

## Observation of Surface Melting

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Ion shadowing and blocking measurements show that the solid-liquid transition at the (110) surface of lead starts at approximately 40 K below the bulk melting point of lead  $T_m$ . The thickness of the liquid surface film increases dramatically as the temperature approaches  $T_m$ .

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Melting is one of the best known phase transitions. For many physical properties of materials the changes upon melting are well understood. Yet the detailed description of the solid-liquid transition on an atomic scale is still a matter of considerable debate. One of the mysteries connected with melting is that under normal conditions superheating of a solid above its melting point is not observed,<sup>1</sup> whereas undercooling of liquids is. A possible explanation for this is that the surface of a solid might already liquify below the bulk melting temperature  $T_m$ . As early as 1910 Lindemann<sup>2</sup> made the observation that a solid melts when the vibration amplitude of its atoms reaches a critical fraction ( $\sim 10\%$ ) of the nearest-neighbor distance. This could imply that for surface atoms, as they have a higher vibration amplitude than bulk atoms,<sup>3</sup> the melting condition is met at a temperature below the bulk melting point. At  $T_m$  the wet surface would then be a vast nucleation center for bulk melting, and superheating would be precluded. Recent theoretical studies<sup>4</sup> and computer experiments<sup>5</sup> have indeed indicated a surface-melting-point depression, but laboratory experiments on real crystals have so far been inconclusive.<sup>6</sup>

In this Letter we report the first direct observation of a reversible melting transition of the surface of a three-dimensional crystal. Temperature-dependent ion-scattering measurements on an atomically clean Pb(110) surface reveal the presence of a liquid surface film on top of, and in equilibrium with, a well ordered substrate. Surface melting is preceded by a gradual disordering of the surface region (premelting).

The Pb specimen was spark cut from a single-crystal lead bar. Chemical polishing produced a mirrorlike surface, which was cleaned in ultrahigh vacuum by cycles of argon-ion bombardment and annealing ( $\sim 1$  h at 590 K), until no impurities were detected with Auger-electron spectroscopy, and the surface was well ordered as seen with both LEED and ion channeling. During the measurements the sample temperature was continuously monitored by a thermocouple and an infrared pyrometer which was carefully calibrated against the bulk melting point of lead. The accuracy of this calibration is estimated to be  $\pm 0.5$  K. The sample was heated by electron bombardment of the back side of

the sample container. The temperature could be stabilized within  $\pm 0.3$  K.

A parallel 97.5-keV proton beam was aligned with the  $[101]$  axis of the lead crystal. In an ideal static lattice, shadowing would completely protect second and deeper layer atoms from being hit by protons [Fig. 1(a)]. Because of thermal vibrations, near-surface atoms also obtain nonzero (but still strongly reduced) hitting probabilities. An electrostatic energy analyzer was used to detect backscattered protons emerging from the crystal parallel to the  $[011]$  axis. Blocking of backscattered protons along this direction further reduces the backscattering yield from subsurface atoms. An energy spectrum [Fig. 1(a)] therefore consists of a peak containing the signal from the exposed surface layers, and a low minimum yield from the small nonshadowed, nonblocked fraction of deeper layers, appearing at lower energies because of the stopping of protons in the solid. If the crystal is covered by a liquid film, coherent shadowing and blocking only occurs below the liquid-crystal interface [Fig. 1(b)]. All atoms in the liquid film fully contribute to the surface signal, thereby increasing the area and width of

