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## Reflection high-energy electron-diffraction study of surface disorder and anomalous expansion of Pb(100)

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The temperature-dependent surface structural behavior of Pb(100) is studied using reflection high-energy electron diffraction. Anomalous surface expansion for temperatures between room temperature to about 500 K is observed. A high density of surface vacancies appears at temperatures above  $\sim 500$  K.

Reflection high-energy electron diffraction (RHEED) is used to study the temperature-dependent structural properties of Pb(100). Compared to low-energy electron diffraction (LEED), estimating the lattice spacing by RHEED is more precise, since the specimen-to-screen distance can be greater, and the distance between RHEED streaks can usually be measured more accurately than distances between LEED spots. The surface sensitivity of RHEED is comparable to that of LEED with the advantage that the probed depth can be varied by changing the incidence angle of the electron beam on the surface rather than changing the primary electron energy, as for LEED.

Several structural studies have been previously performed on fcc(100) metal surfaces near its bulk melting temperature  $T_m$ .<sup>1-7</sup> A recent study on Pb(100) and its vicinal surfaces using medium-energy ion scattering showed that a limited amount of disorder began to form on Pb(100) at temperatures above 500 K, where  $T_m$  for Pb is 600.7 K.<sup>3</sup> The disordered layer thickness on Pb(100) was observed to increase logarithmically up to 2–3 K below  $T_m$  and then saturates at about 1.3 ML's, measured up to  $T_m - 0.05$  K. The maximum amount of disorder on the vicinal surfaces increased with the miscut angle from 1.9 to 3.5 ML's on the 5° and 10° miscut surfaces, respectively. This is in contrast to the divergence of the disordered layer thickness on Pb(110) as  $T_m$  is approached. This behavior, where the disordered layer thickness is finite as  $T_m$  is approached, is known as incomplete surface melting.<sup>3</sup>

Further experiments on Pb(100) with high-resolution low-energy electron diffraction (HRLEED) have shown a weak disordering at  $\approx 570$  K.<sup>5</sup> This disordering is preceded by an anomalous surface expansion at  $T \leq 480$  K and an abrupt generation of surface vacancies beginning at  $\approx 510$  K. An anomalous surface expansion was also observed on Ni(001) using LEED.<sup>4</sup> An x-ray photoelectron diffraction study of Pb(100) showed evidence of a logarithmic growth of the disordered layer thickness beginning at  $585 \pm 5$  K and up to the highest temperatures studied at  $T_m - 2$  K.<sup>6</sup>

Recently, there have been several molecular-dynamics (MD) simulations modeling surface melting of fcc(100) surfaces.<sup>8-10</sup> The simulations by Häkkinen and Manninen<sup>8</sup> examine the (110), (100), and (111) surfaces of copper, from 0 K to  $T_m$ . This study, which uses

effective-medium theory, allows for the direct comparison of the three low-index faces using the same MD potential and identical cell sizes. The results show pronounced disordering of Cu(110), weak disordering of Cu(100) just below  $T_m$ , and superheating of Cu(111). In addition, the high-temperature behavior of vicinal surfaces of Au(100) was studied using the many-body "glue" potential.<sup>9</sup> In these studies, structural modulation in the disordered film was evident on Cu(100) and the vicinal surfaces of Au(100).

In the present paper, we describe an experimental study of the high-temperature structural behavior of Pb(100) using reflection high-energy electron diffraction. The experiment was performed in a vacuum chamber with a base pressure in the low range of  $10^{-10}$  torr. The sample was cut with a fine band saw to twice its final thickness, polished with silicon carbide grit paper, and finally chemically etched in a mixture of 80% glacial acetic acid and 20% hydrogen peroxide until a mirrorlike finish was obtained. The sample was clipped to a resistively heated molybdenum heater mounted on a three-axis manipulator, which also has polar and azimuthal rotation. Two thermocouples placed at different locations on the sample monitored its temperature.

