2D Ising Critical Behavior at an Isomorphous Structural Phase Transition in C_2F_6 Monolayers Physisorbed on Graphite

D. Arndt, St. Faßbender, M. Enderle, and K. Knorr
Technische Physik, Universität des Saarlandes, D-66041 Saarbrücken, Germany

(Received 14 April 1997)

C_2F_6 monolayers physisorbed on graphite have been investigated by heat capacity and x-ray diffraction measurements. With increasing temperature, the adsorbate shows a sequence of three 2D solid phases, all of them having a triangular lattice, followed by the 2D fluid state. One of the transitions belongs to the universality class of the 2D Ising model and is of a new orientational order-disorder type. [S0031-9007(98)05379-4]

PACS numbers: 68.45.−v, 61.50.Ks, 64.60.Cn, 65.40.+g

A large variety of quasi-two-dimensional transitions in monolayer adsorbates has been studied in the last decades. In many cases, the critical behavior can be described in terms of elementary models of statistical mechanics for order-disorder transitions. Concentrating on examples in physisorbed layers on graphite, the melting of the $\sqrt{3} \times \sqrt{3}$ phase of He and H_2 monolayers [1,2] is consistent with the order-disorder transition of the three-states Potts model and the liquid-vapor critical behavior of CH_4 submonolayers [3] with the two-dimensional (2D) Ising model. Both cases are understood in terms of the analogy of lattice gas models with the corresponding spin models. In transitions which involve orientational ordering, the relation of the orientation of the molecule with the spin variable of the models is perhaps somewhat more direct. Here, CO monolayers provide two examples for 2D Ising critical behavior. The transition from the disordered phase to the pinwheel phase in the compressed monolayer [4] and the dipolar head-tail ordering [5] out of the herringbone phase in the submonolayer regime are of this type. For the latter transition, the connection between the real system and spin model is particularly apparent, even though the dipole pattern of the ordered phase is not known. In the present article, we report on a new orientational ordering transition of the 2D Ising type. Strangely enough, the diffraction patterns suggest that the two phases involved are isomorphous.

Hexafluoroethane C_2F_6 monolayers physisorbed on the honeycomb surface of (exfoliated) graphite have been investigated before by x-ray powder diffraction [6]. At low temperatures T, the monolayer is commensurate (C) 2×2 with the substrate lattice. This structure has also been observed for other adsorbed molecules which contain the CF_3 group, namely CF_4 (Ref. [7]), CF_3Cl, and CF_3Br (Ref. [8]). Steric considerations suggest that in all of these cases the molecules rest on the F_3 tripod supplied by the CF_3 group. For C_2F_6, this means that the molecular axis is perpendicular to the substrate. An adsorption on the other, asymmetric and somewhat larger, 1-F_2, 2-F tripod with the axis about parallel to the substrate can be ruled out from these considerations and would also be in conflict with the triangular lattice symmetry. At 80 K, there is a phase transition into an expanded triangular incommensurate (IC) phase which finally melts at $T_m = 115$ K. The temperatures refer to the submonolayer regime in which these phases coexist with the 2D gas (i.e., with practically bare surface regions). In contrast to the more frequent case of C-IC transitions induced by changes of the coverage, the C-IC transition of the present adsorbate is T induced.

C_2F_6 monolayers have been investigated by heat capacity $c(T)$ measurements using the heat pulse technique in an adiabatic calorimeter, the substrate being again exfoliated graphite (Papyex). These measurements show an additional phase transition intermediate in temperature to the C-IC and the melting transition. Therefore, we reinvestigated the adsorbate by exhaustive x-ray powder diffraction measurements (and by some ellipsometric adsorption isotherms, obtained on HOPG. The ellipsometric isotherms are of excellent quality comparable to those measured on Ar, Kr, and Xe on graphite). The coverage θ of the heat capacity and the diffraction experiment is quoted as the number of molecules per four graphite hexagons; thus, the coverage of the ideal 2×2 phase is unity. Figure 1 shows the heat capacity for $\theta = 0.6$. Note that the additional transition ($T_c = 103.6$ K) gives rise to an anomaly considerably stronger than those of the C-IC and of the melting transition. As in the previous study, there is no symmetry breaking at T_c, such as a peak splitting or the appearance of additional reflections, apparent in the diffraction measurements. Thus, both phases, IC2 above and IC1 below T_c, are of triangular symmetry. Profiles of the (10) reflection of the triangular lattice are displayed in Fig. 2. Higher reflections, such as (11) and (20), could not be observed. This problem has been encountered in x-ray and neutron diffraction studies on the high-symmetry triangular phase of many other adsorbates on exfoliated graphite. The lattice parameter a and the coherence length L, i.e., the inverse of the intrinsic width γ^{-1}, of the diffraction peak are shown in Fig. 3. One notes an enormous thermal expansion in the two IC phases, which continues in the liquid state above the

