Evidence for Orientational Glass States in Two Dimensions: Monolayers of $C_2Cl_2F_4$ and C_2ClF_5 Physisorbed on Graphite

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Monolayers of $C_2Cl_2F_4$ and C_2ClF_5 physisorbed on exfoliated graphite have been investigated by x-ray diffraction and heat capacity measurements. Both systems crystallize in a triangular lattice with dynamic orientational disorder at higher temperatures and freeze into an orientational glass state at low temperature. For C_2ClF_5 the orientational glass state is observed only in the extended monolayer region, whereas the monolayer shows long-range orientational ordering in a three-sublattice structure.

Spin glasses and in their wake orientational glasses are the main attempt of solid state physics to address the problem of collective disorder. An orientational glass is formed when a solid phase with dynamic orientational disorder ("plastic" phase) can be cooled down to low temperatures without undergoing a transition into a long-range orientationally ordered phase. In several orientational glasses, such as $Ar:N_2$ mixed crystals, this is achieved by dilution of the active nonspherical species (here N_2) with a spherical partner (here Ar) [1,2]. These glasses have been described theoretically by a spin-glass-like model with the essential ingredients of quenched random site occupation and frustrated intermolecular interactions [3,4]. Alternatively, orientational glass states have been obtained by sufficiently fast cooling of homogeneous undiluted systems, such as cyanoadamantane, through the T region of the disorder-order phase transition [5]. Here the occurrence of the glass state is connected to slow transformation kinetics.

Two-dimensional (2D) orientational glasses have been investigated theoretically [3,6]. For an experimental realization, physisorbed monolayers appear to be the best choice since there are many examples of orientational order-disorder phase transitions in such systems. In fact, the 2D orientational glass state was sought in $Ar:N_2$ [7,8] and $Ar:CO$ [9] monolayers physisorbed on graphite, but both systems encountered the problem of phase separation. The glassiness cited for the low-T pinwheel orientationally ordered phase of $Ar_{0.25}(N_2)_{0.75}$ refers to incomplete compositional ordering rather than to orientational disorder.

In this article we present evidence for a 2D orientational glass state in monolayers of two ethane halides, 1,2-dichlorotetrafluoroethane $C_2Cl_2F_4$, and chloropentafluoroethane C_2ClF_5, physisorbed on exfoliated graphite (Papyex). The films have been investigated by x-ray diffraction and heat capacity, two standard methods in this research field [9]. The monochloride C_2ClF_5 carries a dipole moment of 0.52 D [10]. The dichloride $C_2Cl_2F_4$ has two rotational isomers, *trans* and *gauche,* with dihedral angles of 180° and 62.5°, respectively [11]. The gauche form is dipolar with a moment of 0.81 D [12]; the

trans form is quadrupolar. Both isomers coexist in the gas and in the 3D liquid states, whereas the trans form predominates in the 3D solid state [13]. The *trans* form is the ground state and is approximately 220 K lower in energy than the *gauche* form [11]. Guided by calculations of the binding energies for the haloethanes on graphite [14], one estimates that at $T = 0$ K, the minimum energy configuration of an individual C_2ClF_5 or *trans*-$C_2Cl_2F_4$ molecule is a F_2Cl tripod down orientation, whereas *gauche*-$C_2Cl_2F_4$ is expected to rest on the Cl_2F tripod. The binding energy of the latter orientation should be greater by a few hundred kelvin; this may lead to an enrichment of the *gauche* isomer in the adsorbed layers of $C_2Cl_2F_4$.

Both adsorbates have been characterized by several hundred diffractograms as a function of temperature T and coverage θ. Selected diffraction peaks are shown in Fig. 1. Warren-type profiles based on Lorentzian-, Gaussian-, and squared Lorentzian-shaped structure factors [15] have been fitted to the peaks and the peak position in Q; intensity and the width parameter γ have been extracted (Fig. 2). The γ^{-1} values of Fig. 2 refer to fits with squared Lorentzians, which are the best common choice for all phases observed. The coverage $\theta = 1$ is defined as the minimum quantity of gas which leads to a complete coverage of the exposed graphite (001) honeycomb surface at low T. The diffraction results are complemented by heat capacity measurements $C_V(T)$ at selected coverages; see Fig. 3. Up to the monolayer melting point for all coverages, the 3D vapor pressure is low, as is typical for fully halogenated ethanes and methanes. Therefore site changes of the molecules via the 3D vapor phase are rare, evaporation losses are negligible, and θ is constant in our T-dependent measurements.

