PHYSICAL REVIEW B VOLUME 41, NUMBER 15 15 MAY 1990-II

# Surface melting of Pb(110) studied by x-ray photoelectron diffraction

U. Breuer, O. Knauff, and H. P. Bonzel
*Institut für Grenzflächenforschung und Vakuumphysik, Kernforschungsanlage Jülich G.m.b.H., Postfach 1913, D-5170 Jülich 1, Federal Republic of Germany*

(Received 21 June 1989; revised manuscript received 5 February 1990)

The temperature-dependent forward-scattering intensity of $4f_{7/2}$ core-level photoelectrons at 1344.7 eV kinetic energy was studied for a Pb(110) crystal along the [001] and [$1\bar{1}0$] azimuths. The forward-scattering enhancement peaks, as a measure of crystalline order near the surface, decrease slowly up to about 500 K. Above this temperature a much more pronounced decrease is observed, indicative of a disordering of the Pb(110) surface. A change in the growth law of the disordered layer is seen near 575 K.

Temperature-dependent structural phase transitions at solid surfaces are of great fundamental interest. In particular, processes such as surface roughening and surface melting of metal surfaces[1,2] have received considerable attention in the recent past. The degree of certainty with which these effects can be detected is largely a matter of selecting the right experimental tool for studying surface order.[3,4] One technique that had been proposed for investigating surface melting is x-ray photoelectron diffraction (XPD).[5] In this technique the angle-resolved emission of photoelectrons at kinetic energies greater than 500 eV is directly related to the short-range crystallographic order of the solid because the emitted photoelectrons experience a forward focusing by nearby atoms.[6–8] Therefore, the angular distribution shows intensity enhancements in low Miller-index directions of the bulk lattice. For a single-crystal specimen, these enhancements are a direct measure of crystalline order in the near-surface region.[5,9]

In this paper we report the first successful application of XPD to studying surface disorder at high temperature. We have measured the temperature dependence of the Pb $4f$ photoelectron angular distributions in the range of 200–599.3 K. The angle-dependent forward-scattering enhancements decrease with increasing temperature, at first slowly up to about 500 K, followed by a steep decrease to nearly the melting temperature of Pb at 600.7 K. This steep decrease is interpreted as being due to a massive disordering of the Pb(110) surface, in agreement with earlier studies by Rutherford backscattering[3,10] (RBS) and low-energy electron diffraction (LEED) of the same surface.[4,11] In addition, we detected an anomalous decrease in off-normal forward-scattering intensity for the [$1\bar{1}0$] azimuth near 360 K, which may be indicative of a surface structural change, such as a surface roughening transition.

The experimental setup consisted of a dual-anode x-ray source (Mg,Al), a hemispherical analyzer with an electrostatic lens, and a sample manipulator with a Pb(110) single crystal mounted on axis. The geometrical arrangement of these components was similar to the one previously reported.[12] In short, the angle between the rotation axis of the sample and the lens axis of the analyzer is 90° while that between the rotation axis and the x-ray source is 35°. The analyzer entrance slit lies parallel to the rotation axis which itself is aligned with either the [$1\bar{1}0$] or the [001] direction of the crystal. The polar angle $\theta$ of photoemission is defined as zero when the sample normal is parallel to the analyzer axis. The sample could be rotated to positive and negative polar angles ($\pm 70°$). The chamber contained also a rear view LEED system which was used for checking the azimuthal positioning of the crystal.

The Pb(110) crystal was prepared by spark cutting and polishing, and oriented by x-ray diffraction to an accuracy of 0.1°. Cleaning by Ar sputtering and annealing resulted in a surface that was free of impurities as judged by Auger electron spectroscopy.[4,11] The sample was mounted on a copper plate that could be cooled by liquid nitrogen or heated indirectly. The temperature of the copper plate and the sample was measured independently by two thermocouples. Temperature differences between these were found to be less than 1 K but the temperature of the copper plate was taken as the reference temperature in all experiments. This thermocouple was calibrated at the bulk melting point of Pb at 600.7 K. All photoemission data reported here for the Pb $4f_{7/2}$ core level were taken with Al $K\alpha$ radiation ($h\nu = 1486.7$ eV).

