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NEUTRON DIFFRACTION STUDIES OF MELTING ON PHYSISORBED MONOLAYERS OF CD_4 ON GRAPHITE

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ABSTRACT

The system of methane on grafoil has the unusual property that melting always takes place from an incommensurate phase - an expanded solid phase at coverages less than the full commensurate monolayer coverage, and the familiar compressed solid phase at higher coverages. Detailed line-shape analyses in the fluid and incommensurate solid phases and across the melting transitions show that (a) Lorentzian structure factors account well for the observed fluid lineshapes, with correlation lengths $\sim$ 30A well within the fluid phase; (b) "tails" in the incommensurate solid lineshapes indicate the presence of substantial 'thermal diffuse scattering' and can be fitted with power-law structure factors; (c) The expanded solid has only been observed to melt in a first-order way, whereas melting of the compressed solid is indistinguishable from continuous. However, outside the coexistence region, the approach to the transition region from either side is in all cases indicative of Kosterlitz-Thouless melting.

In an incommensurate phase of a monolayer physisorbed on graphite, the substrate potential in the plane may reasonably be approximated by its constant mean value, and such a system may therefore closely simulate a true two-dimensional system. Melting in two dimensions has been the focus of much theoretical activity. In particular, Kosterlitz and Thouless[1] have proposed that the transition is continuous and proceeds via the unbinding of dislocation and antidislocation pairs. Their work has been extended more recently by Halperin and Nelson[2] using renormalization group theory. We have experimentally studied the melting of monolayers of deuterated methane (CD_4) on exfoliated graphite; CD_4 has a large coherent scattering cross-section for neutrons, and moreover it turns out to have the unusual property of always melting from an incommensurate phase (see below and Fig. (1).

The lineshape calculated by Warren[3] for diffraction from a randomly oriented array of finite two-dimensional crystallites can be modified to account for the known partial orientation of exfoliated graphite surface planes, and has been widely used to characterise the neutron and x-ray diffraction spectra from monolayers physisorbed on these surfaces. The line-shapes are fitted in terms of three parameters: L, the linear dimension of the domains; G, the magnitude of the appropriate reciprocal lattice vector; and an overall multiplicative constant; long-range crystalline order is assumed. The system of methane on grafoil was studied in this fashion by Vora, Sinha and Crawford[4] who reported the phase diagram shown in Fig. 1.

From the value of G it was determined that a $\sqrt{3} \times \sqrt{3}$ commensurate structure is formed at low temperatures and coverages. At low temperatures, above a coverage defined as $\rho = 1.0$, the methane monolayer compresses into a triangular incommensurate phase. (The commensurate-incommensurate transition in methane has been discussed by M. Nielsen at this conference). Both these phases are familiar from studies of many other physisorbed systems, as is the liquid phase obtained for all coverages at high enough temperatures. However, with increasing temperature, the commensurate solid unexpectedly expands before melting and it appears that the expanded solid is always an intermediate stage in the melting of monolayers with $0.6 < \rho < 1.0$.

