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Observation of solid-hexatic-liquid phase transitions of submonolayer xenon on graphite by transmission-electron diffraction

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Two-stage melting of submonolayer xenon adsorbed on single-crystal graphite has been observed using transmission high-energy electron diffraction. Diffraction patterns were obtained from the solid, hexatic, and liquid phases for $11<p<41\times 10^{-3}$ torr and $110<T<120$ K. The aligned solid melts via a hexatic phase to an essentially isotropic liquid within a 1-K interval at constant pressure. The lattice parameter and spot profiles of the hexatic phase are reported, and the order of the transitions discussed in relation to previous thermodynamic and diffraction measurements.

Melting in two dimensions (2D) has aroused a great deal of interest, since the suggestions of Kosterlitz, Thouless, Halperin, Nelson, and Young (KTHNY) that this might occur via a two-stage process involving threading, or Kosterlitz-Thouless (KT) dislocations.[1] There is, in these idealized models, no true long-range order in 2D; a solid monolayer (ML), referred to as a power-law solid (PLS), gives rise to power-law, rather than δ-function, diffraction line shapes. The hexagonal ML solid contains KT dislocations, organized in dipole pairs in the PLS, but free to dissociate at higher temperatures, first into isolated dislocations forming the hexatic phase, and then into disclinations, forming the isotropic liquid. Disclinations are angular defects, where the regions of fivefold and sevenfold coordination present in the core of a dislocation separate to produce orientational disorder.[2]

An extensive search for a realization of this model has alighted on submonolayer xenon adsorbed on graphite as a candidate system.[3–8] High-resolution x-ray studies on oriented polycrystalline substrates have demonstrated long-range positional correlation in the "liquid," approaching 0.2 μm on the best substrates.[3] Experiments on "almost-single crystals" have examined orientational order, and demonstrated the relation between orientational and positional correlation in well-correlated liquids.[4] Thermodynamic studies using volumetric and calorimetric techniques gave clear signatures of the liquid-solid transitions.[5,6] Further single-crystal x-ray studies have been performed, initially in closed cells,[7] and most recently at fixed T as a function of pressure.[8]

The order of the melting transition has also attracted much attention. Whereas the first thermodynamic studies suggested that melting was weakly first order just above the two-dimensional triple point and second order at higher temperatures,[5] subsequent studies with better resolution have argued that two-dimensional melting is a first-order transition up to at least 150 K;[6] this has been queried in a recent diffraction study.[8] The second-order solid-hexatic transition predicted by KTHNY has not been seen in numerous computer simulations, which have always given a first-order transition. The hexatic-isotropic-liquid transition has been fitted to KTHNY theory,[4] but the transition is much sharper than expected; however, a KTHNY transition is modified in principle in the presence of a (hexagonal) substrate orientational field h_6.[2,4]

The main remaining questions are (a) what is the role of h_6, as distinct from interactions in the two-dimensional layer, in inducing long-range orientational order in an incommensurate phase; (b) whether experiment and simulation are prevented from seeing "true" second-order melting behavior because of inadequate sample size or perfection, or inadequate annealing or simulation time; or (c) would a more sophisticated theory give first-order behavior? For example, arrays of dislocations, e.g., KT dislocations in grain boundaries, can also produce split, broadened diffraction spots and other forms of diffuse scattering. It has been suggested that the organization of dislocations into a grain-boundary solid could make the solid-hexatic transition first order.[9] In addition, (d) the order of the hexatic-isotropic-liquid transition needs to be determined, and its relation to point (a) above clarified. We are also concerned whether thermodynamic and diffraction experiments are studying exactly the same transitions.

In this paper, we present transmission-electron diffraction data, from true single-crystal substrates, crossing the solid-hexatic-liquid phase boundaries at pressures and temperatures just above the two-dimensional triple point, located at $T=99$ K, $p=0.18$ mTorr.[10] In comparison with the x-ray work, we record the entire diffraction pattern on film in a few minutes; we can work at constant p and T, rather than at a fixed "fill" of a closed volume; however, our equilibration times are rather less, tens of minutes rather than hours. Problems of crossing phase boundaries along different trajectories are discussed in Refs. 5 and 6, and of lack of equilibrium (at lower temperatures) in Refs. 7, 8, and 11.

