PHYSICAL REVIEW B VOLUME 51, NUMBER 20 15 MAY 1995-II

Thermal diffuse scattering from surface-melted Pb(110)

H. M. van Pinxteren, S. Chandavarkar,* and W. J. Huisman
Fundamenteel Onderzoek der Materie, Institute for Atomic and Molecular Physics, Kruislaan 407,
1098 SJ, Amsterdam, The Netherlands

J. M. Gay
Centre de Recherche sur les Mécanismes de la Croissance Cristalline, Centre National de la Recherche Scientifique,
Campus de Luminy, Case 913, 13288 Marseille Cedex 9, France

E. Vlieg
Fundamenteel Onderzoek der Materie, Institute for Atomic and Molecular Physics, Kruislaan 407,
1098 SJ, Amsterdam, The Netherlands

(Received 4 January 1995)

We report a surface x-ray diffraction study of diffuse scattering from Pb(110). We reproduce the observations by Fuoss *et al.* [Phys. Rev. Lett. **60**, 2046 (1988)]. However, a more extended examination of the observed diffuse intensity demonstrates that it cannot be caused by scattering from a melted surface film. We show that the intensity is due to thermal diffuse scattering.

Surface melting has been investigated by a variety of experimental techniques for several metal surfaces,[1-4] especially for Pb(110).[5-11] So far, only few surface x-ray scattering studies have been reported: two diffraction experiments[12,13] and a reflectivity experiment.[14] In the latter, the density profile of the quasiliquid film on Pb(110) was investigated. Dosch *et al.*[13] measured the (002) Bragg profile of Al(110) to study the surface disordering. Fuoss, Norton, and Brennan[12] observed diffuse scattering on Pb(110), which was interpreted by the authors as scattering from a two-dimensional liquid film of Pb. As the diffuse intensity was observed at all investigated temperatures, it was concluded that the onset temperature for surface melting of Pb(110) is below room temperature. This is in conflict with all other experimental observations, which have demonstrated that Pb(110) is ordered up till at least 450 K.[5-11] At higher temperatures, above 500 K, a so-called quasiliquid film develops, which diverges in thickness on approaching the bulk melting temperature of lead (600.7 K).[5-8,11]

In this report, we present a series of surface x-ray diffraction measurements of Pb(110), in order to resolve the discrepancy between the previous x-ray diffraction study[12] and the other experimental results. The experiments were performed at the surface x-ray diffraction station 9.4 of the wiggler beamline at the Synchrotron Radiation Source in Daresbury, using focused radiation with a wavelength of 1.38Å. The incoming beam was defined by slits to be 0.4-mm horizontally (out-of-plane) and 2-mm vertically (in-plane) and had a total estimated flux of 2×10^{10} photons per second. The angular acceptance of the detector was constrained by slits to be 0.14° along the surface normal and 0.29° in the in-plane direction. The setup has been described elsewhere.[15,16] The sample (12×12 mm^2) was spark cut from a high-purity lead single crystal (99.9999%) and chemically etched in a mixture of 80% acetic acid and 20% hydrogen peroxide to remove the damaged surface layers. After etching, the sample was mechanically polished using a colloidal silica suspension, until a flat and mirrorlike surface was obtained. Finally the oxides were removed by acetic acid. The cleaning of the sample in ultrahigh vacuum and the temperature control have been described in detail in Ref. 5. The miscut angle of the sample was 0.1°±0.1°, and the in-plane mosaicity was 0.15° (full width at half maximum). In this report we will employ a rectangular coordinate frame to describe the fcc(110) surface. Parallel to the surface the unit vectors are $\mathbf{a}_1=[001]_{\text{cubic}}$ and $\mathbf{a}_2=\frac{1}{2}[1\bar{1}0]_{\text{cubic}}$. The unit vector perpendicular to the surface is $\mathbf{a}_3=\frac{1}{2}[110]_{\text{cubic}}$. Reciprocal-space coordinates are given in units of $\{\mathbf{b}_i\}$ with $\mathbf{a}_i\cdot\mathbf{b}_j=2\pi\delta_{ij}$. The momentum transfer, Q, is denoted by the Miller indices (hkl) with $Q=h\mathbf{b}_1+k\mathbf{b}_2+l\mathbf{b}_3$.

