Evidence for Ising and Potts Transitions in the ϵ-ζ Transformation of Two-Dimensional O_2

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Two-dimensional O_2 physisorbed on graphite shows a structural and magnetic phase transition from the paramagnetic to the antiferromagnetic state. A high-resolution specific-heat measurement is presented which reveals that there are two successive phase transitions: first a three-state Potts transition, producing a distorted lattice being still paramagnetic, and second an elastically driven Ising transition from the paramagnetic to the antiferromagnetic state.

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The phase diagram [occupation number versus temperature (ρ'-T plane)] of two-dimensional (2D) molecular oxygen (O_2) has been carefully studied in recent years.[1,2] In the phase diagram, ρ' is the occupation number in units of monolayers of molecules which have their axes oriented parallel to the 2D plane ("lying molecules"). Hence the monolayer of lying molecules is complete at $\rho' = 1$. The O_2 molecule is anisotropic with an egg-shaped form. If one increases the occupation number beyond 1 ($\rho' \geq 1$) the molecules start to lift up their axes. Finally, at $\rho' \approx 1.7$ the axes are oriented perpendicularly to the 2D plane.[3]

The phase diagram of the O_2 film shows interesting features in many aspects. O_2 molecules have spin $S = 1$. Connected with the corresponding magnetic moment, with increasing ρ' first short-range and finally long-range magnetic correlations within the film are observed. The magnetic correlations appear simultaneously with successive erection of the axes of the molecules due to increasing ρ', which shows that a minimum spreading pressure within the film is needed to stabilize magnetic order. It is known that for $\rho' \geq 2.5$ and $T \lesssim 11.5$ K the film is antiferromagnetically ordered and in this state 2D O_2 is believed to be literally a 2D antiferromagnet. The magnetic order disappears at $T = 11.5$ K where the film becomes paramagnetic.[4-6] The corresponding phase transition is ruled by frustation effects of the spin system of the O_2 film and is therefore magnetoelastically driven. Because of the resulting interplay between structural and magnetic ordering forces interesting critical phenomena are anticipated. Besides the structural critical phenomena reported here, 2D O_2 also shows melting phenomena accompanied by unique 2D magnetocaloric effects. This will be described in a forthcoming paper.[7]

We performed a very careful heat-capacity study of the phase boundary between the paramagnetically disordered and the antiferromagnetically ordered state ($\rho' = 2.55$). We also applied magnetic fields of different orientations [parallel ($B_\parallel$) and perpendicular ($B_\perp$) to the 2D film plane]. We used a comparative measuring method, which facilitates separation of background (substrate and adsorption can) and 2D film signal (quotient method[8]). Two samples are coupled together by a thermal weak link (twin calorimeter). One sample ($P_\parallel$) contains a foil of graphite (Grafoil) rolled like a carpet, and the other ($P_\perp$), sheets stacked like a sandwich (each about 6 g of substrate of specific surface area 21 m^2/g). The magnetic field of a superconducting coil ($0 \leq B \leq 5$ T) is oriented such that it is parallel to the axes of the adsorption cells. Therefore, the twin calorimeter allows measurement of magnetic anisotropic behavior without replacing the adsorption cells. For different orientation of magnetic field one has merely to select $P_\parallel$ or $P_\perp$ for film adsorption.

Figures 1 and 2 show specific-heat curves as a function of temperature for the field-free case and with fields of either orientation ($B_{\parallel,\perp} = 1.1$ T).[9] The field-free measurement reveals a strong double peak with $T_{c1} = 11.32$ K and $T_{c2} = 11.65$ K. These structural peaks are superimposed on the T^2 background due to the 2D O_2 film lattice. The field dependence of the two peaks is strongly anisotropic. For a parallel field of $B_\parallel = 1.1$ T the peak at T_{c1} nearly disappears but the peak at T_{c2} survives. For fields $B_\perp$ no change of either peak height or transition temperature is observed. Just before the onset of the first phase transition (T_{c1}) the T^2 background appears to have a weak shoulder at $T_s = 10.9$ K, present in all our measurements, which is not influenced by magnetic fields. The meaning of this precursor is not yet clear.

