

Anisotropy of the Order-Disorder Phase Transition on the Pb(110) Surface

K. C. Prince, U. Breuer, and H. P. Bonzel

Institut für Grenzflächenforschung, Kernforschungsanlage Jülich GmbH, D-5170 Jülich, Federal Republic of Germany

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Surface premelting of lead crystals has been examined by the measurement of integrated LEED beam intensity as a function of temperature. In agreement with previous results, surface premelting on the (110) surface begins well below the bulk melting temperature. Surface premelting is anisotropic in that complete disorder is achieved at lower temperature in the $[1\bar{1}0]$ direction than in the $[001]$ direction. The interface between the ordered and fully disordered phases is atomically sharp for disorder along $[1\bar{1}0]$ but extended along $[001]$, where the substrate acts to preserve partial translational order.

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Surface melting and premelting are subjects of great current interest because of the variety of new phase-transition phenomena which are induced by the presence of the surface.¹⁻¹¹ A number of solids display such effects, including lead,⁵⁻⁷ lead-germanium interfaces,⁸ argon,⁹ germanium,¹⁰ and ice.¹¹ The terminology in this field is not standardized: In the following, we define surface melting to mean complete disordering, with a microscopic structure resembling that of the three-dimensional liquid. By premelting we mean a disordered state in which some residual order is retained.

For the study of premelting, lead is a nearly ideal substrate, because of its simple structure and low vapor pressure. Frenken and co-workers have shown using Rutherford backscattering spectroscopy (RBS) that the Pb(110) surface undergoes a disordering process which was described as complete surface melting for $T > 580$ K (Pb melts at 600.7 K). They obtained a surface melting temperature of 545 K, but they indicated that premelting phenomena became detectable at 450 K.

In this study we have applied LEED to the problem of surface melting. The results are complementary to those of RBS, because LEED investigates long-range order while RBS is sensitive to short-range correlation. LEED has the additional advantage that ordering in specific directions may be studied by the measurement of different diffraction beams, and that it is more surface sensitive than RBS. We present here results which show for the first time that surface premelting is anisotropic. While long-range order is completely lost in the (10) direction ($[1\bar{1}0]$ azimuth) at a temperature of ≈ 565 K, some residual order is retained in the (01) beam ($[001]$ azimuth) up to 590 K.

We prepared single crystals of lead by spark cutting, polishing, and sputtering with Xe, and annealing. Oxygen was the only persistent contaminant and this was removed by cycles of annealing and sputtering. Further details are given elsewhere.¹² Beam intensity, integrated typically over (1-2)% of a Brillouin zone, was measured with a spot photometer and a conventional LEED system. Bartelt, Einstein, and Roelofs¹³ have shown that

under appropriate circumstances, integrated LEED spot intensity may be used to study phase transitions at surfaces.

Figure 1 shows a set of intensity-versus-temperature curves for Pb(110), together with fitted Debye-Waller functions for the (10) and (01) beams. At lower energies, there is in general an anomaly at 540-550 K, above which the intensities decrease much more quickly than expected on the basis of Debye-Waller behavior. The intensity vanishes into the background at about 560 K for the (10) beams and is constant thereafter. For the (01) beam the intensity approaches the background more slowly and stays slightly above it, even at 590 K. In contrast to Pb(110), Pb(111) LEED beams showed no such anomaly and the intensity decreases in Debye-Waller fashion up to 590 K, the upper limit for most of our measurements.¹² This latter observation is consistent with previous LEED results,¹⁴ but the observations for Pb(110) are contradictory. The reasons for this disagreement are unknown.

To extract quantitative information from the anoma-

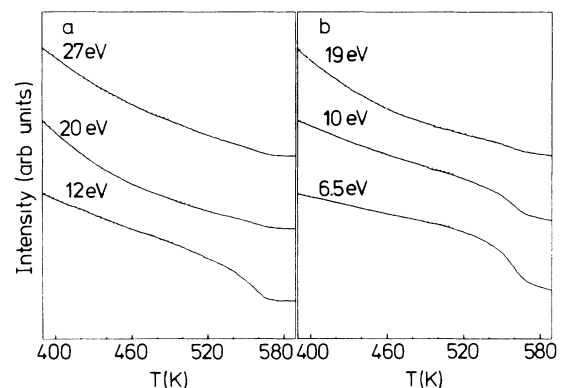


FIG. 1. Intensity vs temperature for Pb(110), together with Debye-Waller functions fitted to the lower-temperature sections of the spectra. (a) (10) beam at primary energies 12, 20, and 27 eV. (b) (01) beam at primary energies 6.5, 10, and 19 eV. For the lowest two energies, a negative bias of 12 V was applied to the sample.

