Orientational disorder and melting of CF₂Cl₂ monolayers physisorbed on graphite

A. Warken, M. Enderle, and K. Knorr

Technische Physik, Bau 38, Universität des Saarlandes, 66123 Saarbrücken, Germany

(Received 25 January 1999)

We present specific heat experiments on CF_2Cl_2 monolayers physisorbed on graphite and determine the entropy changes at the structural and melting phase transitions. The results confirm previously reported x-ray studies where a phase sequence from a low-temperature commensurate hexagonal phase to an incommensurate triangular mesophase and finally the liquid phase was observed. The temperature dependence of the excess entropy reveals that the low temperature phase is orientationally ordered. Angular disorder with respect to reorientation around the surface normal evolves in the mesophase, and is fully developed just below the melting transition where the molecule starts to rotate around an axis parallel to the surface. We observe strong evidence for two-dimensional random exchange or random field behavior at the melting transition of the mesophase due to the bond disorder produced by the rotation about an axis parallel to the surface.

I. INTRODUCTION

Physisorbed monolayers are examples of almost perfect two-dimensional (2D) systems. Although the binding energy of the molecules to the substrate is large compared to the intermolecular potentials, the molecules are able to move almost freely, parallel to the surface, and thus can form a 2D gas, a 2D liquid, and one or more 2D crystalline phases.¹ Of course, the binding energy may prefer a certain orientation of the molecule with respect to the surface normal. Moreover, the corrugation of the substrate leads to constraints both on the lateral and the orientational degrees of freedom parallel to the surface.^{2,3} While the constraints on the lateral degrees of freedom act like an additional 2D interaction which has minima for distances of the molecules equal to a lattice vector of the substrate, and thus can lock the layer into registry with the substrate, the constraints on the orientational degrees of freedom, due to the substrate, can be regarded as an additional anisotropy field which leads to a preferred orientation of the molecule with respect to the substrate. On the other hand, the interaction with the neighboring molecules is lower than in 3D, simply because of the smaller coordination number, usually 6 compared to 12 for compact globular molecules. This point favors the appearance of orientationally disordered phases in 2D.² Even with equal coordination numbers in 2D and 3D, the splitting of a fully ordered system into domains with freely fluctuating domain walls, becomes more and more favorable with decreasing dimension, due to an increase of the entropy gain with respect to the energy loss by building a domain wall. This means that disordered phases are generally more favorable in 2D than in 3D. Even glassy phases have been found in homogeneous monolayers of small molecules.⁴

The molecule of the present study, the polar C_{2v} halomethane CF_2Cl_2 crystallizes in 3D out of the liquid state into an orthorhombic structure (spacegroup Fdd2) which is fully orientationally ordered, the dipole moments all pointing into the *c* direction.⁵ The monolayers adsorbed on graphite form three 2D crystalline phases.⁶ This article deals with the evolution of the specific heat capacity in the temperature range

of the structural phase transition and the melting transition. In contrast to most other heat capacity studies on physisorbed layers, we will also extract the entropy from the data. This allows us to determine the degree of orientational order. The results will be compared to 3D plastic crystals in general. Previous x-ray data and the present specific heat results are then combined to explain the anomalous melting behavior in terms of a 2D random exchange resp. random field model.

The previously established coverage ρ -temperature *T* phase diagram of CF₂Cl₂,⁶ is confirmed and refined by the present study (see Fig. 1). The higher binding energy of the Cl to the substrate suggests that in the low-temperature 2D crystalline phases, the molecules rest on the Cl₂F tripods rather than the smaller F₂Cl tripod. This is confirmed by the x-ray data: the Bragg positions and the resulting area per molecule correspond to the Cl₂F tripod.



FIG. 1. The coverage-temperature phase diagram of CF_2Cl_2 on graphite. *L*: 2D liquid; *G*: 2D gas; 2*L*: second liquid layer; α , β , γ : 2D crystalline phases.