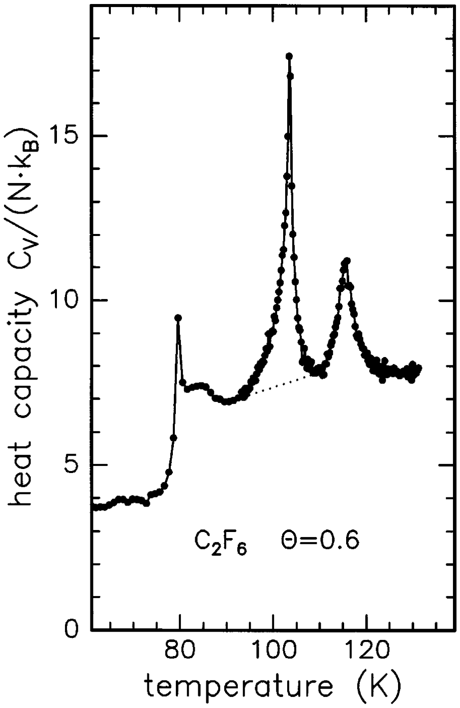

FIG. 1. Heat capacity per particle for a coverage θ of 0.6. The dotted line is the noncritical background used for the determination of the critical contribution.

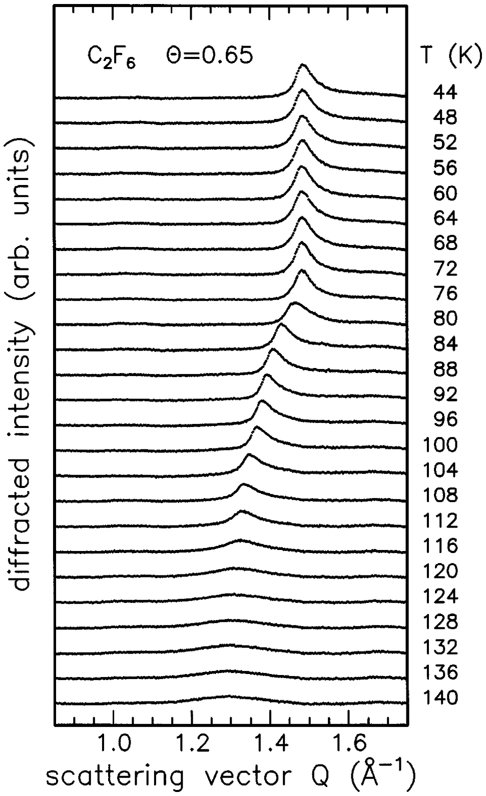

FIG. 2. A series of diffraction patterns for $\theta = 0.65$ showing the principle reflection (10) of the triangular phases. The 2D origin of the reflection is apparent from the asymmetric peak shape (Warren-type profile).

melting temperature. The overall increase of a up to T_m is 11%. At T_c, there is a slight kink in $a(T)$ and a small step in $\gamma^{-1}(T)$. Melting shows up as an anomaly of $c(T)$ with a well defined maximum at T_m. In the diffraction data, the only fingerprint of the melting is the coherence length gradually decreasing to values of the order of two molecular diameters in the liquid state. Although the data suggests that melting is a continuous transition, power law fits to the melting anomaly were not successful. The C-IC transition is of first order with a small latent heat of $4k_B$ K.

The shape of the heat capacity anomaly of the IC1-IC2 transition at T_c calls for an interpretation in terms of critical behavior. Fits to power laws failed, but an excellent description is obtained with the model function $c(T) = -A\ln|T - T_c|$ with $T_c = 103.6$ K and $A = 2.48$, above and below T_c (see Fig. 4). The noncritical part of the heat capacity used in this fit is the linear function of T indicated in Fig. 1. Note that only the slope but not the absolute value of the noncritical background is relevant for the fit.

The heat capacity of the 2D Ising model of a triangular lattice with next-neighbor coupling J can be calculated analytically. In the critical regime, a logarithmic T dependence with a coefficient $A_0 = 0.4991$ is obtained [9]. Thus, apart from the value of the prefactor A, the heat capacity anomaly at T_c follows the 2D Ising model.