Figure 1 shows a radial scan parallel to the surface along the [12] direction as a function of the in-plane momentum transfer, $Q_\parallel$. The angle of incidence was 0.35°, which is below the critical angle (0.39°). Our re-

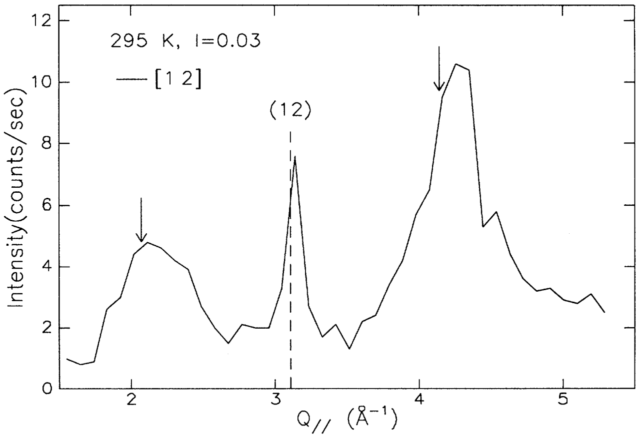

FIG. 1. Radial scan along the [1 2] direction at room temperature as a function of the total in-plane momentum transfer, $Q_\parallel$. The dashed line indicates the position of the (1 2) crystal truncation rod.

0163-1829/95/51(20)/14753(3)/$06.00 51 14 753

sults along the [12] direction are identical to those presented in Fig. 1 of Ref. 12. At room temperature, we also observe two peaks of diffuse intensity at a $Q_{\parallel}$ of 2 and 4 $Å^{-1}$, and a sharp feature at $Q_{\parallel}=3.1$ $Å^{-1}$ (indicated by the dashed line). The latter is an intersection of a so-called crystal truncation rod (CTR), which arises from the discontinuity of the crystal at the surface.[17] At high temperature, the CTR intensity disappears. Measurements at different temperatures between room temperature and 600.3K (the bulk melting temperature of Pb is 600.7 K) revealed an increase of the diffuse intensity with increasing temperature. In Ref. 12, the two peaks at a $Q_{\parallel}$ of 2 and 4 $Å^{-1}$ were interpreted as diffuse scattering arising from a two-dimensional (2D) liquid Pb film on top of a solid Pb substrate. In case of scattering from a 2D liquid film, diffuse peaks may appear in rings in reciprocal space, at constant in-plane momentum transfer. If one assumes that the diameter of a Pb atom is 3.5 Å, which is the bulk nearest-neighbor distance for Pb, diffuse peaks are expected for any radial-scan direction at values of $Q_{\parallel}$ equal to 2, 4 $Å^{-1}$ etc. In Fig. 2, these rings of constant in-plane momentum transfer have been indicated by the dotted circles. Such liquid rings have been observed for a single liquid Pb layer on a Ge(111) substrate.[18] However, Fig. 3 demonstrates that liquid scattering is not the origin of the diffuse peaks on Pb(110). Figure 3 shows radial scans along three different [*hk*] directions. In the [15] and [1 12] direction, similar peaks as those for the [12] direction appear, but at slightly *higher* values for $Q_{\parallel}$. Closer examination of the peak positions in the radial scans reveals that the diffuse peaks are all located on straight lines in between two in-plane Bragg reflections, see Fig. 2. This is clearly demonstrated by Fig. 4 where the open circles show a scan from the (02) to the (11) bulk Bragg peak at $l=0.1$. In between those two reflections there is a continuous streak of diffuse intensity. The radial scans along the [12], [15], and [1 12] direction intersect this streak at the positions indicated by arrows. This intersection causes the peaks at ~2 $Å^{-1}$ in Figs. 1 and 3. Similarly, the peaks at $Q_{\parallel}$ is

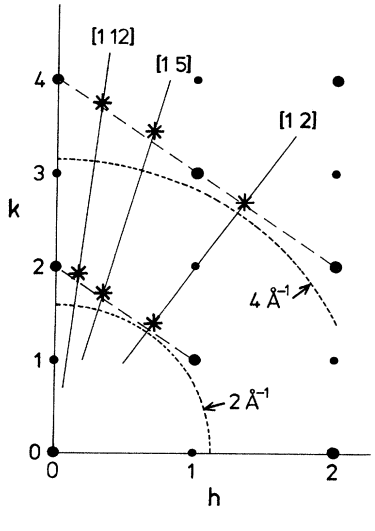

FIG. 2. Reciprocal-space map of the Pb(110) surface, plotted for zero perpendicular momentum transfer ($l=0$). The large solid circles indicate the positions of bulk Bragg peaks. The solid straight lines indicate the direction and the range of the scans, which are plotted in Figs. 1 and 2. The dotted curves are rings at a constant in-plane momentum transfer of 2 and 4 $Å^{-1}$, where contributions from a two-dimensional liquid Pb film are expected. The dashed straight lines indicate the observed streaks of diffuse intensity in between in-plane Bragg peaks. The asterisks denote the positions of the peaks in Figs. 1 and 3.

