tentative model of the c(4×2)-2H phase on the Mo0.95Re0.05(100) surface.

Fig. 2. Intensity of the (1/4, 1/2) spot of the c(4×2) superstructure as a function of hydrogen exposure on the Mo0.95Re0.05(100) surface at 300 eV (T=90 K). (b) Same as (a), but for the (1, 1) integer order spot at 243 eV and 315 eV. (c) Same as (b), but for the Mo0.75Re0.25(100) surface.

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sites observed, a reconstruction of the surface meeting the above mentioned condition has to be considered. Although one can think of a large variety of possible models, we suggest a double-dimer model (Fig. 3b) which is a modification of the widely accepted dimer model accounting for the c(2×2) phases of hydrogen on Mo(100) and W(100) (see e.g. Ref. [12]). Similar to the atomic models for the c(2×2) structures we assume that hydrogen adatoms induce a dimerization of surface atoms. The arrangement of these dimers (Fig. 3b) produces a c(4×2) rather than a c(2×2) periodicity. It should be pointed out that in the present case of the Mo0.95Re0.05(100) surface, like for elemental Mo(100) but different to W(100), the dimer structure is formed around the ideal hydrogen coverage of $\theta_H=0.5$ (assuming an initial sticking coefficient near unity). Thus, we propose a local mechanism to drive the reconstruction: hydrogen atoms adsorbed in bridge positions (cf. Section 4) modify the electronic charge distribution in the vicinity of their adsorption site giving rise to some lateral movement (dimerization) of top layer metal atoms as indicated in Fig. 3b. Local lattice distortions induced by the dimeriza-
tion of Mo atoms might be related to the observed island growth: probably, it is easier to dimerize further Mo atoms by hydrogen when neighbouring Mo atoms have already formed dimers.

Though this reconstruction model is consistent with all our observations, its final confirmation and the quantitative determination of the geometrical parameters must be left to a future LEED intensity analysis.

4. Hydrogen adsorption site

In order to deduce the local adsorption site of hydrogen, specular and off-specular HREELS measurements were performed for the Mo$_{0.75}$Re$_{0.25}$(100) surface at various hydrogen coverages [by restriction to this surface unfortunately no further information could be retrieved for the c(4×2) phase on Mo$_{0.95}$Re$_{0.05}$(100) described above]. We first concentrate on spectra taken for the saturated (1×1)-2H phase as displayed in Figs. 4a–c. In specular reflection (Fig. 4a) only one prominent loss at 130 meV is found, while three vibrational modes at 80, 130 and 157 meV show up clearly in the off-specular spectra (arrows in Fig. 4b). Offering deuterium instead of hydrogen again three off-specular peaks are observed (Fig. 4c) shifted characteristically according to the isotope effect. This proves that the peaks originate indeed from H or D. The existence of three distinct modes rules out the top and four-fold hollow positions as possible adsorption sites, for which parallel modes should be symmetrically degenerate. Applying the selection rule of dipolar scattering on metal surfaces [24], the existence of only a single dipolar active mode (which is further supported by angular profiles of loss intensities not explicitly shown here) clearly determines the symmetry of the adsorption site to be C$_{2v}$, corresponding to a bridge site. This is also expected from the saturation coverage, θ$_H$ = 2. The results are in excellent qualitative and quantitative agreement with earlier findings on elemental Mo(100) [13] and W(100) [25–27] surfaces. Thus, we can adopt the mode assignment given in these publications with the bending mode δ at 80 meV, the symmetric stretching mode ν$_s$ at 130 meV and the asymmetric stretching mode ν$_as$ at 157 meV.

For lower coverages we find, also in even quantitative agreement with the results for elemental Mo(100) [13,21] and W(100) [25,26], considerable shifts of the vibrational energies with hydrogen coverage as displayed in Fig. 5. While the energetic position of the bending mode δ shifts from 58 to 80 meV, the energy for the symmetric stretching mode ν$_s$ decreases from 144 to 130 meV. The asymmetric stretching mode ν$_as$ appears at
the asymmetric stretch mode $v_a$ could not be resolved well enough to decide whether there is also a small dipolar moment as in the case of H/W(100) at low coverages. From the latter observation the existence of a “puckered” surface structure had been derived for hydrogen covered tungsten [26]. Nevertheless, the enormous shift of vibrational frequencies strongly indicates some kind of surface reconstruction, which in the case of W(100) has been unambiguously proven by a variety of different methods [28]. Hence, in the low coverage regime we have to accept some local lattice reconstructions induced by randomly adsorbed hydrogen atoms, although LEED intensity vs. exposure curves (cf. Fig. 2c) give no evidence for that.