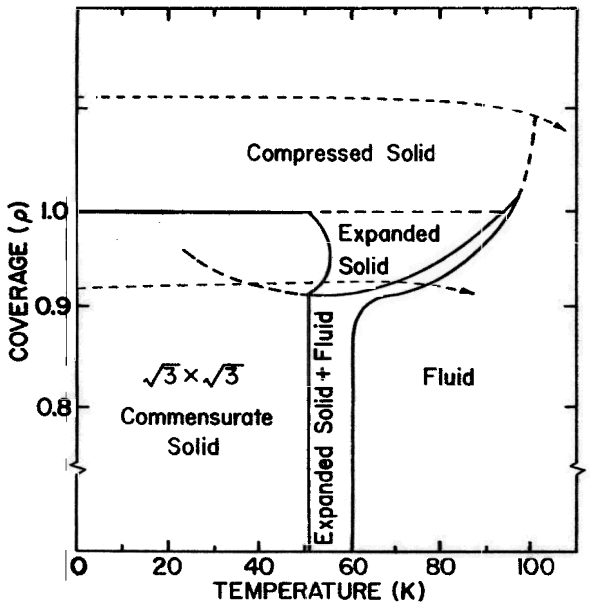

Fig. 1. Phase diagram for CD_4 on graphite (from Ref. 4). The units of coverage are defined such that $\rho = 1.0$ is the highest commensurate coverage at low T. The horizontal dotted lines indicate the trajectories along which the melting transitions were studied (Figs. 4, 6 and 7); the slight downward curves of these trajectories are due to increasing evaporation into the "dead space" in the graphite cell.

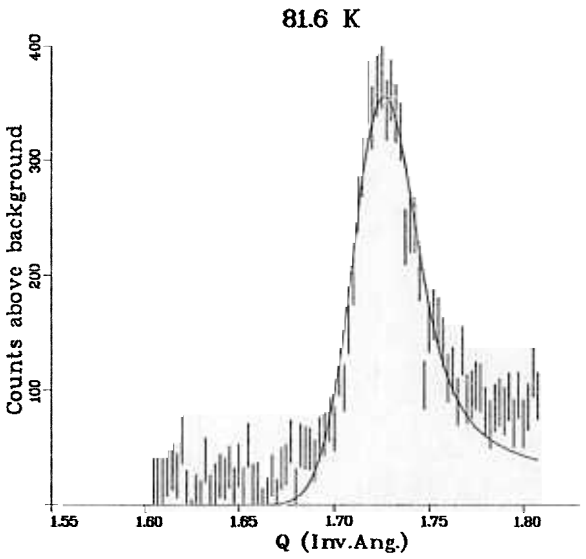

Fig. 2. Lineshape for incommensurate solid CD_4 on ZYX exfoliated graphite at 81.6K. The line is a Warren lineshape fit to the data (i.e. assuming 3D-like correlations and finite size). Note that it is unable to fit the "tail" in the data (in attempting to do so, it has become slightly too wide in the main body of the peak).

The Warren expression for the lineshape is of course inapplicable to fluid phases and solid-liquid coexistence regions, and identifications of such regions in the phase diagram are of necessity made by appropriately interpreting the behavior of the Warren parameters upon entering these regions. Indeed, even an infinite two-dimensional solid is not in principle characterizable in terms of the Warren parameters since long-range order is predicted not to exist. Fig. 2 shows a typical diffuse scan for a compressed solid monolayer of methane on ZYX graphite at 81.6°K and a coverage of $\rho \simeq 1.03$; the Warren lineshape does an adequate job near the peak but does not account for the "tail" at low Q values. These tails are observed in all solid phases (including the registered phase), are substantially larger (in relation to the peak) than is familiar for thermal diffuse scattering in three-dimensional crystals, and indicate the presence of large phonon fluctuations in these quasi-two-dimensional monolayers. The fact that tails exist also in the commensurate solid suggests that the graphite potential wells are particularly weak for methane, and is probably related to the fact that the commensurate monolayer always breaks out of registry before it melts.

In order to analyze lineshapes in cases where the Warren assumption of long-range order is (or may be) incorrect, we have reformulated the Warren expression in terms of a general structure factor S(q), taking into account the fact that the normals to the grafoil surfaces have a distribution $P(\Phi)$ that is peaked around $\Phi = 0$ (partial misorientation) but are completely randomly distributed with regard to rotation about the normals. The structure factor must thus be powder-averaged in the plane:

$$\bar{S}(K') = (2\pi)^{-1} f^2(K') \int_0^{2\pi} d\psi \, S(q) \qquad (1)$$

where

$$\vec{q} = \vec{K}' - \vec{G}$$

$\vec{G}$ is the reciprocal lattice vector; the averaging over orientations of G is represented by the integral over ψ(the angle between $\vec{K}'$ and $\vec{G}$); f(K) is the molecular form factor for methane (which rotates freely at all temperatures relevant here).