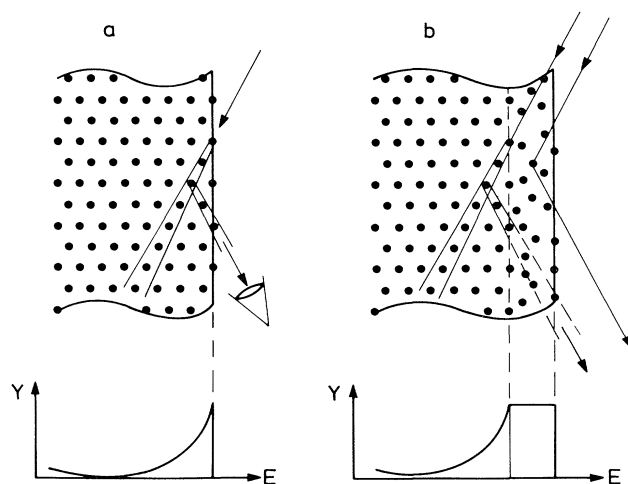


FIG. 1. Energy spectra obtained in shadowing, blocking geometry for (a) a well-ordered crystal surface and (b) a crystal covered by a liquid surface film.

the surface peak (SP). The high energy resolution of our energy analyzer enables us to detect such changes in the SP width on a monolayer scale. The measured resolution function of our analyzer is approximately Gaussian with a full width at half maximum of  $\delta E = 4 \times 10^{-3} E$ , where  $E$  is the ion energy. In the present experiment  $\delta E = 390$  eV. Taking a random stopping power of  $S = 13.7$  eV/Å path length<sup>7</sup> we obtain a depth resolution (full width at half maximum) of 7.1 Å or 4.1 monolayers. An absolute calibration<sup>3</sup> ( $\pm 5\%$ ) converts the SP area into the number of lead monolayers visible to the ion beam and the detector.

Figure 2 displays a selection of measured energy spectra. Up to 500 K the SP shows only a modest increase in area and width, after which it grows spectacularly up to  $T_m$  ( $T_m = 600.7$  K). Just above  $T_m$  the energy spectrum shows absolutely no shadowing or blocking, as is expected for a bulk liquid. The temperature dependence of the number of visible lead layers calculated from the SP area has been plotted in Fig. 3. The reversibility of this dependence was checked up to 595 K. Apart from an almost linear behavior up to 500 K and a strong increase above this temperature, Fig. 3 also reveals a discontinuity in slope near 560 K. Though this feature may seem only very weak it is also present for other experimental quantities, e.g., the SP area for other detection angles and the minimum yield behind the SP.

The interpretation of these results will be presented in two steps. We will first show that the high-temperature SP areas can only be explained by a molten surface. From the SP shape we will then deduce that surface melting already starts at 560 K.

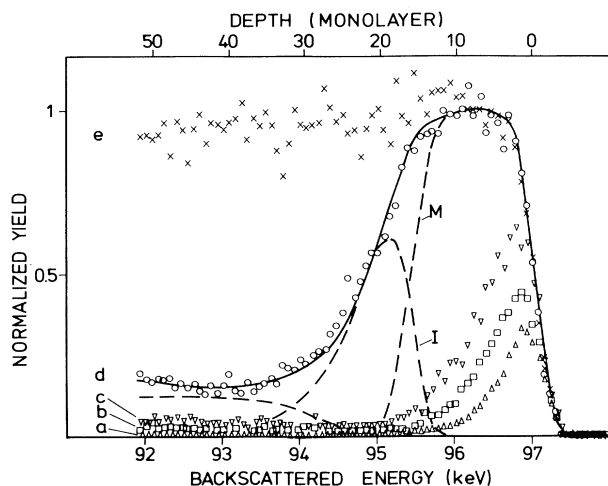


FIG. 2. Experimental energy spectra calibrated with respect to the random height: curve *a*, 295 K; curve *b*, 506 K; curve *c*, 561 K; curve *d*, 600.5 K; and curve *e*, 600.8 K. The fit to spectrum *d* with contributions *M* and *I* is discussed in the text.