In summary, our HREELS measurements show that the local adsorption complexes of hydrogen on the Mo$_{0.75}$Re$_{0.25}$(100) surface must be very similar to those on elemental Mo(100) and W(100) surfaces for the whole coverage regime. This is plausible from the fact that by surface segregation the topmost layer of the clean alloy practically exclusively consists of Mo atoms [8]. The Re accumulated in the second layer (≈50% [8]) has obviously little influence on the local hydrogen bonding configuration, although it prevents any ordered arrangement of the adatoms.

5. Structure of the hydrogen saturated surfaces

In order to retrieve the influence of hydrogen adsorption on the multilayer relaxation of the alloy substrates, the measured LEED I(E) spectra were analysed full dynamically for the hydrogen saturated (1 × 1)-2H phases formed on the unreconstructed surfaces of all three Mo$_x$Re$_{1-x}$(100) samples. According to the results of the previous section, the total coverage is $\Theta_H = 2$ and hydrogen atoms reside in ideal bridge sites, i.e. each bridge site of the unreconstructed surface is occupied. So, the only hydrogen related parameter to be varied in the analysis is the adsorption height $d_H$ in the bridge site above the top substrate plane. With respect to the interlayer distances in the substrate, significant deviations from the bulk value down to at least the sixth layer were found for the clean...
surfaces [8] and thus the first six outermost layer spacings were varied also for the analysis of the hydrogen saturated phase. In principle, the chemical composition of layers could have been taken from the clean surfaces, since hydrogen adsorption at 100 K should not be able to induce any diffusive intermixing of surface atoms. Nevertheless, we have independently fitted the relative concentrations of the four outermost layers to prove the consistency of our analyses.

The intensity analyses for the three surfaces resulted in best fit parameter values summarized in Table 1. The error limits were deduced from the variance of the Pendry R-factor, \( R = \frac{\text{var}(R)}{R(8V_0/\Delta E)^{1/2}} \), whereby \( V_0 = 5 \) eV is the optical potential, \( \Delta E \) is the energy width of the database used and \( R \) is the minimum R-factor achieved for the best theory-experiment fit in each case (the latter values are also given in the table). For comparison, the values determined earlier for the clean surfaces [8] are given in brackets (the error limits are similar to those of the hydrogen phases). For all three phases an excellent level of theory-experiment agreement could be achieved with R-factors in the range 0.14–0.16, a level comparable to that produced for the clean surfaces (0.11–0.14). The good agreement also becomes obvious from a visual inspection of calculated and measured intensity spectra. A selection is displayed in Fig. 7 for the (1 × 1)–2H phase on Mo\(_{6}\)Re\(_{2}\) as an example.

As expected, the average stoichiometries of the layers retrieved for the clean surfaces remain practically unchanged upon hydrogen adsorption within the limits of error. This result is remarkable from a methodological point of view: upon hydrogen deposition the spectra change dramatically and at saturation coverage exhibit no similarities with the clean surface spectra. This is visualized in Fig. 8 for the (10) beam of Mo\(_{6}\)Re\(_{2}\), whereby the change is additionally quantified by the single beam R-factor of 1.03 (we remind the reader that a Pendry R-factor near unity corresponds to spectra with mutually uncorrelated peak positions). With the two data sets so different, the two analyses of the layer dependent stoichiometry