In terms of $\bar{S}(K')$, the observed intensity for a given scattering wave vector $\vec{K}$ may be shown to be

$$I(K) = \int dK' \; K' \; \bar{S}(K') F(K,K') \qquad (2)$$

where

$$F(K,K') = \int dK'' \frac{R(K - K'')}{K''^2} \frac{\theta(K'' - K')}{\sqrt{1 - (K'/K'')^2}} \int_{\beta}^{\pi - \beta} d\Phi \frac{P(\Phi)}{\sqrt{(K'/K'')^2 - \cos^2\Phi}} \quad (3)$$

Here, $R(\Delta K)$ is the instrumental resolution, $\theta(x)$ is a step-function, and

$$\beta \equiv \sin^{-1}\sqrt{1 - (K'/K'')^2}.$$

The misorientation function $P(\Phi)$ is well approximated by a gaussian with a FWHM of about 30^0 for grafoil and 15^0 for ZYX exfoliated graphite.

The Warren lineshape emerges from these expressions if

$$S(q) \propto \exp(-L^2q^2/4\pi)$$

which represents the effects of finite size on a delta-function structure factor. The effect of finite size on other structure factors is far less clear. (A detailed analysis of this effect for two-dimensional systems is in progress and will be reported separately). Nevertheless, we have used theoretical predictions for the infinite-size structure factors in the solid and liquid phases to fit lineshapes obtained in two temperature scans across the melting transitions performed at coverages $\rho = 0.92$ and $\rho = 1.09$. The values of the parameters thus determined, while not quantitatively accurate, may be expected to show illuminating trends.

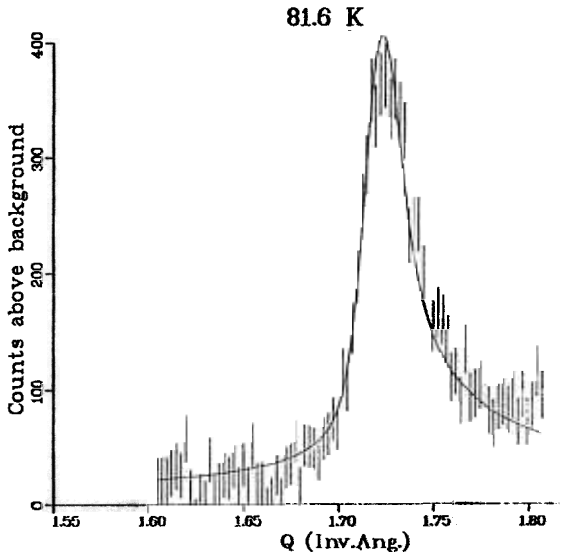

Fig. 3. Same data as in Fig. 2; the line is a fit assuming a power-law structure factor - $S(q) \sim 1/q^{2-\eta}$.

In the case of the solid phases using the power-law structure factors predicted for two-dimensional systems:

$$S(q) \propto \eta\left(\frac{2}{qa}\right)^{2-\eta} \quad (4)$$

(where a is the lattice constant), we are able to obtain excellent fits to both the "body" and the "tail" of each line (e.g. Fig. 3). As already pointed out, the values of η obtained from the fits (Fig. 4) are not exact. However we can say qualitatively that at $\rho = 1.09$, η stays fairly small and suddenly increases for T>95K just near the melting temperature. At $\rho = 0.92$, in the pure expanded solid phase, is considerably larger (which is reasonable since the density is lower) and increases with temperature. (Above 60K, in the coexistence region, the fits are not meaningful).

