

**UC Davis**  
**IDAV Publications**

**Title**

Neutron -Diffraction Study of Phases of CD4 Monolayer Films on Graphite

**Permalink**

<https://escholarship.org/uc/item/5k61s3w8>

**Journal**

Physical Review Letters, 43

**Authors**

Vora Purohit, Parul

Sinha, S. K.

Crawford, R. K.

**Publication Date**

1979

Peer reviewed

order phase transitions which occurs between 27°C and 5°C. In Fig. 4, transverse scans show that these transitions involve changes in the interlayer periodicity from two layers to three layers near 22°C and back to two layers again near 12°C. Finally below 7°C the lattice becomes monoclinic with the  $\tilde{c}^*$  axis tilting as a function of temperature.

We conclude by emphasizing that our results on thick films clearly establish that the smectic-*B* phase of 4O.8 has 3D long-range order. Although it is apparently a solid, unusually low-frequency layer shear modes exist. Furthermore, the energy of interlayer ordering must be weak to account for the observed phase transitions below 27°C. In thin-film experiments we have shown that it is possible to use x-ray diffraction techniques which have thus far demonstrated that the smectic-*B* phase is a 2D crystal. From this basis it is now possible to approach the problem of 2D melting. Improved synchrotron-based x-ray experiments are now in progress.

We have had a number of stimulating discussions with R. J. Birgeneau, W. F. Brinkman, D. S. Fisher, B. I. Halperin, J. M. Kosterlitz, and D. R. Nelson which have been important to

the development of these studies. Also we thank S. C. Davey for technical assistance.

<sup>1</sup>C. Y. Young, R. Pindak, N. A. Clark, and R. B. Meyer, *Phys. Rev. Lett.* **40**, 773 (1978); C. Rosenblatt, R. Pindak, N. A. Clark, and R. B. Meyer, *Phys. Rev. Lett.* **42**, 1220 (1979).

<sup>2</sup>B. Jancovici, *Phys. Rev. Lett.* **19**, 20 (1967); N. D. Mermin, *Phys. Rev.* **176**, 250 (1968).

<sup>3</sup>B. I. Halperin and D. R. Nelson, *Phys. Rev. Lett.* **41**, 121 (1978); D. R. Nelson and B. I. Halperin, *Phys. Rev. B* **19**, 2457 (1979).

<sup>4</sup>J. M. Kosterlitz and D. J. Thouless, *J. Phys. C* **6**, 1181 (1973).

<sup>5</sup>R. J. Birgeneau and J. D. Litster, *J. Phys. Lett. (Paris)* **39**, 399 (1978).

<sup>6</sup>A.-M. Levelut, J. Doucet, and M. Lambert, *J. Phys. (Paris)* **35**, 773 (1974).

<sup>7</sup>A. deVries, A. Ekachai, and N. Spielberg, *J. Phys. (Paris), Colloq.* **40**, C3-147 (1979); A. J. Leadbetter, J. Frost, J. P. Gaughan, and M. A. Mazid, *J. Phys. (Paris), Colloq.* **40**, C3-155 (1979); J. Doucet, A.-M. Levelut, and M. Lambert, *Ann. Phys. (N.Y.)* **3**, 157 (1978).

<sup>8</sup>J. J. Benatter, A.-M. Levelut, L. Liebert, and F. Moussa, *J. Phys. (Paris), Colloq.* **40**, C3-115 (1979).

## Neutron-Diffraction Study of Phases of CD<sub>4</sub> Monolayer Films on Graphite

Parul Vora

*Physics Department, University of Illinois, Chicago, Illinois 60680, and Solid State Science Division Argonne National Laboratory, Argonne, Illinois 60439*

and

S. K. Sinha and R. K. Crawford

*Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439*

(Received 16 April 1979)

Neutron-diffraction studies have been carried out of the various two-dimensional phases of CD<sub>4</sub> physisorbed on graphite and a phase diagram has been constructed. Registered, expanded, and compressed solid phases and a disordered fluidlike phase have been identified. The lattice constant, intensity, and cluster size have been measured as functions of temperature and coverage and the nature of the transitions between the phases has been investigated.

The nature of the various phases of submonolayer atomic or molecular films physisorbed on solid surfaces, and of the transitions between such phases have recently received increasing experimental and theoretical attention.<sup>1-3</sup> The interactions between the adsorbed molecules themselves and with the substrate lead to a rich variety of ordered ("solid"-like) and disordered ("fluid"-like) two-dimensional (2D) phases which may be

commensurate or incommensurate with the substrate.