The sample was cleaned with cycles of 30 min argon bombardment at a temperature of 500 K followed by

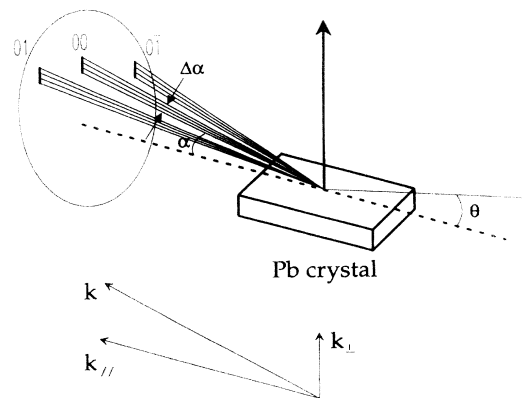


FIG. 1. A schematic diagram of reflection high-energy electron diffraction RHEED. The electron beam is incident on the surface at an angle  $\theta$ , probing the first few atomic layers. The RHEED pattern, which consists of streaks oriented perpendicular to the plane of the surface, is detected on a phosphor screen.

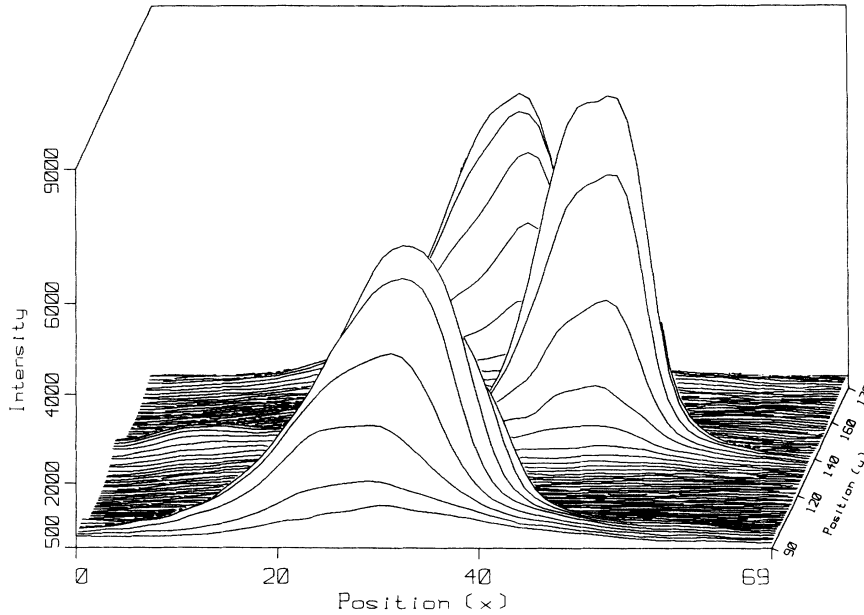


FIG. 2. A three-dimensional picture of a RHEED pattern intensity. The profiles are taken along the streaks. The height of the peak is proportional to intensity (in arbitrary units). From the front to back, the streaks are the 01, 00, and  $0\bar{1}$ , respectively.

5 min annealing at 550 K. The sample cleanliness was checked by Auger electron spectroscopy using a cylindrical mirror electron energy analyzer. The RHEED pattern is monitored by a phosphor screen located 23 cm away from the sample. The RHEED pattern is focused, using a camera lens, into a  $512 \times 512$  charge-coupled-device (CCD) detector. The output of the CCD detector is digitized and stored in a computer for data analysis.

A schematic diagram of reflection high-energy diffraction is shown in Fig. 1. The electron beam is incident along the [011] direction at an angle of  $2^\circ$ – $5^\circ$  with the surface of the sample. In Fig. 1, the central diffraction beam is the 00 streak. The 01 and  $0\bar{1}$  streaks are on the two sides of 00 streak. A three-dimensional plot of a RHEED pattern is shown in Fig. 2. The profiles are taken along the RHEED streaks.

In Fig. 3 we display a set of RHEED profiles taken along the 01 RHEED streak at different temperatures.