| Table 1 | Structural and compositional best fit parameters for all three hydrogen saturated (100) surfaces of Mo\(_{6}\)Re\(_{2}\). The corresponding values for the clean surfaces (taken from Ref. [8]) are given in brackets. |
|-----------------|-----------------|-----------------|
| Interlayer spacings | H\(_{6}\)Mo\(_{6}\)Re\(_{2}\) [clean] | H\(_{6}\)Mo\(_{6}\)Re\(_{2}\) [clean] | H\(_{6}\)Mo\(_{6}\)Re\(_{2}\) [clean] |
| \( \Delta d_1 \) | \(-0.9 \pm 0.4\) Å [\(-11.9\) %] | \(-0.4 \pm 0.3\) Å [\(-11.5\) %] | \(-2.4 \pm 0.5\) Å [\(-11.15\) %] |
| \( \Delta d_2 \) | \(+1.4 \pm 0.5\) Å [\(+3.1\) %] | \(+0.4 \pm 0.5\) Å [\(+4.7\) %] | \(+1.1 \pm 0.6\) Å [\(+4.9\) %] |
| \( \Delta d_3 \) | \(+3.8 \pm 0.6\) Å [\(+7.3\) %] | \(-2.8 \pm 0.6\) Å [\(-3.3\) %] | \(-2.3 \pm 0.7\) Å [\(-3.0\) %] |
| \( \Delta d_4 \) | \(+3.6 \pm 0.8\) Å [\(+7.9\) %] | \(+2.5 \pm 1.1\) Å [\(+5.3\) %] | \(+2.5 \pm 0.9\) Å [\(+5.0\) %] |
| \( \Delta d_5 \) | \(-2.4 \pm 0.8\) Å [\(-2.1\) %] | \(-1.1 \pm 1.1\) Å [\(-2.1\) %] | \(-1.1 \pm 1.2\) Å [\(-1.8\) %] |
| \( \Delta d_6 \) | \(+0.9 \pm 1.6\) Å [\(+1.0\) %] | \(+0.5 \pm 1.7\) Å [\(+1.4\) %] | \(+0.0 \pm 1.9\) Å [\(+0.9\) %] |
| \( d_0 \) | 1.5635 Å | 1.5665 Å | 1.5695 Å |
| Mo concentrations | H\(_{6}\)Mo\(_{6}\)Re\(_{2}\) [clean] | H\(_{6}\)Mo\(_{6}\)Re\(_{2}\) [clean] | H\(_{6}\)Mo\(_{6}\)Re\(_{2}\) [clean] |
| \( c(Mo) \) | 98 ± 12% [99%] | 98 ± 13% [100%] | 92 ± 15% [91%] |
| \( r(Mo) \) | 53 ± 15% [55%] | 72 ± 15% [72%] | 96 ± 12% [85%] |
| \( s(Mo) \) | 88 ± 16% [84%] | 96 ± 18% [90%] | 100 ± 12% [89%] |
| \( t(Mo) \) | 80 ± 15% [72%] | 88 ± 18% [88%] | 100 ± 16% [98%] |
| \( u(Mo) \) | 75% | 85% | 95% |
| Hydrogen height | \( d_0 \) | 1.15 ± 0.13 Å | 1.04 ± 0.14 Å | 1.12 ± 0.13 Å |
| Width of database | 3137 eV [3032 eV] | 2812 eV [1360 eV] | 2695 eV [2694 eV] |
| Pendry R-factor | 0.14 [0.11] | 0.16 [0.12] | 0.14 [0.14] |
can be regarded as independent. So, the close agreement between the corresponding results demonstrates the reliability of the analyses (possibly the error limits given are too conservative). Moreover, the composition of the first two layers determined by low energy ion scattering (LEIS) [29] is also in agreement with the respective present results.

Different to the chemical composition of the surface region its geometrical parameters are free to adjust to the new energetic situation introduced by hydrogen adsorption. Indeed, our analyses – not surprisingly – show that the strong contraction of the topmost layer distance and the related weaker expansion of the second interlayer spacing found for the clean surfaces is almost completely removed upon hydrogen saturation. This behaviour is quite common for hydrogen adsorption on transition metal surfaces [2,3] and can be interpreted by hydrogen acting so as to restore the bonds of the truncated bulk. For the related system H/W(100) an earlier LEED analysis [6] also found in nearly quantitative agreement a derelaxation of the first layer distance resulting in an only 1.3%
in more detail in the following section, this relaxation behaviour is assigned to originate from the oscillatory compositional profile within the surface region.