In this Letter, we present the results of a neutron-diffraction investigation of the various 2D phases of methane adsorbed on exfoliated graphite. Methane was chosen because it is the simplest (spherical) hydrocarbon molecule which can be thus studied and because no detailed information has been available regarding the 2D phases of

this physisorbed system. However, vapor-pressure isotherm measurements of Thomy and Duval<sup>4</sup> had indicated the occurrence of phase transitions in this system, and some preliminary structural investigations have been reported for methane on Graphon powder by Marlow *et al.*<sup>5</sup>

The measurements were carried out using a substrate of preferentially oriented crystallites of exfoliated graphite known as Grafoil<sup>6</sup> having a surface area estimated to be 22 m<sup>2</sup>/g and a mosaic spread estimated to be 30° (full width at half maximum). To utilize the coherent scattering from deuterium, 98% deuterated CD<sub>4</sub> gas was used and introduced into the sample chamber via a capillary from a standard gas-handling system. The plane of scattering was parallel to the planes of the Grafoil chips, corresponding to the average basal plane orientation of the crystallites.

Detector 2 $\theta$  scans were made around the region of the (10) powder peak arising from the triangular methane lattice. These intensity profiles were analyzed after subtracting the intensity of scattering from the empty substrate. These profiles were fitted with line shapes arising from the theory of Warren,<sup>7</sup> modified to include approximately partial orientation effects<sup>8</sup> and instrumental resolution. The three parameters used in the fitting process were the peak amplitude ( $I$ ), the cluster size ( $L$ ) (also roughly interpretable as a correlation length), and the plane spacing ( $d$ ). The main features and novel aspects of these results may be summarized as follows.

From the measured values of the  $d$  spacings in the solid phases, we have identified registered, compressed, and expanded solid phases. The measurements represent the first detailed neutron-diffraction study of the commensurate-incommensurate transition as a function of coverage in these systems, although similar studies using low-energy electron diffraction<sup>8</sup> and x-ray scattering<sup>9</sup> have been carried out for krypton on Grafoil. From the behavior of the  $L$  parameter and the peak amplitude  $I$  as functions of coverage and temperature, fluid phases and coexisting solid and fluid phases have been identified and the phase diagram has been constructed. One of the most remarkable features of CD<sub>4</sub> on Grafoil is its property, at the lower coverages, of expanding out of registry before melting to a fluid, which does not seem to have been previously observed in such systems. Equally remarkable is the fact that the peak in the fluid structure factor appears to be situated at the position of the Bragg peak of the registered solid. Finally, while the behavior of  $I$  vs  $T$  strongly points to a first-order melting transition at the lower coverages (also supported by the fact of a coexistence region), it favors an interpretation in terms of a continuous melting process from the dense solid phase.

Figure 1 shows an example of some of the (10) diffraction peaks (with the Grafoil scattering subtracted) together with the fitted line shapes for various temperatures at 0.8-monolayer coverage. One may observe how the peak appears to move

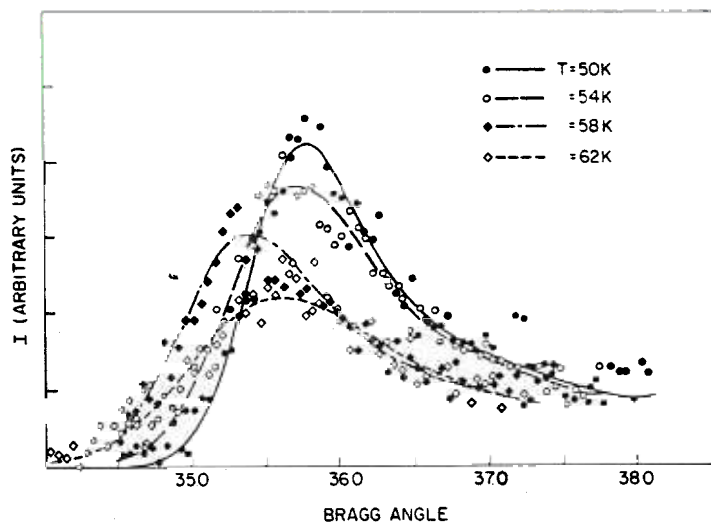


FIG. 1. Some typical (10) diffraction peaks for several temperatures at  $\pi=0.8$  monolayer. The curves represent Warren line-shape fits to the data.

