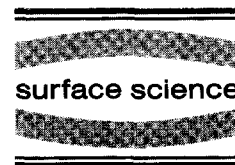




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Structural studies of the Pb(110) surface with ISS and RHEED

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Abstract

The Pb(110) surface undergoes a roughening transition at approximately 400 K. The roughening is seen by ISS in the surface-blocking mode and the surface-channeling mode. The average terrace widths can be estimated from the RHEED experiments. There is also evidence for surface disorder, and the roughening transition is found to be about 30 K higher than the ISS values.

Keywords: Lead; Low index single crystal surfaces; Low energy ion scattering (LEIS); Reflection high energy electron diffraction (RHEED); Surface structure

1. Introduction

After the discovery of surface melting [1] the Pb(110) surface became the subject of many studies. The experiment used medium-energy ion scattering (MEIS). In such experiments, the number of surface atoms “visible” to the ion beam is measured. Under double alignment conditions, the number of visible atoms is a measure of the order of the surface. At 580 K, i.e. 20 K below the bulk melting point, the number of visible atoms increases in accordance with the expected behaviour of a melting surface, where the thickness of the molten layer increases logarithmically with $T/(T_M - T)$, where T_M is the melting temperature and T is the absolute temperature [2]. LEED [3–5], XPD (X-ray photoelectron diffraction) [6] and ISS [7] experiments on the Pb(110) surface gave evidence for a roughening transition at approximately 400 K, i.e. at about $0.70T_M$. The ISS experi-

ments gave independent evidence for the surface melting effect at 580 K [7]. STM studies of the Pb(110) surface show steps with extended frizziness [8,9]. Experiments at elevated temperatures are impossible due to a “jump-to-contact” between the tip and the surface [10]. ISS and RHEED are not troubled by such effects, as many other surface analytical techniques which are sensitive to structural effects. In the present paper we report RHEED data obtained in parallel to the STM studies [9]. From the STM studies we know the terrace sizes and structures and the extent of the frizziness of the steps. The RHEED data are compared with ISS results obtained previously [7,11]. The main concerns are the defect structures and the roughening transition.

2. Experiment

For the experiments, two systems were used, the STM + RHEED and ISS, respectively. The scheme

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of the STM vacuum system is shown in Fig. 1. It is an Omicron STM combined with a LEED and RHEED system. The Staib RHEED electron gun is also used for Auger electron spectroscopy (AES) in combination with a Perkin-Elmer electrostatic energy analyser. The STM and analysis chamber are bridged by a wobble stick. From the analysis chamber, targets are transferred to the preparation chamber for sputtering and annealing. Target temperatures are monitored by thermocouples and an infrared-sensitive pyrometer. A typical STM view of Pb(110) has atomic resolution and, if taken on a large terrace, some streaks or fringes from a neighbouring step are visible [9]. The corrugation amplitudes are of the order of 0.1 Å, quite typical for an fcc (110) unreconstructed surface. AES under this condition shows no impurities. However, from the step pinning observed using STM, it is obvious that impurities are present, albeit on a very low level. A previously described system was used for measuring the ISS data [12]. It is a UHV system with a low-energy accelerator (200 eV to 15 keV), magnetic mass separator and a time-of-flight (TOF) facility. The TOF system is used for ion

scattering in the NICISS mode [13], i.e. TOF spectra of scattered neutrals are measured under a scattering angle of 165° while the angle of incidence of the ions is varied. Alternatively, surface blocking is applied by varying the azimuthal angle and by keeping both the angle of incidence and the scattering angle constant. In the NICISS mode, surface lattice constants and defects can be both measured and detected. The surface-blocking mode yields a real-space projection of the surface crystallographic structure as a series of maxima and minima, where the minima appear at low-index crystallographic directions. The minimum yield is a qualitative measure for defects, i.e. mainly steps. Finally we used surface channeling detection with a position-sensitive detector with the incidence plane cutting a given azimuthal direction, and the beam was incident with small glancing angle, usually about 5° [13,14].