Figure 1(a) shows an experimental polar angle distribution of Pb $4f_{7/2}$ photoelectron peak height at 1344.7 eV kinetic energy for the [001] azimuth. Data are plotted from $\theta = -70°$ to $\theta = 70°$. Forward-scattering enhancements in intensity can be clearly noted in this distribution. To obtain information on the instrumental response function, we measured the distribution of the photoelectron background signal at 1300 eV, also displayed in Fig. 1(a). It has a cosine-type shape but almost no structure. This distribution was fitted by a polynomial that took out the residual peak structure and was then assumed to represent the instrumental response function $I_{\mathrm{RF}}(\Theta)$. The $4f_{7/2}$ intensity distribution corrected for this instrument function was obtained by calculating

$$I_c(\Theta) = F[I(\Theta) - I_{\mathrm{RF}}(\Theta)]/I_{\mathrm{RF}}(\Theta) ,$$

where $F$ is a scaling factor. The distribution $I_c(\Theta)$ is

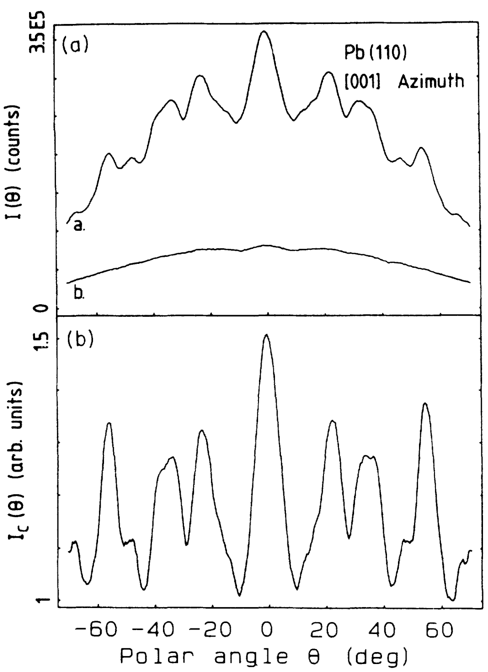

FIG. 1. (a) Measured peak height of Pb $4f_{7/2}$ photoelectrons at 1344.7 eV kinetic energy (a) and background intensity at 1300 eV (b) as a function of polar angle $\theta$ along the [001] azimuth of Pb(110). The sample temperature was 208 K. (b) Corrected intensity distribution $I_c(\Theta)$ for the $4f_{7/2}$ photoelectrons in (a).

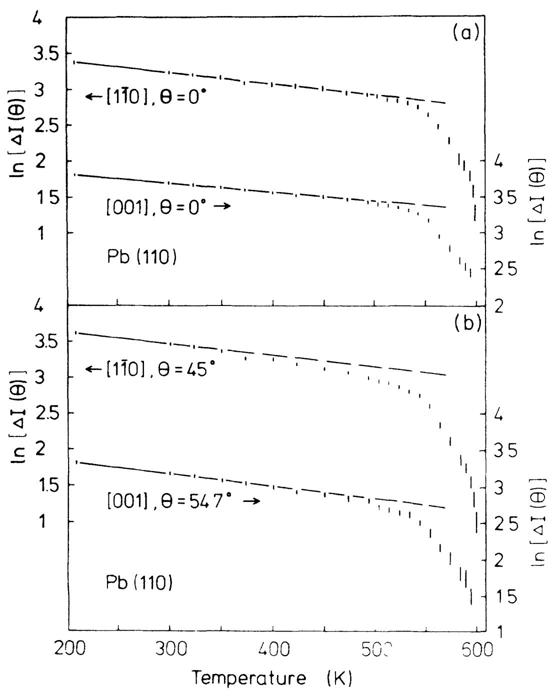

FIG. 2. Plot of $\ln[\Delta I(\Theta,T)]$ vs temperature for the [1$\bar{1}$0] and [001] azimuths. The height of the vertical bars indicates the calculated mean deviation of each measured point. Data sets are shifted against each other to avoid overlap. (a) Peak at $\theta=0°$ for [1$\bar{1}$0] and [001]; (b) Peak at $\theta=45°$ for [1$\bar{1}$0] and $\theta=54.7°$ for [001].

presented in Fig. 1(b) and shows pronounced forward-scattering peaks at 0°, ±22°, ±35° (double peak), ±55°, and additional smaller features. The large peaks can be readily associated with bulk crystallographic directions, and their intensities are a direct measure of the degree of order in the near-surface region. It was therefore the objective of this study to investigate the variation of the intensity enhancements in $I_c(\Theta)$ as a function of temperature of the sample.

