X-Ray and Heat-Capacity Study of Molecular Oxygen Adsorbed on Graphite

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In a comprehensive x-ray scattering and heat-capacity study of O_2 physisorbed onto basal planes of graphite, at least four independent solid phases are found, whose characters differ markedly from previous descriptions. The most important change is for the monolayer δ phase, which is believed to consist of a rectangular lattice with the molecules lying down on the graphite surface. The precise nature of several of the higher coverage phases remains unknown.

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Solid molecular oxygen in both two and three dimensions presents an interesting interplay between orientational, structural, and magnetic degrees of freedom.[1-8] In spite of many years of research, bulk solid oxygen is still not fully understood. However, recent experimental and theoretical work on two-dimensional (2D) solid oxygen, especially in the bilayer regime, has suggested that this system may be rather more straightforward.[1] In order to elucidate further the properties of oxygen films we have carried out a comprehensive study of oxygen on graphite in the one- to three-layer regime by using heat-capacity and x-ray diffraction techniques. We find a richer and more complex phase diagram than that suggested by the previous work.[1] We are only able to provide qualitative models for the observed behavior and indeed it appears that much more work using a variety of techniques will be required before a quantitative understanding is obtained.

The x-ray measurements were performed in transmission through ~1.7 g of *ZYX* exfoliated graphite with Cu $K\alpha$ radiation from a 12 kW rotating anode.[9] Heat-capacity measurements of films adsorbed on 17.3 g of Grafoil have been described[2]; however, the combination of thermodynamic and structural data leads us to a substantially different interpretation of the results. We present all of our O_2 doses in units (f) of the coverage at the commensurate-incommensurate transition of Kr. In this paper we first present our results and analysis. This analysis rests on the observation that the electric quadrupole moment of O_2 is small; thus the dominant *orientational* intermolecular and molecule-surface interactions are steric. Discussions of the differences from previous work will be postponed to the end.

Figure 1 shows our phase diagram. We have relabeled the previously designated α and β phases by ϵ and ζ since, as we discuss below, there is no evident connection between these and the

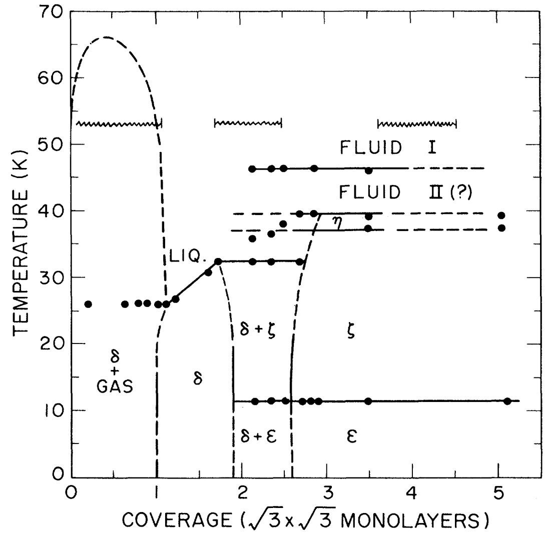

FIG. 1. Proposed phase diagram for O_2 physisorbed on graphite. Filled circles mark the locations of heat-capacity peaks. Horizontal hatched lines indicate quasi-vertical rises in the vapor pressure isotherm. Phase boundaries marked by dashed lines are speculative.

3D O_2 phases. Figure 2 gives a series of x-ray scans through the observed monolayer Bragg peaks; evidently there is a rather complicated progression with increasing coverage at constant temperature. The fitted positions and intensities of the peaks with use of standard 2D Gaussian diffraction theory[9] are plotted in Fig. 3.

Our most important results are for the δ phase. For $f \leq 1.0$, we observe two Bragg peaks at wave vectors $Q = 1.575$ and 2.08 Å^{-1}; this phase melts at a constant temperature of 26 K. In the range $1.1 \leq f \leq 1.9$, the melting temperature increases while both Bragg peaks move to higher Q. This is convincing evidence for solid-gas coexistence for $f < 1.0$ and $T < 26$, a line of solid-liquid-gas triple points, and monophase δ solid above $f = 1.1$.