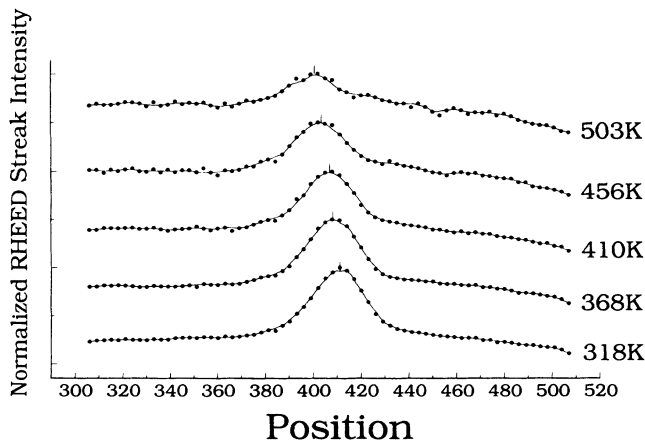


FIG. 3. A set of normalized RHEED profile intensities for the 01 streak plotted at various temperatures. The electron beam is incident at an angle  $\approx 2.7^\circ$  with the surface, which establishes the first in-phase condition. The electron beam energy is 14 keV.

The horizontal axis is the position along the RHEED streak. The vertical axis is the RHEED streak intensity. The peak intensity of each curve is normalized by dividing the intensity at each position by that at the peak. From this set of profiles, we find that the peak position of the streak shifts towards the shadow edge (left side of the figure) as temperature increases. These shifts represent a decrease in the electron momentum component perpendicular to the surface of the sample,  $k_\perp$ , due to the surface expansion as will be described next. Shifts in RHEED streak peak position are related to shifts previously observed in HRLEED  $I$ - $V$  curves with temperature.<sup>5</sup>

In our experiment, the probed depth is obtained by using an empirical relation between electron energy and inelastic mean-free path, along with the measured angle of incidence of the electron beam.<sup>11</sup> For an electron-beam energy of 14 keV and an angle of incidence of  $3^\circ$  from the surface, the probed depth is  $\approx 4 \text{ \AA}$ , reaching about two layers for the Pb(100) surface. If the outgoing electron wave contained contributions from layers deep within the crystal, each reflected coherent wave front from different layers would interfere. The condition of constructive interference is called the in-phase condition, and it can be expressed as

$$k_\perp = 2\pi m / b \quad (1)$$

where  $k_\perp$  is the perpendicular component of the outgoing electron momentum,  $m$  is an integer, and  $b$  is the distance between two atomic layers in the [100] direction.

In the RHEED geometry, the Ewald sphere cuts the reciprocal-lattice rods at a grazing angle. Thus, the diffraction condition in the RHEED geometry results in streaks rather than spots as observed in LEED. It can be shown that

$$\Delta\alpha \approx \frac{\Delta G}{k \sin\alpha} \quad (2)$$

where  $\alpha$  is the electron reflection angle with respect to

the surface,  $\Delta\alpha$  is the angular spread of the reflected beam,  $\Delta G$  represents the width of the reciprocal-lattice rod and  $k$  is the electron momentum. As a result of the small value of incidence angle relative to surface in the RHEED geometry, the position of the peak of the RHEED streak is sensitive to the perpendicular component of momentum transfer.

The angle of incidence of the electron beam on the sample,  $\theta$ , was set such that the perpendicular component of the outgoing electron momentum,  $k_{\perp}$ , equals  $2\pi m/b$ , where  $b=2.48$  Å, the spacing between two atomic layers in the [100] direction. This corresponds to the in-phase condition.

When the surface thermally expands in the vertical direction from  $b$  to  $b+\Delta b$ , the in-phase condition changes to

$$k'_{\perp} = 2\pi m / (b + \Delta b) . \quad (3)$$

This changes the perpendicular component of the electron momentum. The change in  $k_{\perp}$  is described by

$$\Delta k_{\perp} = k'_{\perp} - k_{\perp} = 2\pi m [1/(b + \Delta b) - 1/b] \approx (-2\pi m \Delta b / b^2) . \quad (4)$$

The thermal expansion of the top atomic layers,  $\Delta b/b$ , can be estimated from

$$\Delta b/b = -\Delta k_{\perp} (b/2\pi m) . \quad (5)$$

The change in the perpendicular component of momentum transfer,  $\Delta k_{\perp}$ , can be found from the measured peak position shift along the streak,

$$\Delta k_{\perp} = k \Delta d / L \quad (6)$$

where  $\Delta d$  is peak position shift,  $k=2\pi/\lambda$  is the magnitude of the electron momentum, where  $\lambda$  is the electron wavelength, and  $L$  is the distance between the sample and the phosphor screen.