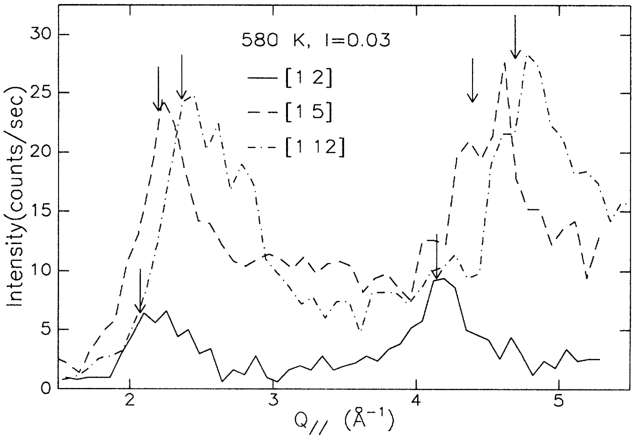

FIG. 3. Radial scans along different directions parallel to the Pb(110) surface as a function of $Q_{\parallel}$. The out-of-plane momentum transfer was kept constant at $l=0.03$. The arrows indicate the positions where lines in the [$\bar{1}$ 1] direction, connecting in-plane Bragg peaks, are intersected by the radial directions. The intensity in the [1 2] scan is significantly lowered by a misalignment of the sample. From a comparison with the measurements at other temperatures, we estimate that the [1 2] intensity should be multiplied by approximately a factor 4.

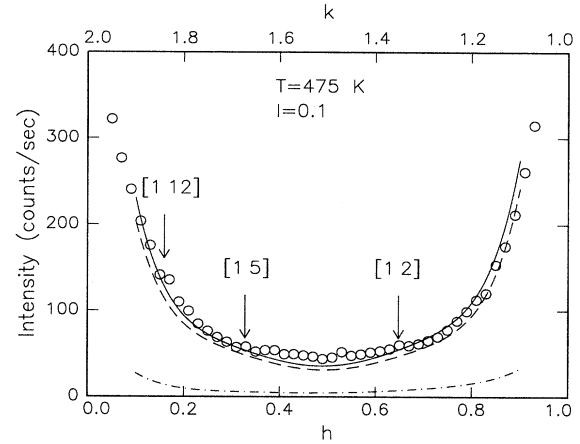

FIG. 4. In-plane scan at $l=0.1$ in between the (0 2) and (1 1) Bragg peaks. The positions where the radial scans intersect this streak of diffuse intensity are indicated by the arrows. The solid curve represents the sum of the single phonon (dashed-dotted curve) and the two-phonon (dashed) contribution to the thermal diffuse scattering. The sum has been scaled to fit the data.

~ 4.5 Å^{-1} are cause by crossing the line connecting the (40) and (22) in-plane Bragg peaks.

We observed an increase of the diffuse intensity with increasing penetration depth of the x rays, indicating that the intensity does not arise from the surface, but from the bulk of the sample. As the amount of diffuse intensity in all directions increased also with increasing temperature, we conclude that the observed scattering is thermal diffuse scattering (TDS) from the bulk of the Pb sample. Bulk TDS gives rise to a continuous distribution of diffuse intensity, and is peaked at lines connecting Bragg reflections. The dashed curve and the dash-dotted curve in Fig. 4 represent the calculated first- and second-order contribution, respectively, to the TDS of Pb. The dispersion curves were obtained from Ref. 19. We have calculated the second-order contribution using the approximation of Walker.[20] Higher-order contributions can be neglected.[21] The sum of the first- and second-order contributions is given by the solid curve. This sum was scaled to fit the data. The shape of the calculation is seen to fit the data quite well, confirming that the intensity can indeed be attributed to TDS.