3028

The high-*T* β phase is triangular and incommensurate. The high symmetry of this lattice in conflict with the low symmetry of the molecule calls for orientational disorder, which is confirmed by the present specific heat data. In the x-ray experiment, the melting of the β phase is evident from a broadening of the (10) diffraction peak which changes over smoothly into the first maximum of the 2D liquid. This suggests that the β phase melts continuously. The lowtemperature phases α (commensurate) and γ (compressed incommensurate) are hexagonal with 9 molecules in the unit mesh. The *p*3 plane group symmetry demands that at least 6 of the 9 molecules are orientationally ordered. The γ phase is a compressed incommensurate but otherwise isomorphous variant of the commensurate $4\sqrt{3} \times 4\sqrt{3} \alpha$ phase. The α - β and γ - β transitions are of first order.⁶

II. EXPERIMENT

The experimental setup has been described elsewhere.⁷ The substrate is exfoliated graphite (Papyex). The active area of the substrate (about 370 m²) has been determined from the measurement of an adsorption isotherm of N₂ at 70 K. The N₂ isotherm shows a substep in the monolayer regime due to the transition from the commensurate $\sqrt{3} \times \sqrt{3}$ into an incommensurate phase. Accordingly, the volumetric coverage ρ will be quoted as number of molecules per 3 graphite hexagons. CF_2Cl_2 gas has been purchased with a nominal purity of 99%. Further purification was achieved by rejecting the fractions of the gas which adsorb first and which adsorb last on the graphite at low temperatures. The heat capacity data were obtained with the conventional adiabatic heat pulse method. Special attention was paid to the thermal isolation of the cell with the result that the temperature drift of the sample was small compared to the temperature changes induced by the heat pulses. Thus, the entropy as an integrated quantity can be determined reliably. Twelve coverages $(\rho = 0.25, 0.35, 0.50, 0.56, 0.61, 0.64, 0.69, 0.73, 0.80, 1.02, 1.62)$ have been investigated for temperatures between 30 and 190 K. The heat capacity of the empty substrate and can were measured in a separate run. Except close to the phase transitions, the heat capacity of the adsorbed layer is a few percent of the total heat capacity.

III. RESULTS

Figure 2 shows the heat capacity per CF₂Cl₂ molecule for some selected values of the coverage, where the contribution of the substrate and the can have been subtracted. Two anomalies are clearly visible: the stronger one at the lower temperature T_s (about 75 K) due to the structural phase transition, α - β or γ - β depending on the coverage ρ , the weaker one at the higher temperature T_m due to the melting of the β phase. From measurements of this type, the boundaries $T_s(\rho)$ and $T_m(\rho)$ of the ρ, T phase diagram have been determined (Fig. 1). The phase diagram thus obtained is in good agreement with that of the diffraction study⁶ as far as the submonolayer and monolayer regime, $\rho < 0.8$, is concerned. A new feature has been detected for higher coverages (ρ =1.02, 1.62), an additional anomaly of the heat capacity at about 105 K. Since the intensity of this anomaly scales with $(\rho - 0.8)$, it has been interpreted as a layering transition, i.e.,



FIG. 2. The heat capacity per molecule in units of k_B for four selected coverages.

as the formation of a second 2D liquid layer out of the bulk (3D) solid. Corresponding corrections have to be made in the phase diagram for $\rho > 0.8$: Below 105 K, the monolayer phases γ , β , 2D liquid coexist with the bulk solid, whereas above 105 K, the first liquid layer coexists with the second liquid layer. In the submonolayer regime, the present heat capacity experiment and accompanying adsorption isotherms produced evidence for the approximate extension of the 2D gas-2D liquid coexistence region. A small hump of the specific heat capacity shows up at ρ =0.25, 150 K and becomes a broad feature at lower temperatures at the next higher coverage. This indicates a phase boundary the tangent of which is parallel to the coverage axis at $\rho = 0.25$, but not at higher coverages. Thus the 2D critical point is at about T_c^{2D} = 150 K. The ratio T_c^{2D}/T_c^{3D} is 0.4; similar values have been observed for other small molecules adsorbed on graphite¹ which confirms the interpretation of the above discussed features of the specific heat capacity and adsorption isotherms. The ratio reflects approximately the number of nearest neighbors that is reduced from 12 to 6 when going from 3D to 2D.