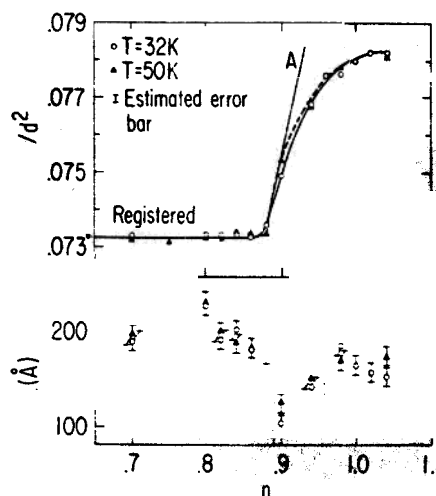


FIG. 2. Plot of  $1/d^2$  and  $L$  vs monolayer fraction  $n$ . The vertical arrow denotes a change in phase as indicated by the text and Fig. 4. The straight line A represents the rate at which  $(1/d^2)$  would increase if all molecules continued to go onto the first monolayer after completion of the registered monolayer.

to smaller  $2\theta$  for  $T > 50$  K indicating an expanded phase after which it broadens and moves back to larger  $2\theta$  as the fluid phase appears.

Figure 2 shows the behavior of  $1/d^2$  (equal to  $2/\sqrt{3}$  times the molecular surface density within the ordered clusters) versus  $n$ , the average monolayer fraction as determined from the isotherm measurements, for  $T = 32$  and  $T = 50$  K. Note that  $n$  is defined relative to the completed compressed monolayer. It is seen that at lower coverages, the registered (commensurate) structure is observed. For  $T = 32$  K and  $n \geq 0.88$ , the area per molecule decreases with increasing coverage and the compressed monolayer is observed. The results indicate that the commensurate-incommensurate transition is *continuous* within experimental accuracy in agreement with the theory of Bak *et al.*<sup>10</sup> The rate of increase of surface density is not as rapid as the increase in coverage, however, indicating that some of the added molecules ( $\sim 9\%$  when  $n = 1$ ) are going elsewhere, possibly on to the second layer (see Fig. 2). When  $n = 1$  is reached, the rate of increase of the surface density diminishes rapidly indicating saturation of the compressed monolayer and the formation of a second layer. Figure 2 also indicates the behavior of  $L$  vs  $n$  at 32 and at 50 K. We see that there is a sudden decrease of  $L$  (manifested as a broadening of the leading edge of the peak) at a

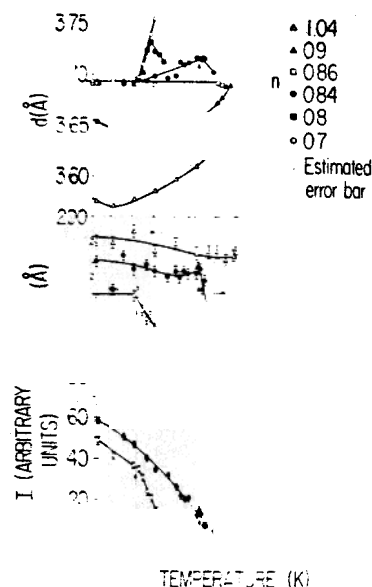


FIG. 3. Plots of lattice plane spacing  $d$ , cluster size  $L$ , and peak intensity  $I$  vs temperature for various coverages. The arrows denote a change in phase as indicated by the text and Fig. 4.

coverage of 0.9, around where the transition to the compressed phase has taken place although  $L$  increases again in the compressed phase. This may indicate the formation of defect regions or microdomain structure at the commensurate-incommensurate transition.<sup>10</sup>

Figure 3(a) shows the behavior of  $d$  vs  $T$  for various representative values of average coverage  $n$ . For  $32 \text{ K} < T < 50 \text{ K}$ , registered or compressed phases are observed depending on coverage, with the compressed phase showing a minimum in the  $d$  spacing at finite temperatures. For  $T > 50 \text{ K}$  (for  $n < 0.88$ ), the registered phase begins to expand linearly with temperature (see Fig. 1). At higher temperatures (for  $n < 0.88$ ) there is another sudden change in behavior where the diffraction peaks broaden anomalously (corresponding to a sudden decrease in  $L$ ) and  $d$  starts to decrease again with increasing temperature. We interpret this as the superposition of a diminishing solid ( $S_{\parallel}$  phase) peak and a broad liquidlike peak centered at the "registered" periodicity. Computer simulations of a superposition of such peaks, in fact, gave the observed qualitative behavior. This behavior is not observed in the compressed phase ( $n > 0.88$ ). Finally at still higher temperatures, for all coverages, the peaks de-

