X-Ray Diffraction Studies: Melting of Pb Monolayers on Cu(110) Surfaces

W. C. Marra,(a) P. H. Fuoss,(a) and P. E. Eisenberger(b)
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 26 March 1982)

This x-ray scattering study of the melting of a monolayer of Pb on the Cu(110) surface reveals an irreversible commensurate-to-incommensurate transition and an anisotropic reversible incommensurate melting transition. This study demonstrates the impressive capabilities of surface x-ray diffraction techniques since (1) kinematic theory can be used to interpret the results, (2) correlation lengths of >1000 Å are easily measured, and (3) high counting rates (>50 000 cps) were measured from a monolayer of Pb.

PACS numbers: 64.70.Dv, 68.20.+t

We report an x-ray study of the solid-liquid phase transition of Pb monolayers on a Cu(110) surface. The experimental technique used was first reported by Eisenberger and Marra.[1,2] In this work, high-resolution x-ray studies revealed melting behavior that was qualitatively the same as that determined by the low-energy electron-diffraction (LEED) studies of Henrion and Rhead (HR).[3] However, our results are quantitatively different and more detailed. Some features of the dislocation mediated melting (DMM) theory[4,5] are consistent with our observations.

The as-deposited Pb films formed a commensurate $p(5\times1)$ structure as reported by HR. After melting and resolidification of the Pb monolayer an incommensurate structure was formed. Commensurate-incommensurate transitions have been the subject of considerable theoretical and experimental study.[6-9] However, this phase transition is qualitatively different since it is a kinetic transition, i.e., not a reversible thermodynamic phase transition, that occurs because of the deposition process. The resulting reversible incommensurate melting transition was studied in detail.

The experiments were performed at the Stanford Synchrotron Radiation Laboratory with $\lambda=1.54$ Å x rays from a focused wiggler source.[2] A 0.07° Soller collimator was used to analyze the diffracted beam. This angular resolution was an order of magnitude sharper than the narrowest Pb reflection. A 1° grazing angle of incidence was used relative to the crystal surface for the diffraction studies. The experiments were performed in the UHV system described by Marra[2] (base pressure 5×10^{-10} Torr). The temperature was controlled to ± 1.5 °C by two type-*J* thermocouples mounted on the sides of the Cu substrate.

The Cu substrate was spark cut and mechanically polished to within 1° of the [1$\bar{1}$0] axis and then electropolished. The substrate was cleaned (by cycles of argon ion sputtering and annealing at 700 °C) until no contaminants were revealed in the Auger spectra. LEED analysis showed that Pb deposited at 120 °C formed a commensurate $p(5\times1)$ structure with 5 times the Cu periodicity along the [110] direction (see Fig. 1). Before the performing of x-ray studies, the ratio of the Cu (60 eV) to Pb (93 eV) Auger peaks was studied over the temperature range of the experiment. The 3-to-1 ratio of the Auger peaks (a monolayer) was unchanged to ± 2% indicating that the x-ray diffraction could be performed at constant coverage.

Data were obtained by the performing of longitudinal x-ray scans along the Cu[110] and transversely along the [001] directions (see Fig. 1). These intensity profiles provided detailed information on the density fluctuations in each direction.[10] The initial x-ray study revealed a room-temperature structure which agreed with LEED results, i.e., a commensurate $p(5\times1)$ Pb overlayer. The peak in Fig. 2(a) at 1.966 Å^{-1} transforms to $\frac{5}{4}$ of the Cu(110) spacing. If the Pb layer were placed on a substrate with smooth troughs

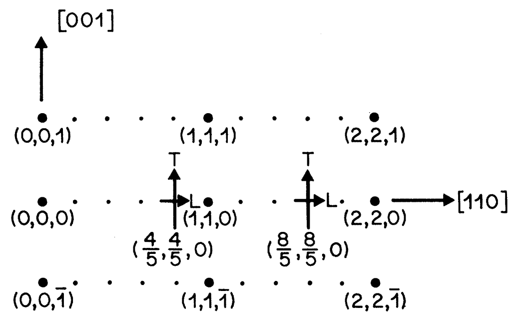

FIG. 1. The two-dimensional reciprocal space of the commensurate $p(5\times1)$ overlayer (Cu, Pb). Detailed studies of the $(\frac{4}{5},\frac{4}{5},0)$ and $(\frac{8}{5},\frac{8}{5},0)$ reflections and the corresponding incommensurate reflections were made with use of longitudinal (L) and transverse (T) scans.