Following the analysis, we set the incidence angle, such that the RHEED pattern is in the first or the second in-phase condition,  $k_{\perp}=2\pi/b$  and  $4\pi/b$ , respectively. A larger peak shift is expected for the second in-phase condition for the same temperature increase. Figure 4 is a

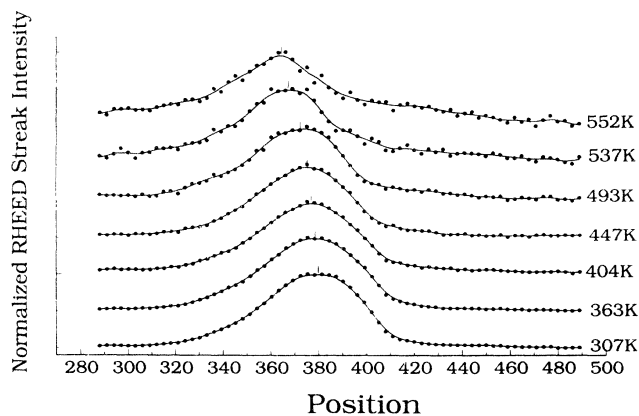


FIG. 4. A set of normalized RHEED profile intensities for the 01 streak are plotted at various temperatures. The electron beam is incident at an angle  $\approx 5^\circ$  with the surface, which establishes the second in-phase condition. The electron beam energy is 15 keV.

set of profiles for the 01 streak on the second in-phase condition. The surface temperature is marked on the side of each profile. It is apparent that the shift is approximately double that of the first in-phase condition, shown in Fig. 3, which is consistent with the above simple model.

From Figs. 3 and 4 we calculate a surface expansion of about 4% in the temperature range from room temperature to 500 K. We observe an anomalous thermal expansion of 7–8 times larger than that for the bulk. This result shows agreement with that previously obtained using HRLEED,<sup>5</sup> which is 3.4% expansion of the top atomic layer spacing in the range from 300 to 480 K. Further consideration of the observed shifts in Figs. 3 and 4 indicates that the rate of RHEED streak peak shift with temperature is larger at higher temperatures. Thus, it appears that the coefficient of thermal expansion normal to the surface increases with temperature, as observed by Cao and Conrad for the Ni(100) surface.<sup>4</sup>

For this simple model to be valid, the thermal expansion parallel to the surface must be much smaller than that perpendicular to it. Thermal expansion parallel to the surface can be monitored by measuring the distance between two adjacent streaks as a function of temperature. Moreover, this simplified analysis depends on the kinematic interpretation of the RHEED pattern and ignores multiple scattering. Therefore, we can only estimate the amount of anomalous expansion. The fact that this estimate is about the same if we use the first or the second in-phase condition is consistent with the assumption that multiple scattering effects have no significant effect on the RHEED peak streak shift.

A set of normalized RHEED streak profiles for the 00 streak at different temperatures is plotted in Fig. 5. A dramatic change in the profile shape is observed when the temperature is raised over 500 K. This implies that a certain structural change has occurred on the Pb(100) surface. A possible reason for that profile change is the generation of surface defects such as vacancies. These defects change the shape of the reciprocal-lattice rods. Generation of surface defects with temperature can be observed in Fig. 6, in which the ratio of background intensity to peak intensity,  $I_{\text{back}}/(I_{\text{peak}} - I_{\text{back}})$ , as a func-

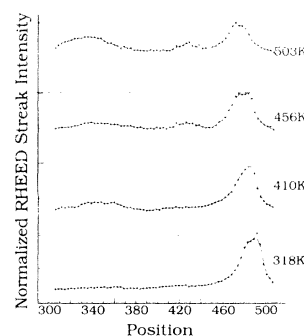


FIG. 5. Normalized RHEED profile intensities taken along the 00 streak at various temperatures. The electron beam is incident at an angle  $\approx 27^\circ$  with the surface, and the electron beam energy is 14 keV. The RHEED profile shape change with temperature is evident.

