Evidence for Kosterlitz-Thouless type orientational ordering of CF$_3$Br monolayers physisorbed on graphite

S. Faßbender, M. Enderle, K. Knorr

Technische Physik, Universität des Saarlandes, 66041 Saarbrücken, Germany

J. D. Noh and H. Rieger

Theoretische Physik, Universität des Saarlandes, 66041 Saarbrücken, Germany

Monolayers of the halomethane CF$_3$Br adsorbed on graphite have been investigated by x-ray diffraction. The layers crystallize in a commensurate triangular lattice. On cooling they approach a three-sublattice antiferroelectric pattern of the in-plane components of the dipole moments. The ordering is not consistent with a conventional phase transition, but points to Kosterlitz-Thouless behavior. It is argued that the transition is described by a 6-state clock model on a triangular lattice with antiferromagnetic nearest neighbor interactions which is studied with Monte-Carlo simulations. A finite-size scaling analysis shows that the ordering transition is indeed in the KT universality class.

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Two-dimensional systems cannot show long-range order by breaking a continuous symmetry at any finite temperature $T$. Nevertheless Kosterlitz and Thouless (KT) demonstrated that the 2D XY-ferromagnet with nearest neighbor interaction and equivalently the planar rotator exhibit a phase transition from an ordered phase with an algebraic decay of the spin correlations to a disordered phase via the unbinding of vortex-antivortex pairs [1].

The KT-concept has been applied successfully to the onset of superfluidity [2] and of superconductivity [3] in thin films and two-dimensional melting [4]. An application to layered magnetic systems with large ratios of the intra- and the inter-layer exchange appears to be more direct, but here the KT transition is masked by the transition to 3D behavior [5]. In the present article we present x-ray diffraction data on CF$_3$Br monolayers physisorbed on graphite and present evidence that the orientational pseudospin ordering is of the KT-type. To our knowledge the present study reports the first observation of a KT-transition in a (quasi)-magnetic system.

Physisorbed monolayers are indeed good approximations to two-dimensional (2D) systems, as evidenced by the fact that phase transitions occurring in such layers can be often described by the 2D versions of elementary models of statistical mechanics such as the Ising or the 3-state Potts model [6].

The halomethane CF$_3$Br is a prolate C$_{3v}$ molecule with a dipole moment of about 0.5 D. Monolayers have been adsorbed on exfoliated graphite and investigated by x-ray powder diffraction. The coverage $\rho$, temperature $T$ phase diagram is rather complex [7] [1]. Here we concentrate on a coverage which is representative of the extended monolayer regime in which the monolayer lattice is commensurate with the graphite lattice. Diffraction patterns are shown in Fig. 1. The peaks of the patterns have been analyzed for position, intensity, and the coherence length, as has been described elsewhere [8] [1]. The commensurate layer melts around 105 K [9]. In the 2D solid state, the diffraction pattern is dominated by the principal Bragg reflection of the commensurate triangular $2 \times 2$ lattice at $Q_p=1.475$ Å$^{-1}$. Just below the melting temperature, this peak is in fact the only one visible. Down to lowest $T$, the peak position is independent of $T$, as imposed by the commensurability with the substrate. The peak width yields a coherence length of about 180 Å throughout the 2D solid state which compares well with the average lateral size of the crystallites of exfoliated graphite usually quoted in the literature. The $2 \times 2$ structure has been also observed for monolayers of CF$_4$ [3], CF$_3$Cl [4], C$_2$F$_6$ [5] on graphite. These molecules and CF$_3$Br have the threefold symmetry and the CF$_3$ group in common. Hence it is plausible to assume that CF$_3$Br stands on the substrate, presumably with the F$_3$ tripod down. An isolated CF$_3$Br would prefer to lie flat on the substrate, but definitely the $2 \times 2$ mesh is too tight to accommodate the molecules in this orientation. On the other hand steric considerations suggest that the lateral $2 \times 2$ packing of perpendicular molecules can tolerate tilt angles of the molecular axis up to 30° with respect to the substrate normal. A tilt is equivalent to a non-zero in-plane component of the dipole moment. We regard this component as pseudospin $S_i$. In this sense the $2 \times 2$ state is disordered with a zero time average of every $S_i$, and is stabilized at higher $T$ by a libration and/or a precession of the molecular axis about the substrate normal.