As far as the value of the prefactor A is concerned, one can reconcile theory and experiment with the following consideration: Across the critical regime, there is a considerable expansion of the lattice; $\partial a/\partial T$ is of the order of 0.015 Å/K, hence J will decrease with increasing T, thereby compressing the critical regime into a narrower T interval compared to the rigid case with constant J. In an approximation to first order, $J(T) = J_c + b(T - T_c)$ with $b = \partial J/\partial a\ \partial a/\partial T$, $J_c = J(T_c)$. Since the internal energy of the model can be written as a product of $J(T)$ times a function f of the variable $T/J(T)$, one finally arrives at the expression $c/c_{\mathrm{Ising}} = A/A_0 = 1 - bT_c/J_c$. Inserting the experimental and theoretical value for the coefficient A and using the relation $T_c/J_c = 4/\ln(3)$ yields $b = -1.1$ and $\partial J/\partial a = -80$ K/Å. This appears to be a reasonable value for the variation of the coupling strength with distance. Alternatively, one may postulate a $J(a)$ dependence of the form $J \propto a^{-n}$. The enhancement factor A/A_0 then requires an exponent of about 13 which is close to the exponent of the repulsive part of the Lenard-Jones potential. The noncritical part of the heat capacity as obtained from this calculation is, in fact, not linear in T as assumed in our data treatment but rather has the shape of a smeared-out step centered at T_c. This explains qualitatively why, in Fig. 4, the data points below T_c lie somewhat above those above T_c.

Since the transition takes place in an IC rather than in a rigid C lattice, one expects that the Ising spins couple to the translational fluctuations (compressible Ising model)

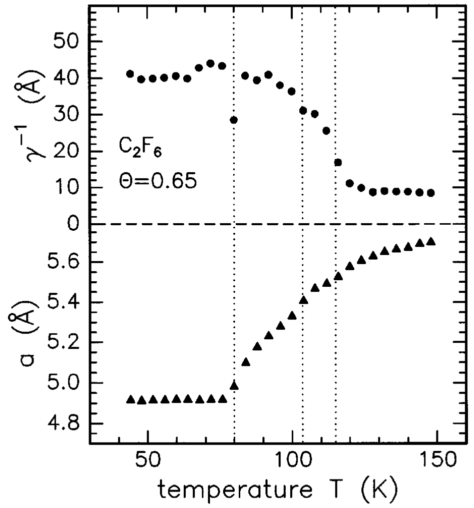

FIG. 3. The lattice constant and the inverse intrinsic width γ^{-1} of the (10) reflection as a function of temperature. The dotted lines give the transition temperatures of the phase sequence C-IC1-IC2-liquid. The low value of γ^{-1} at 80 K is explained in terms of two nonresolved reflections representing the coexisting phases C and IC1.

[10–14]. (Because of the rather peculiar symmetry of the present Ising variable, which will be discussed below, this coupling should not involve uniaxial lattice distortions but only A_{1g} distortions, the corresponding compliance being the 2D compressibility.) The coupling to the lattice may drive the transition to first order. Theory suggests that in cases where the transition is close to second order—as evidenced experimentally by an almost divergent heat capacity—the "pseudocritical" behavior should be still that of the Ising model on a rigid lattice.

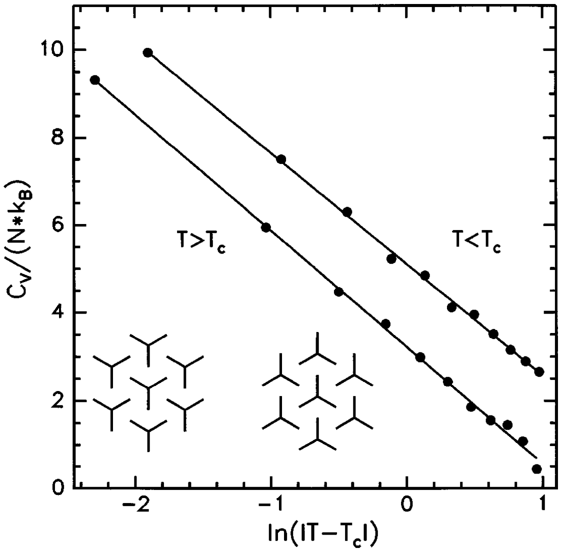

FIG. 4. Plot of the critical part of the heat capacity at the IC1-IC2 transition. The pattern at the bottom is a schematic view of the "+" and "−" domain of the ordered phase IC1. The symbols represent the F_3 tripods of the molecules.

