Magnetic and Structural Phases of Monolayer O_2 on Graphite

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(Received 24 June 1976)

Neutron diffraction studies of O_2 thin films physisorbed on the basal plane of graphite show three distinct two-dimensional crystalline phases, all incommensurate with the substrate lattice. The low-temperature monolayer phase has a distorted triangular structure analogous to the closest-packed plane of bulk α-O_2. As in α-O_2, a magnetic superlattice reflection persisting up to $T = 10$ K indicates a well-developed antiferromagnetic order. Above $T = 10$ K the structure is similar to the closest-packed plane of β-O_2.

Thermodynamic measurements[1] have shown that monolayers adsorbed on Grafoil, a very uniform high-surface-area graphite, behave as essentially two-dimensional (2D) systems. Recently, there have been direct determinations of the crystal structures[2-4] and, in favorable cases, the dynamics[3-4] of these phases by neutron scattering. We report here a study of neutron diffraction from adsorbed O_2, including the first observations of a magnetically ordered phase in a monolayer. The O_2 system is of particular interest since its bulk α phase is the only known homonuclear antiferromagnetic insulator.

The experiments were performed at the cold source of Risø's DR3 reactor on an oriented sample of Grafoil, with momentum transfer Q nominally parallel to the graphite basal planes. The total area for adsorption was determined in an earlier measurement with the same sample cell of the structures of adsorbed D_2 and H_2 monolayers.[3]

Difference spectra, $I(\text{Grafoil}+O_2) - I(\text{Grafoil})$, at $T = 4.2$ K are shown in Fig. 1 for several coverages. The typical shape of a monolayer Bragg peak is asymmetric, as observed in previous monolayer studies.[2] The width of the leading (low Q) edge is determined by the coherence length L of the adsorbed regions, while the broad trailing wing results from 2D scattering off surfaces which are not parallel to the scattering plane.

In all previous structural determinations for gases adsorbed on Grafoil the atomic or molecular centers are found to be arranged on a triangular lattice with six equidistant nearest neighbors. The (10) Bragg peak from this structure lies at $Q_{10} = 4\pi/\sqrt{3}d_0$ which, for the structures observed to date, lies in the region $1.70\ \text{Å}^{-1} < Q_{10} < 2.15\ \text{Å}^{-1}$. The line shapes in Fig. 1 are not compatible with such an interpretation. In particular, the spectrum at coverage $\rho/\rho_0 = 1.96$ shows a well-developed splitting, with maxima at $Q = 2.18\ \text{Å}^{-1}$ and $2.32\ \text{Å}^{-1}$, the high-Q peak having about half the intensity of the low-Q one. (The reference coverage $\rho_0 = 6.37\times10^{-2}\ \text{Å}^{-2}$ is that for a $\sqrt{3}\times\sqrt{3}$ triangular lattice in registry with the graphite basal plane, with one adsorbed molecule for every three carbon hexagons on the surface.)

These nuclear Bragg peaks strongly suggest that the O_2 monolayer has the same structure as the closest-packed (a-b) plane of bulk α-O_2,[5] shown in Fig. 2. The arrows in Fig. 1 indicate the positions and relative intensities of Bragg peaks from such a plane with the known bulk O_2 intermolecular distances. We therefore interpret the split peak in "2D α-O_2" as indicating four nearest neighbors at $d_0 = 3.20$ Å, and two next-nearest neighbors at $d_1 = 3.40$ Å. These values, which are calculated from the observed peaks, are nearly the same as in bulk solid O_2, where $d_0 = 3.20$ and $d_1 = 3.43$ Å. In this structure, the molecular axes are all normal to the plane, giving maximum packing density. From the molecular size, one can estimate that freely rotating O_2

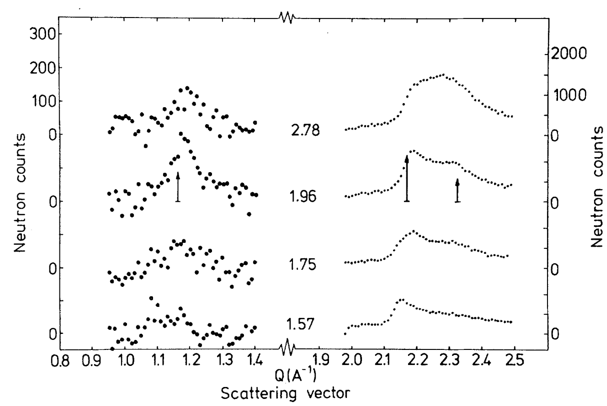

FIG. 1. Neutron diffraction from O_2 adsorbed on Grafoil at $T = 4.2$ K. Coverages are listed as numbers of O_2 molecules per three hexagons on the graphite surface. Displayed on the right-hand side is the difference spectrum $I(Q)(\text{Grafoil}+O_2) - I(Q)(\text{Grafoil})$, while the left-hand side is $I(Q, T = 4.2\text{ K}) - I(Q, T = 20\text{ K})$ (Grafoil $+O_2$). Note the eightfold difference in scales for the two regions.

