X-Ray Scattering Studies of the Melting of Lead Surfaces

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We report x-ray scattering studies of liquid layers on the Pb (110) and (111) surfaces at temperatures substantially below the bulk melting point of Pb. Surprisingly, the initial liquid scattering appears at ≈ 220 K or $< \frac{1}{2} T_m$ on both the (110) and the (111) surfaces. On the (110) surface, analysis of the scattered intensity yields 2–3 monolayers of liquid from 575 to 599 K while substantially less than 1 monolayer of liquid is present on the (111) surface.

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Of fundamental importance in the understanding of melting of three-dimensional crystals is the simple question: Do surfaces melt at a lower temperature than the bulk equilibrium melting temperature (T_m)? The presence of surface melting at low temperatures (premelting) has been invoked to explain the lack of superheating during melting and is consistent with simple intuition regarding vibrations at surfaces. A wide range of theoretical[1,2] and molecular dynamics simulations[3] have predicted that surfaces do, in fact, melt below T_m.

Experimentally, there is evidence of premelting of adsorbed gases on graphite surfaces from heat-capacity measurements.[4] Premelting of Ge(111) surfaces has been postulated from an anomalous attenuation of low-energy electron-diffraction peaks from the crystal lattice.[5] Lastly, ion-channeling results suggest that the Pb(110) surface melts at up to 50 K below the Pb melting temperature of 600 K and that up to 20 molten layers are present on the surface at temperatures very close to the melting temperature.[6,7]

In this Letter, we report an x-ray scattering experiment that has directly measured liquid correlations on Pb(110) and Pb(111) surfaces. The results of this experiment both conflict with the earlier measurements of melting on the Pb(110) surface and indicate that initial stages of premelting may occur at very low temperatures ($< \frac{1}{2} T_m$).

The Pb samples used for this experiment were cut from commercially produced 13-mm-diam, 25-mm-long single crystals by spark cutting 10-mm-long right cylinders. The surfaces of these cylinders were oriented to within 0.1° of the crystallographic planes by repeated polishing in acetic acid and hydrogen peroxide and subsequent x-ray alignment. After alignment of the surfaces, they were mechanically polished flat with 0.3-μm alumina and then lightly etched to remove the damaged layer. This process left a highly reflective surface which had a macroscopic figure error of 10 mrad, full width.

The samples were subsequently cleaned in ultrahigh vacuum by repeated sputtering and annealing at 523 K (the chamber had a base pressure of $\approx 1 \times 10^{-9}$ Torr and a maximum pressure of $\approx 5 \times 10^{-9}$ Torr with the sample at 600 K). The surface composition was checked with Auger analysis and insignificant contamination was found over the course of our measurements.

During the experiment, the temperature was controlled by our heating the sample holder to a fixed temperature and allowing the entire system to come to thermal equilibrium. The thermocouples were calibrated (*in situ*) with an ice bath and boiling water, and, at the conclusion of the experiment, by the melting of a polycrystalline Pb cylinder of the same size as the single-crystal samples. This procedure gave an estimated absolute accuracy of ±0.25 K.

Our experiments were performed in the grazing-incidence x-ray scattering geometry.[8] With this geometry, x rays impinge on the surface at a grazing angle (ϕ) and are observed at a second grazing angle (ϕ'). In order to illuminate the entire surface, a grazing angle of 5 mrad was chosen. Hence, these measurements have been performed with a depth sensitivity of ≈ 350 Å (primarily limited by absorption) although a reflected x-ray beam was observed and monitored throughout the experiment to ensure maximum surface sensitivity.

These experiments were performed on beam line X16A at the National Synchrotron Light Source with a UHV diffractometer. Both of these instruments are described elsewhere.[9,10] X16A produces a 1-mm-diam spot containing $\approx 5 \times 10^{10}$ photons/sec at 9500 eV with a stored current of 100 mA. With a grazing angle of ≈ 5 mrad, the sample has a projection of 0.05 mm and 5% of those photons are intercepted. We estimated the scattering from 1 monolayer of Pb liquid by looking at the scattering from a 200-Å-thick amorphous $GeSe_2$ layer under identical experimental conditions. The measured rate of scattering from this film was ≈ 410 photons/sec.