3. Results

After cleaning the Pb sample and obtaining a good STM result, the targets were brought to the

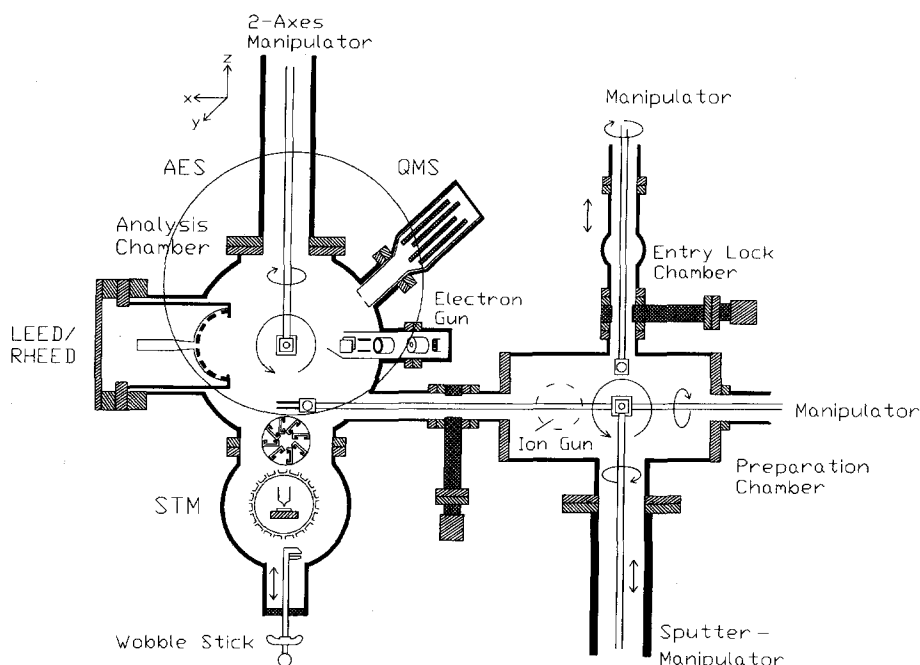


Fig. 1. Schematic view of the apparatus.

RHEED position. There, the temperature was varied in situ and patterns were taken using the LEED screen and a video camera for the data handling. At 300 K the pattern taken along the [110] azimuth shows the expected main diffraction maxima forming a Laue circle, evidence for disorder as weak streaks and weak additional maxima, as well as a characteristically shaped diffuse background (Fig. 2). The profile analysis of the main maxima (FWHM corresponds roughly to $2\pi/N_a$ with N_a being the average terrace width) gives a size estimate of the average terrace size along the chosen direction of 190 Å. This is clearly smaller

than the RHEED transfer width, which is found to be 1000 Å. From the STM data, an average length of 150 Å is found. Since the spot profile is smooth, the terrace width distribution should be rather random. The additional intensity outside the Laue circle can be identified as being due to transmission effects. The $\langle 110 \rangle$ steps are not perfect at room temperature; they have single and multiple atom kinks, such that the electrons pass through extensions of the steps. By varying the glancing angle of the electron beam this part of the background varies, as is usual for transmission effects in RHEED. The diffuse background has been observed in an equivalent situation, i.e. the disordered Pt(110) surface above the

