PHYSICAL REVIEW B VOLUME 41, NUMBER 13 1 MAY 1990

Pb/Ge(111) 1 × 1: An anisotropic two-dimensional liquid

F. Grey*
Max Planck Institute for Solid State Research, D-7000 Stuttgart 80, Federal Republic of Germany

R. Feidenhans'l, J. Skov Pedersen, and M. Nielsen
Risø National Laboratory, DK-4000 Roskilde, Denmark

R. L. Johnson
II. Institute for Experimental Physics, Hamburg University, D-2000 Hamburg 50, Federal Republic of Germany

(Received 29 January 1990)

We report x-ray measurements of a ring of diffuse scattering due to a single layer of liquid Pb in the 1 × 1 phase of Pb/Ge(111), above 180 °C. The ring is part of a cylinder in reciprocal space, and its radial position differs significantly from that of the first ring due to bulk liquid Pb. The ring is found to be azimuthally anisotropic, due to interaction with the substrate.

Several differences are expected between the x-ray-scattering pattern of a two-dimensional (2D) liquid and its 3D counterpart. An isotropic 3D liquid produces spherical shells of diffuse scattering, whereas a 2D liquid will give rise to cylindrical shells of scattering. In both cases, measurements in a fixed diffraction plane will reveal rings of intensity, but as we shall discuss here, the radii of the rings due to 2D and 3D liquids will be different, even if the liquids have the same radial pair distribution function. Further, for a 2D liquid on a periodic substrate, the interaction between the solid and the liquid will alter the x-ray scattering pattern significantly.

In a reflection high-energy electron-diffraction study of Pb/Ge(111)1 × 1, diffuse cylinderlike scattering has been observed about the origin in reciprocal space, characteristic of a 2D liquid phase.[1] The first ring of scattering was estimated to be at $q = 2.0$ Å^{-1}, shifted with respect to the position of the first ring for bulk Pb,[2] $q = 2.19$ Å^{-1}. The rings appeared to be isotropic, implying no interaction between the periodic part of the substrate potential and the 2D liquid. However, in a low-energy electron-diffraction study, no rings of diffuse scattering were observed, and it was suggested that the 1 × 1 phase was a 2D solid.[3] X-ray standing-wave measurements support a 2D solid model,[4] while photoelectron spectroscopy results are ambiguous.[5]

The x-ray scattering measurements reported here were made at the wiggler line *W*1 of the Hamburg Synchrotron Radiation Laboratory (HASYLAB). Pb was deposited onto the clean substrate surface at the Flipper II photoemission beamline. One monolayer (ML) coverage is defined here as one Pb atom per top-layer atom of the unreconstructed surface. The sample was transferred in vacuo to a small ultra-high-vacuum chamber which was mounted on the x-ray diffractometer at *W*1. Temperature was measured by a W/Rh thermocouple in contact with the backside of the Ge sample, which was directly heated. The temperature was stabilized to 0.1 °C, and the estimated error is ±5 °C. The x-ray wavelength was 1.350 Å. Measurements were made in the grazing-incidence mode, where the incidence angle of the x rays to the surface was 0.22°, or 80% of the critical angle α_c to suppress bulk diffuse scattering. A linear position-sensitive detector (PSD) was used, subtending 3° perpendicular to the surface and 0.6° in the surface plane. A detailed description of sample preparation and scattering technique can be found in Ref. 6.

