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The melting of submonolayer ethane adsorbed on graphite : a LEED study

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Résumé. — Nous avons étudié la fusion d'une sous-monocouche d'éthane adsorbée sur un monocristal de graphite par Diffraction d'Electrons Lents (DEL). La phase solide S_1 possède une maille rectangulaire commensurable $4 \times \sqrt{3}$ avec une structure moléculaire en chevrons. A $T = 65$ K, S_1 se transforme en un liquide de réseau I_1 de symétrie hexagonale, commensurable 2×2 . Lorsqu'on augmente la température, I_1 perd son ordre positionnel et d'orientation des liaisons de manière continue. A 95 K, la figure de DEL est un anneau diffus, caractéristique d'un liquide isotrope.

Abstract. — The melting of ethane submonolayers has been studied by Low Energy Electron Diffraction (LEED). The solid phase S_1 has a $4 \times \sqrt{3}$ rectangular commensurate structure with a herring-bone packing. At $T = 65$ K, S_1 melts into a lattice fluid I_1 having the hexagonal symmetry of a 2×2 commensurate structure. With increasing T , I_1 continuously loses its positional and bond orientational orders. At $T = 95$ K, the LEED pattern shows a diffuse ring, characteristic of an isotropic fluid.

Melting in two dimensions (2D) has attracted much attention since Kosterlitz and Thouless presented their theory of dislocation-mediated melting and suggested that this transition should be continuous [1]. Since then, theories [2-4], experiments [5-12] and computer simulations [13-15] have brought about a lot of controversial matter. For instance, Abraham [15], Migone *et al.* [10] and Hurlburt *et al.* [12] have shown that a seemingly continuous melting transition can be observed to be first order under careful investigation, using more appropriate techniques. However, recent X-rays experiments, seemed to show a continuous melting into a hexatic phase for an incommensurate monolayer of xenon adsorbed on single crystals of exfoliated graphite [16]. Melting transitions from commensurate phases have also been reported and are generally considered to be disordering transitions [17].

This Letter describes a LEED study of the melting of submonolayer ethane films adsorbed on graphite single crystals. This transition is particularly interesting for it occurs from a com-

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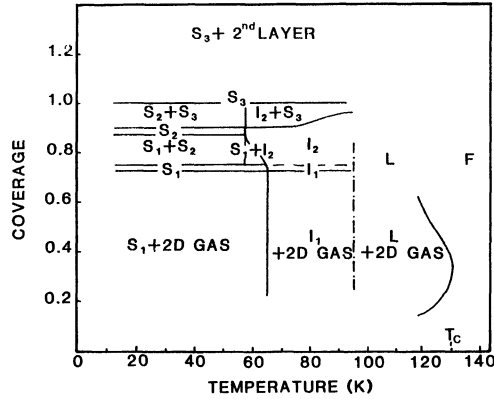


Fig. 1. — Tentative phase diagram of ethane monolayer adsorbed on graphite [34]. Coverage of one monolayer corresponds to that of the phase S_3 . See table I for characteristics of the various 2D phases.

mensurate solid phase having a herring-bone structure. The system ethane/graphite has been studied previously by numerous techniques : classical volumetry [18], elastic [19-21] and inelastic [22] neutron scattering and LEED [23]. A more complete study of the structure and thermodynamics of ethane adsorbed on graphite has been performed and will be presented later [24]. It has allowed us to complete the 2D phase diagram of reference [23]. As shown in figure 1, it features three solids S_1 , S_2 and S_3 , two intermediate phases I_1 and I_2 and fluid phases L and F. Table I

Table I.

Phase	Structure	Area/molecule	Temperature range
S_1	Rectangular Commensurate $4 \times \sqrt{3}$ Herring-bone packing C-C // surface	21 \AA^2 (2 molecules/cell)	$T \lesssim 65 \text{ K}$
S_2	Rectangular Commensurate $10 \times 2\sqrt{3}$ Packing unknown	17 \AA^2 (12 molecules/cell)	$T \lesssim 57 \text{ K}$
S_3	Triangular Commensurate $\sqrt{3} \times \sqrt{3}$ C-C \perp surface	15.7 \AA^2	$T \lesssim 85 \text{ K}$
I_1	Triangular Commensurate 2×2 Close-packed	21 \AA^2	$T \lesssim 90 \text{ K}$
I_2	Triangular Incommensurate Close-packed	$21 \text{ \AA}^2 < a < 16.5 \text{ \AA}^2$	$T < 90 \text{ K}$

presents the characteristics of the various 2D phases. In the present work, we have studied the sequence of phases $S_1 \rightarrow I_1 \rightarrow L$ in more details and tried to determine the nature of the intermediate phase I_1 .