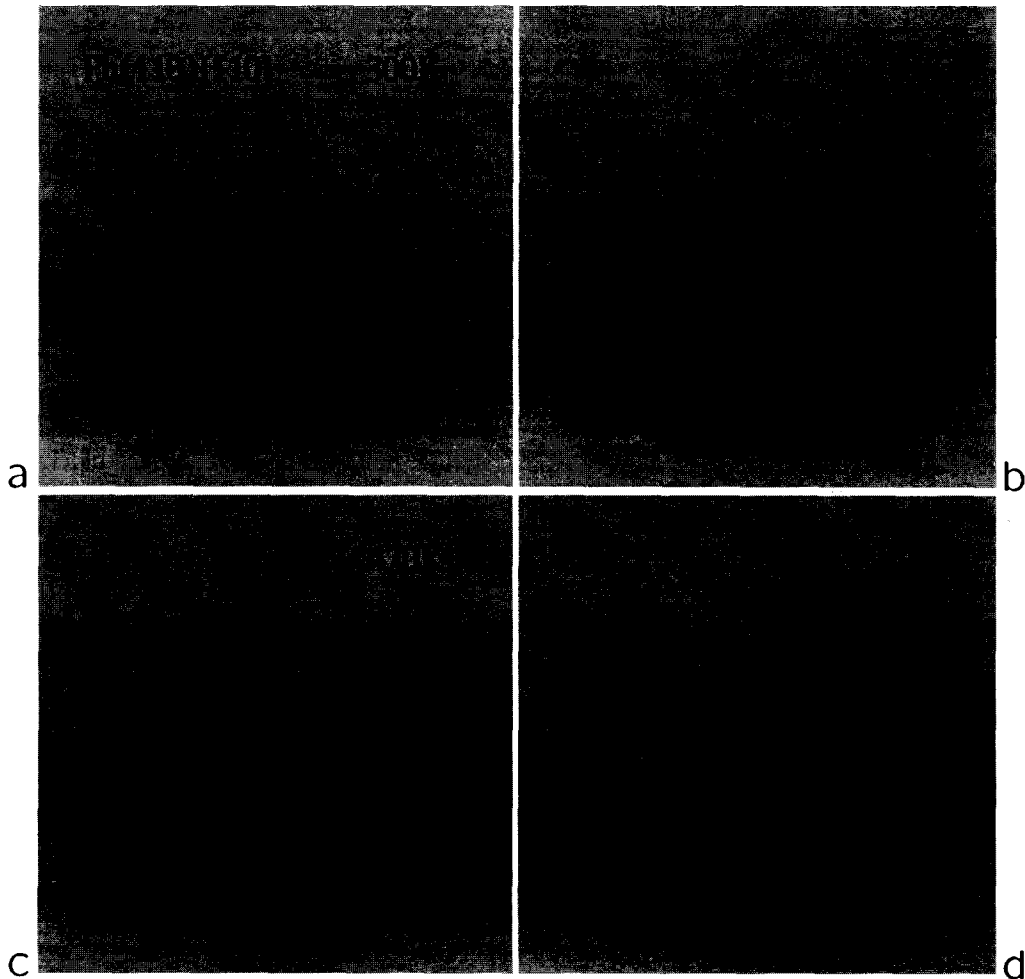


Fig. 2. RHEED patterns at different temperatures $E_e = 12$ keV, $\phi = 3.7^\circ$.

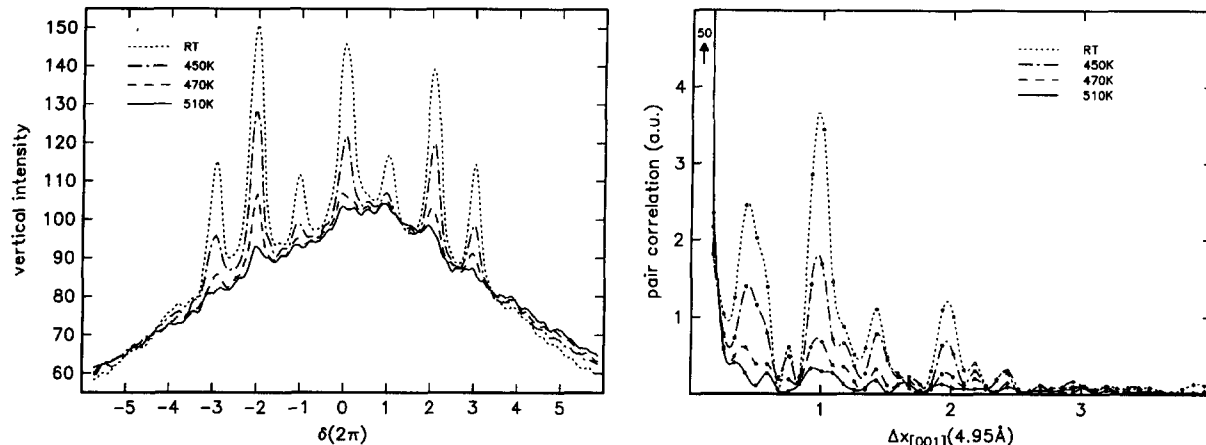


Fig. 3. (a) Vertically added sections through RHEED patterns. (b) Inverse Fourier transformation (related to the pair-correlation or Patterson function).

$(1 \times 2) \leftrightarrow (1 \times 1)$ transition temperature [15]. Calculations show that this background is due to steps; these steps are counted as missing atoms for a given terrace. This effect becomes obvious in the Fourier transform of the RHEED intensities as a contribution to the pair correlation function at zero (Fig. 3b). Fig. 3a is the sum of the vertical intensities of the RHEED patterns. The intensities decrease with increasing temperature without significant changes of the spot profiles, as expected from the Debye–Waller behaviour of thermal vibrations. At about 450 K we find a discontinuity in the integral intensities for all observed main diffraction maxima (Fig. 4). Note that this happens at the same value for the different beams. The