The densest two-dimensional solid phase of Pb/Ge(111), the β phase, is completed at $\Theta = \frac{4}{3}$ ML, and has a $\sqrt{3} \times \sqrt{3}R30°$ unit cell which is a close-packed Pb structure, slightly distorted from an ideal bulk Pb(111) layer.[6,7] The reciprocal space of the $\sqrt{3} \times \sqrt{3}R30°$ surface is shown in the inset of Fig. 1. Beyond $\Theta = \frac{4}{3}$ ML, Pb grows as sub-micron-sized 3D crystallites ("clusters"), which are epitaxially oriented by the substrate.[3] The coverage Θ can be varied *in situ* by desorption at temperatures above 350 °C. The transition to a 1 × 1 phase, where fractional-order reflections are absent, is reversible and occurs at a temperature which depends on coverage. Above $\Theta = \frac{4}{3}$ ML, the transition to a 1 × 1 phase occurs at 330°, but at a coverage of about 1.25 ML (no 3D clusters present), the transition is at 180 °C. This agrees with reflection high-energy electron-diffraction (RHEED) observations.[1]

We find that the 3D clusters melt abruptly at $T_m = 302$ °C, in other words, before the transition to a 1 × 1 phase.[8] On melting, the clusters remain as droplets on the surface.[3] The first ring of liquid scattering due to the 3D droplets can thus be observed while the β phase is solid. A radial scan through this ring at 310 °C, along a direction 10° to (1,1), is shown in Fig. 1(a), with $\Theta = 4$ ML. The position of the ring, $q = 2.18 \pm 0.02$ Å^{-1}, agrees with the value measured for bulk Pb.[2] At the same coverage and at 230 °C (below the island melting temperature), there is no indication of a ring [Fig. 1(b)]. But in the 1 × 1 phase at 223 °C and $\Theta = 1.25 \pm 0.05$ ML, there is a ring of scattering at the position $q = 2.05 \pm 0.02$ Å^{-1} and with full width at half maximum $\Delta q = 0.30 \pm 0.05$ Å^{-1} [Fig. 1(c)]. This ring is shaded in the inset of Fig. 1.

The shift in position is consistent with the expected

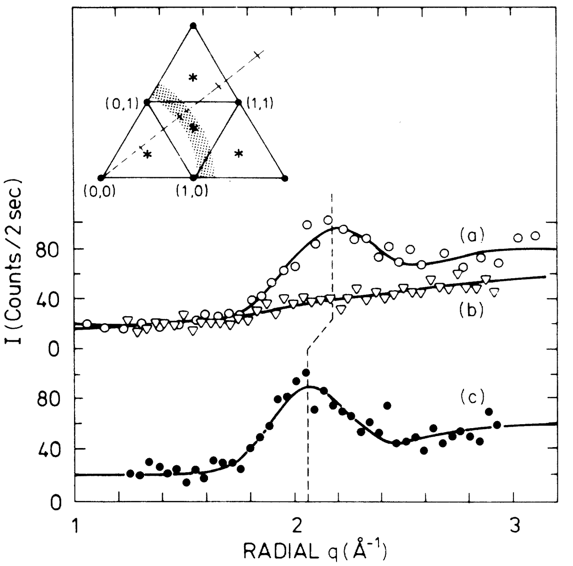

FIG. 1. (a) Radial scan 10° to (1,1) through liquid ring, at $\Theta=4$ ML and $T=310\,^{\circ}$C; 3D phase liquid, 2D phase solid. (b) Same scan at $T=230\,^{\circ}$C; 3D and 2D phases solid. (c) Same scan at $T=223\,^{\circ}$C and $\Theta=1.25$ ML; 3D phase absent, 2D phase liquid. Fitted curves are Gaussian on a Gaussian background, which is due to TDS (see text). The dashed vertical line indicates fitted midpoint of ring. The inset gives the reciprocal space of the Ge(111) surface. The surface notation is adopted: (1,1) is bulk (2,−2,0). Fractional-order reflections due to the $\sqrt{3}\times\sqrt{3}R30°$ superstructure are indicated by stars. The ring of scattering observed in the 1×1 phase is shaded. The dashed line represents a radial scan 10° to the (1,1) direction, inverse Å units are indicated by the tickmarks.

difference between 3D and 2D liquid scattering. The scattered intensity of a liquid is given by[9]

$$I(\mathbf{q})=Nf^2(\mathbf{q})\left[1+\rho\int[g(\mathbf{r})-1]e^{i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r}\right],$$

where $g(\mathbf{r})$ is the liquid pair distribution function, N the number of scatterers, $f(\mathbf{q})$ the atomic form factor, and ρ the mean liquid atomic density, the integral being over all space.