All $4f_{7/2}$ peak height distributions $I(\Theta)$ of Pb(110) for the [1$\bar{1}$0] and [001] azimuths were obtained and corrected in the same fashion, as illustrated in Fig. 1. The temperature dependence of these $I(\Theta)$ distributions was studied by evaluating the relative intensity enhancement defined as

$$\Delta I(\Theta,T)=\frac{[I_c(\Theta,T)]_{\max}-[I_c(\Theta',T)]_{\min}}{[I_c(\Theta',T)]_{\min}} \tag{1}$$

for a particular peak at $\Theta$ and a nearby minimum at $\Theta'$ (for a given azimuth). It was observed that this quantity decreases with increasing temperature. All of these data are collected in Fig. 2 which is a plot of $\ln\Delta I(\Theta,T)$ versus temperature. Figure 2(a) shows two sets of data for $\theta=0°$ for [1$\bar{1}$0] and [001] azimuths. These data belong essentially to the same peak looked at from two different azimuths. The reason that the intensities are not equal is due to the finite angular resolution of the spectrometer and second-order intensity contributions from other close-by scattering directions that add into the main peak. Because of the twofold symmetry of the surface, these contributions are not equal for the [1$\bar{1}$0] and [001] azimuths.[8] Figure 2(b) compares the behavior of the $\theta=45°$ peak in the [1$\bar{1}$0] azimuth with the $\theta=54.7°$ peak in the [001] azimuth. These latter data probe the directional anisotropy of disordering.[4,11]

At first glance the data in Figs. 2(a) and 2(b) are quite similar: There is a linear decrease in $\ln\Delta I(\Theta,T)$ with increasing temperature up to about 500 K. Above this temperature the slope gradually increases and above 560 K the intensities drop quite rapidly. The constant rate of decrease over the wide temperature range 208–500 K in Fig. 2(a) is expected on the basis of increased thermal diffuse scattering due to the larger vibrational amplitude of Pb atoms. To a first approximation, i.e., for uncorrelated and isotropic thermal vibrations, the intensity decrease in this region is described by the commonly used Debye-Waller factor $I=I_0\exp[-(\Delta\mathbf{k})^2\langle u^2\rangle]$, where $\Delta\mathbf{k}$ is the change in electron momentum during a single-scattering event and $\langle u^2\rangle$ the mean-square displacement of vibrating atoms.

The temperature-dependent peak intensity at $\theta=45°$ for [1$\bar{1}$0] could not very well be fitted by a single straight line in the temperature range 200–500 K. Repeated measurements at 350–400 K revealed that there was an anomalous decrease in intensity in this temperature region. None of the other peak intensities showed such an effect to this extent. We believe that this slope change is a characteristic of the [1$\bar{1}$0] azimuth and that it can be explained by increasing anharmonic vibrations or motion of atoms along this particular azimuth direction. On the other hand, surface atoms on a (110) surface are close packed along [1$\bar{1}$0] such that a large increase in vibrational amplitudes is not possible without a concomitant surface structural change. This change could be the formation of additional adatom-vacancy pairs, as expected for the onset of surface roughening. The interpretation is supported by observations of Heyraud and Métois who concluded from particle growth experiments of Pb that the (110) surface should undergo a roughening transition near 390 K.[13] Most recently Yang *et al.*[14] also reported a roughening transition for Pb(110) at 415 K.

The strong decrease in ln $\Delta I(\Theta,T)$ above 500 K in Fig. 2 is interpreted as the beginning of surface disordering and surface melting.[3,10] When the data are normalized with respect to the exponential Debye-Waller behavior seen at $T<500$ K, a forward-scattering intensity corrected for thermal diffuse scattering, $\Delta\hat{I}(\Theta,T)$, is obtained that can be directly related to the order-parameter function of a surface order–disorder transition.[4,11] This relationship has been derived in simple kinematic framework. Photoelectrons excited within the ordered crystal experience forward scattering by nearby atoms leading to the observed angular emission pattern. These electrons are scattered elastically and inelastically by atoms in the disordered overlayer of thickness $l(T)$. This causes an attenuation of the primary forward-scattering intensity enhancement (for a particular direction $\Theta$) that is exponential with $l(T)/\lambda$, where $\lambda$ is the effective mean free path of electrons. The growth of the disordered layer as a function of temperature is given by $l(T)=ca_0\ln[T_m-T_0/(T_m-T)]$,[4,15] where $c$ is a constant, $a_0$ the correlation length in the liquid phase, $T_m$ the melting temperature of Pb, and $T_0$ the onset temperature of disorder. With these inputs the temperature dependent intensity is derived as[11]

$$\Delta\hat{I}_j(\Theta,T)=k_1(T_m-T/T_m-T_0)^{2ca_0/a_j}+k_2(T_m-T/T_m-T_0)^{ca_0/\lambda\cos\theta}\,, \qquad (2)$$

