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Interlayer relaxation of W(1 1 0) studied by surface X-ray diffraction

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Abstract

The structure of the clean, unreconstructed W(1 1 0) surface was investigated by surface X-ray diffraction. The analysis of the integer order crystal truncation rods up to a maximum momentum transfer of four reciprocal lattice units indicates a contraction of the first interlayer distance by $\Delta d_{12} = -2.7(5)\%$ relative to the bulk interlayer distance ($d_{\text{bulk}} = 2.238$ Å). The relaxation of the second interlayer spacing is found to be smaller than 0.3%. Within the error bars our results agree with recent low energy electron diffraction studies. However, Δd_{12} is lower than predicted by recent calculations (−4.1%). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: X-ray scattering, diffraction, and reflection; Tungsten; Surface structure, morphology, roughness, and topography

1. Introduction

The structure analysis of clean and adsorbate-covered crystal surfaces is an important field in surface science, since the atomic arrangement within the first layers is intimately related to their physical, chemical and catalytic properties [1]. Among the wide variety of surface structural studies, the experimental and theoretical analysis of clean metal surfaces has been a matter of interest for a long time. In general, it is found that the first (d_{12}) and second (d_{23}) normal interlayer spacing are compressed and expanded relative to the bulk, respectively. When going deeper into the crystal, these displacements are rapidly damped and are often oscillatory [2]. However, often discrepancies exist between different investigations with respect to the magnitude of the relaxation as well as their extent into the bulk.

In this context, there is renewed interest on the structure of the W(1 1 0) surface. Apart from its use as an important substrate material for the growth of magnetic ultra-thin films such as Fe/W(1 1 0) [3–6] it has been investigated since the early days of quantitative analysis of low energy electron diffraction (LEED) data [7–11]. In contrast to these investigations which found an unrelaxed surface, more recent *I–V*-analyses indicate a

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Table 1
First and second interlayer relaxations for W(1 1 0) as derived from experimental and theoretical investigations

	$\Delta d_{12}/d_{bulk}$ (%)	$\Delta d_{23}/d_{bulk}$ (%)	Method	Year	Reference
Experiment					
	0.0		LEED	1974	[7]
	0.0 ± 3.0		LEED	1975	[8]
	0.0		LEED	1976	[9]
	< -2.0		HEIS[a]	1987	[10]
	1.0 ± 2.0		PED[b]	1993	[11]
	-3.1 ± 0.6	0.0 ± 0.9	LEED	1997	[12]
	-3.0 ± 1.3	0.2 ± 1.3	LEED	1999	[13]
	-2.2 ± 1.0	0.0[c]	SPLEED[d]	2000	[14]
	-2.7 ± 0.5	0.0 ± 0.3	SXRD	2000	This work
Theory					
	−1.4	−0.4	TB[e]	1988	[15]
	−2.1	+0.7	ECT[f]	1993	[16]
	−5.0	+4.6	TB[e]	1994	[17]
	−3.6	+0.2	DFT[g]	1997	[12]
	−4.1	−0.4	DFT-FLAPW[h]	1999	[18]

[a] High energy ion scattering.
[b] Photoelectron diffraction.
[c] Fixed parameter.
[d] Spin-polarized LEED.
[e] Tight binding approximation.
[f] Equivalent crystal theory.
[g] Density functional theory.
[h] Density functional theory-full potential linearized augmented plane wave.

relaxation in the −2% to −3% range for d_{12} and an almost unrelaxed spacing for d_{23} [12–14]. Moreover, theoretical work yielded different results in the range between −1.4% and −5% [12,15–18]. Table 1 provides an overview over the experimental and theoretical results.

Although LEED is still the most commonly applied technique for surface structure analysis, surface X-ray diffraction (SXRD) has evolved to be a powerful tool for analyzing the surface atomic arrangement. This is because of the development of high-brilliance synchrotron X-ray sources as well as due to the applicability of the single scattering theory, which allows a simpler interpretation of the scattered intensities compared to LEED. However, in many cases limited resolution, especially along the surface-normal is a disadvantage of SXRD. This is especially important for the determination of small relaxations as often encountered for low index metal surfaces. This might be the reason why SXRD has only been applied in exceptional cases for this purpose [19,20].