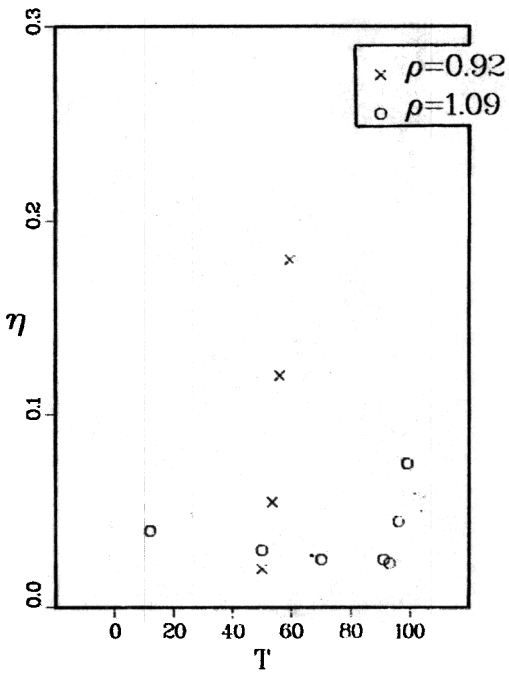

Fig. 4. η vs. T for expanded ($\rho = 0.92$) and compressed ($\rho = 1.09$) incommensurate solid CD_4 on grafoil.

Turning now to the liquid phase, the structure factor is predicted by Halperin and Nelson[2] to be approximately

$$S(q) \propto \frac{\xi^{2 - \eta^*}}{(q^2\xi^2 + 1)^{1 - \eta^*/2}} \quad (5)$$

Here η^* is the value of η for the solid at melting and ξ is a correlation length (at $T = T_c$, $\xi \to \infty$ and $S(q)$ reduces to Eq. 4 with $\eta = \eta^*$). The

description in terms of the distance q from a reciprocal lattice point is applicable because of the postulated existence of a hexatic phase. The temperature dependence of ξ is predicted by these authors to be

$$\xi = \xi_o \exp [A(T - T_o)^{-\nu}] \qquad (6)$$

where ν is calculated by Halperin and Nelson to be 0.369...and T_o is the transition temperature.

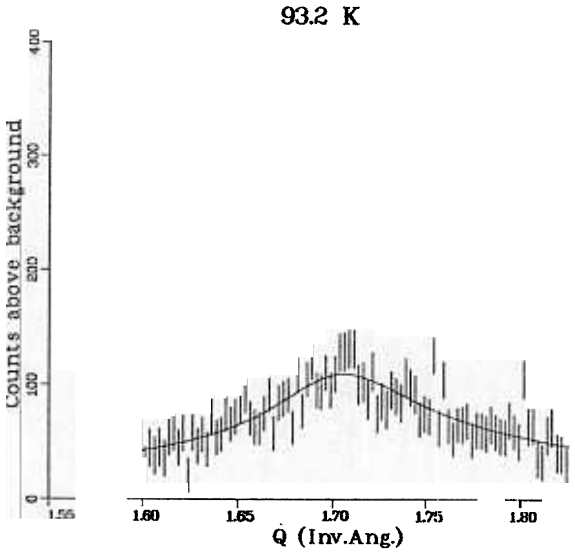

Fig. 5. Lineshape at 93.2K for the same system as in Figs. 2 and 3 (CD_4 on ZYX exfoliated graphite); the line is a fit assuming a Lorentzian structure factor $S(q) \propto A/(1 + q^2\xi^2)^{1-\eta^*/2}$.

We have fitted liquid lineshapes to Lorentzian structure factors (corresponding to the approximation $1-\eta^*/2 \simeq 1$) and find good fits (eg., Fig. 5). The values of ξ well inside the liquid phase are quite large ($\sim$ 30 Å). Further, we find that

(a) for ρ = .92 the lineshapes may be plausibly fitted near the melting transition with a sum of solid and liquid structure factors, with relative weights changing across the transition in such a way as to keep the total amount of material constant. Thus our identification in Ref. 4 of a solid-liquid coexistence region (indicative of a first-order transition) is consistent with our fits.