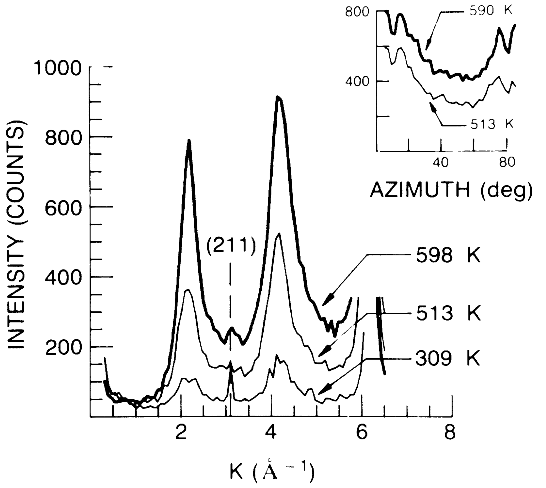

FIG. 1. X-ray scans along the Pb($1\bar{1}2$) azimuth for various temperatures. Inset: Azimuthal scans through 2.05 Å^{-1} for the highest and lowest temperatures. Note the disappearance of the ($1\bar{1}2$) peak at 3.05 Å^{-1} and the strong increase in diffuse scattering.

Given the differences in atomic scattering factor and film thicknesses, we estimate that a single liquid layer of Pb should scatter ≈ 32 photons/sec into our detecting aperture.

Figure 1 shows radial scans along the ($1\bar{1}2$) azimuth from the Pb(110) surface for various temperatures. As is clearly seen, a strong diffuse component appears at momentum transfers [$k = 4\pi \sin(\theta)/\lambda$] of 2 and 4 Å^{-1} as the temperature is increased from 308 to 597 K. Azimuthal scans (rotation about the surface normal at constant momentum transfer) are shown in the inset and demonstrate that these peaks in the diffuse spectrum are also rotationally diffuse. Unlike a three-dimensional liquid, there is a weak orientational dependence to the peak of the structure factor at 2 Å^{-1}. We emphasize that these are rings in reciprocal space (i.e., the peak intensity is at a constant radial momentum transfer) and are not diffuse streaks connecting Bragg points.

The sharp feature at 3.05 Å^{-1} which disappears with increasing temperature is a ($1\bar{1}2$) "forbidden reflection." Such reflections are generated by the surface discontinuity of the crystal and are strongest for flat, abrupt interfaces.[11] The disappearance of this reflection with increasing temperature suggests that the surface is roughening.[12] In addition, weak superlattice peaks were present near room temperature and disappeared with increasing temperature. Similar features have recently been associated with the presence of an ordered array of atomic steps and used to study the roughening of Cu surfaces.[13] The diffuse scattering in Fig. 1 is not centered on simple multiples of the underlying crystal and has the form of rings in reciprocal space. Hence, it is not directly coupled to the roughening of the surface.

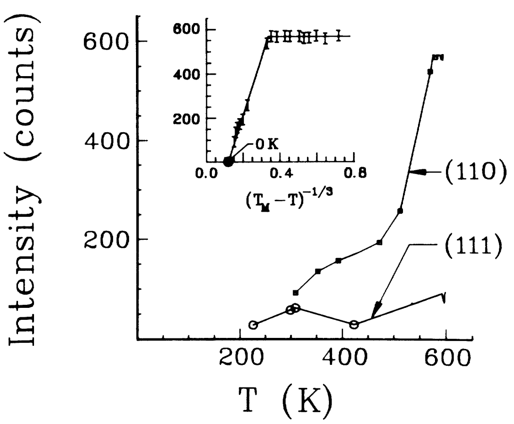

FIG. 2. Integrated intensity of the diffuse peak at 2.05 Å^{-1} as a function of temperature for the Pb(110) surface (squares) and the Pb(111) surface (circles). The (111) datum point at 410 K may be anomalously low because of unusual storage-ring conditions. Inset: (110) data replotted as a function of $(T_m - T)^{-1/3}$.