A Monte Carlo computer simulation of the experiment was performed to determine which surface structure could be responsible for the large number of visible lead layers near  $T_m$ . In these calculations typically  $10^5$  ion tracks through a slab of forty atomic layers were constructed (with use of a Molière scattering potential), along which the hitting (detection) probability of each layer was collected by the nuclear-encounter probability method.<sup>8</sup> Lattice vibrations were modeled by Gaussian probability densities<sup>9,10</sup> of the atoms around their equilibrium positions (quasi-harmonic approximation<sup>11</sup>). The bulk thermal-vibration amplitude  $\sigma_b$  (defined as the one-dimensional rms thermal displacement of bulk lead atoms) varies smoothly from 0.18 Å at room temperature to 0.28 Å just below  $T_m$ .<sup>11</sup> This causes the SP area calculated for a bulklike solid surface to follow curve I in Fig. 3. Curve II is obtained by also accounting for enhanced surface-vibration amplitudes and relaxations of the first two interlayer distances.<sup>3</sup> At 500 K the measured SP areas already exceed those in curve II. At 600.5 K the discrepancy amounts to as much as 20 extra visible lead layers. This large difference cannot be overcome by simply raising  $\sigma_b$  in the simulation. The necessary  $\sigma_b$  would be unrealistically high ( $\sim 1$  Å), the SP in the resulting energy spectrum would not reach the random height, and the minimum yield would be over 60% in contrast to the observed 15%. The only way to make the simulation fit the high-temperature SP area, SP height, and minimum yield is to keep  $\sigma_b$  at 0.28 Å and to have at least 15 layers of disorderly positioned (fully visible) lead atoms covering the surface. The observa-

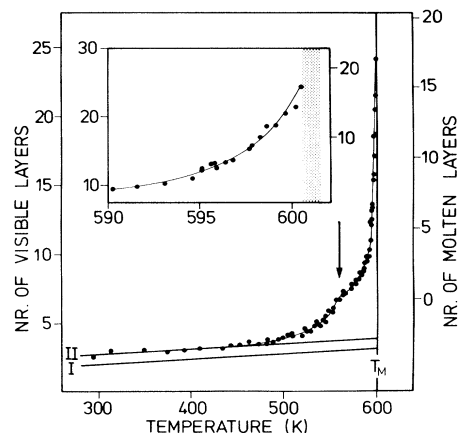


FIG. 3. Calibrated surface-peak area as a function of temperature. The vertical line indicates the bulk melting point  $T_m$ . The inset is an expanded view of the highest 10-K interval. The shaded band therein corresponds to the calibration uncertainty in  $T_m$ . The arrow indicates the surface melting point. Curves I and II and the right-hand vertical axis are discussed in the text.

tion of LEED spots from Pb(110) up to the very melting point by Goodman and Somorjai<sup>6</sup> has been interpreted by these authors as evidence against the presence of a liquid surface film. The information in their paper is too limited to decide whether or not they could actually have observed diffraction features from the substrate, strongly reduced in intensity by the liquid overlayer.<sup>6</sup>

SP shapes were used to determine the surface melting temperature  $T_s$ . If the difference between the energy spectrum at  $T_s$  and each of the higher-temperature spectra is completely caused by an additional number of liquid layers at high temperatures, it should be possible to construct all high-temperature spectra by addition of a liquid film spectrum to an accordingly energy-shifted copy of the spectrum at  $T_s$  ("interface peak"), as shown in Fig. 1(b). Of course each energy spectrum above  $T_s$  would do equally well as interface spectrum, all differences between spectra above  $T_s$  being the result of differences in melt depth. So  $T_s$  is the lowest temperature for which adding liquid-film spectra should result in good fits to higher-temperature spectra. The outlined procedure works remarkably well with use of the spectra down to about 560 K as interface spectrum, and starts to fail below this temperature. We therefore identify  $\sim 560$  K as the surface melting point of Pb(110). The fit to spectrum *d* in Fig. 2 has been produced by addition of the calculated signal (*M*) from 16.5 molten lead layers (including the multiple-scattering contribution at lower energies caused by this liquid film) to a shifted copy (*I*) of spectrum *c* (561 K). Melt depths obtained in this way are indicated on the right-hand vertical axis of Fig. 3.

