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Structure and Melting of Submonolayer Ethane Films on Graphite

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Elastic neutron diffraction has been used to study the structure and melting of submonolayer ethane films physisorbed on exfoliated graphite. Analysis of the relative intensity of seven Bragg reflections of the film yields the molecular orientation in the close-packed solid structure observed below 63 K. At higher temperatures a novel melting process occurs which we tentatively interpret as a first-order transition to an intermediate phase followed by continuous transition to the disordered state.

Elastic neutron diffraction has developed rapidly in the past few years[1] as a method of studying the structure of gases physisorbed on high-surface-area powdered substrates. Because of the penetrability of the probe, neutron scattering has the advantage that films can be examined under high vapor pressure for samples similar to those on which thermodynamic measurements such as vapor-pressure isotherms and specific heats can be performed. In this way the technique has been useful in elucidating the phase diagrams of simple gases physisorbed on various exfoliated graphite substrates.[2] Nonetheless, even in the most favorable circumstances[3] only a few Bragg reflections of the film have been observed so that a conventional structure determination fitting a large number of Bragg angles and peak intensi-

ties to a model structure factor is difficult. To date, only the neutron diffraction experiment of Suzanne *et al.* on nitric oxide adsorbed on graphite[4] has attempted to use the relative intensities of several Bragg reflections to infer the orientation of an adsorbed molecule. However, their analysis was limited to determining only one orientational parameter in a model structure.

We have recently begun to study the elastic diffraction of neutrons from deuterated ethane films adsorbed on graphite. We have found these films to be exceptionally favorable for neutron scattering studies because of the large number of Bragg reflections observable. Analysis of the neutron diffraction pattern of the low-temperature solid phase yields not only the two-dimensional (2D) unit cell but also the three Euler angles spec-

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ifying the orientation of the adsorbed molecules. The temperature dependence of the diffraction patterns suggests a novel melting process which is initiated by a structural transformation to an expanded phase.

The neutron scattering experiments described here were conducted at the Institut Laue-Langevin (ILL) in Grenoble and at the University of Missouri Research Reactor Facility (MURR). The ILL measurements were performed on the two-axis D1B spectrometer with an incident neutron beam of wavelength 2.52 Å and a Papyex substrate as described previously.[4] Experiments at MURR were on the two-axis D-port spectrometer at a wavelength of 1.29 Å with a Grafoil[1] substrate. Both exfoliated graphite substrates had a surface area of ~ 20 m²/g and were aligned with the scattering vector Q parallel to the foil planes. The deuterated form of the gas (C_2D_6) was used to enhance the coherent neutron cross

section of the film.

In Fig. 1(a) we show the elastic diffraction pattern obtained with 1.29 Å neutrons incident upon a 0.8-layer C_2D_6 film adsorbed on Grafoil at a temperature of 8.6 K. The background scattering from the substrate has been subtracted. Seven peaks can be distinguished in the difference spectrum, the most intense of which clearly exhibit the "sawtooth" profile characteristic of diffraction from a 2D polycrystal.[1] The diffraction pattern was reproducible at the longer neutron wavelength of 2.52 Å except near $Q = 3.1$ Å⁻¹ where the graphite scattering is particularly strong relative to that of the film.

To analyze this diffraction pattern, we first attempted to find a 2D unit cell which would index the observed reflections. The van der Waals dimensions of the molecule together with the assumption of close packing suggested an oblique cell containing one molecule as shown in Fig. 2. The cell of minimum area which we have found to index the diffraction peaks has primitive vectors $|\vec{a}| = 4.91$ Å, $|\vec{b}| = 3.89$ Å, and the included angle $\theta = 86.4°$.[5]

Since calculations based on empirical atom-atom potentials had indicated a negligible distortion of the ethane molecule when adsorbed on a

FIG. 1. (a) The diffraction pattern $(\lambda = 1.29$ Å$)$ from a 0.8-layer C_2D_6 film adsorbed on Grafoil at 8.6 K. Arrows at the top mark angles at which Bragg reflections from the graphite and the aluminum sample holder occur. The observed pattern is compared with calculated spectra for different angles of the C-C bond with respect to the surface: (b) 90°, (c) 0°, and (d) 24°. The spectra are normalized so that the strongest peak of the calculated and observed spectrum, respectively, have equal intensity. The tilted configuration in (d) gives the best agreement with the observed spectrum.