In the present investigation we discuss the SXRD analysis of the clean W(1 1 0) surface relaxation. The results demonstrate the applicability and straightforward analysis of diffraction data obtained with high k-space resolution to determine even small relaxations with high precision. We find a first interlayer contraction of $\Delta d_{12}/d = -2.7(5)\%$ and an almost one order of magnitude smaller relaxation of the second interlayer spacing within an error bar of less than 0.3%.

2. Experiment and theory

The experiments were performed at the beamline ID3 of the European Synchrotron Radiation Facility (ESRF) in Grenoble using a six-circle-ultra-high-vacuum diffractometer (base pressure 7×10^{-11} mbar) running in the z-axis mode [21,22]. The W(1 1 0) crystal was cleaned by heating several times in 10^{-6} mbar oxygen partial pressure for 30 s at 1500°C. After a final 10 s flash at 2000°C only

minor traces of carbon contamination (less than 1% of 1 ML) could be detected by Auger-electron spectroscopy.

Integrated X-ray reflection intensities were collected at a wavelength of 0.73 Å by transverse scans, i.e. rotating the crystal about its surface normal while the X-ray incidence angle was kept fixed at 1.0° with respect to the sample surface. This large value about six times the critical angle of total reflection has been used in order to avoid possible systematic errors due to a slight bending of the crystal. When scanning in the transverse direction, the resolution is limited by the sample mosaic spread, which was 0.1°. After correcting the intensities for active sample area as well as for the polarization, and Lorentz factor [23,24], a total of 100 symmetry independent structure factor intensities, $|S(q)|^2$, along three crystal truncation rods (CTRs) were derived. The standard deviations, σ, were derived from the reproducibility of symmetry equivalent reflections and from the counting statistics. In general, σ is in the 5–10% range.

The scattered intensity $|S(q)|^2$ along the CTRs is calculated analytically by summing the scattering amplitudes of the unit cells along the crystal axes:

$$|S(\vec{q})|^2 = \left| \sum_{n_1=-\infty}^{\infty} e^{i2\pi h n_1} \sum_{n_2=-\infty}^{\infty} e^{i2\pi k n_2} \sum_{n_3=-\infty}^{\infty} e^{i2\pi \ln_3} \right|^2 \times |F(h\,k\,l)|^2 \quad (1)$$

where $F(h\,k\,l)$ corresponds to the structure factor of one unit cell and $q = (h\,k\,l)$ is the scattering vector. In Eq. (1) the crystal is assumed to be infinite along the a- and b-axes (summation from $n_{1,2} = -\infty$ to ∞), but semi-infinite along the c-axis (summation from $n_3 = -\infty$ to 0). The summation in Eq. (1) leads to:

$$|S(\vec{q})|^2 = |F(h\,k\,l)|^2 \sum_h \delta(h) \sum_k \delta(k) \frac{1}{4\sin^2(\pi l)} \quad (2)$$

In Eq. (2), $\delta(h)$ and $\delta(k)$ represent delta functions. They reflect the point like nature of the reciprocal lattice along a^* and b^*. On the other hand, the rod like shape along c^* is represented by the $\sin^2(\pi\ell)$ term, where the reflection index ℓ is a continuous parameter. This is a consequence of the broken crystal periodicity along c. The singularities at the bulk Bragg positions (ℓ integer in Eq. (2)) are removed by taking into account the finite penetration depth of the X-rays into the crystal due to absorption and extinction. This can be done by introducing the exponential damping term $e^{-c/\mu}$, where μ is the penetration depth in units of c. However, for the analysis of the CTR data away from the bulk Bragg-reflections this represents only a minor correction and can be neglected in the following discussion.