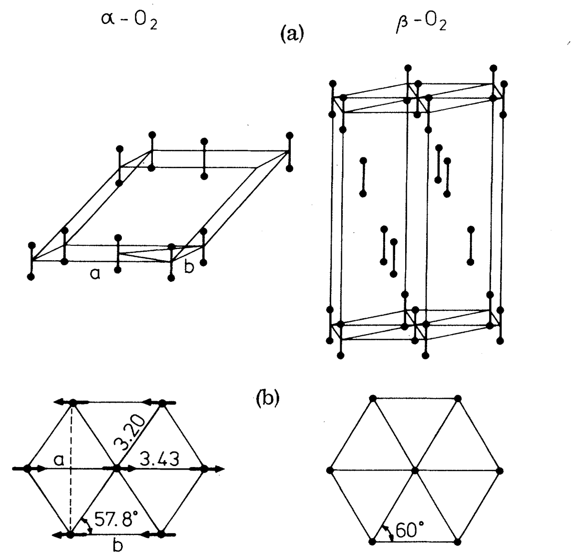

FIG. 2. (a) The structures of α-O_2 and β-O_2. (b) The structures of the closest packed planes in α-O_2 and β-O_2. The molecular axes are perpendicular to the plane. Arrows indicate the directions of the magnetic moments. Note the doubling of the magnetic unit cell in the a direction. The β phase has no long-range magnetic order.

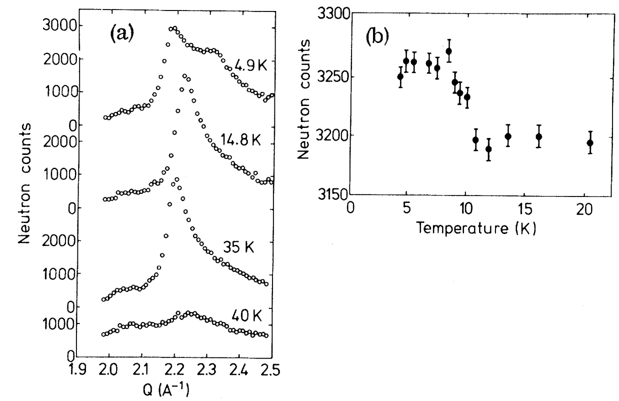

FIG. 3. (a) Temperature dependence of structural peaks for coverage $\rho = 1.96$, corresponding to 1.16 monolayers for the observed structure. (b) Scattering intensity at $Q = 1.16$ Å^{-1}, the peak of the magnetic sublattice reflection, as a function of temperature, for $\rho = 1.96$. The count rate 3200 corresponds to the background scattering from Grafoil in this region of Q.

molecules parallel to the surface would occupy linear dimensions about 40% greater. An orientationally ordered structure of molecules parallel to the substrate would presumably have dimensions intermediate between these extremes.

Since it is known from neutron-diffraction observations of magnetic superlattice reflections that bulk α-O_2 is antiferromagnetic,[6] we searched for similar indications in the monolayer. The weak reflection at $Q = 1.16$ Å^{-1} is interpreted as indicating a magnetic doubling of the unit cell along the same axis as in the bulk basal plane. In this structure all moments are confined to the plane, with the four nearest neighbors antiferromagnetically coupled and the magnetic moments pointed along the direction defined by the two ferromagnetically coupled neighbors (Fig. 2). The relative intensity of the superlattice peak is compatible with such an interpretation, using the previously determined magnetic form factor.[7] From the width of the leading edge of the superlattice peak[2] we estimate the range of magnetic order L_{mag} to be ~125 Å, the same as inferred from the structural peak, and in agreement with previous determinations of the effective coherence size of the Grafoil substrate.[2]

Figure 3 displays the temperature dependence of the magnetic and structural peaks at coverage $\rho = 1.96\rho_0$. In the region $T \sim 10$ K there are both magnetic and structural transitions. There is some indication that the magnetic transition is not first order, but the data do not permit more precise conclusions. High-temperature series expansions for a 2D, $S = 1$ Heisenberg system[8] give a divergent susceptibility at $T_c \approx \frac{9}{5}J$, while the bulk value for J in O_2 is 5.75 K[9] giving T_c(2D) ≈ 10.3 K in (presumably fortuitous) agreement with the observed transition temperature $T = 10$ K. In the transition region the structure evolves continuously to a phase having all neighbors equidistant at $d_0 = 3.27$ Å, reminiscent of bulk β-O_2 ($d_0 = 3.31$ Å). Concomitant with the approach to an equilateral triangular structure, the intensity of the magnetic peak decreases. Figure 3 gives only an approximate notion of the sublattice magnetization, since only the values at $Q = 1.16$ Å^{-1} are plotted and the position of the maximum shifts with the structural change.