where $a_j$ is the correlation length in the disordered phase for a particular azimuth $j$, and $k_1,k_2$ are constants. It can be shown that the second term in Eq. (2) dominates if $2\lambda\cos\theta/a_j$ is considerably larger than one. With $\lambda$ for electrons of 1344 eV energy[16,17] and $a_j=1.75$ Å for the [1$\bar{1}$0] azimuth,[4] this condition is fulfilled. Hence a plot of $\ln\Delta\hat{I}_j(\theta,T)$ versus $\ln(T_m-T)$ according to Eq. (2) should exhibit straight-line sections when the above assumptions are fulfilled, and in particular when the logarithmic growth law holds. Such a plot is shown in Fig. 3 for the [1$\bar{1}$0] azimuth and the $\theta=0°$ and 45° peaks. Three different regions can be recognized in this plot. Firstly, at lower temperature there is a region I with a negligible or small slope ($\theta=45°$), which shall not be further evaluated here. Secondly, there is a nearly straight-line section between about 536 and 580 K with appreciable slopes. Because of a small continuous curvature, it is not clear whether a logarithmic growth law holds in this temperature range. The average slopes are $-0.60$ and $-0.86$ for $\theta=0°$ and 45°, respectively. Extrapolation yields an onset temperature $T_0$ of 530±5 K.

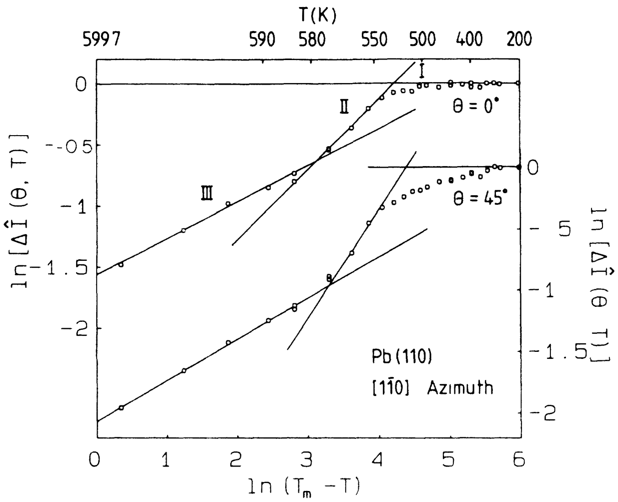

FIG. 3. Plot of ln[$\Delta\hat{I}(\Theta,T)$] vs ln ($T_m-T$) for the $\theta=0°$ and 45° peak along the [1$\bar{1}$0] azimuth. The three different kinetic regions are indicated by straight lines.

The third region in Fig. 3 shows extended straight lines for $T>580$ K, thus proving the logarithmic growth law for high temperatures. The slopes are $-0.29$ and $-0.38$ for $\theta=0°$ and 45°, respectively. Note the approximate factor of 2 in the slopes of regions II and III for each peak. The experimental data thus demonstrate unambiguously that the surface disordering of Pb(110) does not obey a single growth law over the whole temperature range 530–600 K.

Further evaluation of the [1$\bar{1}$0] azimuth data is carried out for region III. It is predominantly this temperature range that has been evaluated previously in RBS experiments of Pb(110) surface melting.[3,10,18] Most recently, the growth law for surface melting in this temperature range was chosen with the factor $c=0.5$ (Ref. 18) instead of $c=1$.[4,10,11] Theoretically, the factor of $c=0.5$ is well founded for Pb because the density difference in the solid and liquid phase is small.[4,15] With $c=0.5$ we evaluate the slopes in Fig. 3 in terms of the limiting value of $ca_0/\lambda\cos\theta$ governing the second term in Eq. (2). With published data of $a_0$ for Pb(110) of 6.3 Å (Refs. 10 and 18) and 4.68 Å (Ref. 19), one obtains an effective mean free path of electrons in Pb of 11 and 8 Å, respectively, for both peaks in Fig. 3. This range of 8–11 Å for electrons of 1345 eV kinetic energy appears to be reasonable in view of recent overlayer damping experiments that were carried out to obtain directly the effective attenuation length from an XPD intensity distribution.[20]

Both regions II and III can be readily associated with surface disordering of Pb(110) as detected previously by RBS (Ref. 10) and LEED.[4] The onset temperature determined here is also close to that reported previously.[4,10] On the other hand, there is clearly a change in the growth law between regions II and III but as long as the logarithmic growth is not proven in region II, an unambiguous evaluation of the data in this region cannot be pursued. The nearly linear behavior and the factor of 2 in the slope suggest a logarithmic growth law with $c=1$, as it was used for the evaluation of LEED (Ref. 4) and earlier RBS data[10] but there is no theoretical backup for this choice.[15,21] It is remarkable, however, that the present XPD data of region II and the previous LEED intensity data[4] fall into the same temperature range and that they support the identical growth kinetics. Thus the present study is fully consistent with the LEED investigation of Pb(110).