On cooling, two additional features develop in the diffraction pattern which finally, below 40 K, can be regarded as Bragg peaks at $Q=0.851$ Å$^{-1}$ and 2.253 Å$^{-1}$. They are easily identified as superlattice reflections brought forth by a tripling of the 2D mesh leading to a $2\sqrt{3} \times 2\sqrt{3}$ commensurate hexagonal lattice. The $(h,k)$ indices of Fig. 1 refer to this superlattice. The $(20)$ reflection, which should occur at 1.703 Å$^{-1}$, is absent. Below 40 K, the coherence length derived from the width of the superlattice reflections is again 180 Å and is thus imposed by the substrate. The global structure of the low temper-
ature state must be consistent with the hexagonal plane group p3 with three molecules in the supercell. Regarding the molecules as rigid, there are five positional parameters, namely the translational coordinates $x,y$ and the three Eulerian angles of one molecule. The low number of reflections does not allow a rigorous determination of these parameters, nevertheless one can make some semi-quantitative statements. A perpendicular orientation of the molecules in combination with a staggered azimuthal angle of the $\text{CF}_3$ group about the substrate normal is not sufficient to explain the superlattice intensities. The cell tripling must involve tilts of the molecular axes away from the perpendicular direction, presumably in combination with slight displacements of the molecule centers out of the original positions. A satisfactory agreement of measured and calculated intensities (including the accidental absence of the (20) reflection) is obtained with tilts of about $20^\circ$ pointing toward a next neighbor such that the pseudospins form an antiferro-“magnetic” $120^\circ$ Neél-pattern on a 2D triangular lattice.

In case of a conventional order-disorder transition, the integrated intensities of the superlattice reflections would be a measure of the order parameter and should hence vanish when approaching the critical temperature from below. (See ref. [9] for such a transition for $\text{C}_2\text{F}_5\text{Cl}$ on graphite). This is however not what is observed in the experiment on $\text{CF}_3\text{Br}$ monolayers. On heating the superlattice peaks broaden while keeping approximately their integral intensity until they are finally lost in the background. The temperature evolution of the (21) reflection is shown in Fig. 2 together with fits of a theoretical profile. The $T$-dependence of the coherence length $\xi$ as determined from the intrinsic width of this peak is shown in Fig. 3. The solid line of this figure is a fit of the KT-expression

$$\xi = A \exp(B(\frac{T}{T_K} - 1)^{-1/2})$$  \hspace{1cm} (1)
monolayers shows an anomaly extending from 35 K to 40 K which is just the \( T \)-range where \( \xi \) saturates. However it does not allow a quantitative analysis of the critical scaling behavior since the anomaly is very weak.

Do \( \text{CF}_3\text{Br} \) monolayers meet the theoretical requirements for a KT-transition? Clearly the pseudospin correlations are bound to a plane, thus the system is 2D with respect to the relevant degrees of freedom at the phase transition. The pseudospin is presumably not a strictly isotropic planar rotator but experiences a crystal field which breaks the continuous azimuthal symmetry. It has been shown however that — at least for the planar \( \text{XY} \) ferromagnet — the KT-behavior is stable with respect to small crystal fields of 6-fold symmetry [16]. The site symmetry of the monolayers is indeed 6-fold, but the ordered structure approached is not ferro- but antiferroelectric. Antiferro-type ordering on a triangular lattice is affected by frustration with the consequence that the helicity, a discrete 2-fold symmetry, enters into the problem. The order–disorder transition is then described by a confluence of the Ising and KT universality classes [17,18] with an Ising type anomaly of the specific heat, but the spin correlations of the disordered phase still follow the \( \text{KT} \)-form of \( \xi(T) \) as we will demonstrate now.