Now we discuss and interpret the measured re-

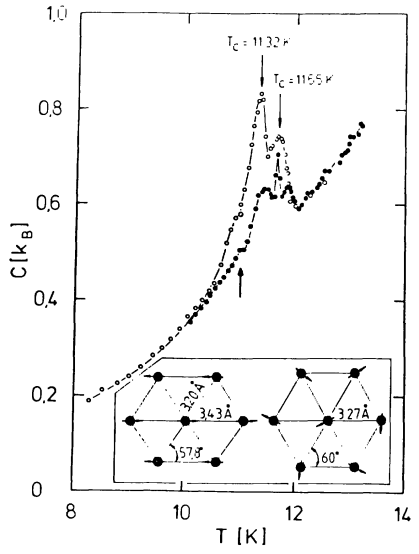

FIG. 1. Specific heat per O_2 particle in units of k_B as a function of temperature. Gas adsorbed in $P_{\parallel}$. Open dots: field-free case; full dots: $B_{\parallel} = 1.1$ T. Left inset: distorted unit cell of the antiferromagnetic state ($T < 11.3$ K); right inset: hexagonal unit cell of the paramagnetic state ($T > 11.6$ K). Note that this hexagonal unit cell may be a simplification. There are evidences (Stephens *et al.*, Ref. 1) that the hexagon is slightly deformed. This deformation, however, is negligible compared with the large deviation from the hexagonal symmetry in the antiferromagnetic state (left inset). The lower arrow indicates the shoulder mentioned in text.

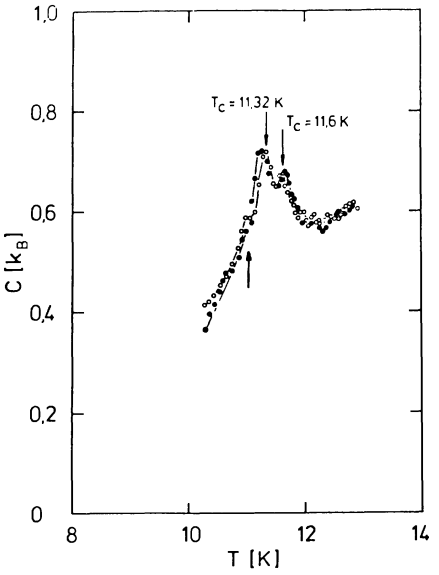

FIG. 2. Specific heat per O_2 particle in units of k_B as a function of temperature. Gas adsorbed in $P_{\perp}$. Open dots: field-free case; full dots: $B_{\perp} = 1.1$ T. The lower arrow indicates the shoulder mentioned in text.

sults in terms of Ising, Potts, and Heisenberg models. Consider the hexagonal lattice of 2D O_2 in the paramagnetic state. The unit cell is shown in the right inset of Fig. 1. O_2 molecules (spin $S = 1$) are placed at each corner and additionally at the center of the hexagon. There is direct antiferromagnetic exchange interaction between neighbor spins which tends to align them antiparallel. On a hexagonal lattice it is not possible to realize an antiparallel configuration for all pairs of neighbor spins. This has the consequence that such a system does not have a well-defined ground state. However, magnetoelastic distortions can cause four nearest neighbors to be antiferromagnetically aligned and two nearest neighbors to be ferromagnetically aligned with respect to the spin of the central particle. Because of the distortion, the four antiferromagnetically coupled particles move in, thereby increasing their magnetic overlap with the central particle, and the two ferromagnetically coupled particles move out, thereby decreasing their magnetic overlap (left inset of Fig. 1). Hence, for the phase transition from the paramagnetic lattice with hexagonal symmetry to the antiferromagnetic lattice with rhombohedral symmetry two steps are needed. First the lattice is distorted, and second the spins are ordered. Then the question arises whether lattice distortion and magnetic order occur at the same or at successive temperatures and whether an intermediate phase lies between the two states. The specific-heat measurement reveals two separated transition temperatures. This suggests the conclusion that there are two successive phase transitions.

Domany and Riedel[10] examined the properties of the discussed phase transitions with the aid of a phenomenological Landau-Ginzburg-Wilson Hamiltonian (LGWH). The LGWH consists of three parts. First, a magnetic part H_m, which has the symmetry of a Heisenberg system with cubic anisotropy. Second, a distortive part H_d, which—because of the three equivalent possibilities for deformation of the hexagon (left inset of Fig. 1)—has the symmetry of the three-state Potts model. Third, a coupling part H_c, which via magnetoelastic coupling links the magnetic and elastic degrees of freedom. Which part of the LGWH dominates at the phase transition (H_m or H_d) is determined by the coefficients r_m and r_d of the quadratic terms in H_m and H_d, respectively. If $r_m > r_d$, as one lowers the temperature

first the lattice distortion takes place and then magnetic order sets in. If $r_m < r_d$ just the reverse is true.