Figure 2 shows the integrated intensity of the 2-Å^{-1} peak as a function of temperature. This integrated density was calculated by our fitting the peak at each temperature with a Lorentzian line shape and a constant background. Because the azimuthal dependence of the peak intensity did not significantly vary with temperature, it was not included in the integration. At low temperature, these data exhibit a linear slope which, if extrapolated, intersects zero at ≈ 220 K. Above 500 K, there is a sharp increase in the diffuse scattering until a pla-

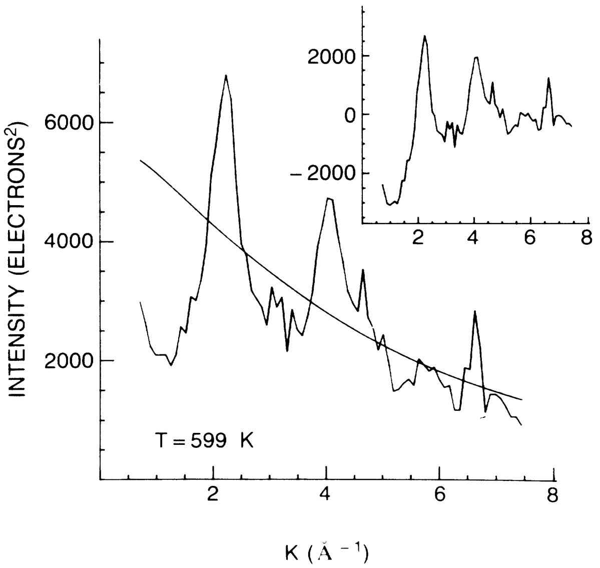

FIG. 3. Normalized scattering from the Pb(111) surface, the calculated independent scattering, and the reduced scattering (inset). The normalization was performed with standard radial distribution function techniques.

teau is reached at 568 K. The inset in Fig. 2 recasts the data with a predicted $(T_m - T)^{-1/3}$ dependence.[2] At low temperatures, an overall $(T_m - T)^{-1/3}$ dependence is found which linearly extrapolates to zero intensity at 0 K. At high temperatures, a temperature-independent region is found which extends to the maximum temperature measured ($\approx 1°$ below T_m). These intensities were reversible and reproducible from two different samples.

The average scattering intensity from the (110) surface (at 599 K) is ≈ 100 photons/sec and corresponds to ≈ 3 layers of liquid on the surface. There is substantial uncertainty in this number within a range of 1 to 4 monolayers. This uncertainty comes from (in order of declining importance) (1) uncertainty in the exact structure factors of the 2D liquid, (2) subtraction of substrate contributions, and (3) calibration of the absolute scattering rate.

Figure 3 shows the scattering at 599 K from the Pb(111) surface. These data were obtained with a 2θ scan at constant θ. The θ value was chosen such that the crystal was rotated 30° from the $(2\bar{2}0)$ setting. These data clearly show that a liquidlike scattering is produced from the Pb(111) surface at temperatures below the bulk melting temperature. The scattering rate from this surface (shown in Fig. 2 as a function of temperature) is an order of magnitude weaker than that from the (110) surface and yields an estimate of $< \frac{1}{2}$ monolayer of liquid at 1° below the melting temperature.

We have analyzed these data in more detail using standard radial distribution function techniques. In the analysis of three-dimensional liquids, correlation functions are related to the normalized intensity by the relationship[14]

$$I(k) = Nf^2 + Nf^2 \int_{r=0}^{\infty} 4\pi r^2 [\rho(r) - \rho_0][\sin(kr)/kr]\,dr, \tag{1}$$

where $\rho(r)$ is the density of atoms at a distance r, ρ_0 is the average density of atoms, and N is the total number of atoms. However, for the case of two-dimensional liquids, the scattering should be more closely related to[15]

$$I(k_R,k_z) = Nf^2 + 2\pi N f^2 \int_{z_{\min}}^{z_{\max}} \int_0^{\infty} [\Gamma(R,z) - \Gamma_0] J_0(k_R R) e^{ik_z z} R\,dR\,dz, \tag{2}$$

where k_R and k_z are the momentum transfers parallel and perpendicular to the surface, $\Gamma(R,z)$ is the average density per unit area, Γ_0 is the average number of atoms per unit area, and $J_0(x)$ is the zero-order Bessel function.