Figure 3 shows that at 560 K the SP area already exceeds the value from curve II by 3 monolayers of lead atoms. As we stated above these atoms are not contained in a liquid overlayer. Again the SP shape was used to determine the nature of these extra visible atoms. For 97.5-keV protons the energy loss observed along the  $\langle 110 \rangle$  rows of a well-ordered lead crystal is enhanced by a factor of  $\sim 3.5$  over the random stopping power<sup>7</sup> (a detailed account of this observation will be given in a later publication). The width and height of the SP are therefore very sensitive to the order in the surface region contributing to the SP. From the SP shape we have determined the enhanced stopping power to remain constant up to about 500 K, after which it gradually reduces to the random value, having an intermediate value at 560 K. This indicates that the extra atoms becoming visible between 500 and 560 K are positioned far out from the  $\langle 110 \rangle$  rows. As they are not forming a liquid overlayer these disorderly positioned atoms are necessarily distributed over a certain depth interval, and form a transition layer which could be described either as a defected crystalline layer

(e.g., dislocations, interstitials, etc.) or as a partially ordered liquid film.<sup>5</sup>

We now propose the following model for surface melting. Below 500 K the Pb(110) surface is perfectly ordered. Above this temperature a transition layer is formed with the characteristics of a defected solid or a partially ordered liquid, resulting in 3 additionally visible lead monolayers at 560 K. Above 560 K this transition layer becomes buried under a liquid surface film. As the temperature is further raised towards  $T_m$ , transition layer and melt front continuously progress into the bulk.

Our experimental findings are in qualitative agreement with recent theoretical predictions. Using Landau theory of phase transitions, Lipowsky and Speth<sup>12</sup> have argued that a semi-infinite system undergoing a first-order transition in the bulk may exhibit critical behavior at its surface, i.e., surface quantities behave continuously although bulk quantities are discontinuous. This theory, when applied to melting, predicts the liquid film thickness *l* to diverge as  $l = l_0 \times \ln[T_0/(T_m - T)]$ , with constants  $l_0$  and  $T_0$ , as  $T_m$  is approached from below. Within the accuracy of our temperature calibration our data are consistent with such behavior.

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<sup>5</sup>J. K. Kristensen and R. M. J. Cotterill, *Philos. Mag.* **36**, 437 (1977); J. Q. Broughton and L. V. Woodcock, *J. Phys. C* **11**, 2743 (1978); J. Q. Broughton and G. H. Gilmer, *J. Chem. Phys.* **79**, 5105 (1983), and *J. Chem. Phys.* **79**, 5119 (1983). Preliminary molecular-dynamics simulations of surface melting of simple metals with use of pair potentials obtained from pseudopotential theory, volume energy, and single-ionic contributions indicate the occurrence of surface premelting in the form of 1 to 3 disordered layers, which, at

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<sup>7</sup>H. H. Andersen and J. F. Ziegler, *The Stopping and Ranges of Ions in Matter* (Pergamon, New York, 1977), Vol. 3.

<sup>8</sup>J. H. Barrett, *Phys. Rev. B* **3**, 1527 (1971).

<sup>9</sup>The choice of non-Gaussian probability distributions

would not affect our conclusions.

<sup>10</sup>Correlated vibrations were not considered in the simulations, as they would not seriously alter the results.

<sup>11</sup>E. V. Zaroquentsev, S. P. Kravchuk, and T. M. Tarusina, *Fiz. Tverd. Tela (Leningrad)* **18**, 413 (1976) [*Sov. Phys. Solid State* **18**, 239 (1976)], and references therein. An independent determination of  $\sigma_b$  from the width of measured bulk blocking minima confirms these results.

<sup>12</sup>R. Lipowsky, *Phys. Rev. Lett.* **49**, 1575 (1982); R. Lipowsky and W. Speth, *Phys. Rev. B* **28**, 3983 (1983).