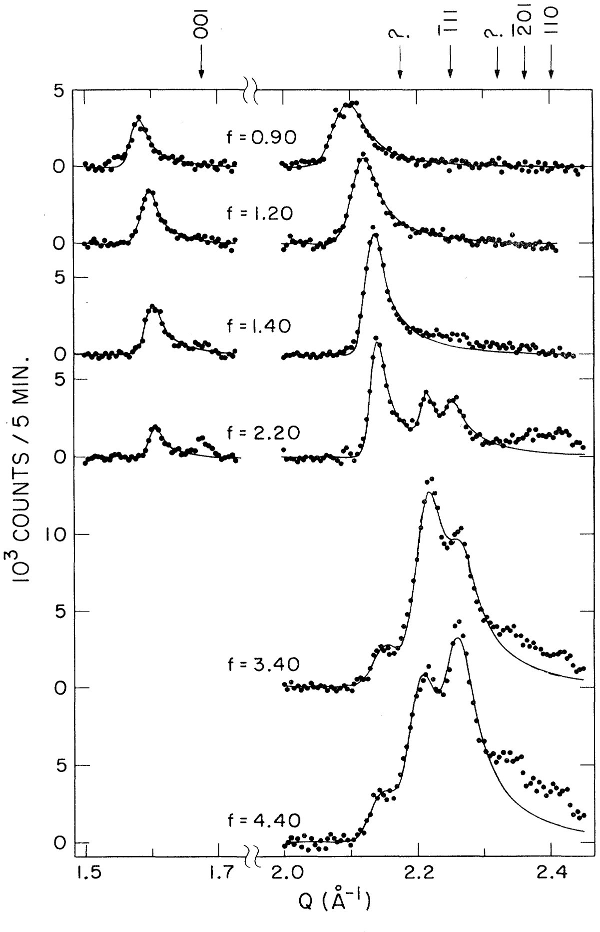

FIG. 2. X-ray scattering profiles at several coverages; temperature = 15 K. Graphite background [4 × 10^4 counts/(5 min)] has been subtracted. Data reproduced over a period of six months. Arrows at top indicate 3D α-O_2 peaks (including two not indexed) from Ref. 3. Smooth curves are line shapes fitted according to the model of Ref. 9: resolution = 0.009 Å^{-1} half-width at half maximum (HWHM), vertical mosaic = 14° HWHM.

From the observed diffraction peaks, the structure clearly cannot be triangular. By considering various possible models, we conclude that the most physically plausible structure is centered rectangular, with incommensurate lattice vectors $a = 3.17$–3.25 and $b = 7.85$–7.98 Å. This simple structure is close packed if the molecules are parallel to the b axis. Each molecule is then surrounded by two neighbors at 3.17–3.25 Å, and four at 4.23–4.31 Å. This agrees qualitatively with Etters, Pan, and Chandrasekharan,[4] who predict 3.17 and 4.99 Å. The two observed peaks index as (02) and (11). This structure accounts for the 1:3.5 ratio of the integrated intensities of the two peaks within the ± 10% experimental error[10]; moreover, the obvious alternatives do not reproduce the x-ray data. Thus for $f \leq 1.9$, the molecules lie in the plane to optimize the carbon-oxygen van der Waals interaction while the O_2 steric forces control the in-plane structure.