The discrepancy between the absolute values of the volumetric coverage and the crystallographic coverage ρ_x calculated from the lattice parameters is a common observation for studies on exfoliated graphite. Here, the upper critical coverage for the pure commensurate α phase is $\rho_x=0.56$, that of the γ and β phases in their most compressed states $\rho_x=0.6$. For comparison, the α - γ boundary of the ρ , T phase diagram in Fig. 1 is at $\rho=0.64$, the maximum ρ for the β and γ phases 0.8. This discrepancy is due to molecules in irregular sites where they do not contribute to the Bragg peaks nor to the heat capacity anomalies at the phase transitions. The number of irregular sites per regular site is not a constant, it varies with the specific production parameters of the substrate but also with age, i.e., the number of thermal cycles. In particular, at higher coverages, for the γ and β phase, there are definitely extra molecules outside the 2D and 3D crystal lattices which may nevertheless influence the structural and thermal behavior of the monolayer.⁷

Altogether, the heat capacity curves are very similar for all coverages within the submonolayer and monolayer regime. The anomaly related to the structural phase transition is almost δ -function shaped for submonolayers (see Fig. 2 for $\rho = 0.5$). This suggests that the transition is of first order and that the temperature interval of the α - β phase coexistence is very narrow, in agreement with the x-ray study. The anomaly is slightly broader in the monolayer regime when the surface is completely covered with the adsorbate. It appears plausible that the transformation α - β or γ - β proceeds less freely at complete coverage and that correspondingly, the coexistence region is somewhat wider. The transition temperature T_s varies slightly with ρ (Fig. 1). The values for the γ - β transition are a little bit lower than those for the α - β transition. This may be due to the fact that the α phase is stabilized, with respect to the γ phase, by the commensurability with the substrate, which acts like an additional interaction term.

Since the melting anomaly is very small (see Fig. 2) the scatter of the data does not make it possible to fit analytic expressions for the critical behavior to the data. Hence, we cannot decide whether the transition is of second order or a smeared-out first order transition. However, a comparison to CF₃H monolayers is in order: CF₂Cl₂ as well as CF₃H form an incommensurate triangular 2D solid in which the molecules rest on an asymmetric tripod (Cl₂F and F₂H, respectively). Nevertheless, the melting behavior is different. The abrupt disappearance of the Bragg peaks and the δ -function shaped anomaly of the specific heat capacity identify the melting of the triangular phase of CF₃H as a first order transition.⁷ For CF₂Cl₂, the gradual broadening of the diffraction peaks suggests a transition of second order.⁶ Above ρ =0.64, T_m decreases with increasing ρ and eventually, for $\rho=0.80$, the tiny melting anomaly disappears in a background of enhanced heat capacity which extends for all coverages in this region from T_s across the β phase to well above the melting temperature. The anomalous slope of the $T_m(\rho)$ boundary in this ρ range is connected with a negative thermal expansion coefficient of the β phase.⁶ Part of the apparent broadening of the melting transition may result from the finite slope of the phase boundary. A possible explanation for the negative slope as well as the broadening based on the temperature dependence of the orientational disorder is given after the discussion of the entropy change with temperature.

Figure 3 shows the excess entropy ΔS (per molecule, in units of k_B) related to the structural phase transition (α - β for ρ =0.5 and 0.61, or γ - β for ρ =0.69 and 0.8) and to the melting of the β phase. ΔS is determined from the excess part of the heat capacity above a noncritical background. This background has been obtained by fitting a smooth curve to the data, which interpolates between the noncritical regimes below 70 K and above about 150 K (dashed lines in Fig. 1). This procedure is to some degree arbitrary and leads to some error of the asymptotic high-temperature value of ΔS (Fig.



FIG. 3. The "excess" entropy ΔS (which is part of the total entropy connected with the structural phase and the melting transition) per molecule in units of k_B for the four coverages of Fig. 1. The temperature scale refers to $\rho=0.50$. The other curves are shifted to the right in steps of 50 K.

3). Nevertheless the whole set of data gives convincing evidence for the picture developed below.