The domains of stability of the different 2D phases being known, we can set the conditions of substrate temperature and pressure of 3D ethane gas in the chamber in order to have a pure I_1 or L phase (coverage 0.7 on the phase diagram of Fig. 1).

The study has been made from photographs and negatives employing ILFORD HP5 film (400 ASA) taken with 35 mm Nikon camera and an exposure time of 30 s. We have used a computer controlled photodensitometer to measure the spot intensity. The response of the film has been supposed linear. A more careful analysis would take account of the film response *versus* intensity. A calibration will be made in the future but would probably not change the qualitative features of the present results.

We have first studied the $S_1 \rightarrow I_1$ transition. In previous works [19, 23], it has been tentatively interpreted as being a transition to an orientationally disordered solid. As pointed out in reference [23], this transition is somewhat analogous to the orientational order-disorder transition observed at 27 K for nitrogen adsorbed on graphite [25, 26]. As for nitrogen, the densities of S_1 and I_1 are equal (Table I). However, the analogy is limited : in the case of ethane, the molecules no longer remain in their original sites ($S_1 : 4 \times \sqrt{3} \rightarrow I_1 : 2 \times 2$). Furthermore I_1 has a shorter positional order correlation length L than S_1 . Measurements on LEED patterns show that $L \simeq 50 \text{ \AA}$ for I_1 close to the $S_1 \rightarrow I_1$ transition (70 K), in agreement with previous neutron diffraction experiments [21] which give also $L = 120 \text{ \AA}$ for S_1 .

We think at the present time that unlike the commensurate disordered phase of N_2 /graphite, I_1 is a lattice fluid. According to this picture, molecules are translating and rotating, but on average, their centres of mass spend most of the time on 2×2 sites. To argue for the lattice fluid model, we have considered recent results on the measurements of the mobility of ethane molecules in the I_1 phase by quasi-elastic neutron scattering (QENS) [27]. They show translational diffusion above 65 K and an increase of mobility with temperature. Furthermore, NMR experiments have shown an increase of mobility above 65 K [28]. It is also worth noticing that the value of the ratio

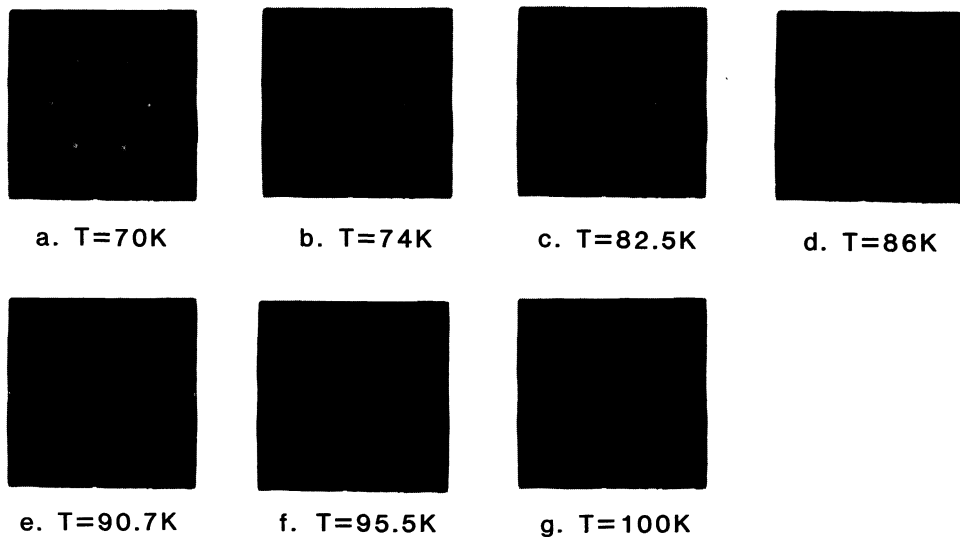


Fig. 2. — LEED patterns of ethane submonolayer adsorbed on graphite showing the continuous change in the positional and bond orientational orders of the lattice fluid I_1 . Figure 2a shows a rather well correlated 2×2 commensurate phase. At 95.5 K, figure 2f, the spots have merged into a broad, diffuse ring, and the fluid phase is no longer commensurate (distance between molecules in the 2×2 phase : 4.92 \AA).