As the coverage is increased from $f = 1.9$ to 2.6

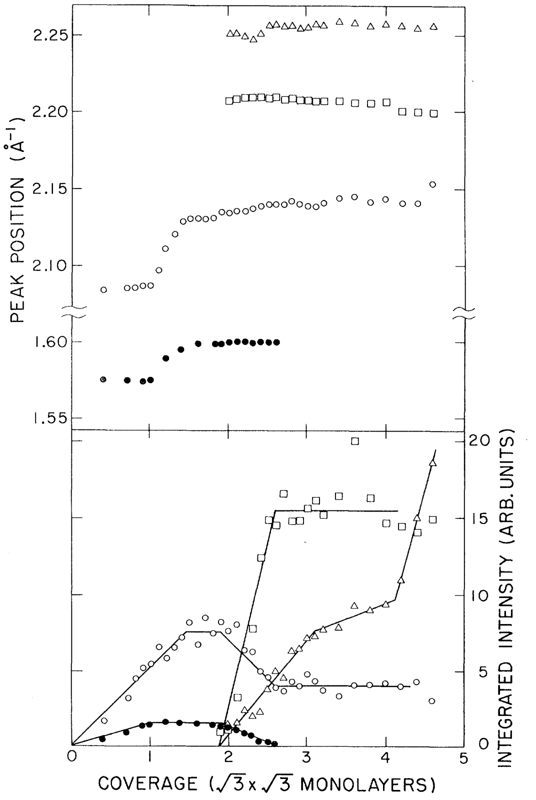

FIG. 3. Peak positions and intensities vs coverage at 15 K. Lines are drawn as guides to the eye.

we observe a linear tradeoff between the δ phase and two higher coverage phases: ϵ below ~11.4 K and ζ above. The ζ phase is characterized by three principal Bragg peaks at 2.14, 2.21, and 2.25 $Å^{-1}$. We cannot distinguish between the 2.14 $Å^{-1}$ ζ phase peak and the δ phase (11) peak at this same position for $f > 1.4$. No other prominent Bragg peaks are observed. As shown in Fig. 3, throughout the δ-ζ coexistence and up to three full layers, the peak positions remain essentially constant while the intensities undergo a strong evolution. The positions of these peaks imply an interatomic spacing ~3.3 Å, close to that of a single triangular plane of the bulk β phase. The δ-ζ first-order transition thus corresponds to a structural change in which the O_2 molecules reorient themselves from parallel to perpendicular to the graphite plane. This transition is clearly driven by the competition between the oxygen-carbon and the oxygen-oxygen van der Waals interaction, the latter becoming dominant at higher coverages. Unfortunately, because of our limited diffraction data, we cannot offer a unique model for the structure of the ζ phase. Possibilities include a small monoclinic distortion from hexagonal symmetry and, alternatively, incommensurate successive layers. We should also note that at coverages as low as $f = 2.2$ small amounts of bulk O_2 appear to be nucleated, as seen from the extra scattering at 1.68 and 2.3–2.4 $Å^{-1}$ in Fig. 2.

We now consider the behavior with increasing temperature in the multilayer region. At low temperatures ($T \leq 11.4$ K), bilayer O_2 is antiferromagnetic with a structure which, according to Nielsen and McTague,[1] is close to that of bulk α-O_2. At 11.4 K there is a transition from the ϵ phase to the ζ phase which we assume to be paramagnetic. We shall comment on the nature of the magnetic transition below. We show in Fig. 4 a series of x-ray scans from 15.0 to 39.0 K for $f = 2.70$; we did not take x-ray data below 15.0 K. As the temperature is increased toward 36 K the three ζ peaks move to smaller Q and the central peak grows in intensity at the expense of the other two.