FIG. 2. Structure of the ethane submonolayer: (a) The 2D unit cell. (b) Definition of the orientational parameters α, β, and ψ. For clarity in labeling, the molecule is not drawn to scale. The zero of α corresponds to the configuration in Fig. 4 of Ref. 6. (c) Projection (to scale) of the ethane molecules on the 2D unit cell. Circles represent approximate van der Waals radii of the D atoms. (d) Illustration of the tilting of the molecules with respect to the surface. Atoms numbered 2, 4, 7, and 8 are nearly coplanar.

graphite basal plane,[6] we assumed each cell to
be occupied by a rigid molecule with an orienta-
tion described by the three Euler angles α, β,
and ψ defined in Fig. 2(b). The relative intensity
of the Bragg reflections was then calculated from
the Warren theory of diffraction for 2D poly-
crystals[7] in the form appropriate to neutron scat-
tering.[8] The Debye-Waller factor was set equal
to unity[9] in order to limit the number of fitting
parameters to the three Euler angles in the geo-
metrical structure factor. In comparing calcu-
lated with observed intensities, we chose not to
estimate integrated peak intensities in Fig. 1,
since overlapping of the Bragg reflections asso-
ciated with their sawtooth shape introduced large
uncertainties. Instead, the initial step of the
sawtooth was assumed proportional to the inte-
grated intensity.[10] The peak overlap necessitated
taking a separate background level for each re-
flection as shown by the horizontal lines in Fig. 1.

The Euler angles of the molecule were varied
systematically to find the best agreement between
the calculated and observed Bragg intensities.
The results are shown in the lower portion of
Fig. 1 for a series of representative orientations.
Figure 1(b) shows the best fit which could be ob-
tained with the C-C bond constrained to be per-
pendicular to the surface ($\beta = 90°$, α varied) while
Fig. 1(c) shows the best fit obtained with the C-C
bond constrained parallel to the surface ($\beta = 0$,
α and ψ varied). Of these, the worst fit occurs
for the perpendicular configuration in which only
the first three Bragg reflections are calculated
to be observable and these do not have the cor-
rect relative intensity. Although better agree-
ment is achieved in the parallel configuration,
there are still discrepancies such as the negli-
gible intensity predicted for the (1$\bar{2}$) peak. Be-
cause of the missing peaks, neither of these cal-
culated spectra would be improved by including
a Debye-Waller factor or changing the background
level assumed for each peak.

We have obtained the best fit to the observed
spectrum when the C-C bond is tilted at an angle
of 24° with the surface. The calculated intensi-
ties for this orientation are shown in Fig. 1(d)
and the corresponding crystal structure is illus-
trated in Figs. 2(c) and 2(d). Calculations of the
2D crystal structure of ethane using empirical
interatomic potentials and including both the in-
termolecular and graphite contributions to the
potential energy are now in progress.[11] We note
that previous calculations[6] neglecting the inter-
molecular interaction predicted the C-C bond to

be parallel to the graphite basal plane rather than
the tilting that we have inferred here.

The sensitivity of the calculated structure fac-
tors to the molecular orientation is easily under-
stood. The molecule is sufficiently large with re-
spect to the 2D unit cell that a small rotation
moves an atom through a significant fraction of a
lattice spacing. In practice, we were able to
bracket the observed diffraction pattern between
calculated spectra for which the Euler angles of
the molecule differed by 10°. In this way we es-
timate an error of $\pm 5°$ for the Euler angles.[12]