If the liquid is isotropic $[g(\mathbf{r})=g(r)]$ then the integral in the above expression reduces to Fourier-sine transform in 3D,

$$\int_0^\infty (4\pi r/q)[g(r)-1]\sin(gr)dr\,,$$

and a Fourier-Bessel transform in 2D,

$$\int_0^\infty 2\pi r[g(r)-1]J_0(qr)dr\,;$$

the difference being simply due to the different integration elements for 3D and 2D. For simplicity, we consider an idealized pair distribution function, $g(r)=\delta(r-a_0)+1$, often called the Ehrenfest model. For $a_0=3.5$ Å, the bulk Pb-Pb bond length, the transform will have its first maximum at 2.21 Å^{-1} in 3D and at 2.01 Å^{-1} in 2D. The predicted positions agree within 2% with measurement.

To confirm the two-dimensional nature of the liquid in the 1×1 phase, scans of parallel momentum transfer $q_{\parallel}$ through the ring were made at finite perpendicular momentum transfers, $q_z=0.96$ and 1.44 Å^{-1}, by varying the detector takeoff angle. For scans 0°, 10°, and 20° to the (1,1) direction, the ring maximum remains at $q_{\parallel}=2.05\pm0.03$ Å^{-1}. Two of these scans are shown in Fig. 2. The constancy of the ring's position, for varying q_z, clearly indicates that the ring extends as a cylinder in reciprocal space. (We note that, except for these scans, all measurements discussed here were made with the average exit angle α_f, equal to α_c, hence $q_z=0.04$ Å^{-1}.)

In radial scans extending further from the origin, we observe a second peak at $q\simeq3.2$ Å^{-1}, which becomes particularly intense near the (1,1) direction (Fig. 3). To determine whether this feature is due to the Pb layer, we use the fact that for scattering from the very surface of a crystal, there is an increase of intensity at incidence or exit angles near α_c.[10] The PSD analyzes the scattered intensity as a function of exit angle α_f and the insets in Fig. 3 show the PSD trace at both peak positions in the radial scan. While the characteristic intensity increase at $\alpha_f=\alpha_c$ is apparent for the first ring of intensity, it is absent for the second feature. Further measurements reveal this feature to be a streak of intensity along the (−1,1) direction, extending from the (1,1) bulk reflection. This streak is present, though weaker, at room temperature, and we attribute it to anisotropic bulk thermal diffuse scattering (TDS).[9] We are unable to detect a second ring of liquid scattering, and estimate its intensity to be < 10% of the first ring.

A 60° azimuthal scan at the maximum of the 2D liquid ring at 243 °C shows a weak azimuthal modulation of the ring intensity [Fig. 4(a)]. The line in Fig. 4(a) is a three-Gaussian fit. On cooling below about 210 °C, intensity builds up at the azimuthal angle $\omega=0°$, which is defined here as the (1,1) direction [Fig. 4(b)]. This peak is the tail of the $(\frac{2}{3},\frac{2}{3})$ reflection at 2.09 Å^{-1} in the $\sqrt{3}$ phase