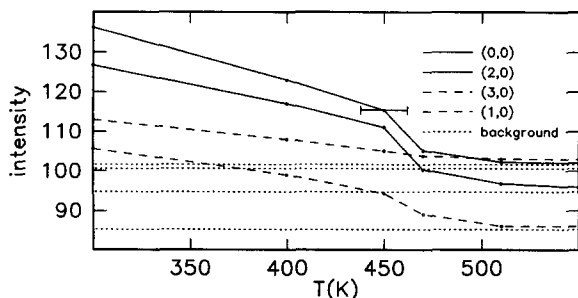


Fig. 4. Integral diffraction spot intensity at varying temperatures. The background of the curve is represented by the line which is near the corresponding spot intensity at 550 K. (2,0): in-phase, (0,0): still in-phase, (1,0): out-of-phase scattering condition, (3,0): intermediate.

strongest diffraction beams ((2,0) and (0,0)) are more sensitive to positional disorder than to the presence of steps since they are from in-phase scattering of different terraces. So, the value found by this kind of evaluation probably estimates the temperature more at the end phase of the roughening.

When comparing this temperature behaviour with the ISS data from the surface-blocking experiment (Fig. 5a) we identify the discontinuity with the roughening transition. The experimental data [16] are the minimum yields of the low-index surface half channels of a surface-blocking pattern. The experiment was performed with 2 keV Ne at an angle of incidence of 11° and a scattering angle of 165° . The “random” or high-index direction (this was chosen in the maximum of the blocking spectra) yield decreases with increasing temperature, whereas the low-index yields increase with increasing temperature. The temperature-dependent yields were calculated using a quasi-2D model which takes into account the crystallographic structure of the surface half channels and thermal vibrations as random displacements of the surface atoms according to the Debye model (Fig. 5b). Steps are not included in the calculations, so that differences between the calculations and the experiments are due to the step formation and other possible defects, i.e. kinks in steps which run parallel to the channel under consideration. In

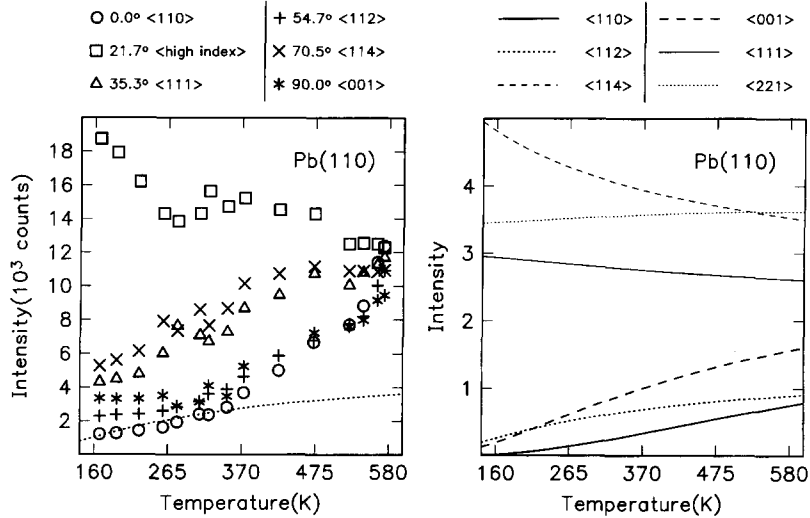


Fig. 5. Temperature dependence of the backscattering intensity in five low-index directions. Angle of incidence $\phi = 10.5^\circ$, 2 keV $\text{Ne}^+ \rightarrow \text{Pb}(110)$, Scattering angle $\theta = 165^\circ$. Left: experiment, right: calculation.

comparison with the experiment the calculations give qualitatively the correct behaviour, with consideration of the roughening, which is not included in the calculation. The high-index intensity is rather flat; $\langle 111 \rangle$ and $\langle 114 \rangle$ decrease slightly, whereas $\langle 110 \rangle$, $\langle 112 \rangle$ and $\langle 001 \rangle$ show the expected increase. This increase is due to the incomplete shadowing of the atoms in the channel by the thermal vibrations, as observed in bulk channeling. However, in this case, the vibrations along the beam direction are responsible. The $\langle 221 \rangle$, $\langle 114 \rangle$ and $\langle 111 \rangle$ directions behave differently compared to the lower-indexed directions, and the critical angle for these channels is very close to the incidence angle (7.0° , 9.3° and 11.0° compared to 11°). So, there is almost no channeling left, the backscattered intensity is about maximal, and each distortion in the surface would lead to a rather large drop of that intensity. For instance, holes in the row would hardly influence the intensity of a low-indexed channel, since they do not disturb the channeling motion. Rather, they would cause a decrease of the signal of the three highest-indexed directions. This is the explanation for the significant deviations of the experimental signal from the predictions below 370 K. The deviations between the experimental and calculated yields of the three low-indexed directions are mainly due to the