Independent of the coverage, the entropy change at the structural phase transition in Fig. 3 is about $1.1 \approx \ln 3$, while the excess entropy up to a temperature just below the melting anomaly, ΔS_t , is 1.8 which is approximately ln 6. These values are independent of whether the transition is α - β (commensurate-incommensurate) or γ - β (incommensurateincommensurate). As suggested by the adsorbate-substrate potentials and known from x-ray results,⁶ in the β and α phases, the molecules rest on their Cl₂F tripods. In the β phase, they are surrounded by 6 neighbors which produce a sixfold anisotropy of the nearest-neighbor interaction potential. In spite of the low symmetry of the molecule, the anisotropy is sixfold in case the molecules are dynamically disordered with respect to their azimuthal orientation. The anisotropy is also only sixfold, in case they are sufficiently far apart so that their noncylindrical shape produces only higher-order terms. Accordingly, there are six distinguishable equivalent azimuthal orientations for every molecule in the β phase. For this model of discrete azimuthal orientations, the entropy increase from a completely ordered state to one with fully developed azimuthal disorder is ln 6. Applied to the present system, this suggests that the low-temperature phases, α and γ , are fully ordered and that the azimuthal disorder is eventually reached in the β phase at temperatures close to the melting transition. Thus, the β phase can be regarded as an orientationally disordered 2D phase. At temperatures closer to the α phase, still within the β phase, the molecules are obviously prevented at any particular moment from adopting some of the six orientations because of the orientations of the neighbors at that instant. This means that the symmetry of the nearest-neighbor interaction potential has become lower because of the asymmetric shape of the molecules-either via reduced distances or via slower and slower jumps between the six orientations. Independent of the positive or negative thermal expansion coefficient which changes sign at $\rho = 0.64$, all coverages show an entropy change from about $k_B \ln 3$ at the low-temperature end of the β phase to $k_B \ln 6$ at the high-temperature end. Hence, all coverages experience the lowering of the symmetry of the interaction potential, independent of whether the lattice contracts or expands with decreasing temperature. Therefore, the reason for the lowering of the symmetry of the interaction potential must be slower movements due to smaller thermal energy. In the α phase, the molecules evolve long-range correlations with threefold symmetry. Close to the α transition but still in the β phase, these correlations will be of short range but nevertheless determine the number of equivalent orientations, which can no longer be sixfold but only threefold. The situation is the same at the phase transition between the two incommensurate phases γ and β . At the phase transition, the molecule locks into one of three equivalent orientations which are favored by the short-range correlations.

In contrast, for the triangular phase of CF₃H, $\Delta S_t = 1.3$,⁷ hence the azimuthal disorder is never completed below the melting transition, presumably because of stronger correlations between the CF₃H molecules. Note that the dipole moment of CF₃H is more than three times larger, namely 1.5D compared to 0.4D for CF₂Cl₂. Furthermore, the F₂H tripod of CF₃H is somewhat more asymmetric than the Cl₂F tripod of CF₂Cl₂.

Melting leads to a further increase, ΔS_m , of the entropy. ΔS_m is of the order of 0.7 in CF₂Cl₂ for the coverages of Fig. 3. The asymptotic high-temperature value of the excess entropy, $\Delta S_{\infty} = \Delta S_t + \Delta S_m$ is about 2.5. This value also applies to $\rho = 0.8$, although there is no distinct melting anomaly of the heat capacity. Clearly, ΔS_m should at least to some extent be due to translational degrees of freedom, i.e., to the loss of the quasi-long-range 2D crystalline order. The translational aspect of melting in two dimensions,⁸ whether melting is a phase transition of first or second order, whether it is a one step process or proceeds via a hexatic mesophase, and the role played by various types of defects are still under discussion. Of course, the melting process can involve additional degrees of freedom. For the present molecule, melting may, e.g., be connected with flips of the molecule from the Cl₂F tripod onto the F₂Cl tripod. This alternative orientation supplies a second set of 6 azimuthal states which increase the value of the orientational entropy to ln 12, remarkably close to the experimental value. If we assume that the orientational order is entirely removed at the melting transition for both CF_3H and CF_2Cl_2 , the different amount of orientational order that is left to be removed at the melting transition may explain why the melting appears to be first order in CF₃H and second order in CF₂Cl₂.