We suggest relating the Ising variable, which is relevant to the transition at T_c, to the discrete azimuthal orientation of the molecule about its axis. We recall that this axis is perpendicular to the substrate. The inset of Fig. 4 shows the orientational pattern of the lower F_3 tripods that are in contact with the substrate in the two domains "+" and "−" of the ordered phase IC1. Above T_c, in the disordered phase IC2, the molecules perform hindered rotations about their axes, with an increasing preference for the orientations + and − as the temperature is lowered towards T_c. It is this preference for two special azimuthal orientations which corresponds to the Ising anisotropy in a spin model.

Is the x-ray structure factor different in the ordered and the disordered phases? The molecule consists of two CF_3 groups which are rotated by 60 deg with respect to each other. The lower CF_3 groups of the + domain have the same azimuth as the upper CF_3 groups of the − domain, and vice versa. In our schematic picture, the projection of the molecule onto the 2D plane, therefore, corresponds to a star with six arms, no matter whether the molecules are in the + or the − domain of the ordered phase. A mixture of + and − molecules as in the disordered phase IC2 has the same projection and, hence, the same 2D structure factor as in the ordered single domain state of the IC1 phase. In a more realistic calculation, the extension of the molecule perpendicular to the substrate is taken into account. The structure factor is now modulated along the (hk) Bragg rods. The modulation depends on the node index and is, at least for a general reflection (hk), different in the ordered and the disordered phases. However, for the principal reflection (10)—which is the only one observable in the present experiment—the structure factor is still identical for the two phases. Thus, the absence of changes at the IC1-IC2 transition in our diffraction data is perfectly understandable.

The overall structural behavior of the C_2F_6 monolayers is as follows: Throughout the 2D solid state, the molecule is oriented perpendicular to the substrate. The transition from the C phase at low T into the expanded IC state appears to be induced by the thermal excitation of translational and small-amplitude librational modes rather than by reorientation jumps. Azimuthal disorder is achieved via a separate, isomorphous, Ising-type phase transition. The apparently continuous melting [14] of the monolayers then involves not only the loss of translational symmetry but also that of the perpendicular alignment of the molecules with respect to the substrate.

A comparison to monolayers of ethane C_2H_6 physisorbed on graphite is appropriate. Here, a phase transition which involves a change of the orientation from flat to perpendicular can be induced by increasing coverage [15]. In the perpendicular state, the thermal excitation of the rotations about the molecular axis progresses gradually with increasing T (Refs. [16,17]), rather than via an order-disorder transition, as in the present system.

This work has been supported by the Deutsche Forschungsgemeinschaft (Projekt Kn234/6).

[1] M. Bretz, Phys. Rev. Lett. **38**, 501 (1977).
[2] H. Freimuth and H. Wiechert, Surf. Sci. **162**, 432 (1985); F.C. Motteler and J.G. Dash, Phys. Rev. B **31**, 346 (1985).
[3] H.K. Kim and M.H.W. Chan, Phys. Rev. Lett. **53**, 170 (1984).
[4] Y.P. Feng and M.H.W. Chan, Phys. Rev. Lett. **71**, 3822 (1993).
[5] H. Wiechert and S.-A. Arlt, Phys. Rev. Lett. **71**, 2090 (1993).
[6] A.R.B. Shirazi and K. Knorr, Mol. Phys. **78**, 73 (1993).
[7] B. Croset, C. Marti, P. Thorel, and H.J. Lauter, J. Phys. (Paris) **43**, 1659 (1982).
[8] K. Knorr, Phys. Rep. **214**, 113 (1992).
[9] R.M.F. Houtappel, Physica (Utrecht) **16**, 425 (1950).
[10] M.E. Fisher, Phys. Rev. **176**, 257 (1968).
[11] A.I. Larkin and S.A. Pikin, Sov. Phys. JETP **29**, 891 (1969).
[12] J. Sak, Phys. Rev. B **10**, 3957 (1974).
[13] D.J. Bergman and B.I. Halperin, Phys. Rev. B **5**, 2145 (1976).
[14] K.J. Strandburg, Rev. Mod. Phys. **60**, 161 (1988).
[15] J.M. Gay, J. Suzanne, and R. Wang, J. Chem. Soc. Faraday Trans II **82**, 1669 (1986).
[16] J.P. Coulomb and M. Bienfait, J. Phys. (Paris) **47**, 89 (1986).
[17] S. Zhang and A.D. Migone, Phys. Rev. B **42**, 8674 (1990).