TABLE I. Solid-hexatic and hexatic-liquid transition temperatures on warming and cooling (in parentheses).

	Transition temperature (K)	
Pressure (mTorr)	(sol-hex)	(hex-liq)
11	110.6 (110.3)	111.6 (111.1)
22	115.9 (115.4)	116.8 (116.2)
41	118.2 (118.0)	119.2 (118.7)

The experimental techniques used are described fully in Ref. 11. Briefly, a thin (<100 Å thick) graphite crystal is enclosed in an environmental cell, at sample holder temperature T and Xe gas pressure p. Small (400 μm diameter) holes in the cell allow the entry of the 100-keV electron beam and the exit of the lowest-order Xe and graphite-diffracted beams. An improvement made for this work was to collect the directly transmitted beam with a Faraday cup; this allowed us both to measure the electron dose accurately, and gave a lower background for detecting weak features in the diffraction pattern.[12] Temperatures were measured with a silicon diode to ±0.1 K, and pressures with a 1–1000 mTorr Baratron gauge to ±5%. We define 1 ML as the complete filling of commensurate $\sqrt{3}\times\sqrt{3}R30°$ structure with an assumed lattice parameter $a_c=4.260$ Å; this structure gives a Xe(10) diffraction peak at $g_c=4\pi/\sqrt{3}a_c=1.703$ Å^{-1}. The resulting ML density, $N_0=6.363\times10^{14}$ atoms cm^{-2}. This is up to 13% higher than some other definitions;[5] coverage comparisons must be done with great care.

Sets of diffraction patterns were obtained at three separate pressures, $p=11$, 22, and 41 mTorr in the temperature range $110<T<120$ K. The temperature was increased or decreased very slowly (0.1 K in about 8 min). Diffraction patterns characteristic of the three phases (aligned solid-hexatic-isotropic liquid) were observed as very weak features on the fluorescent screen, and were recorded photographically, with exposures of around 1–2 min for the solid, and up to 7 min for the liquid. Subsequently these patterns were examined visually and then quantitatively using the Photometric Data System densitometer at the Royal Greenwich Observatory, Cambridge.

The temperatures of first appearance of the hexatic and isotropic ring patterns on heating, and of the hexatic and solid patterns on cooling were observed. These transition temperatures are recorded in Table I. It is seen that there is a slight hysteresis between warming and cooling, averaging ±0.2 K in the expected sense, which could well be instrumental in origin. The main result, however, is that the two transitions are indeed separate and reproducible, with a shift with pressure that is consistent with previous studies of the melting line.[10] The width of the hexatic phase is 0.9 K on average, with a spread between 0.7 and 1.0 K for individual measurements; the accuracy is certainly not better than 0.1 K, and the sensitivity around 0.05 K.

The solid phase is incommensurate, with a large misfit in the lattice parameter of up to 10% with respect to the graphite, which has been measured to ±0.1% accuracy, as shown in Fig. 1. This incommensurate aligned (IA) phase occurs along the melting line, consistent with previous single-crystal x-ray data.[4,7,8] Here, we determine this alignment to be within ±0.1°. A study of the rotated (IR) phase at intermediate misfits, at lower pressures and temperatures, and of IAIR transitions is presented elsewhere.[12]