lous decrease in LEED intensity, we must eliminate the influence of Debye-Waller effects and compare the result with an appropriate model. The first step is easy: We subtract the background intensity, and divide by a Debye-Waller function obtained from a least-squares fit of the low-temperature part of the data. Typical curves are shown in Fig. 2. They show constant intensity up to about 500 K, indicating a good fit, and thereafter there is a sharp decrease associated with disordering. The (10) beam is consistently lower in intensity at a given temperature than the (01) beam, indicating the anisotropy of disorder. We now wish to describe quantitatively the decrease in intensity above 500 K. Theory indicates that the thickness of the disordered layer grows logarithmically with temperature, and that the interface between the ordered and disordered phases is delocalized.² To test whether our LEED results are consistent with these predictions, we assume a simple model. The intensity contribution from depth z is equal to the square of the order parameter multiplied by $\exp(-z/\lambda \cos\theta)$, where λ is the inelastic mean free path and θ is the direction of the diffracted beam relative to the surface normal inside the solid. This is a kinematical model, although LEED at room temperature is a dynamical process, but a dynamical calculation is impossible because of the complexity of the problem.

The distance l from the surface to the substrate-disordered-phase interface grows logarithmically²:

$$l = l_0 \left| \ln \left(\frac{T_m - T}{T_m - T_0} \right) \right| = l_0 \left| \ln \left(\frac{t}{t_0} \right) \right|,$$

where l_0 is a characteristic length, T_m is the bulk melting temperature, and T_0 is a characteristic temperature identified as the temperature for the onset of surface disordering.

Two cases can be treated easily. First, if the substrate-disordered phase is localized over distances

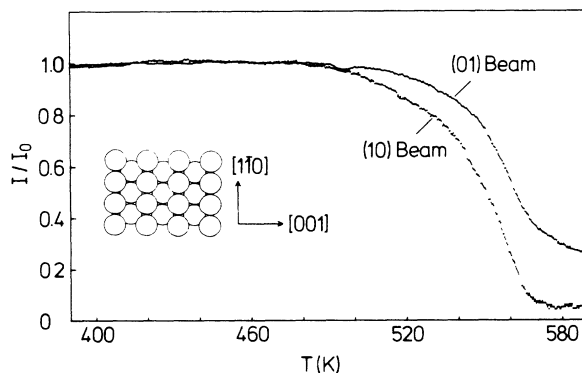


FIG. 2. Pb(110), decrease in intensity of LEED beams due to disordering. Measured intensity minus background has been divided by the Debye-Waller factor and plotted against temperature.

small compared with λ , which is comparable to the lattice parameter, the interface is atomically sharp. This type of interface resulted from calculations by Trayanov and Tosatti^{15,16} for a van der Waals solid. The order parameter in the z direction is a steplike function, and LEED intensity decays because the disordered overlayer absorbs intensity. The absorption takes place for the incoming electrons penetrating the disordered layer as well as for the outgoing diffracted electrons in the direction θ . Hence the total electron path length where attenuation is important is $l + l/\cos\theta$. The temperature-dependent intensity is then

$$I/I_0 = (t/t_0)^\alpha, \quad \alpha = (1 + \sec\theta)l_0/\lambda. \quad (1)$$

The diffraction angle θ for the (10) beam and 12.3-eV kinetic energy was calculated in the free-electron limit by the assumption of an inner potential of 10 eV. The expression is independent of the assumption of kinematical scattering.

The second case which can be treated easily is an interface which is much broader than λ . If we assume exponential decay of the order parameter in the disordered phase, with interface width s_0 , we obtain

$$I/I_0 = (t/t_0)^{2l_0/s_0}. \quad (2)$$

This result is formally similar to the case above, but the exponent is independent of λ and hence of the diffraction angle θ . If we plot the logarithm of intensity against $\ln(T_m - T)$ we should obtain a straight line whose intercept with the temperature axis is $\ln(T_m - T_0)$, from which we obtain T_0 . In one case the slope is $(1 + \sec\theta)l_0/\lambda$ and in the other $2l_0/s_0$.

A log-log plot of the corrected intensities in Fig. 2 is shown in Fig. 3. The data for the (10) and (01) beams both exhibit straight-line sections over a limited temperature range. The slopes of these sections are 4.5 and 1.7 for (10) and (01), respectively, underlining the direction-

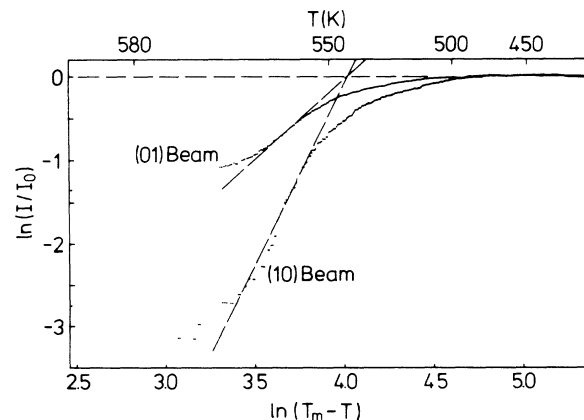


FIG. 3. Logarithm of intensity, corrected for Debye-Waller effects, vs logarithm of the melting temperature minus temperature.