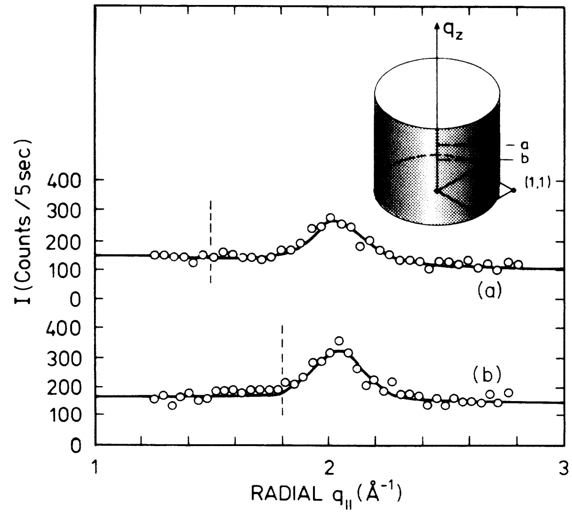

FIG. 2. Radial scans along (1,1) direction through the liquid ring at $\Theta\simeq1.2$ ML, $T\simeq240\,^{\circ}$C, at (a) $q_z=0.96$ Å^{-1} and (b) $q_z=1.44$ Å^{-1}. Vertical dashed lines indicate the intersection point of a sphere of radius 2.05 Å^{-1} with these scans. The inset indicates the scans and cylinder in reciprocal space.

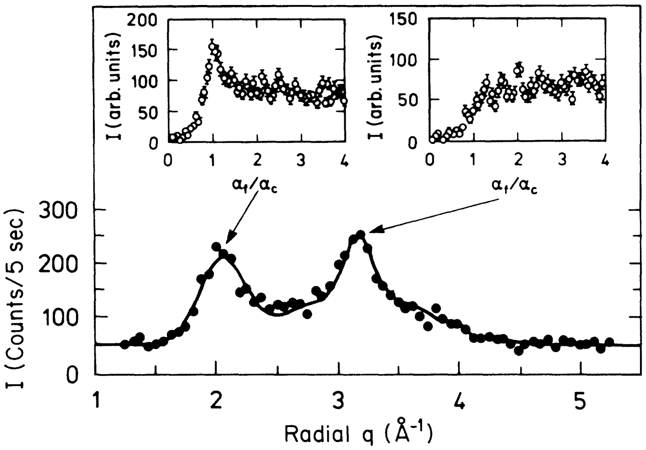

FIG. 3. Radial scan 7.5° to (1,1) at $T=223\,^{\circ}\mathrm{C}$. Insets shows PSD traces at positions of the two peaks in the radial scan. The peak at 3.2 Å^{-1} is attributed to anisotropic TDS of bulk Ge.

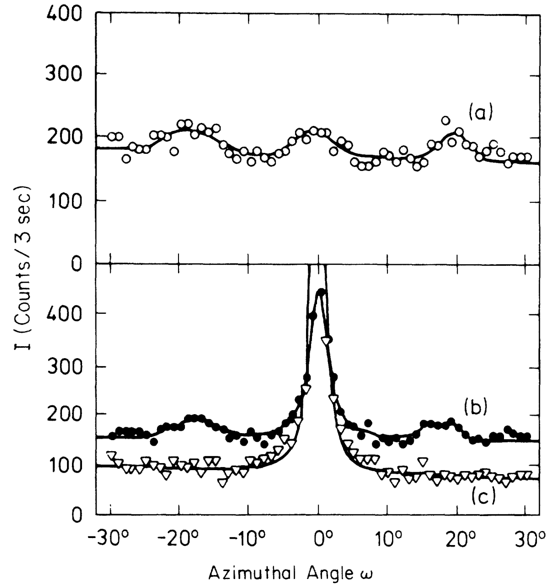

FIG. 4. Azimuthal scans at $q=2.05$ Å^{-1}, showing the anisotropy of the 2D liquid ring. (a) At 243 °C; the line is a three-Gaussian fit. (b) At 183 °C, just above the 2D melting transition. (c) At 166 °C, below the transition. The side peaks disappear below 180 °C, and the base line intensity falls simultaneously to background (70 counts/3 sec).

(Fig. 1). The side peaks in Fig. 4(a), which are not on high-symmetry directions, disappear abruptly on cooling at about 180 °C, and the base line falls simultaneously to background level [Fig. 4(c)]. The coexistence of β phase and liquid scattering in the range 210°–180° is attributed to a two-phase ($\beta+1\times1$) region in the phase diagram.