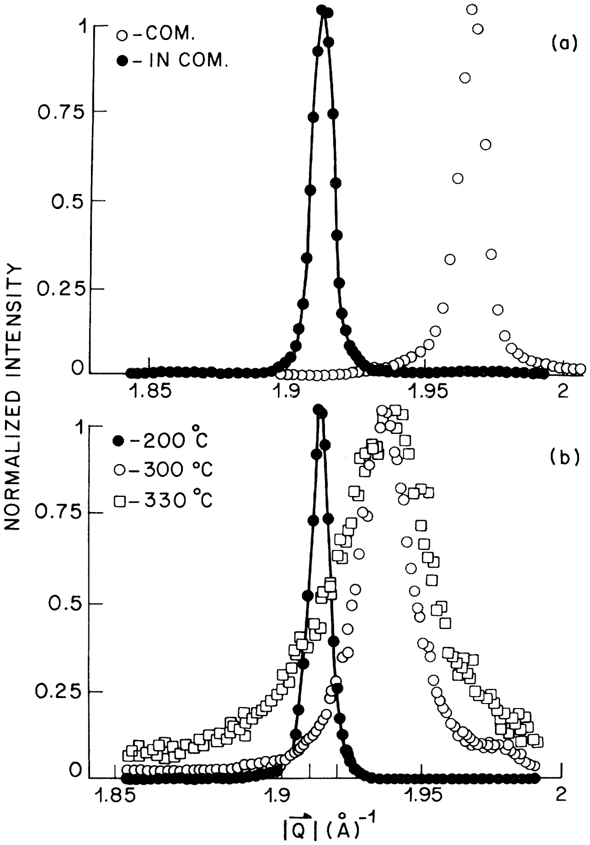

FIG. 2. FOR (top) of the commensurate (open circles) and incommensurate (filled circles) solid. FOR's (bottom) as a function of temperature showing the changing line shapes as the solid melts.

along [110] we would expect peaks at 1.795 Å^{-1} (corresponding to the nearest-neighbor spacing for bulk Pb) and its harmonics. Since the substrate makes a small perturbation along [110], the peak at 1.966 Å^{-1} is the strongest superlattice peak because it corresponds to this near-neighbor spacing. The line shape in Fig. 2(a) is not the Gaussian expected from infinite long-range order. This result is consistent with the Frank and Van Der Merwe[11] (FV) growth mechanism discussed below.

Upon heating, this structure melted at 320 °C. When cooled an incommensurate structure formed which exhibited reversible melting at 240 °C. In Fig. 2(a) are x-ray data taken on this incommensurate structure at 200 °C. The peak intensity corresponds to 50 000 cps and the width to correlation lengths of ~ 1000 Å. This counting rate is two orders of magnitude higher than predicted by a Z^2 extrapolation of our synchrotron studies of the Ge[001]2×1 surface.[12] This is due to the long correlation lengths for the Pb and Cu(110).

FV suggested that, depending upon the lattice misfit between the monolayer and substrate, a metastable commensurate monolayer can be deposited at low temperature. However, this metastable state can be destroyed by heating the crystal to overcome the activation barrier for generating dislocations and forming the incommensurate structure. Figure 2(a) reveals a broader commensurate-solid diffraction peak than for the incommensurate solid. This is consistent with the formation of islands in the commensurate structure whose registry with the substrate depends on the choice of five sites which would limit island size.

We fitted the experimental line shapes by the follow function:

$$I(q) = \alpha H(Q) + \beta L(Q) + C, \tag{1}$$

where α and β are variable coefficients, $H(Q)$ and $L(Q)$ are the solid (low temperature) and liquid (high temperature) line shapes, Q is the momentum transfer, and C is an experimentally determined background. The commensurate-solid line shape along [001] was a Gaussian. The incommensurate solid has a Lorentzian squared line shape along [110] and a Gaussian line shape along [001]. The Gaussian line shape along [001] indicated that the monolayer was commensurate in that direction. The liquid had Lorentzian line shapes for scans along both [110] and [001].

In Fig. 2(b) are [110] scans taken at 200, 300, and 330 °C on the incommensurate phase. As the temperature is increased the peaks broaden (indicating shorter correlation lengths) and move towards higher Q. The shift towards higher Q is surprising because it implies a contraction of the monolayer upon melting. However, in domain-wall models of the incommensurate phase[9] the structure consists of commensurate regions separated by domain walls at regular intervals. In the DMM theory[5] regions smaller than the correlation length retain solidlike properties in the liquid phase. Thus, a shift of the structure towards commensurability in the liquid phase is consistent with current theories.