Although a logarithmic growth law with $c=1$ is not in agreement with theory, a *change* in growth kinetics with temperature is consistent with the present theoretical framework of Landau theory.[21] The growth law is obtained as a derivative of the short-range interaction between the "crystal/liquid" and the "liquid/vapor" interfaces.[4,14] This interaction energy can be viewed as a Laplace transform of $(T_m - T)$, with coefficients that are positive as well as negative. Hence, $l(T)$ need not be a monotonic function but can have inflection points.[21]

In conclusion, the present XPD results of the Pb(110) surface order–disorder transition illustrate a change in growth law near 575 K and are therefore fully consistent with the RBS investigation[3,10,18] *and* with a LEED study of the same surface.[4,11] The data for the $[1\bar{1}0]$ azimuth were evaluated with the growth law $l(T)$ on the basis of $c=0.5$, yielding an effective attenuation length of electrons. Furthermore, the present XPD study produced evidence for a (110) surface roughening transition near 360 K. Last but not least, the results presented here demonstrate the excellent utility of XPD for investigating surface structural phase transition.

We are grateful to Dr. D. A. Wesner, Dr. H. Löwen, Dr. K. C. Prince, and Dr. K. Kern for valuable discussions, to F. P. Coenen for assistance with the experimental setup, and to U. Linke for the excellent preparation of Pb single crystal.

---

[1] J. F. van der Veen, B. Pluis, and A. W. Denier van der Gon, in *Chemistry and Physics of Solid Surfaces VII*, Vol. 10 of *Springer Series in Surface Sciences*, edited by R. Vanselow and R. Howe (Springer, Berlin, 1988), p. 455.

[2] D. Nenow and A. Trayanov, Surf. Sci. **213**, 488 (1989).

[3] J. W. M. Frenken and J. F. van der Veen, Phys. Rev. Lett. **54**, 134 (1985).

[4] K. C. Prince, U. Breuer, and H. P. Bonzel, Phys. Rev. Lett. **60**, 1146 (1988); R. Lipowsky, U. Breuer, K. C. Prince, and H. P. Bonzel, *ibid.* **62**, 913 (1989).

[5] R. Trehan and C. S. Fadley, Phys. Rev. B **34**, 6784 (1986).

[6] C. S. Fadley, Prog. Surf. Sci. **16**, 275 (1985).

[7] H. C. Poon and S. Y. Tong, Phys. Rev. B **30**, 6211 (1984).

[8] M. L. Xu and M. A. van Hove, Surf. Sci. **207**, 215 (1989).

[9] H. Li and B. P. Tonner, Phys. Rev. B **37**, 3959 (1988).

[10] J. W. M. Frenken, P. M. J. Marée, and J. F. van der Veen, Phys. Rev. B **34**, 7506 (1986).

[11] U. Breuer, H. P. Bonzel, K. C. Prince, and R. Lipowsky, Surf. Sci. **223**, 258 (1989).

[12] D. A. Wesner, F. P. Coenen, and H. P. Bonzel, Phys. Rev. B **33**, 8837 (1986).

[13] J. C. Heyraud and J. J. Métois, J. Cryst. Growth **82**, 269 (1987).

[14] H. N. Yang, T. M. Lu, and G. C. Wang, Phys. Rev. Lett. **63**, 1621 (1989).

[15] R. Lipowsky, Ferroelectrics **73**, 69 (1987), and further references therein.

[16] D. Chadwick, A. B. Christie, and M. A. Karolewski, Surf. Interf. Anal. **11**, 144 (1988).

[17] P. Cadman and G. M. Gossedge, J. Electron Spectrosc. Relat. Phenom. **18**, 161 (1980).

[18] B. Pluis, T. N. Taylor, D. Frenkel, and J. F. van der Veen, Phys. Rev. B **40**, 1353 (1989).

[19] H. Löwen and T. Beier (unpublished).

[20] U. Breuer, O. Knauff, and H. P. Bonzel (unpublished).

[21] H. Löwen (private communication).