roughening, i.e. the enhanced step formation at about 400 K, where the $\langle 110 \rangle$, $\langle 112 \rangle$ and $\langle 001 \rangle$ experimental intensities bend upwards at about 400 K, whereas on the perfect surface the intensities start to level off. For a direct comparison, the calculated $\langle 112 \rangle$ intensity is plotted in the experimental data of Fig. 5a. The roughening is also found in the channeling experiment [11]. At room temperature the $\langle 110 \rangle$ and $\langle 112 \rangle$ half channels produce “half moon”-shaped channeling patterns which become almost circular when passing through the roughening transition. The aspect ratio of the channeling pattern visualises this effect by the transition from semi-axial to semi-planar channeling (Fig. 6). At about 570 K the aspect ratio reaches 1.0 as expected for the quasi-liquid-like surface. The roughening temperature is where the $\langle 110 \rangle$ signal passes a discontinuity, i.e. between 360 and 400 K. The curve for the $\langle 112 \rangle$ direction shows the same behaviour, but with the discontinuity temperature about 70 K higher. This can be explained by the special structure of the $\langle 112 \rangle$ semi-axial surface channels. $\langle 112 \rangle$ is the only direction along which the channel is not bordered by atoms in the bulk direction. Therefore, the projectiles can penetrate more and bulk channeling is more probable than along $\langle 110 \rangle$. This reduces the central intensity in the channeling pattern and

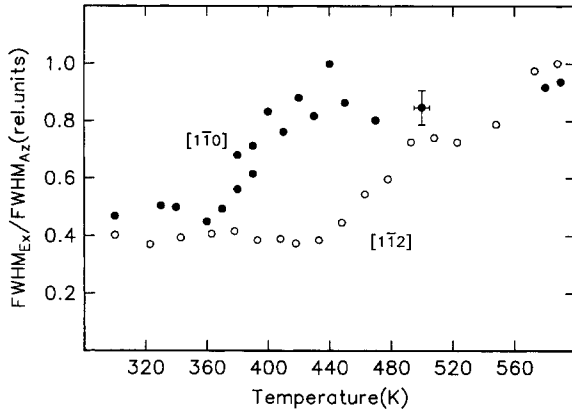


Fig. 6. Temperature dependence of the surface channeling patterns of Pb(110) for the $\langle 1\bar{1}0 \rangle$ and $\langle 1\bar{1}2 \rangle$ directions expressed by the aspect ratio of the pattern, i.e. the FWHM in the direction perpendicular to the surface/FWHM in the azimuthal direction.

emphasizes its anisotropy. Additionally, the $\langle 112 \rangle$ rows are part of the energetically very stable $\langle 111 \rangle$ planes, extending into the bulk. In order to move the atoms out of these planes, a higher temperature is most probably needed. The temperature difference of about 30 K between the value obtained from ISS and RHEED is due to the fact that a sudden decrease, especially of the in-phase diffraction maxima, indicates a complete roughening transition, whereas the distortion of channeling patterns is caused by a small amount of misplaced atoms or additional steps and is assumed to happen at the beginning. Another reason is probably the larger probing depth of the electrons.

It is worth noting that both the electrons and the ions are fast probes, i.e. 15 orders of magnitude faster than STM. So, the thermal fluctuations (frizzes) seen in STM play no major role in RHEED and ISS. The increased step density at the roughening transition causes more transmission effects and hence a decrease of the main diffraction-spot intensity. In ISS the steps cause dechanneling which is azimuthal-dependent, due to the preference of low-index step directions to be formed at lower temperatures.

4. Discussion

The main result of the present work is the new data on the roughening transition of Pb(110) in

the temperature range between 400 and 450 K. At a roughening transition the surface spontaneously creates new steps, the stability of which is rather low. In case of Pb(110), this is manifested by the large frizzes of the $\langle 110 \rangle$ steps in the STM measurements [8,9]. The frizziness is counteracted by the fact that narrow terraces are stabilized by the repulsive step-step interaction. Different theoretical models are discussed in the literature. One model is the surface-on-surface (SOS) model [17], in which the solid is broken into columns of different heights. The surface consists of mesa-like structures with height differences of one lattice constant a . The energy of such a mesa is proportional to its circumference L (in lattice units) multiplied by the energy difference J between neighbouring columns. The free energy of such a system is then