Assume for the moment that the coupling part were switched off. Then suppose that the magnetic part describes a transition at $T_c{}^m$ ($T_c{}^m$ corresponds to r_m) and the distortive part at $T_c{}^d$ (corresponding to r_d). Now switch the coupling on. What is the effect of the coupling? When $T_c{}^m > T_c{}^d$, the system first undergoes a phase transition to the magnetic ordered state, by the coupling term inducing a magneto-elastic distortion of the 2D lattice. This mechanism yields a single transition of cubic Heisenberg character. When $T_c{}^m < T_c{}^d$, as a first step the distortive part of the LGWH initiates a three-state Potts transition. This transition produces a nonmagnetic intermediate phase. Then the coupling lowers the coefficient of *one* component of the three-component magnetic order parameter. As a second step this component undergoes an elastically driven Ising transition to the antiferromagnetic state.

Now refer to the experimental results. Obviously the experiment selects out of the two theoretical possibilities the one describing a *two*-phase transition. Moreover, the experiments suggest that the system does not correspond to a Heisenberg model with cubic anisotropy. Instead, we may conclude that, as predicted by theory, the peak at $T_{c1} = 11.32$ K corresponds to an Ising transition ($T_{c1} = T_c{}^m$) and the peak at $T_{c2} = 11.65$ K corresponds to a Potts transition ($T_{c2} = T_c{}^d$). How can we get more evidence for this interpretation? There are two possibilities. First, we could try to do a very careful investigation of the specific-heat temperature dependence close to the T_c's and determine the critical exponents of the transitions. By this means, it might be possible to identify the transitions as Ising- and Potts-like, respectively. At present, however, the accuracy of measurement needed to do such an investigation is far beyond the accuracy available even in high-resolution specific-heat experiments. Second, we could test the nature of the transitions by investigating anisotropic behavior with magnetic fields. What kind of anisotropic behavior is anticipated with magnetic fields? It is obvious that for either field applied ($B_\parallel$ or $B_\perp$) there should be no change of the magnetoelastic Potts transition. The Ising transition, on the contrary, should reveal strong anisotropic behavior. We start with the discussion of $B_\parallel$. Assume that we are in the antiferromagnetic state. If a sufficiently strong field of parallel orientation is applied, we will eventually reach the spin-flop phase, in which the spins of the two sublattices are oriented perpendicular to the field direction, at the same time precessing clockwise and anticlockwise around the field.[11] This is just the definition of the Heisenberg xy model, which in 2D, as is well known, at best shows a flat cusp at T_c. Consider now $B_\perp$. Since the field is now oriented perpendicular to the plane of spins, no influence on the Ising transitions is expected at all, apart from a slight shift of T_c dependent on field strength.

Figures 1 and 2 suggest that the experiments with magnetic fields reveal exactly the anticipated behavior and that there is agreement with the anisotropic properties with magnetic field predicted by theory. Figure 2 shows that the specific heat nearly does not change for a perpendicular field $B_\perp$. For parallel fields $B_\parallel$, however, T_{c2} survives but T_{c1} disappears.

A comparison of Figs. 1 and 2 needs additional comments since one could judge from these figures that $P_\parallel$ and $P_\perp$ show different behavior even without applied fields. The peaks of Fig. 2 appear to be a little less pronounced than the peaks of Fig. 1. Note that for investigation of anisotropic behavior with magnetic fields we do not change the orientation of the magnetic field or the orientation of the sample within the field, but we switch from one cell to the other of the twin arrangement. In all previous measurements $P_\parallel$ of both cells proved to have the better surface homogeneity and the larger effective adsorption area. We think that this is due to the different kind of preparation of the two cells. $P_\parallel$ contains *one* elongated sheet but $P_\perp$ contains many little disks (about 150) of Grafoil with the consequence that in case of $P_\perp$ the surface is much more disturbed. This is believed to be the reason for the slightly different behavior between the two cells. We checked that besides the difference in size of the Grafoil sheets there is no reason why the cells should behave differently.

There are neutron-diffraction experiments which also investigate the lattice distortion and the magnetic order near the phase transitions considered here.[6] Unfortunately, the question whether magnetic order and lattice distortion appear at the same temperature was not investigated. Careful consideration of Figs. 11 and 12 of this investigation, however, reveals that the lattice distortion takes place between 11.68 and 11.86 K and the magnetic ordering at a slightly

lower temperature (about 11.3 K). This would be in excellent agreement with the results of the present investigation.[12]

In 3D, many systems are known which because of frustration effects show magnetic-order phase transitions accompanied by lattice distortion phenomena. There are, however, only a few[13] systems known for which the lattice distortion has the function of a predecessor, in the sense that only after a delay in temperature is magnetic order accomplished. Therefore, our specific-heat results represent a behavior of matter which is rarely known from the 3D world and is to our knowledge unique for the behavior of 2D matter.

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