Two effects should be noted. First, the transition from a Gaussian line shape to a Lorentzian line shape along [001] occurs at the same temperature as melting along [110]. However, the correlation length along [001] does not change until ~ 340 °C. This is consistent with the results of HR and indicates that the melting is an anisotropic two-dimensional phase transition. Second, in Fig. 2(b), at 300 °C a satellite peak appears at 1.978 Å^{-1}. As the temperature is increased to 330 °C, this peak seems to be fading (although it is difficult to resolve from the broadening main peak). This satellite peak may be due to domain-wall interactions.[9,13]

Figure 3 shows the change in peak intensity (I_p) versus temperature for the (1.566, 1.566) superlattice reflection (room-temperature wave vectors). This second-order reflection (SOR) and the first-order superlattice peak (FOR) at (0.777, 0.777) were studied in detail. Data on I_p versus temperature show that a phase transition occurs near 240 °C. Figure 3 also shows the concentration of liquid scattering versus temperature as derived from our line shape analysis with the normalization

$$\int \alpha S(q) dq + \int \beta L(q) dq = 1. \qquad (2)$$

Clearly above 260 °C the system is liquidlike, well below the bulk Pb melting temperature of 327 °C. The shift in melting temperature from the as-deposited commensurate solid (320 °C) to the incommensurate melting temperature (240 °C) may be due to a lower entropy of the incommensurate solid.

Similar results were obtained for the first-order reflection but the transition is ~ 10 °C broader. These results appear to be characteristic of a second-order-phase transition. However, a first-order transition broadened by sample inhomogenities could explain these results since scanning electron micrographs revealed roughness on the 2000-Å scale over a significant portion of the surface.

DMM theories[4,5] predict that the peak value of the structure factor,[14] $S(0)$, for the liquid phase is

$$\ln[S(0)] \propto (2 - \eta_G)\ln(\xi), \qquad (3)$$

where ξ is the correlation length (in this case proportional to $1/\Delta Q$, where ΔQ is the half width at half maximum of the peaks). In Fig. 4 we have evaluated the slope $2 - \eta_G$ above 263 °C. The FOR yields $\eta_1 = 0.356 \pm 0.1$ and the SOR yields $\eta_2 = 1.264 \pm 0.3$. Nelson and Halperin[4] have shown that η_G is proportional to $|\vec{G}|^2$ where $\vec{G}$ is a reciprocal-lattic vector.

In summary, our results show that a nonequilibrium commensurate monolayer of Pb is formed during evaporation of Pb on a Cu(110) surface. This layer irreversibly transforms to an incommensurate solid upon melting and resolidification. The melting of the incommensurate solid has been studied by use of the (0.777, 0.777) and (1.566,1.566) superlattice reflections. The incommensurate Pb monolayer melts at 240 °C and long-range correlations break down along the incommensurate [110] at a lower temperature than along the commensurate [001].

Our results on the liquid phase agree with the predictions of DMM theory in that (1) a Lorentzian line shape is found, (2) there is a Q^2 dependence to the critical exponent (η_G), and (3) η_G is in the right range. This agreement may be coincidental since the Lorentzian squared line shapes of the solid phase may indicate random pinning of the overlayer[15] and an artificial second-order transition.

In conclusion, we would like to emphasize the relative ease with which these measurements can

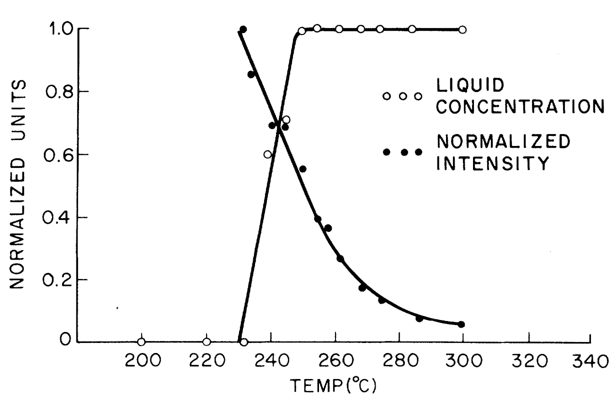

FIG. 3. The peak intensity of the second-order Pb reflection and the fraction of liquid vs temperature.