After evaluation of Eq. (2) for the specific case of the W(1 1 0) surface [1] one obtains:

$$|S(\vec{q})|^2 = \left| \frac{f_W}{1 - e^{-i\pi(h+k+\ell)}} + \sum_i \theta_i f_W e^{i2\pi(hx_i + ky_i + \ell z_i)} \right|^2 \quad (3)$$

The total scattering amplitude of the bulk truncated crystal is given by the first term on the right side, where the parameter f_W represents the atomic scattering factor of the W-atoms. For the consideration of surface relaxations additional W-layers have to be included. This is represented by the second term where θ_i represents the occupancy of the ith layer. Since (also in the present setting [1]) the bulk W-structure it is characterized by a body centred structure there is a phase shift of $(h + k + l)$ between successive layers since the vector between consecutive layers is $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. According to Eq. (3) normal surface relaxations can be included by shifting the W-atoms in the layers (i) out of their bulk positions at $z_{i=1} = 0.5$, $z_{i=2} = 1.0$, etc.

3. Results and discussion

The structure refinement was carried out by least squares refinement of the calculated structure factor amplitudes, $|S(q)|$ to the measured ones. In Fig. 1 the solid symbols represent the measured

[1] We use a sample setting corresponding to a primitive (p) (1×1) surface unit cell which is related to the bulk bcc setting according to the relations: $[1\,0\,0] = (1/2)[\bar{1}\,1\,1]_{bcc}$, $[0\,1\,0] = (1/2)[\bar{1}\,1\,\bar{1}]_{bcc}$ and $[0\,0\,1] = [1\,1\,0]$.

ones (after taking the square root of the structure factor intensities) for the (0 1 ℓ), (2 0 ℓ) and (1 1 ℓ) rods. Calculated structure factor amplitudes are represented by the different lines, where several first interlayer relaxations ($\Delta d_{12}/d_{\mathrm{bulk}} = 0\%$, -2.7%, -4%) were assumed. Even from direct inspection of Fig. 1 it is evident, that neither the model of a bulk truncated crystal (dashed line) nor one assuming a crystal with a -4% relaxed first layer spacing (dotted line) fit the data well. For a bulk truncated crystal the CTRs are symmetric about the anti-phase condition. In contrast, an interlayer contraction leads to a shift of the CTR minimum to larger q_z-values.

A quantitative parameter of the fit quality is the unweighted residuum (R_{u}). [2] It is shown in Fig. 2 versus ($\Delta d_{12}/d_{\mathrm{bulk}}$). A clear minimum is observed for 2.7% contraction. An error bar of about 0.5% for Δd_{12} can be deduced from the R_{u} versus Δd_{12} curve when a maximum increase of up to 10% for R_{u} is assumed not to be significant. The solid line in Fig. 1 represents the corresponding calculated CTRs. For data points along the (0 1 ℓ) rod close to the Bragg reflection at $\ell = 3$ there is some disagreement between fit and data which is larger than the standard deviation. We tentatively attribute this to some experimental systematic error, however, this does not have any influence on the results for the interlayer relaxations. This is because they are determined by the asymmetry of the CTRs along the rods. These most surface sensitive parts of the rods are fitted very accurately as can be seen in Fig. 1.

In a second step we also tried to vary the second interlayer spacing d_{23}. However, variation of d_{23} led in any case to a deterioration of the fit. The error bar for the determination of d_{23} is estimated from R_{u} and its correlation with d_{12}. We estimate an error of about 0.3% for d_{23}.

Table 1 compares the results derived from experimental and theoretical work carried out over the last 25 years. It can be seen that for Δd_{12} there