Neutron diffraction patterns at other fillings
and temperatures demonstrate that the submono-
layer structure of ethane is stable between cov-
erages of 0.4 and 0.8 layers and at temperatures
up to 60 K. As shown in Fig. 3(a), the diffraction
pattern from a 0.4-layer film at 60 K is similar
to that in Fig. 1 except, as noted above, near
$Q = 3.1$ Å^{-1}. However, above 60 K the spectra be-
gin to change dramatically. At 62.5 K [Fig. 3(b)],
the (10), (11), and (20) Bragg peaks of the low-
temperature solid have disappeared while the (01)
peak is still present but with reduced intensity.
In addition, a new peak appears at $Q = 1.47$ Å^{-1}.
Only this peak remains at 65 K [Fig. 3(c)], broad-
ening continuously about the same Q value above
70 K [Figs. 3(d) and 3(e)]. A similar temperature
dependence is observed in the diffraction patterns
of the 0.8-layer film.
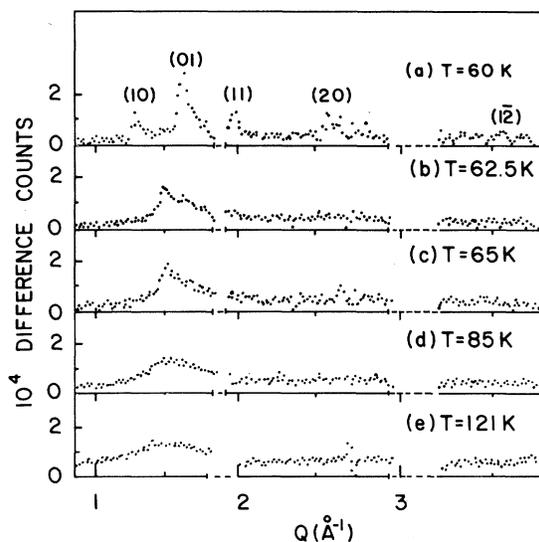
FIG. 3. Temperature dependence of the diffraction
patterns ($\lambda = 2.52$ Å) for a 0.4-layer C_2D_6 film adsorbed
on Papyex. The graphite background has been sub-
tracted. Dashed lines on the abscissa correspond to
the position of the most intense substrate peaks.

Our preliminary interpretation of these results is that the melting of the submonolayer film is preceded by an expansion from the low-temperature solid to an intermediate phase which is at least partially ordered. This transition is first order as evidenced by the coexistence of the two phases between 60 and 65 K. We identify the single-peak diffraction pattern at 65 K with the pure intermediate phase and tentatively interpret the broadening of the Bragg peak observed above 70 K as a continuous loss of the long-range order present in the intermediate phase.[13]

The structure of the intermediate phase is difficult to determine from the single-peak diffraction pattern of Fig. 3(c). The d spacing of 4.26 Å inferred from the Bragg angle suggests an epitaxial phase. The peak can be indexed as the (10) reflection of a triangular lattice having a nearest-neighbor distance of 4.92 Å. This structure can form in 2×2 epitaxy on a graphite basal plane and has the virtue of allowing only two other reflections, the (11) and (20), in the Q range of Fig. 3. Although evidence of a (20) reflection is obscured by the intense graphite scattering near $Q = 3.1$ Å^{-1}, the (11) reflection at $Q = 2.55$ Å^{-1} should be observable (a peak appears at this Q vector in the low-temperature phase). Therefore, the (11) peak would have to be extinguished by the structure factor or, in the case of orientational disorder, a molecular form factor. The possibility of an orientationally disordered solid phase is now being investigated both experimentally by quasielastic neutron scattering[13] and theoretically by calculations with empirical potentials.[11,14] Experiments are also in progress to investigate the structure of the ethane films at coverages above a monolayer.

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[10]This approximation was found to hold reasonably well for the first two Bragg reflections which overlap the least. We are investigating whether the fitting procedure can be improved by adapting the profile refinement method for 3D powder diffraction developed by H. M. Rietveld [Acta Crystallogr. 22, 151 (1967)] to the analysis of the film spectra. Profile analysis will also elimate the need to assume a separate background level for each Bragg peak.

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[12]This, of course, assumes that the 2D unit cell has been correctly identified.

[13]An alternative interpretation is that there is only short-range order in the intermediate phase, and between 60 and 65 K this liquidlike phase coexists with the low-temperature solid. However, the relatively large intensity of the intermediate-phase peak in Fig. 3(b) and the narrow width of its leading edge do not appear to support this view. Quasielastic neutron scattering experiments by J. P. Coulomb and M. Bienfait are now in progress to elucidate the nature of the melting process.

[14]The empirical potentials are also being used to calculate the energy barriers to translational motion (Ref. 11). For example, parallel chains of the rod-shaped molecules could "unlock" and slide parallel to each other.