The anisotropy of the ring is similar to patterns seen for intercalation compounds such as $C_{24}Rb$.[11] The detailed analytical description of such anisotropy is complex, the main features being a sixfold modulation of the rings about the origin, and the appearance of secondary rings about the innermost Bragg points.[12] We tentatively identify the peak at 0° as due to the sixfold modulation, and the peaks at $\pm(18.8°\pm1.2°)$ as due to the crossing of secondary rings about the (1,1) bulk Ge reflections with the primary ring. Assuming secondary rings have the same radius as the primary ring, the intersection should occur at $\pm(19.5°\pm1.0°)$.

In conclusion, we have made a study of the liquid scattering of a single Pb layer adsorbed on Ge(111). In the past, x-ray scattering from a 2D liquid has been observed for intercalation compounds, where effectively thousands of layers are scattering.[11] Two-dimensional liquid phases of adsorbed monolayers on crystalline substrates have also been inferred indirectly from changes in line shape of diffraction groups for a variety of systems.[13] Our measurements show, however, that it is possible with synchrotron radiation to directly observe a cylinder of x-ray scattering from an adsorbed liquid monolayer. We draw attention to the fact that even under optimal conditions (subcritical angle of incidence, adsorbate much stronger scatterer than substrate) bulk diffuse scattering can swamp 2D liquid scattering. Finally, contrary to previous RHEED observations, we observe the liquid scattering to be azimuthally anisotropic. This is presumably a general feature of 2D liquids on periodic substrates.

We thank the staff of HASYLAB for their help. This work was supported by the German Federal Minister for Research and Technology, the Max Planck Society, and the Danish National Research Council.

---

*Mailing address: Risø National Laboratory, DK-4000 Roskilde, Denmark.

[1] T. Ichikawa, Solid State Commun. **49**, 59 (1984); **46**, 827 (1983).

[2] R. Kaplow, S. L. Strong, and B. L. Averbach, Phys. Rev. **138**, A1336 (1965).

[3] J. J. Metois and G. Le Lay, Surf. Sci. **133**, 422 (1983).

[4] B. N. Dev, F. Grey, R. L. Johnson, and G. Materlik, Europhys. Lett. **6**, 311 (1988).

[5] B. P. Tonner, H. Li, M. J. Robrecht, Y. C. Chou, M. Onellion, and J. L. Erskine, Phys. Rev. B **34**, 4386 (1986).

[6] F. Grey, Ph.D. thesis, Copenhagen University, 1988 (unpublished), also available as Report No. Risø-M-2737 on request to Risø library.

[7] R. Feidenhans'l, J. S. Pedersen, M. Nielsen, F. Grey, and R. L. Johnson, Surf. Sci. **178**, 927 (1986).

[8] This T_m is 25 °C below the T_m of bulk Pb. A similar depression of T_m has been seen in Pb-Ge foils: R. H. Willens, A. Kornblit, L. R. Testardi, and S. Nakahara, Phys. Rev. B **25**, 290 (1982). For the discussion here, however, only the difference between T_m of the clusters and of the β-phase matters.

[9] B. E. Warren, *X-Ray Diffraction* (Addison-Wesley, Reading, MA, 1968).

[10] R. Feidenhans'l, Surf. Sci. Rep. **10**, 105 (1989).

[11] J. D. Fan, O. A Karim, G. Reiter, and S. C. Moss, Phys. Rev. B **39**, 6111 (1989).

[12] G. Reiter and S. C. Moss, Phys. Rev. B **33**, 7209 (1986).

[13] Several examples of the melting of rare gases on graphite and other substrates exist, see K. Strandberg, Rev. Mod. Phys. **60**, 161 (1988), and references therein. An example of a chemisorbed system is the melting of Pb/Cu(110) by W. C. Marra, P. H. Fuoss, and P. E. Eisenberger, Phys. Rev. Lett. **49**, 1169 (1982). X-ray scattering from a 2D quasiliquid Pb layer of premelted Pb(110) has been reported by P. H. Fuoss, L. J. Norton, and S. Brennan, Phys. Rev. Lett. **60**, 2046 (1988), but no direct evidence is presented that the observed scattering was from the surface or that it formed cylinders.