crease rapidly in intensity indicating the loss of the solid phase. Figure 3(b) indicates the temperature dependence of the parameter  $L$  for three representative values of  $n$ . This parameter is most sensitive to the slope of the leading edge of the diffraction peak. Note that the rms graphite crystallite size determined from the width of the graphite reflection is  $\sim 400 \text{ \AA}$  and the thickness is  $\sim 100 \text{ \AA}$ . At lower coverages, the rather rapid decrease of both peak intensity and cluster size  $L$  with increasing temperature is interpreted as arising from the loss of solidlike regions in a coexistence region with a low-density fluid as the fluid boundary is approached. In the compressed phase ( $n > 0.88$ ) the  $L$  parameter decreases slightly but does not change significantly until very close to melting. This is similar to the behavior observed by Horn *et al.*<sup>11</sup> in monolayers of Kr on Grafoil. Figure 3(c) indicates the peak intensities versus temperature for the above three coverages. For  $n \leq 0.80$  two regions of roughly linear decrease of intensity can be distinguished, the boundary being at 50 K, the temperature of the registered- to expanded-solid transition. For the higher coverages, the intensity appears to curve downwards with increasing temperature in a manner more reminiscent of a continuous phase transformation. On the basis of the above data we have constructed the tentative phase diagram shown in Fig. 4. We have indicated a region of commensurate phase  $S_I$  separating the incommen-

surate-phase regions  $S_{II}$  (expanded) and  $S_{III}$  (compressed). The phase diagram also indicates the existence of a "fluid" phase which coexists in some temperature ranges with the solid  $S_I$  and  $S_{II}$  phases as indicated. For the lower concentrations and temperatures, the fluid phase would correspond to a low-density "vapor" and would not be observed in the neutron-diffraction patterns. At higher concentrations and temperatures, the fluid would have a much higher density and would presumably give rise to a broad liquidlike diffraction peak. As mentioned above, we observe a sudden change of the peak shape on crossing the line  $AB$  to a broad low-amplitude shape which appears to be a superposition of a solidlike and a liquidlike peak. Note that we have not distinguished here between liquid and vapor fluid phases since the neutron experiments alone are unable to distinguish a coexistence region of such phases. It would not be inconsistent with our data, however, to have such a coexistence region above 60 K for  $n < 0.8$ . The phase boundaries could then be modified in Fig. 4 to demarcate  $S_{II} + V$ ,  $S_{II} + L$ , and  $L + V$  phases, and 60 K would then be the 2D triple point. Coulomb, Bienfait, and Thorel<sup>12</sup> have used mobility measurements to indicate that a liquid-gas coexistence region should exist. No information regarding the solid phases and the solid-liquid coexistence region are available from these measurements, however. The phase diagram in Fig. 4 bears a good qualitative resemblance to the phase diagram for  $\text{CH}_4$  on graphite calculated by Ostlund and Berker from renormalization-group theory.<sup>13</sup> These authors, however, assume that only registered solid and fluid phases exist. The remarkable fact about the present system is that the solid-fluid transition in general (except possibly for a narrow concentration range) takes place from an incommensurate solid phase. In such a case one might expect the Halperin-Nelson theory<sup>14</sup> to apply which would favor a continuous transition. However, the effect of the substrate potential may seriously modify their results. Our present results indicate such a continuous transition from the compressed incommensurate solid to the fluid phase but the melting from the expanded solid phase probably takes place in a first-order manner. Theory<sup>14</sup> indicates that above the true 2D solid-liquid transition temperature (where the pair correlation function changes from a power-law form to an exponential) there is a temperature range over which orientational correlations exist before an isotropic liquid phase is reached.

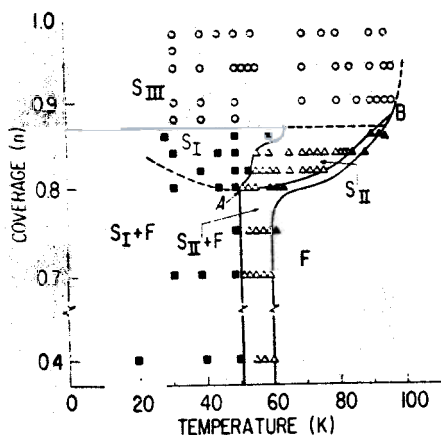


FIG. 4. Phase diagram for  $\text{CD}_4$  on graphite.  $S_I$ ,  $S_{II}$ , and  $S_{III}$  indicate, respectively, registered, expanded, and compressed solid phases and  $F$  indicates a fluid phase. Each point represents a measurement of the (10) peak.



