Melting and Wetting Behavior in Oxygen Films

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At high coverages and low temperatures oxygen on exfoliated graphite takes the form of a bilayer film plus bulk solid clusters. A transition at 47 K is interpreted as prewetting in which a thick film is formed. Evidence for this transition is seen in heat-capacity and magnetic-susceptibility measurements.

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Oxygen, the only magnetic gas which retains its magnetic moment in condensed phases, possesses many interesting properties in the adsorbed state. The system of oxygen on exfoliated graphite has received considerable attention and much of the phase diagram is well understood.[1] Our interest here is focused on melting and possible wetting behavior. In an extensive series of experiments we have measured the magnetic susceptibility and heat capacity of oxygen films on Grafoil exfoliated graphite from submonolayer to multilayer coverages.

In Fig. 1 we have plotted the loci of various transition features obtained from our data. The great majority of these features are seen in both susceptibility and heat capacity. A transition can, however, quite often be detected in the susceptibility data when it has become too weak to be seen in the heat-capacity data. Some proposed phase boundaries taken from Ref. 1 are shown by dashed lines. (In this paper coverages will be defined with reference to the "$\sqrt{3}\times\sqrt{3}$" commensurate monolayer which we shall call a "mon.")

A melting[2] transition of the film occurs at 25.5 K below 1 mon. and shifts upward in temperature above this coverage. At 1.6 mon. (one fully compressed δ monolayer) the transition temperature becomes constant at about 32 K and features associated with it rapidly diminish. The phase boundary represented by this constant-temperature section has been associated with the upper bound of $\delta+\zeta$ coexistence.

As the 32-K features diminish, new features (shown in Fig. 1 by solid circles) grow rapidly in strength and increase in temperature, eventually to about 42 K. We shall refer to these below as the "40-K" features. They reach maximum size at 3 mon., then decline somewhat at higher coverage. We believe that the local decrease of the temperature of the "40-K" features to 38 K at 3 and 3.5 mon. is associated with completion of the bilayer. (Repeating these runs gave reproducible behavior.) Above 1.5 mon. a transition is seen at a constant temperature of 47 K. Evidence of this transition has been seen previously in heat-capacity measurements,[3] but our susceptibility measurements can now detect a feature at coverages as low as 1.5 mon. The size of the features associated with the transition increases more rapidly above 3 mon. Figure 2 shows the coverage dependence of the area under the peaks for these various features.

We believe that for "apparent" coverages great-

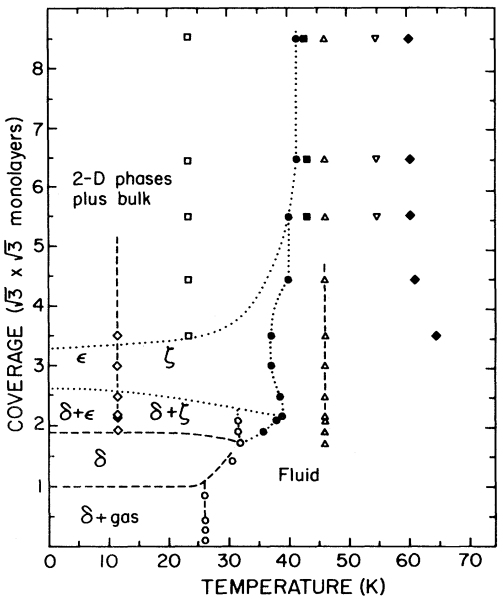

FIG. 1. Phase diagram of oxygen on graphite. Dashed lines are taken from Ref. 1. Dotted lines are suggested by the present work. Locations of features from the present work are shown with various symbols: open lozenges, 2D ϵ-ζ transition; open squares, 3D α-β transition; open circles, δ melting; closed circles, ζ melting (40-K feature); closed squares, 3D β-γ transition; triangles, 47-K feature; inverted triangles, 3D (γ) melting; closed lozenges, "60-K" transition referred to in text.

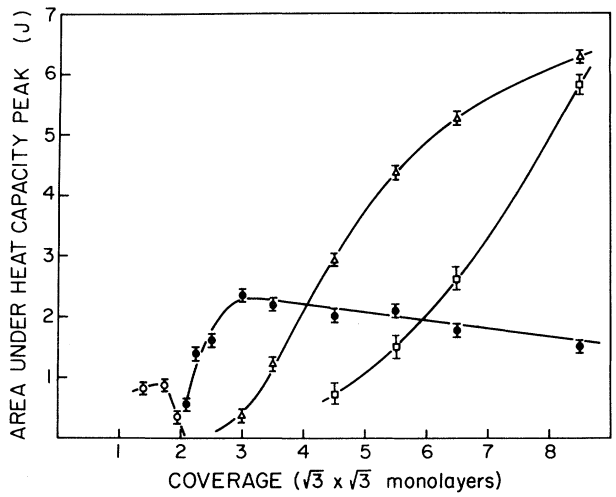

FIG. 2. Integrated heats under various heat-capacity peaks: open circles, δ melting; closed circles, ζ melting (40-K feature); triangles, 47-K feature; squares, 24-K 3D α-β transition (multiplied by 10).

er than 3 mon., which corresponds to about two compressed fluid monlayers, two-dimensional (2D) film actually ceases to thicken. Instead, condensation in cracks and contact regions between the Grafoil platelets nucleates "bulk" islands which account for the disposition of the added gas, a situation discussed in connection with other gases by Dash.[4] This picture is borne out by the appearance of the 24-K α-β transition (see Fig. 1) of bulk oxygen above a coverage of 3 mon. Stoltenberg and Vilches[3] and Heiney *et al.*[1] have also observed experimental evidence for this "bilayer plus bulk solid" picture.