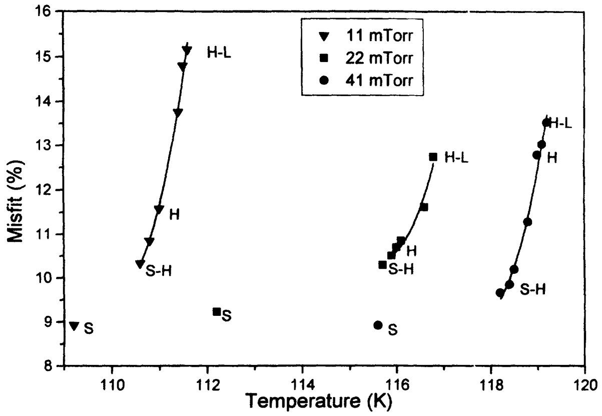

FIG. 1. Misfit at the three pressures measured, as a function of (increasing) temperature. The solid lines are second-order polynomials to $m(T)$, where the misfit $m=(g_x-g_c)/g_x$. The points S are reference points in the solid phase; S-H indicates composite solid-hexatic line shapes, and H-L points close to the hexatic-isotropic-liquid transition. Similar diffraction patterns were obtained on cooling with a temperature shift of around 0.4 K. See text for discussion.

Analysis of spot profiles was made by digitizing 400×400 points (on 20-μm centers) around the diffraction spots. These were subsequently subjected to 5×5 smoothing, density calibration, and background-fit routines, and spots optimally fitted to combination Gaussian plus Lorentzian (GL) profiles. Some examples from the 22-mTorr data are shown in Fig. 2. This GL profile has been found to fit lower temperature data well,[13] and fits this data well too, though possibly for different reasons. Other authors have found that if the exact theoretical shape is convoluted with finite size and mosaic spread, then the fits obtained can be nonunique.[8] Yet others have used empirical forms without further justification.[14] By adopting very simple functional forms we hope to avoid such problems here.

Gaussian profiles can arise from a distribution of KT dislocations, the width reflecting the dislocation density ρ.[13] It is notable that the lowest temperature points at the three pressures of Fig. 1 all have predominantly Gaussian profiles, with a radial width (half width at half maximum) $\sigma_R=2$–3×10^{-2} Å^{-1}. This corresponds to positional correlation lengths $2\pi/\sigma$ in the range 300–200 Å, smaller than the instrumental resolution, which is better than 1000 Å.[13] Numerically, for randomly distributed dislocations, $\sigma_R^2=C\rho$, with the constant $C=33.5$,[13] so that $\rho=1.2$–2.7×10^{11} cm^{-2}. However, if dislocations are present as closely spaced dipoles, as envisaged for the PLS,[1,2,9] then the density could be even higher. The x-ray results show that positional correlation lengths in well-annealed solids near the melting line can be more than a factor of 10 larger than those observed here;[4,7,8] this argues that any unpaired dislocations are not intrinsic, but, as in three-dimensional solids, are introduced as a consequence of condensation and/or freezing at a finite rate. We have argued elsewhere[12,13] for the geometric necessity of dislocation climb in relation both to adjustment of the lattice parameter to temperature or pressure changes, and to forming grain boundaries between oppositely rotated phases.