The nature of the low-density ($\rho < 1.7\rho_0$) δ phase is less clear. Antiferromagnetic correlations are implied by the low-Q magnetic scattering, while the shape of the structural group, with excess intensity in the high-Q wing, suggests the existence of magnetostrictive fluctuations, but lack of long-range structural order. Furthermore, the areal density of the δ phase is somewhat less than that of the α and β phases, but still too great to permit the molecule to tilt more than ~10° from the vertical.

In Fig. 4 we show a tentative phase diagram. The transition between the δ and fluid phases is

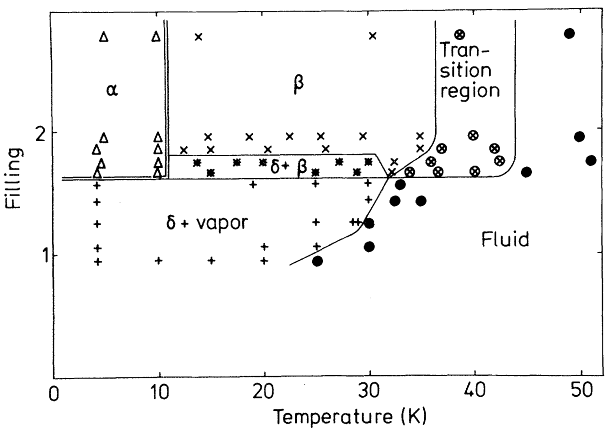

FIG. 4. Phase diagram for O_2 adsorbed on Grafoil. There are three distinct solid phases, labelled α, β, and δ. The δ–α transition line occurs at monolayer completion. In the "transition region" the β-phase Bragg reflection gradually fades out. The measurements indicate that the α-to-β transition may be continuous but it occurs over a narrow temperature range. The nature of the δ-to-α transition is not known.

sharp, as evidenced by an abrupt disappearance of the Bragg peak [presumably the peak in $S(Q)$ for the 2D fluid is too broad for observation under the conditions employed]. In contrast to this the intensity of the (10) peak in the β phase decreases gradually in the temperature range labelled "Transition region." In the area labelled $\delta+\beta$, Bragg peaks of both phases are in evidence, the relative intensity of the β peak increasing with coverage. The δ-β transition thus appears to be of first order, and occurs upon monolayer completion as determined by the known graphite area and the observed lattice spacing. It thus seems that a finite surface pressure is required to stabilize the α and β structures relative to the less dense δ phase.

The overall behavior of adsorbed O_2 in the monolayer regime is strikingly similar to bulk O_2, whose magnetic properties are well understood in terms of the electronic states of isolated molecules, slightly perturbed by pairwise interactions with neighbors.[10,11] The ${}^3\Sigma_g^-$ ground state of O_2 has the electronic configuration

$$\sigma_g^2(1S)\sigma_u^{*2}(1S)\sigma_g^2(2S)\sigma_u^{*2}(2S)\sigma_g^2(2p_z)\pi_u^2(2p_x) \times \pi_u^2(2p_y)\pi_g^*(2p_x)\pi_g^*(2p_y),$$

and by Hund's rules the two unpaired π^* electrons form a triplet $S=1$ spin state. Two such molecules aligned as in bulk and 2D O_2 can interact attractively via perturbative admixture of low-lying ionic states only if, as required by the Pauli principle, their molecular spins are not parallel. This leads to an effective Hamiltonian of the Heisenberg form, $E_{12}=|J|[\vec{S}_1\cdot\vec{S}_2-1]$, and an antiferromagnetic ground state.

English and Venables[11] have shown that both the nuclear and magnetic structures of bulk α-O_2 and β-O_2 can be understood in terms of a stack of 2D sheets of O_2 molecules, with the molecular axes normal to the sheets. To the accuracy of our measurement this is also true for O_2 monolayers on graphite. All of the observed properties appear consistent with a 2D array of molecules whose orientation, interaction, and magnetic properties are not significantly affected by the substrate. In particular, the observed structures are some 60% more dense than the $\sqrt{3}\times\sqrt{3}$ registered structure.[1,2]

The authors wish to acknowledge helpful discussions with O. Vilches and F. Hanson. J. P. M.'s research was supported in part by the National Science Foundation.

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