The dichloride $C_2Cl_2F_4$ has been characterized additionally by ellipsometric isotherms, 100 K $< T <$ 185 K, obtained on high-oriented pyrolytic graphite. In passing, we note that these isotherms are of high quality with almost horizontal monolayer plateaus and almost vertical monolayer steps, comparable in quality to those of the rare gases obtained with this method [16].
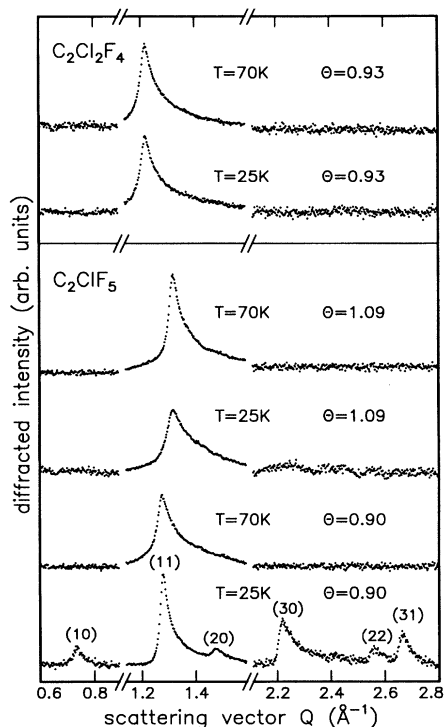
FIG. 1. X-ray diffractograms of $C_2Cl_2F_4$ and C_2ClF_5 physisorbed on exfoliated graphite at different temperatures T and coverages θ. The peaks of the commensurate phase of the monochloride are indexed in terms of a 4×4 structure. (Note that the low momentum transfer and the high momentum transfer parts of the three-part diffractograms are multiplied by a factor of 3.)

FIG. 2. Temperature dependence of the Q position and the inverse halfwidth γ^{-1} of the principal diffraction peak of C_2ClF_5 for two different coverages θ. γ is the FWHM of the squared-Lorentzian structure factor [15].

lar down to 23 K, the lowest temperature measured, as indicated by the persistence of the single diffraction peak. Guided by the temperatures of orientational order-disorder transitions in physisorbed layers of comparable molecules such as the halomethanes and, in particular, the second haloethane of the present study, one expects that the orien-

The θ, T phase diagrams are conventional in most aspects. At intermediate temperatures the monolayers of both molecules crystallize in a triangular lattice, which is incommensurate with the graphite substrate. The lattice parameter for both systems compares favorably with the size of the molecule. The high symmetry of the triangular lattice is incompatible with the low molecular symmetry and therefore requires that the molecules are orientationally disordered. Such 2D plastic triangular phases have been observed before for a number of molecules adsorbed on graphite with comparable deviations from sphericity, e.g., N_2 [17,18], CF_3Cl [19]. As expected for a plastic phase, the lattice parameter varies strongly with spreading pressure (for C_2ClF_5 see Q position in Fig. 2), which in turn is controlled by T and θ. The melting temperatures of the layers range from about 100 K for submonolayers of C_2ClF_5 to about 160 K for $C_2Cl_2F_4$ in the extended monolayer regime. Melting is apparent only from a decrease of the inverse peak width γ^{-1} (Fig. 2) and does not lead to an anomaly of the heat capacity.