Whether or not the melting anomaly is dominated by the addition of the last orientational degree of freedom, namely the flipping of the molecule between FCl₂ and ClF₂ tripods, the entropy of melting ΔS_m is very small, both in absolute units and with respect to that part of entropy which is released in the preceeding orientational disordering process, ΔS_t . ΔS_m values of similar magnitude have been reported for the triangular phases of CF₃H (Ref. 7) and CF₄ (Ref. 9) monolayers adsorbed on graphite. Analogous observations have been made in 3D molecular crystals. In fact, low values of the entropy of fusion have been taken as the thermodynamic criterion for the existence of an orientationally disordered "plastic" mesophase.¹⁰ Values of ΔS_t and ΔS_m of several 3D molecular crystals have been compiled in this reference. Concentrating on CF₄ and CCl₄, the molecules

which are most closely related to CF₂Cl₂, the tabulated ΔS_m values are 0.96 and 1.21, ΔS_t values are 2.71 and 2.45, respectively. Thus, the ratio $\Delta S_t / \Delta S_t$ is about the same as for the 3D plastic crystals and for the present example of a 2D plastic crystal, while the ratio of corresponding quantities $\Delta S_i^{2D} / \Delta S_i^{3D}$ (i=m,t) is about equal to $\frac{2}{3}$.

We come back to the observation that the increase of the entropy at the melting transition is small compared to the increase at the orientational phase transition and the increase within the β phase due to orientational disorder. We also pay attention to the fact that ΔS_m of approximately $k_B \ln 2$ can entirely be accounted for by the orientational Ising type degree of freedom which corresponds to flips of the molecule from the Cl₂F tripod onto the F₂Cl tripod. Hence the translational part of the entropy increase at the melting transition must be vanishingly small compared to the Ising-type $k_B \ln 2$ contribution of the orientational disorder. Naturally, we conclude that in our case the melting is dominated by the disordering of the discrete orientational degree of freedom and hence is of 2D Ising type. Although the specific heat capacity data at $\rho = 0.5$ do not allow us to distinguish between a power law divergence and a logarithmic divergence, they nevertheless support divergent behavior of one or the other kind. The shape of the melting anomaly of the specific heat capacity at $\rho = 0.5$ is at least not in contradiction with the $\ln |T - T_c|$ anomaly of the 2D Ising model.

Keeping this in mind, the idea of gradually reduced orientational order up to the melting transition (with complete orientational disorder just above the melting transition) as implied by the temperature dependence of the entropy provides an explanation for the negative thermal expansion above $\rho=0.64$: Close to the melting transition, with increasing temperature, more and more molecules start to flip between the Cl₂F tripod and the F₂Cl tripod. Because the F₂Cl tripod needs less surface area, the lattice contracts as more and more molecules are standing on the F₂Cl tripod.

Furthermore, the amount of molecules in the β phase standing on the F₂Cl tripod also increases with coverage, as a smaller surface area is more favorable at higher coverages. The Bragg-peak positions at about 90 K at ρ =0.64 and ρ =0.8 (Ref. 6) reveal a decrease of the average molecule distance by about 3%, implying that about one half of the molecules are standing on the (11% smaller in area) F₂Cl tripod at ρ =0.8.

The interactions involving one or more molecules on the F₂Cl tripod differ from those between molecules on Cl₂F tripods. Such random interactions are known to influence long-range order significantly. According to an argument by Harris,¹¹ the phase transition remains sharp in spite of the bond disorder, only if the specific heat of the pure system behaves like $|T - T_c|^{-\alpha}$, α being negative. For positive α , a broadening of the phase transition and a shift of the transition towards lower temperatures with increasing number of "wrong" bonds are predicted. This still holds for a 2D Ising phase transition with logarithmic specific heat anomaly as shown explicitly by Harris.¹¹ Even without knowing the universality class of the melting transition, we can rely on the experiment at $\rho = 0.5$ which shows a distinct melting anomaly of the heat capacity with either logarithmic divergence or a power law with positive α , but certainly not a power law with negative α . Accordingly, we can expect the melting transition to shift to lower temperatures and to broaden more and more, the more molecules are flipped from the FCl_2 tripod to the F_2Cl tripod.