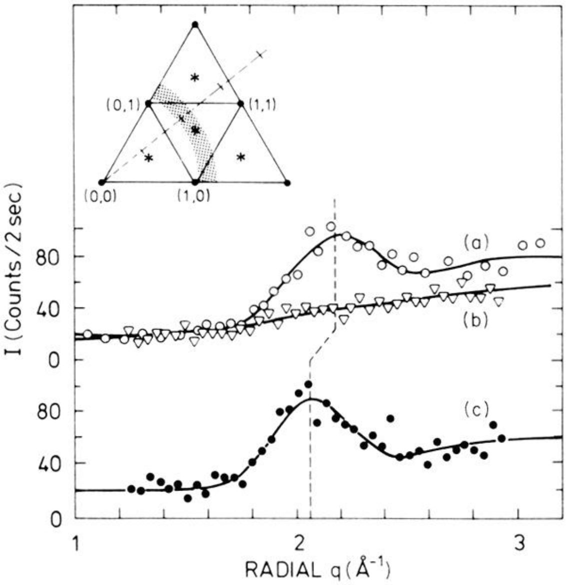

FIG. 1. (a) Radial scan 10° to (1,1) through liquid ring, at $\Theta = 4$ ML and $T = 310\,^\circ\mathrm{C}$; 3D phase liquid, 2D phase solid. (b) Same scan at $T = 230\,^\circ\mathrm{C}$; 3D and 2D phases solid. (c) Same scan at $T = 223\,^\circ\mathrm{C}$ and $\Theta = 1.25$ ML; 3D phase absent, 2D phase liquid. Fitted curves are Gaussian on a Gaussian background, which is due to TDS (see text). The dashed vertical line indicates fitted midpoint of ring. The inset gives the reciprocal space of the Ge(111) surface. The surface notation is adopted: (1,1) is bulk $(2,-2,0)$. Fractional-order reflections due to the $\sqrt{3}\times\sqrt{3}R30^\circ$ superstructure are indicated by stars. The ring of scattering observed in the 1×1 phase is shaded. The dashed line represents a radial scan 10° to the (1,1) direction, inverse Å units are indicated by the tickmarks.

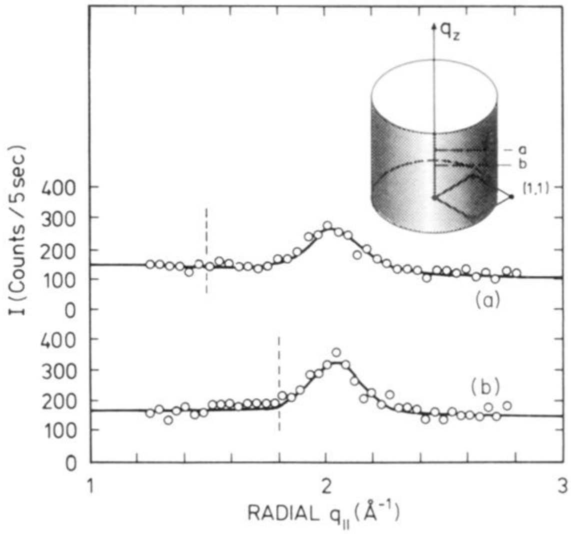

FIG. 2. Radial scans along (1,1) direction through the liquid ring at $\Theta \simeq 1.2$ ML, $T \simeq 240\,^{\circ}\mathrm{C}$, at (a) $q_z = 0.96$ Å^{-1} and (b) $q_z = 1.44$ Å^{-1}. Vertical dashed lines indicate the intersection point of a sphere of radius 2.05 Å^{-1} with these scans. The inset indicates the scans and cylinder in reciprocal space.