What type of low-T states evolve out of the plastic phase on cooling? For $C_2Cl_2F_4$ the 2D lattice remains triangu-
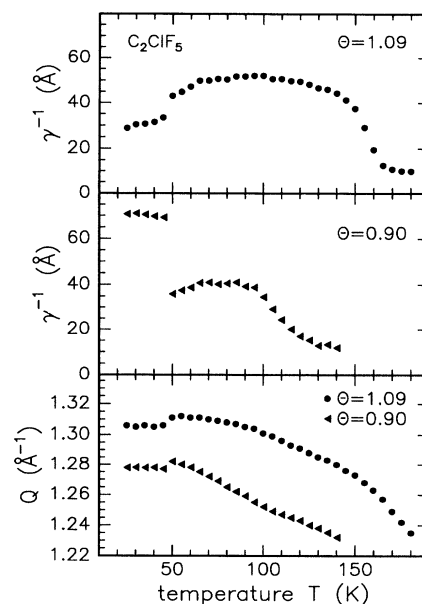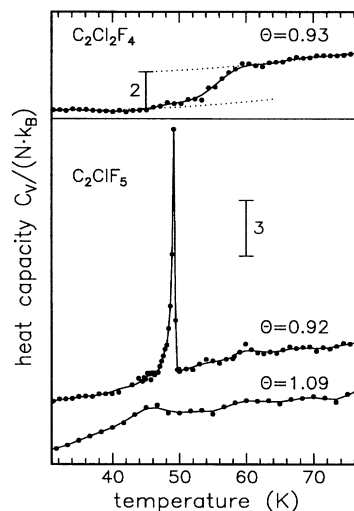

FIG. 3. Low-temperature region of heat capacity curves of $C_2Cl_2F_4$ and C_2ClF_5 physisorbed on exfoliated graphite at different coverages θ. The curves shown for the submonolayer are representative for all coverages $\theta \leq 1$ of each molecule.

tational degrees of freedom should be frozen-in at that temperature. For $C_2Cl_2F_4$ this freezing obviously occurs without the system undergoing a transition into a long-range orientationally ordered phase. Instead, the molecules form an orientational glass. The freezing process does not lead to apparent anomalies in the temperature dependence of the lattice parameter, the width, or the intensity of the diffraction peak. On the other hand, a steplike anomaly with an amplitude of about $2Nk_b$ is observed in the heat capacity at about 56 K (Fig. 3). We suggest that this anomaly stems from the arrest of the orientational degrees of freedom. Similar anomalies have, in fact, been observed in a computer simulation on 2D orientational glasses [6].

A deeper insight into the 2D glassy freezing can be obtained for the monochloride C_2ClF_5. Here it is only in the extended monolayer regime, $1.04 < \theta < 1.09$, that neither diffractometry nor heat capacity measurements can detect a structural phase transition, thus suggesting a low-T orientational glass with a triangular center-of-mass lattice. The monolayers and submonolayers of this system undergo a conventional ordering phase transition into a long-range orientationally ordered phase. As shown in Fig. 1 for $\theta = 0.90$, the low-T phase is characterized by a number of diffraction peaks in addition to the principal peak. Two of the additional peaks are easily identified as overtones (30) and (22) of the principal peak (11), which are absent in the high-T plastic phase. As is the case for 3D systems, this observation already suggests that the orientations and positions of the molecules are more defined in the low-T phase than in the plastic phase. The remaining peaks, (10), (20), and (31), are compatible with a commensurate 4×4 supercell. The Miller indices given in Fig. 1 refer to this cell. We note that the incommensurate lattice of the plastic phase is close in lattice spacing to a higher order commensurate $\frac{4}{3}\sqrt{3} \times \frac{4}{3}\sqrt{3}$ lattice (with $Q_{(10)} = \pi/a_c$, where a_c is the graphite lattice constant). Therefore we conclude that there is a phase transition from the incommensurate triangular plastic phase to an ordered hexagonal commensurate phase with a unit cell which is about tripled with respect to the high-T phase. Thus the low-T cell contains three molecules which—as required by hexagonal symmetry—form a triad grouped about an axis of threefold symmetry and which mutually differ in orientation by $120°$ (as given by the projection of the C-Cl bond onto the surface). The structure is shown in Fig. 4. Such a ground state, which one might call the dipolar analog of a "Néel antiferromagnet," has been treated in theoretical studies of nonspherical entities and spins on triangular lattices [20]. The transition into the ordered phase is of first order, as can be deduced from the sharp anomaly of the heat capacity at the transition temperature $T_C = 48$ K (Fig. 3) and from the discontinuous onset of the intensities of the additional diffraction peaks. On crossing T_C from above, the monolayer expands upon ordering (Fig. 2). This suggests that the molecules settle
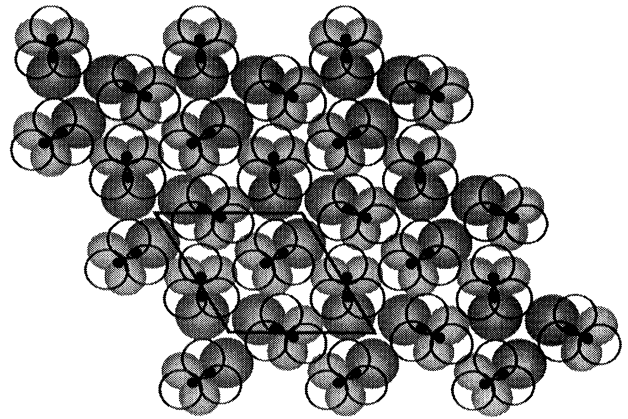