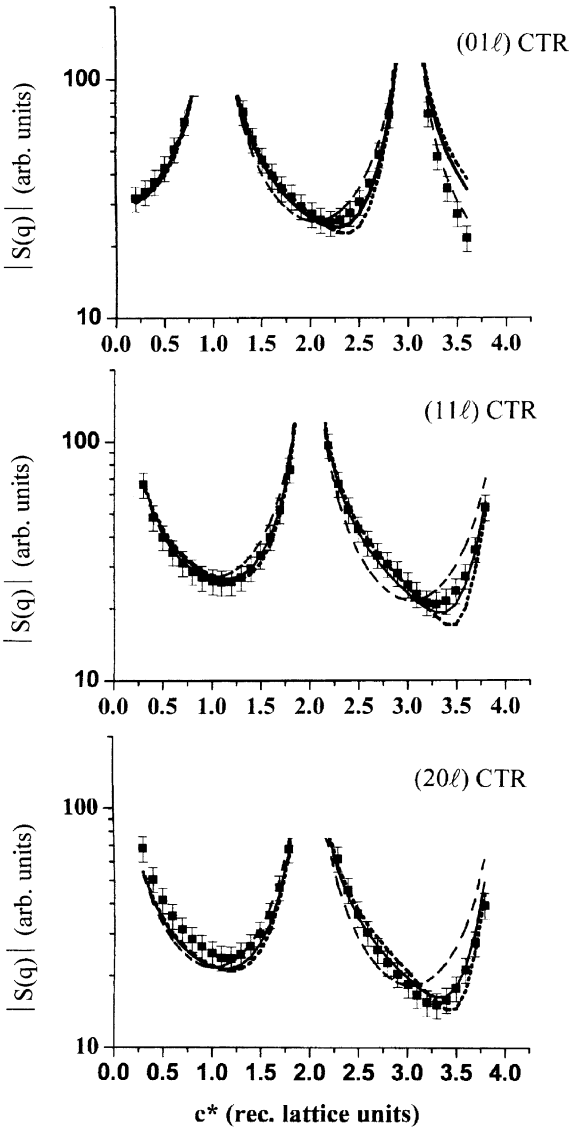

Fig. 1. Measured (symbols) and calculated (lines) structure factor amplitudes along the (1 0 ℓ), (1 1 ℓ) and (2 0 ℓ) CTRs. Dashed and dotted lines represent calculations for a bulk truncated surface ($\Delta d_{12}/d = 0$) and a $\Delta d_{12}/d = -4\%$ contracted interlayer spacing, respectively. The solid line represents the best fit to the data with $\Delta d_{12}/d = -2.7\%$.

is considerable convergence between experiment and theory over the years; the gap has closed from up to 5% in 1993/1994 [11,16,17] to at most 0.5–1.4% since 1997. Moreover, there is now considerable consensus that d_{23} is almost bulk-like. The

[2] The unweighted residuum (R_{u}) is defined as: $R_{\mathrm{u}} = \sum ||F_{\mathrm{calc}}| - |F_{\mathrm{obs}}|| / \sum |F_{\mathrm{obs}}|$, where F_{obs} and F_{calc} are the observed and calculated structure factors, and the summation runs over all observed reflections.

convergence of the results can be attributed to both, improved experimental analysis methods and more elaborate calculation techniques. Nevertheless, for $(\Delta d_{12}/d_{\text{bulk}})$ there is still some disagreement between experiment and theory, where in general the experimentally derived relaxation is smaller than the theoretically predicted.

Enhanced thermal expansion of the top layer as compared to the deeper layers can only account for some minor fraction (in the present case about 0.3%) of the difference. In order to provide a rough estimate we recall that a detailed temperature dependent analysis of the W(1 0 0)-(1×1) surface by spin polarized low energy electron diffraction (SPLEED) [25] has indicated that the thermal expansion coefficient of the top layer is about two to three times larger than the bulk expansion coefficient ($\alpha = 4.5 \times 10^{-6}$ after Ref. [26]). This is quite a large factor, but is in agreement with theoretical predictions [27]. Since the theory used for calculating the interlayer relaxations assumes a crystal at $T = 0$ K, measurements at higher temperatures are expected to yield larger interlayer distances d_{12} than predicted by theory. Using a linear extrapolation and assuming the same factor for W(1 1 0) this thermal expansion effect can explain at most 0.3% difference between experiment and theory. Moreover, thermal expansion is related to anharmonic vibration potential. In the present case no significant anharmonicity could be determined. In X-ray diffraction (harmonic) thermal disorder is represented by the Debye parameter $B = 8\pi^2\langle u\rangle^2$. We allowed for a variation of the (isotropic) Debye–Waller factor of the first layer W-atoms while keeping deeper layers constant at the bulk value of the Debye parameter $B = 0.15$ Å^2 ($\langle u^2\rangle = 0.0019$ Å^2 at 300 K) [10]. No enhancement for the surface atoms could be determined. This is at some variance with calculations by Dobrzynski et al. [28] and the high energy ion scattering experiments by Smith et al. [10] which indicate an enhancement of the first layer thermal disorder for the W(1 1 0) surface relative to the bulk by a factor of 1.2 parallel to the surface and up to a factor of 2–3 perpendicular to the surface. Although the *relative* vibration enhancement is quite large for the normal direction the *absolute* vibration amplitudes are a factor of four smaller as compared to most other metal crystals (e.g. $B \approx 0.6$ Å^2 for Cu, Ag, Al, etc.). Consequently, the *absolute* differences between bulk and surface vibrations are quite small. This might be the reason why with the present data set it is not possible to determine the thermal surface anisotropy and the surface anharmonicity as has been done in some previous studies [29,30].