As a final parameter of our structural analyses we consider the hydrogen adsorption height determined for the three surfaces. As displayed in the table, the height is in the range 1.04–1.15 Å with, however, rather large error limits (±0.14 Å) involved due to the weak scattering of hydrogen. In view of the latter, the agreement with the result of $d_{H} = 1.17$ Å reported for H/W(100) [6] is reasonably good. Taking an average value of $d_{H} = 1.10$ Å for the present alloy systems, the Mo–H bond lengths amount to 1.92 Å. This corresponds to a hard sphere radius for hydrogen of $r_H = 0.55$ Å which lies very near the atomic radius (1.53 Å) and by all means well within the usually observed range for H–metal systems [1–3].

6. Discussion of the impact on alloying

In our investigation HREEL spectra have revealed that the local adsorption configuration of hydrogen on the Mo$_x$Re$_{1-x}$(100) alloy surface resembles in great detail that of an elemental Mo(100) surface. This behaviour is easily explained by the detected almost complete segregation of Mo atoms to the surface. Due to the occupation of bridge positions – which has only been reported for bcc(100) surfaces as yet – the adatoms are only coordinated with top layer (Mo) atoms (bond length $\approx 1.9$ Å). The large distance of second layer atoms ($\approx 3.1$ Å) prevents any significant electronic overlap. Consequently, the energetics of the adsorption complex are dominated by the bridge-sited adatom and the atoms of the top substrate layer, which is the same for the pure metal and the alloy surface. We are suspicious that this simple situation is more the exception rather than the rule for alloy surfaces.

The situation looks strikingly different when regarding the ordering behaviour of the adsorbate. While for elemental Mo(100) a variety of different superstructures as a function of coverage and temperature are reported [12,21], the addition of Re almost completely prohibits an ordered contraction. Yet, our results exhibit also a very surprising and until now unknown feature: relaxations of deeper lying layers remain practically unaffected by hydrogen adsorption. So, we have the curious situation that right at the surface the interlayer distances are practically bulk-like, whilst going deeper into the surface the spacings start to oscillate around the bulk value with an amplitude dying gradually away. The whole scenario is elucidated as a bar graph in Fig. 9. As will be discussed
arrangement of hydrogen adatoms as well as substrate reconstructions. Though we cannot exclude some residual direct influence of second layer Re atoms, the main reason for the missing ordering most likely lies in the nature of the H–H interaction. As usually accepted for metal surfaces, the latter is dominated by indirect interactions mediated via spatial charge density fluctuations within the substrate (e.g. Ref. [30]). Since in the rather open atomic structure of bcc(100) surfaces layer atoms are not in direct contact with each other, any electronic charge flow requires at least some contribution from the second layer. Obviously, Re atoms being accumulated and randomly distributed within this second layer locally modify these fluctuations. As a consequence, the H–H interaction gets at least a random component which suppresses hydrogen ordering. In principle, the same reasoning holds also for hydrogen induced (ordered) substrate reconstructions. This is evident in cases where rearrangements of substrate atoms are locally induced in the vicinity of an adsorbed hydrogen atom because then ordered substrate reconstruction is simply a consequence of hydrogen ordering. Obviously, there is a minimum (bulk) concentration of Re necessary to prohibit the reconstructive ordering. For $x = 0.95$, i.e. 5% bulk Re concentration, the segregation of Re in the second layer is already rather weak and – possibly as a consequence – still a c(4 × 2) superstructure is observed. Yet, as described in Section 3, the structural properties of the latter are already rather different from the corresponding superstructure on the elemental Mo(100) surface. This is indicative of a non-negligible influence of Re even at this low 5% bulk concentration. It is also consistent with the lifting of the reconstruction of the elemental Mo(100) surface at this low concentration. For reasons discussed above, any charge density wave – which is frequently made responsible for the reconstruction (e.g. Ref. [12]) – must be partly located within the second layer where Re is randomly accumulated. Therefore, such a periodic fluctuation of electronic charge can hardly develop or is at least sufficiently modified to prevent an ordered reconstruction.