From the above considerations follows that the pseudospins formed by the \( \text{CF}_3\text{Br} \) dipoles are arranged on a triangular lattice, interact antiferromagnetically with nearest neighbors [19] and have 6 preferred orientations. Hence the model that captures the universal features of the orientational ordering transition should be the antiferromagnetic six-state clock model on a 2D \( N = L_x \times L_y \) triangular lattice (see Fig. 1). The six-state clock spin is a planar spin pointing toward discrete six directions; \( \text{S} = (\cos \theta, \sin \theta) \) with \( \theta = \frac{2\pi n}{6} \ (n = 0, 1, \ldots, 5) \). The Hamiltonian of this model reads

\[
\mathcal{H} = 2J \sum_{\langle i,j \rangle} \cos(\theta_i - \theta_j) , \tag{2}
\]

where the sum is over nearest neighbor site pairs \( \langle i,j \rangle \) and \( J > 0 \) is the antiferromagnetic coupling strength. The overall factor 2 is introduced for a computational convenience. It is a limiting case of an antiferromagnetic \( \text{XY} \) model with infinite anisotropy field \( \cos p\theta \ (p = 6) \).

The antiferromagnetic coupling on a triangular lattice induces a frustration. As a result the system has 12-fold degenerate ground states with three-sublattice structure. Global spin rotations by multiples of \( 2\pi/6 \) and also Ising like transformation that inverts all helicities formed by the spins on elementary triangles (see Fig. 4) transforms one ground state into another. Therefore the model possesses a \( C_6 \) (6-fold clock) \( \times Z_2 \) (Ising) symmetry and we expect that there are two phase transitions associated with the spontaneous breaking of the \( C_6 \) and \( Z_2 \) symmetry.

We performed extensive Monte-Carlo simulations of the model (2) using conventional single spin-flip dynamics with up to \( 10^8 \) Monte-Carlo steps per spin and lattice sizes up to 384×192 and studied its phase transition with a thorough finite size scaling analysis. Here we focus on the breaking of the \( C_6 \) symmetry that is indicated by the x-ray diffraction experiments reported above, the details of the breaking of the \( Z_2 \) symmetry (which happens at a slightly higher temperature and turns out to be in the Ising universality class) will be reported elsewhere [20].

The order parameter for the \( C_6 \) symmetry is the sublattice magnetization

\[
m_A = \frac{1}{N} \sum_{i \in A} \exp(i\theta_i) , \tag{3}
\]

where the sum runs over only sites in the \( A \) sublattice \( (m_B \) and \( m_C \) can be defined similarly). Analogously the spatial spin correlation function is defined as

\[
\langle \theta_i \theta_j \rangle = \frac{1}{N} \sum_{i \in A} \sum_{j \in A} \exp(i(\theta_i - \theta_j)) , \tag{4}
\]
The magnetic susceptibility with a fit to the expected KT-form.

\[ C_m(r) = \left( \frac{3}{N} \sum_{i \in A} \cos(\theta_i - \theta_{i+r}) \right) \]  

(4)

and the susceptibility is given by \( \chi_m = N \langle m_A^2 \rangle \).

The transition temperature is estimated using the dimensionless ratio of moments (or Binder parameter)

\[ B_m = 1 - \frac{\langle m_A^2 \rangle}{3\langle m_A^2 \rangle^2}, \]  

(5)

which is shown in Fig. 5 and yields the critical temperature \( T_{C_6} = 1.035 \pm 0.0005 \). We extract the correlation length from the correlation function \( C(r) \) defined in (4) via

\[ \xi^2 = \frac{\sum_r r^2 C_m(r)}{\sum_r C_m(r)}. \]  

(6)

Our data are shown in Fig. 5 in a log-log plot of \( \xi^m(T) \) versus \( T - T_{C_6} \) with \( T_{C_6} \) from above. They fit nicely to the KT-form [6] with \( A = 2.54 \) and \( B = 0.193 \). Note that the non-universal number, \( B \), differs significantly from the one for the experimental data, which is not unusual for microscopically different systems in the KT universality class (see e.g. [21]). The susceptibility, also shown in Fig. 5, follows the expected KT-form \( \chi_m = A'\exp(B'(T - T_{C_6})^{-1/2}) \), too. We also checked other quantities (like the decay of \( C_m(r) \) at \( T_{C_6} \)) and found everything to be consistent with a KT-scenario.

In summary, our measurements show that CF\(_3\)Br molecules physisorbed on graphite are arranged in a commensurate triangular lattice. On cooling, a Néel-type \( 120^\circ \) pattern is approached. The growth of the critical correlations has been followed over a wide temperature range. It finally stops when the correlation length reaches the size of the substrate crystallites. The behavior is consistent with the KT-scenario. An antiferromagnetic 6-state clock model on a triangular lattice, which we studied numerically, describes the universal features of this ordering transition well.

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