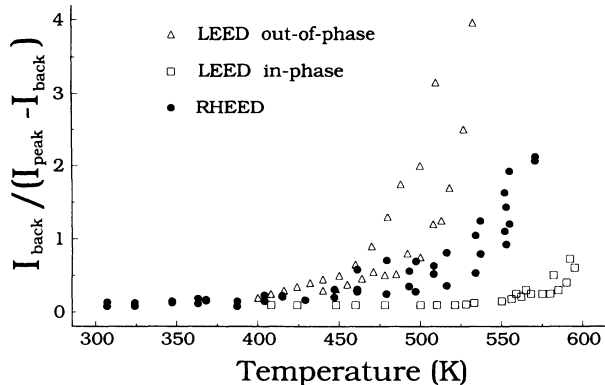


FIG. 6. The ratio of the background intensity to the peak intensity  $I_{\text{back}}/I_{\text{peak}} - I_{\text{back}}$  plotted as a function of temperature. Our RHEED data are represented by solid circles. Open triangles and squares are HRLEED data for out-of-phase and in-phase conditions, respectively, taken from Ref. 5 (see text).

tion of temperature is plotted. Our data are represented by solid circles. The background level is the intensity measured at a location between the 00 and 01 streaks. Similar ratios taken from HRLEED measurement by Yang *et al.*<sup>5</sup> are also plotted. The open triangles are ratios for the out-of-phase condition, empty squares are for the in-phase condition.

In the LEED data of Yang *et al.*<sup>5</sup> the ratio  $I_{\text{back}}/(I_{\text{peak}} - I_{\text{back}})$  for the in-phase condition is observed to remain very small below 540 K. This indicates that thermal diffuse scattering is not important at temperatures less than 540 K. Following the theoretical calculation of Pimbley and Lu,<sup>12</sup> a high ratio for an out-of-phase condition indicates generation of high density of vacancies beginning at  $480 < T < 540$  K for the LEED data of

Yang *et al.*, and beginning at  $\sim 530$  as shown in our RHEED data. The background intensity  $I_{\text{back}}$ , is proportional to  $2n(1-n)[1 - \cos(k_{\perp}b)]$ , where  $n$  is the vacancy concentration at the surface. To describe the temperature dependence of that ratio, the above relation was modified by Yang *et al.*<sup>5</sup> such that

$$I_{\text{back}} \propto 2n(1-n)[1 - \cos(k_{\perp}b)](1 + k_{\perp}^2 \langle u_{\perp}^2 \rangle), \quad (7)$$

where  $\langle u_{\perp}^2 \rangle$  is the mean-square vibrational amplitude perpendicular to the surface. When the in-phase condition is satisfied ( $k_{\perp}b = 2m\pi$ , where  $m$  is an integer), there is no background intensity. However, the background intensity reaches maxima for the out-of-phase condition when high density of surface vacancies are present.<sup>5</sup> Thus, results shown in Figs. 5 and 6 can be related to the generation of high density of surface vacancies when the temperature is raised over  $\sim 500$  K. The data shown in Fig. 6 do not account for the difference in the probing depth of our RHEED experiment when compared with that for LEED. According to the conditions reported in Ref. 5, the probing depth in the LEED experiment is expected to be somewhat larger. Moreover, the RHEED background was taken without any energy filtering.

In conclusion, we have used a simple model to extract from RHEED profiles the surface expansion normal to the surface. Anomalous surface expansion of about 4% in the temperature range from room temperature to 500 K was observed. This is 7–8 times larger than that in the bulk. High density of surface vacancies appear at temperatures above 500 K.

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