Up to the highest measurement temperature of 600.3 K, we observe no sign of liquid scattering, although it was shown in Refs. 5, 8, and 11 that at this temperature approximately 10 ML of Pb atoms have lost their crystalline order. We can roughly estimate the intensity expected for 1 ML of liquid Pb (1) by comparing our experimental configuration with the one of Grey *et al.*[18] who observed liquid rings from approximately 1 ML of liquid Pb, and (2) by calculating the intensity from the theory of scattering from a liquid.[22] This leads to expected count-rates between 0.2 and 1 count per second per ML. At 580 K, one expects a quasiliquid layer with a thickness of 3 ML,[8] i.e., 0.6–3 counts per second in Fig. 3. This is on the edge of being observable. The fact that even at 600.3 K we don't see liquid rings seems to indicate that the system is not behaving in the way one would expect. Maybe the large thermal vibration amplitude at the surface leads to a reduced (spherical) correlation between adatoms and, thus, to a reduced intensity in the liquid rings. On the other hand, a large fraction of the total intensity may remain at the bulk Bragg positions due to the periodic potential of the underlying substrate. The fact that 2D liquid rings have to date only been observed in the case of an isolated layer on top of a well-ordered substrate,[18] seems to indicate that the substrate region below the quasiliquid layer plays an important role.

In summary, we have shown that the observed diffuse intensity from Pb(110) is not caused by the melted film on this surface, as was claimed previously,[12] but is due to bulk thermal diffuse scattering instead. With this interpretation, the observations using surface x-ray diffraction no longer indicate a larger amount of disorder at room temperature than was found using other techniques.

The authors would like to thank the Daresbury Staff for their assistance during the measurements. We thank R.J.I.M. Koper for carefully polishing the sample and A.J. Riemersma for spark cutting. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) and was made possible by financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

---

[*] Present address: Exxon PRT, Building 510E, Brookhaven National Laboratory, Upton, NY 11973.

[1] J. F. van der Veen, in *Phase Transitions in Surface Films 2*, edited by H. Taub, G. Torzo, H. J. Lauter, and S. C. Fain, Jr. (Plenum, New York, 1991), p. 289.

[2] A. Pavlovska, M. Tikhov, Y. Gu, and E. Bauer, Surf. Sci. **278**, 303 (1992).

[3] A. W. Denier van der Gon, R. J. Smith, J. M. Gay, D. J. O'Connor, and J. F. van der Veen, Surf. Sci. **227**, 143 (1990).

[4] A. Hoss, M. Nold, P. von Blanckenhagen, and O. Meyer, Phys. Rev. B **45**, 8714 (1992).

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

[6] U. Breuer, O. Knauff, and H. P. Bonzel, Phys. Rev. B **41**, 10 848 (1990).

[7] K. C. Prince, U. Breuer, and H. P. Bonzel, Phys. Rev. Lett. **60**, 1146 (1988).

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

[9] S. Speller, M. Schleberger, A. Niehof, and W. Heiland, Phys. Rev. Lett. **68**, 3452 (1992).

[10] J. W. Herman and H. E. Elsayed-Ali, Phys. Rev. Lett. **68**, 2952 (1992).

[11] A. W. Denier van der Gon, H. M. van Pinxteren, J. W. M. Frenken, and J. F. van der Veen, Surf. Sci. **244**, 259 (1991).

[12] P. H. Fuoss, L. J. Norton, and S. Brennan, Phys. Rev. Lett. **60**, 2046 (1988).

[13] H. Dosch, T. Höfer, J. Peisl, and R. L. Johnson, Europhys. Lett. **15**, 527 (1991).

[14] B. Pluis, J. M. Gay, J. W. M. Frenken, S. Gierlotka, J. F. van der Veen, J. E. Macdonald, A. A. Williams, N. Piggins, and J. Als-Nielsen, Surf. Sci. **222**, L845 (1989).

[15] E. Vlieg, A. van 't Ent, A. P. de Jongh, H. Neerings, and J. F. van der Veen, Nucl. Instrum. Methods A **262**, 522 (1987).

[16] C. Norris, M. S. Finney, G. F. Clark, G. Baker, P. R. Moore, and R. G. van Silfhout, Rev. Sci. Instrum. **63**, 1083 (1992).

[17] I. K. Robinson, Phys. Rev. B **33**, 3830 (1986).

[18] F. Grey, R. Feidenhans'l, J. S. Pedersen, M. Nielsen, and R. L. Johnson, Phys. Rev. B **41**, 9519 (1990).

[19] B. N. Brockhouse, T. Arase, G. Caglioti, K. R. Rao, and A. D. B. Woods, Phys. Rev. **128**, 1099 (1962).

[20] C. B. Walker, Phys. Rev. **103**, 547 (1956).

[21] S. L. Schuster and J. W. Weymouth, Phys. Rev. B **3**, 4143 (1971).

[22] B. E. Warren, *X-ray Diffraction* (Dover, New York, 1990).