(b) The melting of the ρ = 1.09 monolayer is considerably sharper and we were not able to fit the rapidly changing lineshape to a sum of solid and liquid structure factors with constant total amount.

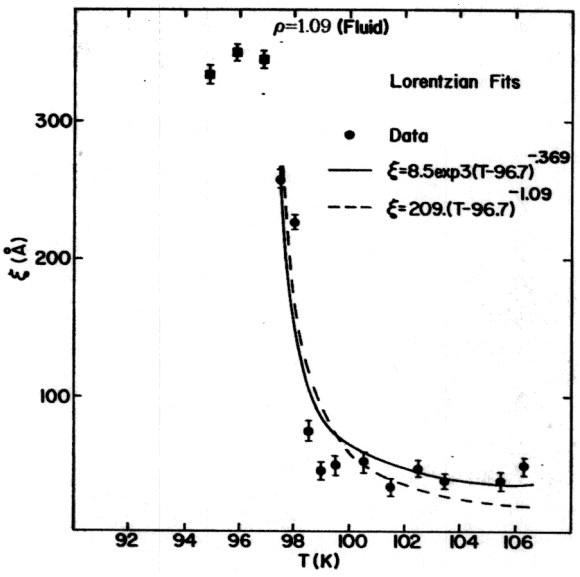

Fig. 6(a) Temperature dependence of ξ for ρ = 0.92.

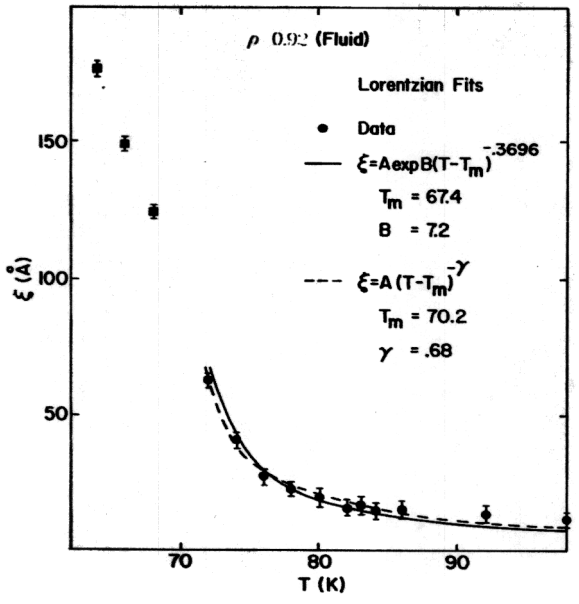

Fig. 6(b) Temperature dependence of ξ for ρ = 1.09.

Fig. 6 (a) and (b) show the behavior of ξ in the liquid as a function of temperature. In both cases ξ is fairly constant at $\sim$ 30Å and then

rapidly increases with decreasing temperature. When ξ reaches a few hundred angstroms it tends to level off; we are limited here both by the not-fully-understood effects of finite size and by the spectrometer resolution (S(q) is independent of ξ for $q \gg \xi^{-1}$). Fig. 6 (a) and (b) also show fits of the Halperin-Nelson prediction (Eq. 6) for $\xi(T)$ using ξ_o and T_c as parameters; also shown is a fit to

$$\xi \sim A\,(T - T_c)^{-\nu}$$

The largest values of ξ have been excluded from these fits for the reasons mentioned above. It can be seen that owing to the relatively small number of points, it is not really possible to distinguish between the models and to demonstrate the validity of Eq.(1); however, ξ does show strong 'precursor' behavior above the transition that is unknown in three dimensional fluids and is consistent with Eq. (6). Fig. 7 shows a plot of ln I vs ln ξ, where I is the amplitude of the Lorentzian. In both cases a reasonable straight line is observed with a slope slightly less than 2 as predicted by the theory [see Eq. (5)]. Also shown are points corresponding to temperatures clearly in the solid (for ρ = 1.09) or coexisting solid/fluid (for ρ = 0.92) phases, for which the Lorentzian structure factor is presumsbly not valid. In each case, a departure of the plot from linearity is observed which also helps to identify the transition. It may be recalled (Fig. 4) that in the incommensurate solid phase, the ρ = 0.92 coverage had a higher η; from the slopes in Fig. 7, this coverage can be also seen to have the higher η^*. Note that this is very qualitative since there is an intervening coexistence region for this coverage.