FIG. 4. Structure of the low-T phase of the $\theta = 1$ monolayer of C_2ClF_5 (plane group $P3$). The molecules are represented by the projection of their van der Waals contour on the surface. The inferred commensurate 4×4 cell is indicated. The 1-F, 1-F, 2-Cl tripod is shaded, the C atoms are drawn in black. Because the unfavorable relation of six Bragg intensities as input data and at least five structural parameters (one x, y-center-or-mass position and three Eulerian angles), the structure shown is an "educated guess" rather than the result of a rigorous structural calculation.

such that they lie flat on the surface, presumably resting on the 1-F, 1-F, 2-Cl tripods. However, in the high-temperature plastic phase, the molecules stand on the 2-F, 2-F, 2-Cl tripods and are rapidly reorienting around the C-C axis, allowing for a higher molecular density. Upon ordering, the Bragg peaks sharpen and change their profile from more Lorentzion-like above T_C to Gaussian below T_C, which in our fits with squared Lorentzians manifests itself as a jump to higher γ^{-1} values (Fig. 2).

In the extended monolayer regime the layer attains neither commensurability nor long-range orientational ordering, as can be seen from the positions of the diffraction peaks and the absence of the superlattice peaks (see Fig. 1 for $\theta = 1.09$). Thus the system freezes into the orientational glass state. Nevertheless two features are reminiscent of the phase transition occurring for $\theta \leq 1$: At about 46 K there is still a cusplike anomaly of the heat capacity (Fig. 3) and an expansion of the lattice upon cooling (Fig. 2). The diffraction peaks of the extended monolayer broaden significantly below 50 K (Fig. 2), suggesting that the triangular lattice of the glass state is either inhomogeneously strained or has a short translational coherence length.

Turning to discussion, we note that even for the 3D orientational glasses it is still not yet decided whether freezing into the glass state is a dynamic process, in which the orientational relaxation time slows on cooling until it exceeds any experimental observation time or a static phase-transition-like arrest. A 2D system is definitely

closer to or probably below the lower marginal dimension for static freezing and, hence it is likely that the freezing of the present systems is a dynamic phenomenon. The origin of the glass formation in the present monolayers is by no means clear, and may be even different for the monchloride and the dichloride, in spite of the similarity of the two molecules. If the dichloride monolayer were in fact a mixture of the two isomers, one would infer a triangular lattice with lattice sites randomly occupied by *gauche*-dipoles and *trans*-quadrupoles, a situation which calls for spin-glass-type random bond models [3]. On the other hand, a triangular lattice of spins or pseudospins with discrete orientations and an "antiferrotype" coupling is highly frustrated and hence susceptible to the formation of topological point and line defects. It has been shown theoretically that this situation can lead to slow. i.e., glassy, orientational relaxation, even for the undiluted, homogeneous case, which leave the system in a long-lived metastable state [21].

The example of the monochloride shows that the role of the substrate cannot be ignored. The orientational ordering of the monochloride is due to a combined effect of an antiferrotype intermolecular coupling and of surface corrugation. Either interaction individually favors the tripling of the cell. As soon as the coverage is increased beyond $\theta = 1$ and the monolayer is compressed, the 4×4 commensurability is lost and the long-range orientational ordering is replaced by glassy freezing. Thus the glass state of C_2ClF_5 could be a short-range variety of the ordered phase. The freezing may be again due to the slow relaxations mentioned above. Alternatively, perhaps the incommensurability of the adsorbate with respect to the substrate leads to local surface potentials which vary from site to site. In that sense, one may refer to models which describe the formation of the orientational glass in terms of a structural instability where long-range ordering competes with local freezing in random fields [3,22].

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