From the experimental point of view another reason why the contractions are determined to be too low might be contamination of the surface due to insufficient surface preparation and – more importantly – due to adsorption from the residual gas. As an example, the LEED measurements of Arnold et al. [12] have shown that hydrogen adsorption on W(1 1 0) reduces the interlayer contraction from 3.1% for the clean surface to about half this value. However, a contamination-induced reduction of the interlayer relaxation can be ruled out within the error bars of our experimental uncertainty, since intensities of symmetry equivalent rods measured during 1–3 h did not show any significant time dependence.

Apart from varying the interlayer relaxation and thermal disorder, in addition surface roughness was taken into account. For the description of the roughness, Robinson [31] has developed an atomistic model assuming a geometric distribution of layer occupancies within the coherence width (in the present case about 500 Å as deduced by the longitudinal width of the reflections), where the layer occupancy is 1.0 for layer 0, layer 1 has a fraction of β occupied sites, layer 2 has a fraction of β^2 and so on. The parameter β can be converted to σ_{rms}, the root mean square elevation of the surface which is given by $\sigma_{\text{rms}} = (d \times \sqrt{\beta})/(1-\beta)$, where d is the layer spacing perpendicular to the surface (for W(1 1 0): 2.237 Å). Increasing roughness leads to a steeper decrease of the CTR but not to an asymmetry of the intensity distribution as layer relaxation does [32]. Values for β are in the range between 0.0 and 0.5 depending on the material and preparation. In general, semiconductor surfaces exhibit flatter surfaces than metals. For the W(1 1 0) surface we determine $\beta = 0.05$ (5) which corresponds to $\sigma_{\text{rms}} = 0.5$ Å. This is a quite small value for a metal surface and reflects the high degree of flatness which might be attributed to the high temperature surface preparation.

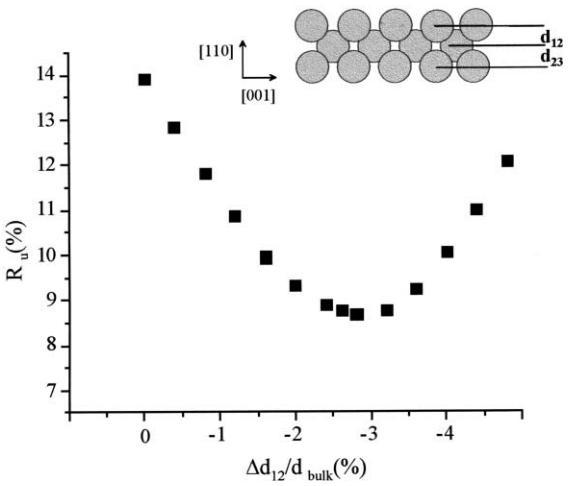

Fig. 2. Plot of the unweighted residuum, R_u, versus the first interlayer relaxation, $\Delta d_{12}/d_{bulk}$. The minimum of the curve indicates the best fit for the layer relaxation $\Delta d_{12}/d = -2.7\%$.

In summary, we have presented a SXRD investigation of the clean W(1 1 0) surface. The analysis of the CTRs reveals a first layer contraction of 2.7(5)% with no changes of the second layer spacing relative to the bulk within about 0.3%. Within the error bar this is in agreement with recent investigations by LEED. The crystal surface was found to be very flat for a metal sample as expressed by the roughness parameter $\beta = 0.05$ (5). The present investigation has shown that SXRD, with its simple interpretation of intensities, is an excellent tool for determining accurate values for the interlayer relaxations of metals, which has so far been a domain of LEED investigations.

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