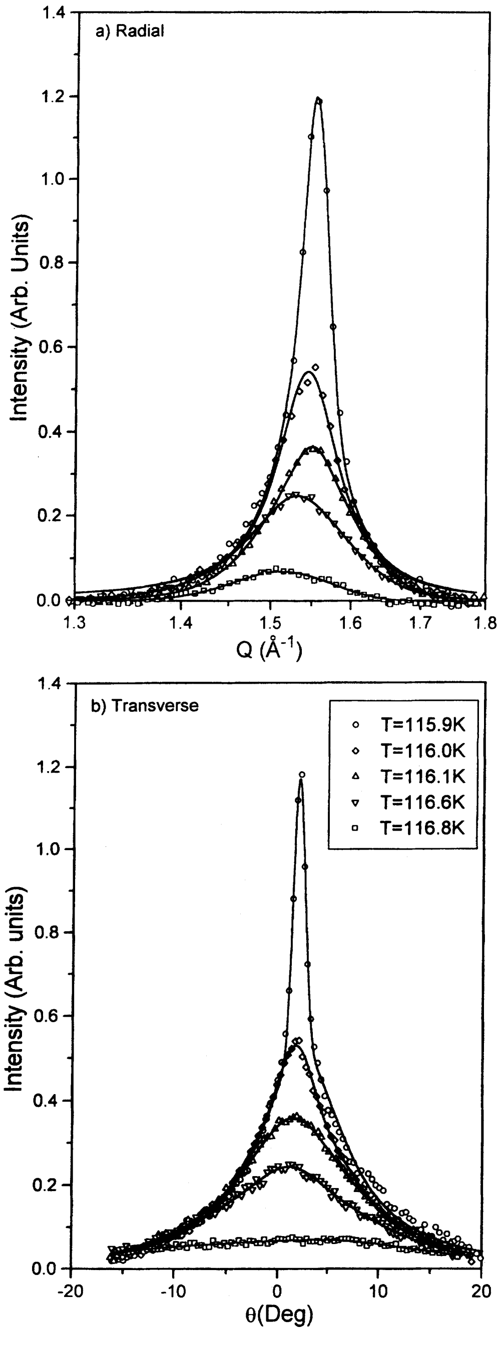

FIG. 2. Radial (a) and transverse (b) profiles through selected diffraction spots for $p=22$ mTorr. The lines are Lorentzian plus Gaussian (LG) fits as explained in the text.

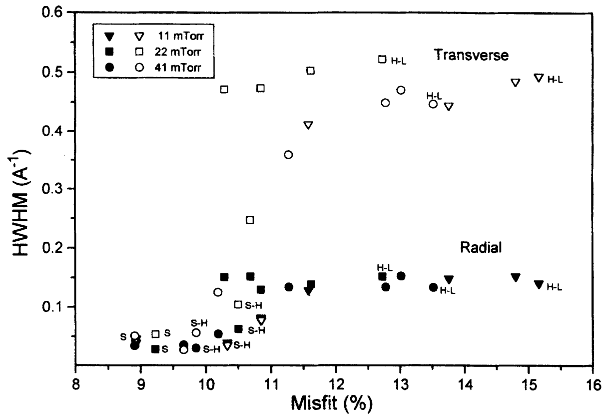

FIG. 3. Half-widths of radial and transverse profiles as a function of misfit. See text for discussion.

Lorentzian profiles, or close approximations to them, can arise either from disorder in the domain-wall system,[13] or from the PLS.[3,4,8] The mosaic broadening used in conjunction with the Lorentzian to describe the hexatic for $116<T<138$ K (Ref. 4) is close to our combination GL curves, and gives comparable transverse half-widths.

The hexatic profiles observed in the present work cannot be fit well with just a Lorentzian, but the G/L amplitude ratio is lower than in the solid. The radial and transverse half-widths of all the spots on Fig. 1 are shown in Fig. 3 as a function of misfit. There is a rapid transition, between 10% and 11% misfit, from the solid values, with transverse and radial widths essentially equal, to constant values appropriate to the hexatic. These values $\sigma_T=0.48\pm0.04$, and $\sigma_R=0.14\pm0.02$ Å^{-1}, are clearly characteristic of the hexatic phase near the melting line in the range $110<T<120$ K. The ratio $\sigma_T/\sigma_R=3.4\pm0.6$; this value is close to the estimated value of 3–4 suggested in Ref. 4 when account is taken of the substrate orientational field h_6; it is also close to the experimental value for Xe/Ag(111), where h_6 is thought to be smaller than for Xe-graphite;[14] but more detailed calculations seem to be lacking.

Figure 3 shows that there is indeed a well-defined hexatic phase with characteristic σ_R and σ_T, but Fig. 2 shows that the amplitude decreases while the widths stay more or less constant as the misfit increases. The final state is, as near as we can tell, an isotropic two-dimensional liquid. For example, the transverse data [Fig. 2(b), not all of it portrayed] shows the transition from solid-hexatic coexistence (the lowest temperature curve shown, with a two-component shape) to isotropic liquid. There is a reduction in peak amplitude $A(T)$ from the reference solid of a factor of 10 at the solid-hexatic transition, and a further factor of 10 within a temperature change of 1 K. On a plot similar to Fig. 1, ln$A$ versus T is locally a straight line, so that $A=A_0\exp(-E/kT)$; for T around 115 K, the factor of 10 in 1 K means that the energy (E/k) is in the region of 30 000-K units, around 2.6 eV. This is a huge energy for an activated process at 115 K, and would suggest that the two-dimensional liquid is created in relatively large patches. The fact that the solid and hexatic phases are so well aligned with the substrate means that a part of this energy must be due to h_6.