In a slightly different line of reasoning we include the defects of the substrate: They will not destroy long-range order as long as the system is homogeneous, i.e., consisting of only one type of molecules, those that are standing on their Cl_2F tripods. As soon as we have molecules with two types of physisorption energies, the defects of the substrate act as random fields to the system. No doubt the substrate has an abundance of defects. Because the lower critical dimension for the random field Ising problem is three, in two dimensions the phase transition is destroyed by random fields.¹² This is an even stronger argument why the melting transition must broaden significantly and shift to lower temperatures with increasing number of molecules standing on their F₂Cl tripods.

IV. CONCLUSION

 CF_2Cl_2 monolayers give a fine example for an orientational order-disorder transition preceding the melting transition. The entropy changes derived from our specific heat capacity experiments show that the orientational disorder achieved in the β phase close to the melting temperature is complete, in the sense that the six azimuthal states expected for a molecule resting on an asymmetric tripod in a triangular lattice are accessible. There is no evidence for a partial orientational disorder in the low-temperature phases, as proposed in a previous diffraction study. The existence of an azimuthally disordered mesophase is a peculiarity of the 2D system. The 3D system directly solidifies into an orientationally ordered phase. The low melting entropy compared to the preceding contribution by orientational disorder qualifies the system as an example of a 2D plastic crystal. Indeed, we argue that the melting anomaly itself is dominated rather by orientational disorder with respect to the discrete degree of freedom that corresponds to flips of the molecule between the Cl₂F tripod and the F₂Cl tripod than by disorder of the translational degrees of freedom. Thus, the melting shows the characteristics of a 2D Ising phase transition. Increasing coverage in the plastic β phase leads to an increased number of molecules on the smaller F2Cl tripod and introduces random interactions as well as random fields (due to the different sensitivity of Cl₂F and F₂Cl to defects of the substrate) into the system. The melting anomaly becomes broadened and shifted to lower temperatures as expected for a 2D Ising random exchange or random field system. Altogether our specific heat capacity data provide convincing evidence that the melting of the β phase of CF₂Cl₂ on graphite can be regarded as an example for the random exchange and random field problem in two dimensions.

- ¹For a review, see *Phase Transitions in Surface Films*, edited by J. G. Dash and J. Ruvalds (Plenum Press, New York, 1981); and *Phase Transitions in Surface Films II*, edited by H. Taub, G. Torzo, H. J. Lauter, and S. C. Fain, Jr. (Plenum Press, New York, 1991).
- ²K. Knorr, Phys. Rep. **214**, 113 (1992).
- ³D. Marx and H. Wiechert, Adv. Chem. Phys. **95**, 213 (1996).
- ⁴ St. Faßbender, C. Steimer, D. Arndt, and K. Knorr, Surf. Sci. **388**, 201 (1997).
- ⁵J. K. Cockroft and A. N. Fitch, Z. Kristallogr. 197, 121 (1991).

- ⁶K. Knorr and E. Civera-Garcia, Surf. Sci. 232, 203 (1990).
- ⁷D. Arndt and K. Knorr, Mol. Phys. **95**, 91 (1998).
- ⁸K. J. Strandburg, Rev. Mod. Phys. **60**, 161 (1988).
- ⁹Q. M. Zhang, H. K. Kim, and M. H. W. Chan, Phys. Rev. B 34, 8050 (1984).
- ¹⁰N. G. Parsonnage and L. A. K. Staveley, *Disorder in Solids* (Clarendon Press, Oxford, 1978).
- ¹¹A. Brooks Harris, J. Phys. C 7, 1671 (1974).
- ¹²K. Binder, Y. Imry, and E. Pytte, Phys. Rev. B 24, 6736 (1981);
 K. Binder, Z. Phys. B: Condens. Matter 50, 343 (1983).