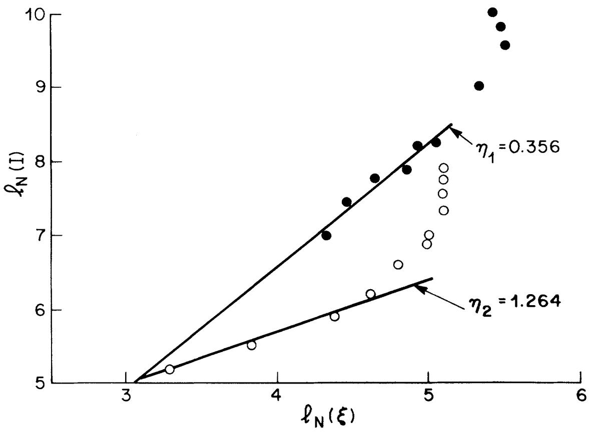

FIG. 4. $\ln(I_p)$ vs correlation length for the FOR (filled circles) and SOR (open circles).

be made and interpreted. First, these data are interpreted with kinematic scattering theory. Secondly, the high resolution of x-ray scattering enables straightforward analysis of 1000-Å correlation lengths. Finally, and perhaps most important, is that high signal rates are possible (50 000 cps for the FOR) with high signal-to-background ratio ($S/B = 500$ for the FOR). These capabilities should make this technique not only feasible but also practical and further experiments should stimulate advances in understanding two-dimensional phase transitions, the growth of thin films, and the behavior of small clusters on surfaces.

We acknowledge useful discussions with D. Moncton, R. Birgeneau, and W. Brinkman. The experiments were performed at the Stanford Synchrotron Radiation Laboratory which is supported by the National Science Foundation through the Division of Materials Research and by the National Institutes of Health through the Biotechnology Resource Program in the Division of Research Resources (in cooperation with the U. S. Department of Energy).

(a) Present address: Bell Laboratories, Holmdel, N. J. 07733.

(b) Present address: Exxon Research and Engineering Company, Linden, N. J. 07306.

[1] P. Eisenberger and W. C. Marra, Phys. Rev. Lett. 46, 1081 (1981).

[2] W. C. Marra, Ph.D. thesis, Stevens Institute of Technology, 1981 (unpublished).

[3] J. Henrion and G. E. Rhead, Surf. Sci. 29, 20 (1972).

[4] D. R. Nelson and B. I. Halperin, Phys. Rev. B 19, 2457 (1979).

[5] S. Ostlund and B. I. Halperin, Phys. Rev. B 23, 335 (1981).

[6] P. W. Stevens, P. Heiney, R. J. Birgeneau, and P. M. Horn, Phys. Rev. Lett. 43, 47 (1979); R. J. Birgeneau, E. M. Hammonds, P. Heiney, P. W. Stevens, and P. M. Horn, in *Ordering in Two Dimensions*, edited by S. K. Sinha (Plenum, New York, 1980), and references therein.

[7] D. E. Moncton, P. W. Stevens, R. J. Birgeneau, P. M. Horn, and G. S. Brown, Phys. Rev. Lett. 46, 1533 (1981).

[8] M. D. Chinn and S. C. Fain, Jr., Phys. Rev. Lett. 39, 146 (1977).

[9] S. N. Coppersmith, D. S. Fisher, B. I. Halperin, P P. A. Lee, and W. F. Brinkman, Phys. Rev. B 25, 349 (1982).

[10] Y. Imry, CRC Crit. Rev. Solid State Mater. Sci. 8, 157 (1979).

[11] F. C. Frank and J. H. Van Der Merwe, Proc. Roy. Soc. London, Ser. A 198, 216 (1949).

[12] W. C. Marra, P. H. Fuoss, and P. Eisenberger, unpublished.

[13] J. Villain, in *Ordering in Two Dimensions*, edited by S. K. Sinha (Plenum, New York, 1980), and references therein.

[14] P. Dutta, S. K. Sinha and P. Vora, in *Ordering in Two Dimensions*, edited by S. K. Sinha (Plenum, New York, 1980), and references therein.

[15] R. J. Birgeneau, private communications.

High-Pressure Melting Curve of ^{4}He

P. Loubeyre, J. M. Besson, and J. P. Pinceaux
Physique des Milieux Très Condensés, Université Pierre et Marie Curie, F-75230 Paris Cedex 05, France

and

J. P. Hansen
Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie,
F-75230 Paris Cedex 05, France

(Received 26 July 1982)

The melting curve $P(T)$ of ^{4}He has been measured from 220 to 360 K (8 to 16 GPa); it is found to exhibit a well-defined cusp point at 299 K and 11.65 GPa. The cusp, together with estimates of the relative volume change, points to the existence of a triple point and a new high-pressure phase in solid ^{4}He. The melting curve below this point is accurately fitted by theory on the basis of a modified Aziz interatomic potential.

PACS numbers: 67.80.Gb, 62.50.+p, 64.70.Dv, 64.70.Kb

Knowledge of the thermodynamic behavior of helium at high densities is important not only because of the fundamental character of this element, but also because it may serve as a model for the properties of highly compressed insulators. The law of corresponding states allows an