Previous x-ray work has correlated this amplitude variation with the radial width of the Lorentzian, finding that $A(\sigma_R)$ decreases strongly as σ_R increases, the data favoring a power law $(\sigma_R)^{-x}$, with $x=-1.71$.[4] That data correspond to a very narrow region near the solid-hexatic transition for $116<T<140$ K, where $\sigma_R<0.1$,[4] or <0.04 Å^{-1},[3,8] where the misfit is around 6–7.5 %. The x-ray technique has not followed the patterns further out into the hexatic-liquid region; the scattering is just too weak. The present data correspond to a broader region where the misfit is somewhat larger, and σ_R extends to about 0.15 Å^{-1}, which according to Fig. 3 seems to be a limiting value.

Our conclusions are that the aligned solid-liquid and hexatic-liquid transitions are at most weakly first order in this temperature range, and are about 0.9 K apart. With an experimental resolution of 0.1 K in temperature, 0.1% misfit and 0.1° orientation, the changes across both transitions are very subtle, and are driven primarily by thermal expansion, reminiscent of the Lindemann melting criterion.[15] At the solid-hexatic boundary, the misfit is essentially continuous, and the angular rotation broadens very rapidly as the misfit passes 10%, to around 15° characteristic of the hexatic phase. But soon after this transition is underway, the hexatic-liquid transition starts. In this second transition, the misfit increases rapidly with increasing temperature, and diffracted intensity is transferred from the hexatic to the isotropic liquid.

Comparison with previous thermodynamic measurements[5,6] is, of course, more difficult, because the techniques are so different from ours. However, it seems justified to make the following points. These papers are cast in terms of one transition, whereas we have shown here that there are in fact two sequential transitions. Most emphasis has been placed on high values of the isothermal compressibility K_T as a function of pressure. Here we see (Fig. 1) a corresponding rapid increase in misfit $m(T)$ at constant pressure, most obviously in the second (hexatic-liquid) transition, where the misfit m increases by 2–4 % as diffraction intensity is transferred from the hexatic to the liquid phase over a narrow temperature interval <1 K. The rapid changes in density n and density steps of order 2% seen in the thermodynamic measurements[5,6] are therefore not inconsistent with our measurements. If anything, we might deduce larger density changes based on a misfit-density relation $n=(1+m)^{-2}$, which is appropriate to a perfect solid;[11] but perfect solid models are certainly not correct near the melting transition. Smaller changes could, of course, also result from sample heterogeneity.

It is reasonable to conclude that thermodynamic studies were more sensitive to the hexatic-liquid transition, in which there is a substantial density change, whereas the high-resolution x-ray line-shape studies[4,7,8] were more sensitive to the solid-hexatic transition with long correlation lengths, where the density change is considerably less. Thus the two groups of workers have not been studying quite the same transition, hence the confusion in the literature. It is worth reinforcing that our study spans both transitions.

The composite diffraction line shapes, which result from these consecutive transitions, mean that extremely homogeneous samples, sensitive temperature and pressure control are required to make stronger statements about the order and energies associated with the separate transitions. Despite the success of KTHNY (with h_6 in addition) in predicting the ratio of transverse to radial widths in the hexatic phase, it remains true that no current theory based on second-order behavior predicts transitions that are as sharp as those observed. This implies that the spatial organization of the dislocations, and thermal expansion via anharmonic lattice vibrations, are also important in determining the fine details of the melting of monolayer xenon on graphite. Theoretical progress may be possible in future, building on previous calculations, which take (some of) these factors into account.[16]

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