Also in Fig. 3 is a fit to the independent scattering and, in the inset, the reduced scattering. To this point, standard three-dimensional techniques work remarkably well. However, calculation of a spherical radial distribution function from this scattering pattern results in distribution functions which are strongly negative and hence quite unphysical (Fig. 4). (The shaded regions indicate negative density.) In contrast, a Bessel-function transform yields a very physical $\Gamma(R)$ with a sharp peak at 3.05 Å and a distribution which rapidly approaches the average density. The area of this peak is consistent with a sixfold-coordinated liquid. In addition, the peak at 1.8 Å is consistent with the projected atomic positions of correlated 2D liquid layers. The data from the (110) surface were acquired along high-symmetry directions and substrate contributions preclude a similar real-space analysis.

Our results from the (110) surface differ substantially from those of Frenken *et al.* In particular, their ion-channeling results yield a rapidly increasing thickness for the liquid layer near T_m and a liquid thickness of ≈ 10 layers at 599 K. In addition, they report no indication of a liquid layer below $\frac{3}{4} T_m$, while we see an appreciable signal at much lower temperatures. On the other hand, their reflection high-energy electron-diffraction results suggest that 3 liquid layers are present at 565 K and that result is in agreement with our results. Our results for the Pb(111) surface are in essential agreement with those of Frenken *et al.* in that less than a monolayer of liquid is present at temperatures very close to T_m.

It is difficult to reconcile the differences between our results and those of Frenken *et al.*, but two possibilities

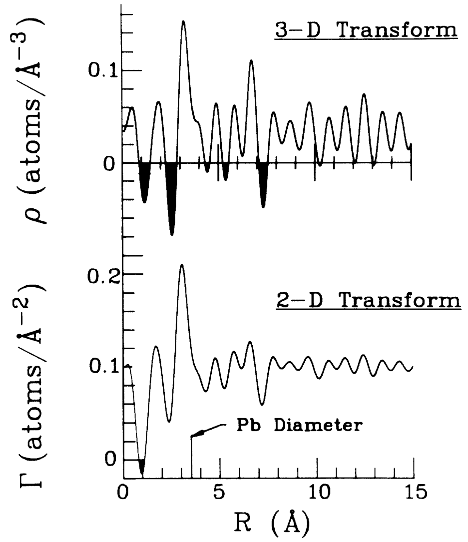

FIG. 4. Real-space distribution functions calculated from the normalized scattering in Fig. 3 with use of a three-dimensional transform [see Eq. (1)] and a two-dimensional transform [see Eq. (2)]. The shaded areas of the distributions indicate areas of negative atomic density.

should be mentioned. First, the surface sensitivity quoted earlier is calculated with a conservative algorithm. In the most favorable case, the x-ray penetration depth could be as short as 20 Å and would result in a saturation of the intensity if the liquid thickness exceeded this depth. Calculations demonstrate that this effect cannot be the sole source of the discrepancy. Second, there is an implicit assumption in our analysis that the intensity of scattering is directly proportional to the thickness of the liquid layer, i.e., the structure factor is thickness independent. While this is experimentally verified for the in-plane component of the structure, a highly correlated liquid might have significant variations along the surface normal.

In summary, we observe diffuse scattering from liquid layers on the Pb (110) and (111) surfaces at temperatures substantially below the bulk melting point of Pb. Surprisingly, liquid scattering is observed at $< \frac{1}{2} T_m$ on both the (110) (at 300 K) and the (111) (at 210 K) surfaces. On the (110) surface, analysis of the scattered intensity yields 2–3 monolayers of liquid from 575 to 599 K, while substantially less than 1 monolayer of liquid is present on the (111) surface. The overall trend of the (110) data at low temperature agrees with a scaling proportional to $[(T_m - T)/T_m]^{-1/3}$ but the intensity is constant above 575 K. In addition, the plateaus in the scattered intensity suggest layer-by-layer melting at low temperature. From the presence of ordered steps on the Pb(110) surface and from the similarity of the low-temperature behavior between the (110) and (111) surfaces, we speculate that steps may be the source of the initial liquid fraction on these surfaces and propose that a future experiment measure the liquid fraction as a function of step density.

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