We have given some thought to a picture in which the first and second layers melt independently. In this picture the 47-K transition would be associated with melting; however, the detailed behavior of the various features cannot be reconciled with this interpretation. Specifically, if the 47-K transition *were* to be identified as melting it would, because of its higher temperature, presumably have to be that of the first layer. Thus, one would identify the "40-K" transition with the second layer. However, the 47-K features are absent at low coverages and do not grow appreciably until two fluid monolayers are completed. The "40-K" features, on the other hand, have increased to maximum size by this coverage. It is therefore much more reasonable to associate the latter with melting of the whole film and this requires us to view the film between 40 and 47 K as fluid. This is consistent with the observation of liquidlike scattering by Stephens *et al.*[2] above 39 K.

Our interpretation of the low-temperature features is that the transitions indicated by open and solid circles in Fig. 1 are the melting of δ- and ζ-oxygen, respectively, as suggested by the dotted boundaries. Over a small coverage range at which these phases coexist, both melting transitions can be present.

As for the 47-K feature, we note that it grows above 3 mon., the coverage at which the 24-K α-β-transition susceptibility feature of "bulk" oxygen is first seen, although a "pretransitional" feature is evident in the susceptibility at a coverage as low as 1.6 mon. (An indication of the amount of bulk solid is given by plotting the area under the 24-K heat-capacity peak.) The fact that the feature increases in strength with increasing coverage militates against explanations in terms of one- or two-layer behavior. We suggest that the 47-K feature indicates a prewetting phase boundary which becomes a wetting transition at bulk solid-gas coexistence. The increasing strength of the feature as one approaches the actual wetting transition follows naturally in this picture.

The bulk β-γ transition is accompanied by a great structural change and loss of magnetic order. We should quite generally expect that such a bulk transition would change the wetting characteristics of the system. Thus, the prewetting transition could be driven by the β-γ transition, although the two transitions need not be coincidental, even at bulk coexistence. Indeed, it is certainly the experimental fact that the temperature of the prewetting feature is remarkably constant over the entire coverage range. It should be noted that, in our picture of the 47-K transition, the bilayer fluid film phase vanishes at the transition as the γ solid wets the substrate. Above 47 K only γ solid is present and this melts at the bulk solid melting temperature of 54 K. The 47-K feature in the magnetic susceptibility (also seen in Fig. 3) is such that there is strong deviation from simple Curie-Weiss behavior over a wide temperature range on both sides of the transition. We believe that the film is paramagnetic above 40 K and this behavior therefore indicates a considerable change in the average interaction between oxygen moments, as would be expected in a restructuring of the adsorbate of the type suggested.

Gilquin[5] has measured stepped isotherms for O_2 on graphite between 54.9 and 66.7 K, indicating

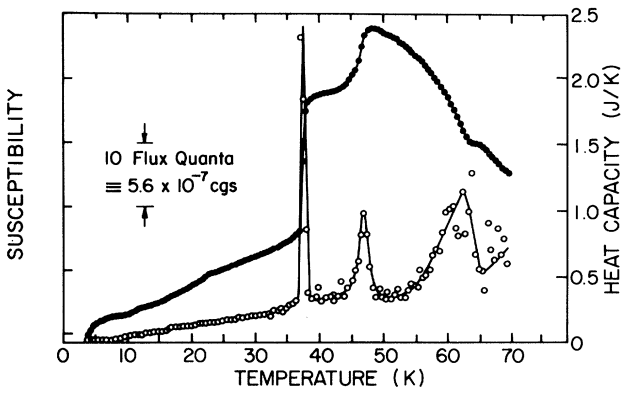

FIG. 3. Magnetic susceptibility and heat capacity of 3.5-mon. film vs T. Closed circles, susceptibility; open circles, heat capacity.

layering in this system. Thus, a wetting-prewetting transition at 47 K should presumably proceed through a sequence of layer transitions. This would be somewhat different from the "usual" wetting-prewetting behavior discussed by Ebner and Saam[6] and Cahn[7] in which there is a single "thin-thick" transition.

Finally, we note the presence of a transition at about 60 K. Above this "60-K" transition the temperature dependence of the susceptibility is that of bulk oxygen. The transition is accompanied by a sharp heat-capacity peak for coverages between 4.5 and 8.5 monolayers. The critical points in which the four layer transitions determined by Gilquin[5] terminate are all close to 60 K. Our measurements appear to be consistent with these values.

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