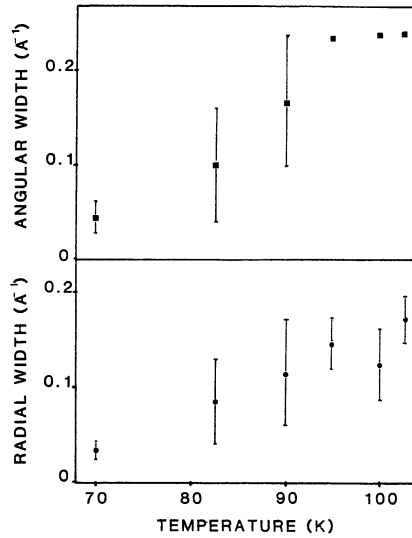


Fig. 3. — Angular and radial widths of the I_1 spot versus temperature. The widths increase continuously with T . Above 95 K, the angular width is constant which means that the pattern is ring-like.

of the temperature of the $S_1 \rightarrow I_1$ transition to that of the 3D triple point $T(S_1 \rightarrow I_1)/T_t(3D) = 0.72$ is very close to the ratio of the temperature of melting to the 3D triple point $T_M(2D)/T_t(3D)$ of commensurate krypton (0.73) [29] or nitrogen (0.75) [30]. As expected, it is larger than the same ratio for various incommensurate adsorbates on graphite (0.62 for Xe [31] and CH_4 [32]). This is another argument in favour of the fluid like nature of I_1 if we admit that the barrier to translational motion for ethane molecules rotating above the surface is of the same order of magnitude as the rare gases or CH_4 . The lattice fluid model also explains the lack of long range order observed for I_1 .

We have also studied the I_1 lattice fluid with increasing T . Figure 2 shows a series of LEED patterns at different T . As said before, they correspond to the pure I_1 phase and then pure L phase. Close to the $S_1 \rightarrow I_1$ transition ($T = 70$ K), the 2×2 triangular commensurate structure is observed. At higher T , the spots elongate angularly and give gradually a ring like pattern observable at $T \geq 95$ K. At the same time, the fluid becomes incommensurate expanded (4.45 Å, i.e. + 4 %, at $T = 100$ K). Figure 3 shows the variation of the radial and angular widths of the spots versus temperature. It can be seen that the angular and radial widths change continuously with increasing T . Unlike for xenon and the interpretation of the results published in reference [16], we think that the bond orientational order of ethane on the graphite surface is due to the substrate field. When T increases, the residence time in 2×2 sites decreases, reducing the range of order in the fluid. This shorter residence time is confirmed by the increase of translational mobility with T shown by QENS [27]. It is interesting to notice that the parameter increases, i.e. is no longer that of the 2×2 structure when the bond orientational order is lost. Hence the I_1 lattice fluid loses its 2×2 modulation and becomes an isotropic fluid at a disorder line located around 95 K as shown in figure 1 (vertical dash-dotted line).

As a conclusion, the melting of the S_1 phase of ethane submonolayer occurs *via* an intermediate phase I_1 which is a lattice fluid having the 2×2 modulation. The $S_1 \rightarrow I_1$ transition occurs at 65 K. An increase of temperature decreases the positional and bond-orientational orders of the lattice fluid in a continuous manner. Above 95 K, the fluid loses its 2×2 modulation and becomes isotropic. Finally, we cannot definitively rule out the existence of a plastic phase between the solid S_1 and the lattice fluid I_1 in a very narrow temperature range. Let us recall that a plastic phase exists for 3D ethane between 89.9 K and 90.3 K [33].

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