In conclusion, our detailed lineshape analyses show that:

(1) The substantial excess scattering in the solid phases can be explained in terms of power-law structure factors.

(2) While methane always melts from an incommensurate phase, there is an identifiable solid-liquid coexistence region at low coverages but not at high coverages. Thus the compressed solid may be melting in a continuous way.

(3) In both cases, however, the precursor behavior in the liquid correlation length, and the fact that the coverage with the higher η below the transition has the higher η^* above it, are qualitatively consistent with theoretical predictions. Thus it may be that dislocation unbinding has identifiable effects whether or not it is the primary process very close to the transition temperature.

This work was partially supported by the U.S. Department of Energy.

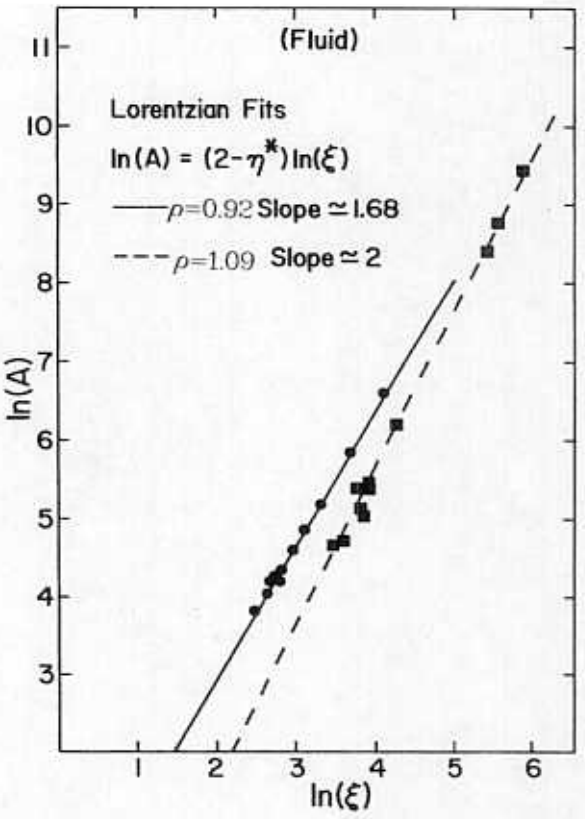

Fig. 7. Dependence of the scale factor A on for the two coverages, showing the different slopes (i.e. different values of η^*) in the two cases.

References:

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2. B. J. Halperin and D. R. Nelson, Phys. Rev. B 19, 2457 (1979).

3. B. E. Warren, Phys. Rev. 59, 693 (1941).

4. P. Vora, S. K. Sinha and R. K. Crawford, Phys. Rev. Lett. 43, 704 (1979).

5. See, e.g. Y. Imry, CRC Crit. Rev. in Sol. State and Mat. Sciences 8, 157 (1979).

DISCUSSION

O. Vilches:

Could you comment on the discrepancies between

the French neutron scattering data and the isotherm work and the phase diagram you showed?

The isotherms show that there is a liquid-vapor coexistence region. Why not put it in your phase diagram?

P. Dutta:

Early data reported by Bienfait and coworkers did not show an expanded phase. They have now studied the system further (see Glachant et al., these proceedings) and have identified the expanded phase. Since Vora et al. did not attempt to distinguish the liquid from the vapor phase, there are now no discrepancies regarding the qualitive features of the phase diagram.