$$F = U - TS = (J - kT \ln z)L/a,$$

where z is the number of neighbours of each column. This estimate shows that below a transition temperature T_R the surface may minimize the free energy either by minimizing the numbers of mesas and/or the circumference of the mesas. Above the critical temperature the free energies of the steps vanish and many bordering lines of any given length exist. This state of the surface is then described by the divergence of the height-height correlation function. Other more realistic models are based on the considerations related to crystal growth, nucleation, and the formation of 2D terraces [18,19]. Again, the energies of the steps become an important parameter in the estimates of possible phase transitions. Macroscopic models are based on the Wulff construction, which describes the equilibrium shapes of the crystals [20]. Consequently, the anisotropy of the surface energies γ can be derived from the equilibrium shape of crystals using the Wulff construction, as for example for Pb [21]. At low temperatures, small crystals form stable, step-free facets which meet at sharp edges or are separated by "rounded" step-rich areas. Stable facets are described by a discontinuity in the derivative of γ . At the roughening temperature, the discontinuities vanish and steps are formed on the facets: the crystal becomes "rounder". The roughening transition for Pb(110)

is found at about 390 K. A LEED, $\Delta\Phi$ and light-scattering study found roughening at a temperature of 400 K [4]. A LEED study [3] reports $T_R = 415$ K, and an XPD study [6] gives $T_R = 400 \pm 10$ K. These values are in good agreement with the ISS [11] $T_R = 390 \pm 10$ K and the RHEED value $T_R < 450$ K, respectively. Theoretical data from the embedded-atom model predict $T_R = 450$ K [22]. Note that the roughening temperature determined by the blocking spectra is approximately 20 K less than that determined through channeling. The reason is the presence of holes [7], which already disturb blocking, but hardly ever effect the shape of the channeling pattern.

Another aspect of the ISS [7] data is the lack of anomalies in the surface atoms' thermal vibrations. The ISS data show an increase of the surface thermal vibrational amplitudes up to 400 K, strictly following the Debye model. A deviation from the Debye model would have been clearly visible by comparison of angle of incidence spectra with calculations, done in Ref. [7]. There is also almost no change of the widths of the RHEED diffraction spots, nor an appreciable change in the background up to 510 K (Figs. 2 and 4), which is qualitative evidence for a regular Debye–Waller behaviour. Roughening without other structural changes is reported for the (110) surfaces of other fcc metals, Ag, Al, Cu, In and Ni [22–38]. For Ag(110), no anomalous thermal vibrations are observed in a He-atom diffraction experiment [7]. For Cu(110), enhanced thermal vibrational amplitudes are found in the temperature range of the roughening transition [33–35]. A theoretical study predicts anharmonic effects for the Cu(110) and the Al(110) in the temperature range of the roughening [39].

For surfaces where the roughening occurs in combination with a phase transition, e.g. Au(110), Ir(110) and Pt(110) [40–46], no vibrational anomalies have been found in the cases of Au and Ir [40,46], i.e. the measured mean thermal displacements of the surface atoms follow the Debye law. For Pt(110), no data have been reported with respect to the thermal vibrations. This (perhaps incomplete) survey shows that in general, the roughening is not accompanied by anomalous thermal vibrations.

Possible advantages and disadvantages of the different methods have often been discussed; even so, HLEED (or SPALEED) or RHEED have comparable instrumental responses. Apart from theory, which is easier for RHEED than for LEED, since the interaction is so fast that no exchange and correlation terms are needed, it is in general more difficult to obtain clear RHEED images for the higher-indexed directions. This seems to disagree with the fact that the shape of HLEED spot profiles of Pb(110) along $\langle 001 \rangle$ and $\langle 110 \rangle$ in principle show no difference [3]. On the other hand, on the same surface no proper Laue circles could be observed in the $\langle 001 \rangle$ direction by RHEED, but the image is dominated by transmission effects and the spots are streaky, while conventional LEED and STM give clear images. In in-situ comparisons of most (110) metal surfaces the LEED images look clearer than the RHEED images along $\langle 001 \rangle$. This is mainly due to the geometry, i.e. the Ewald sphere is large compared to the reciprocal lattice constant and is cut by the reciprocal rods with a small angle. Therefore, deviations of the shape of the reciprocal rods along the beam direction are amplified (by a factor of > 10). For the anisotropic (110) surfaces, for which a higher degree of disorder is expected along $\langle 001 \rangle$, this seems to be a disadvantage, because strongly disturbed diffraction images are difficult to evaluate quantitatively. This also implies a higher sensitivity, which in general is no disadvantage.

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