al anisotropy. Extrapolation of the straight-line sections for both beams yields a critical temperature of 543 ± 3 K. This temperature agrees well with the corresponding value of 545 K obtained by Frenken, Maree, and van der Veen.⁷

Since the (10) intensity becomes indistinguishable from the background near 570 K, i.e., well below T_m , we conclude that the thickness of the interface between ordered and fully disordered Pb along this azimuth must be smaller than the maximum thickness of the disordered layer visible by the electron beam with 12-eV primary energy. Because this maximum thickness is about 2λ , and λ (12 eV) is small,¹⁷ the interface must be atomically sharp for order in the $[1\bar{1}0]$ direction. In other words, the data for the (10) beam in Fig. 3 should correspond to case (1) above, with the slope being $(1 + \sec\theta)l_0/\lambda$. Using the value of $l_0 = 6.23$ Å obtained by Frenken, Maree, and van der Veen⁷ for Pb(110) we calculate $\lambda = 3.5$ Å, which is reasonable.¹⁷ With this value of λ we estimate the thickness of the disordered layer as a function of temperature from the data of Fig. 2. This is shown in Fig. 4 and compared to the total number of disordered layers obtained in Ref. 7. The agreement is excellent. Because of the low value of λ at 12-eV primary energy, LEED is incapable of probing disordered layers thicker than about 2 monolayers at 570 K.

The (01) beam intensity in Fig. 2 does not reach the background at 590 K, a fact which indicates that for this azimuth the width of the interface must be larger than about 2λ . Hence we argue that the behavior in the $[001]$ direction is typical of case (2) above, corresponding to a delocalized interface of thickness s_0 . The slope in Fig. 3 then is equal to $2l_0/s_0$ which yields $s_0 \approx 8$ Å based on the same l_0 as before.⁷ Because λ is small at 10 eV, the upper limit of the information depth is the same as for the (10) beam. However, since the interface thickness for the (01) beam is now larger than λ , the measured intensity of this beam is not a good measure of disordering processes for thicknesses greater than about 7 Å, i.e., for $T \gtrsim 570$ K. Therefore the change in slope in Fig. 3 for

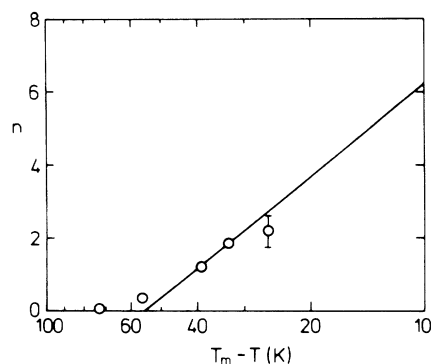


FIG. 4. Number of disordered layers vs logarithm of reduced temperature. The line taken from Ref. 7 represents the number of "molten" plus disordered layers.

the (01) beam data at higher temperatures cannot be easily evaluated.

The overall result is then a self-consistent picture of the anisotropic disordering of the Pb(110) surface. The order parameter in the $[1\bar{1}0]$ direction is characterized by an atomically sharp interface ($s_0 < \lambda$) whereas in the $[001]$ direction it is about 8 Å wide ($s_0 > \lambda$). The critical temperature of disordering for both directions is near 543 K in good agreement with the RBS study.⁷ It is reasonable that T_0 is the same for both azimuths because disordering in the two azimuths is a correlated process.

Some insight into the reason for the anisotropy of surface disordering is obtained by consideration of the solid-liquid interface. The liquid may be regarded as a randomly close-packed phase¹⁸ in which the interatomic distance is only slightly larger than in the solid. (The volume change of lead on melting is 3.5%, giving an average bond-length change of 1.2%.) Metallic bonding requires high coordination number, and to minimize interfacial free energy, this high coordination must be continued across the solid-liquid interface. This is easy for the (111)-liquid interface, which is expected to be sharp. However for the atomically "rough" (110) surface this transition is difficult. Good packing can still be achieved in the $[1\bar{1}0]$ direction, but not in the $[001]$ direction where the interatomic distance is $\sqrt{2}$ times larger than the distance of close packing. An interface with low interfacial energy is only possible if the liquid structure partly resembles that of the substrate. There is therefore a tendency for the interface to delocalize, and for order to decay slowly into the liquid in the $[001]$ direction (see, e.g., Broughton, Bonissent, and Abraham¹⁹). This description applies to the solid-liquid interface at the melting point, but the same principles apply to the premelted surface.

In conclusion, we have demonstrated the anisotropic nature of surface premelting on Pb(110). The onset temperature is in good agreement with the value obtained from RBS, and the thickness of the disordered layer is also consistent. The previous controversy between LEED and RBS results^{7,14} has been resolved.

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