It is possible that the broad liquidlike peaks which are indicated by the data at temperatures beyond the line *AB* may be due to such orientationally ordered regions modified by the periodic potential of the substrate. The Warren line-shape theory used to fit the intensity profiles is in any case not rigorously valid except possibly in the registered solid phase since it does not take into account a continuous decay of particle correlations with distance. More detailed measurements and analysis in terms of various types of pair correlations functions are underway. The details regarding possible critical behavior of both the order parameter and the pair correlations near the transitions are also presently under study. Detailed vapor-pressure-isotherm and specific-heat measurements to verify our proposed phase diagram would be helpful. Quasielastic scattering studies of the diffusion of  $\text{CH}_4$  on the graphite surface have also been carried out<sup>15</sup> and further details will be published shortly.

We wish to acknowledge helpful discussions with S. H. Chen, S. C. Fain, Jr., L. Kadanoff, R. J. Birgeneau, P. M. Horn, S. Doniach, J. McTague, L. Passell, and J. White. One of us (P.V.) would also like to thank J. W. Garland for continuing advice and encouragement. This work

was supported by the U. S. Department of Energy.

<sup>1</sup>J. Phys. (Paris), Colloq. **10**, C4 (1977).

<sup>2</sup>J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1978).

<sup>3</sup>A. N. Berker, S. Ostlund, and F. A. Putnam, Phys. Rev. B **17**, 3650 (1978).

<sup>4</sup>A. Thomy and X. Duval, J. Chim. Phys. **67**, 1101 (1970).

<sup>5</sup>I. Marlow, R. K. Thomas, T. D. Trewern, and J. W. White, J. Phys. (Paris), Colloq. **10**, C4-19 (1977).

<sup>6</sup>J. K. Kjems, L. Passell, H. Taub, J. G. Dash, and A. D. Novaco, Phys. Rev. B **13**, 1446 (1976).

<sup>7</sup>B. E. Warren, Phys. Rev. **59**, 693 (1941).

<sup>8</sup>M. D. Chinn and S. C. Fain, Jr., Phys. Rev. Lett. **39**, 146 (1977).

<sup>9</sup>P. W. Stephens, P. Heiney, R. J. Birgeneau, and P. M. Horn, to be published.

<sup>10</sup>P. Bak, D. Mukamal, J. Villain, and K. Westowska, Phys. Rev. B **19**, 1610 (1979).

<sup>11</sup>P. M. Horn, R. J. Birgeneau, P. Heiney, and E. M. Hammonds, Phys. Rev. Lett. **41**, 961 (1978).

<sup>12</sup>J. P. Coulomb, M. Bienfait, and P. Thorel, Phys. Rev. Lett. **42**, 733 (1979).

<sup>13</sup>S. Ostlund and A. N. Berker, private communication.

<sup>14</sup>B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. **41**, 121 (1978).

<sup>15</sup>S. K. Sinha, S. H. Chen, R. Diehl, and R. K. Crawford, to be published.

## Theory of Minority-Carrier Injection

J.-C. Manificier and H. K. Henisch

*Department of Physics and Materials Research Laboratory, The Pennsylvania State University  
University Park, Pennsylvania 16802*

and

J. Gasiot

*Centre d'Etudes Electroniques des Solides, Université des Sciences et Techniques du Languedoc,  
34060 Montpellier, France  
(Received 19 January 1979)*

It is shown that minority-carrier injection into trap-free semiconductors at low current densities can lead to a local field maximum and resistance increase. These features disappear at high current densities, and only then is the more familiar expectation of a resistance decrease fulfilled.

As is well known, the transport equations which govern carrier-injection (and all related) processes cannot be solved in analytic form without the introduction of simplifying approximations (e.g., the assumption of space-charge neutrality, the neglect of free-carrier space charges, etc.). The relationships are, however, very complex, and the extent to which these assumptions affect the physics of the situation cannot be safely left

to intuitive judgment. In this situation two other approaches are possible: (a) recourse to computer-derived solutions of the complete equations and (b) linearization of the equation without *ad hoc* assumptions, leading to a "small-signal theory." Approach (b) was described in four previous papers.<sup>1-4</sup> One of the (several) results they yielded was the prediction of a local resistance increase as a result of minority-carrier injection