However, the most prominent finding of our LEED analyses is the unusual behaviour of the interlayer spacings upon hydrogen exposure. It certainly requires the postulation of an additional mechanism for the relaxation of interlayer distances. As a general observation, the break of vertical periodicity at a metal surface causes an inward relaxation of the free electronic charge density, which leads to an enhanced bonding between first and second layer. This contraction of the outermost layer distance is usually accompanied by an (already considerably smaller) expansion of the next spacing until bulk-like conditions are more and more re-established by electronic screening with further increasing depth. Generally, this effect is more pronounced the more open a surface is (e.g. Ref. [31]). Hydrogen bonding at a metal surface restores to a certain extent the electronic charge above the surface and thus leads to a derelaxation of the interlayer spacings, i.e. hydrogen acts in such a way as to re-establish bulk conditions at the surface. In accordance with these predictions we find also for the random alloy surfaces an almost complete derelaxation of the first two interlayer spacings. The unexpected and so far unique result of the present analyses, however, is the persistence of relaxed spacings between deeper layers in spite of hydrogen adsorption. The mere existence of such unusually deep-going relaxations at the clean surfaces was already attributed to the presence of an oscillatory segregation extending also deep into the surface [8]. This role of oscillatory segregation is further supported by the present hydrogen adsorption experiments, which so reveal a second mechanism for (sub) surface relaxations in random alloy surfaces. Obviously, the hydrogen adatoms modify only the uppermost two layer spacings, i.e. their influence is electronically screened within a distance of about 4 Å. This is in accordance with typical screening lengths in metals. Consequently, deviations of layer spacings from the bulk value deeper in the surface have to originate from below the very surface. The layer dependent segregation observed for Mo$_{x}$Re$_{1-x}$(100), i.e. the deviations from bulk stoichiometry, act as additional (multiple) breaks in the vertical periodicity. As a consequence, they involve some (electronically mediated) geometrical relaxations within the screening length. As for Mo$_{x}$Re$_{1-x}$(100) the segregation is oscillatory; the
relaxation induced turns out to be oscillatory as well. If the alloy’s constituents are different in size, sterical reasons might add to the modification of layer spacings. Yet this is practically not the case for Mo-Re, and so an electronically mediated relaxation mechanism must dominate. This type of relaxation has principally to be expected for any compositional discontinuity, not only in the segregational zone of an alloy surface, but also at buried interfaces of heteroepitactic metal systems.

Finally, we point out that the compositional profiles of the Mo-Re(100) surfaces as derived in the present analyses were generated during annealing the samples at elevated temperatures followed by a rather rapid cooling process. So, elemental distribution in the surface reflects the equilibrium condition of clean surfaces not even at the very adsorption temperature, but at some elevated temperatures. Certainly, this state does not necessarily correspond to the equilibrium of the hydrogen covered phase. One might speculate whether the latter is identical with a surface which is more or less bulk-like with respect to both layer spacings and layer compositions. Yet, there is no chance to check for this speculation as hydrogen desorbs at temperatures far below the onset of surface atom interdiffusion, allowing thermal equilibrium to be established.

7. Summary

Hydrogen adsorption on the (100) surfaces of the randomly disordered alloy Mo-Re(100) was investigated for \( x = 0.75, 0.85 \) and 0.95 by means of vibrational spectroscopy and low energy electron diffraction. The data analysis for the hydrogen saturated surfaces with coverage \( \Theta_H = 2 \) found the adsorption site to be two-fold coordinated, i.e. hydrogen resides in bridge sites and the adsorption height is according to a hydrogen radius in the usual range of 0.5–0.6 Å. The adatom–substrate adsorption cluster is very similar to that found for adsorption on elemental Mo(100). This is not surprising in view of the finding that the top alloy layer practically exclusively consists of Mo atoms which have segregated to the surface. In contrast, the ordering behaviour at submonolayer coverage is very different from that on the pure metal, in particular no long range ordering is observed. These strong modifications upon alloying are interpreted to come from the enrichment of the minority constituent in the second layer, in particular by its random distribution which prevents the development of long range order in the adsorbate. The structure determinations reveal that the H adsorption at full coverage lifts almost completely the relaxation of the two outermost layer spacings, but only of those. The relaxation of deeper layers – which still show some layer dependent composition deviating from bulk stoichiometry – is left practically unmodified compared to the clean surface according to the usual electronic screening of the adatoms’ influence. This points towards an electronically mediated correlation between the relaxation of layer spacings and compositional discontinuities in subsequent layers, which also accounts for the unusually deep multilayer relaxation found for the clean surfaces.

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References