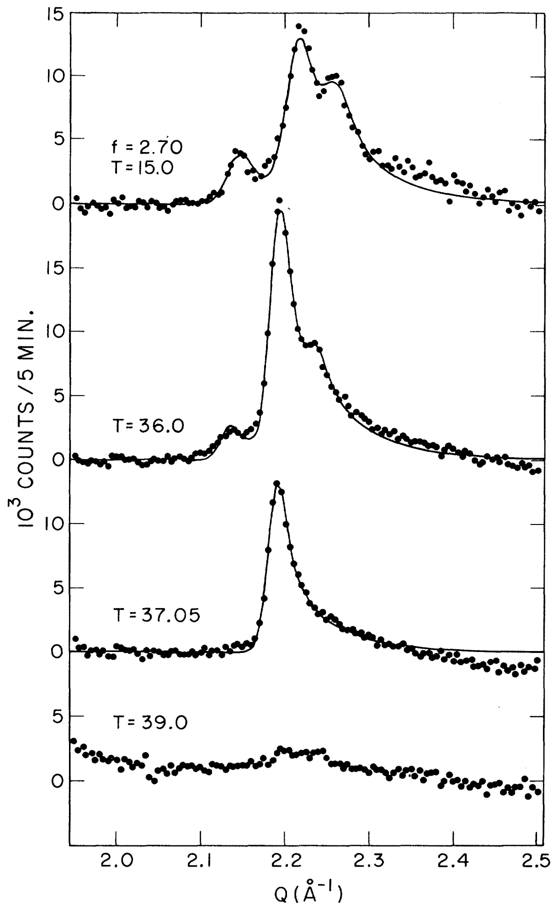

FIG. 4. X-ray scattering profiles at several temperatures, fixed coverage $f = 2.70$, which show evolution through ζ, η, and fluid II(?) phases.

A sharp heat-capacity peak at 36 K signals the transition to a phase with only one Bragg peak, identified as η in Fig. 1. However, we cannot distinguish whether the ζ-η transition is first or second order. The η-phase diffraction pattern is consistent with a simple 2D triangular lattice; indeed the lattice constant is identical to the in-plane spacing of rhombohedral 3D β-O_2 stable at the same temperature. We therefore infer that the η phase indeed has the same stacked triangular structure of precessing tipped molecules.[3] A heat-capacity peak at ~39 K indicates a sharp transition to a fourth phase. The diffraction pattern at 39.0 K is shown at the bottom of Fig. 4. We find no evidence for any prominent Bragg peaks although a strong peak could be hidden under the graphite (002) peak centered at 1.876 $Å^{-1}$. There does appear to be liquidlike scattering around 2.2 $Å^{-1}$ although this is not completely certain. Accordingly, we have labeled this phase fluid II(?), the question mark signifying our uncertainty. Finally at ~46 K a fourth specific-heat peak is observed. This highest-temperature phase must certainly be a fluid.

The study of the evolution from surface to bulk phases is also an interesting problem; for O_2 we find that the $f = 2.6$–5 heat-capacity peaks and x-ray profiles do not connect onto the 3D α, β, and

γ phases with increasing coverage. Rather, as Gregory showed for the magnetic susceptibility,[5] 3D transitions appear above ~3 monolayers with no apparent relation to the adsorbed phases. The presence of 3D Bragg peaks for coverage as low as $f = 2.2$ further supports this viewpoint.

These results differ from those of Nielsen and McTague (NMc) in a number of important respects. Firstly, NMc did not observe the 1.58 Å^{-1} peak at low coverages and hence they incorrectly identified the δ phase as triangular. Because of their use of Grafoil as a substrate, NMc were unable to resolve the three ζ phase peaks and hence they incorrectly identified the ζ phase as triangular. NMc did not observe the ζ-η transition. Finally NMc locate the phase boundaries at markedly different coverages from our independent specific-heat and x-ray studies. We do not understand this discrepancy, although it could be related to the amount of bulk O_2 nucleated in the cell.

Clearly, much more work remains to be done before we will be able to claim a reasonable understanding of O_2 on graphite. Since one of the most interesting aspects of O_2 is the magnetism, we conclude this paper with some conjectures on the magnetic behavior. Domany and Riedel[6] have suggested that the antiferromagnetic transition for this triangular X-Y system should fall in the universality class of the 2D Heisenberg model with cubic anisotropy. However, they considered only collinear structures. We believe instead that if the ζ phase were triangular, then one would observe a second-order transition into a noncollinear three-sublattice triangular structure with the neighboring spins at 120° to each other. This transition may be either followed or preempted by a *first-order* transition into a distorted two-sublattice collinear structure. Indeed we suggest that such a model describes the β-α transition in bulk O_2 very well. The rhombohedral β phase exhibits pronounced three-sublattice short-range order,[11] while the structure of α-O_2 is a stack of distorted triangular sheets.[1,3] In any case our diffraction results show that the ζ phase does not have a simple triangular structure. It does not seem worthwhile to speculate on the possible nature of the ζ-ϵ transition until the structures are properly solved.

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