PHYSICAL REVIEW B VOLUME 22, NUMBER 6 15 SEPTEMBER 1980

Heat capacity of O_2 films adsorbed on Grafoil

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(Received 14 April 1980)

Measurements of the heat capacity of adsorbed O_2 films are reported. Coverages extend from a small fraction of a monolayer up to multilayers and bulk formation in the temperature range between 7 and 58 K. We show melting of the first-layer solid with an apparent triple line, the appearance and disappearance of the two-dimensional α-β film transition, the α-δ and β-δ coexisting regions, and the appearance of the bulk melting and the three-dimensional α-β transformation at a reduced temperature. While most of our low-coverage features qualitatively agree with neutron and susceptibility studies, our results suggest that a more complex layer structure may exist.

I. INTRODUCTION

Various authors have recently investigated O_2 adsorbed on graphite. The main interest stems from the fact that the O_2 molecule possesses a magnetic moment, leading in three dimensions (3D) to paramagnetic gas, liquid, and solid (γ) phases, a short-range-ordered antiferromagnetic (β) solid phase, and a long-range-ordered antiferromagnetic (α) solid phase.

McTague and Nielsen[1-3] have studied O_2 adsorbed on Grafoil and ZYX graphite[4] using elastic neutron scattering. Their measurements start at 0.6 monolayer coverage and go up to about the completion of the second layer. They reveal a rich phase diagram. For the monolayer portion, they show the existence of a triangular two-dimensional (2D) solid (δ solid) incommensurate with the underlying graphite lattice. This 2D solid melts at or above 25 K, the melting temperature increasing with coverage. In the bilayer regime, two different solid phases exist. The low-temperature phase ($T < 11.8$ K) is almost identical to the most dense planes of 3D α-oxygen (isosceles-triangular lattice), and shows the same type of antiferromagnetic order. The high-temperature phase ($11.8\text{ K} < T < 36$ K) has a density identical to the most dense planes of 3D β-oxygen (triangular lattice) and shows no long-range magnetic ordering. Although the 2D phases have the same lattice parameters as in 3D, the α-β transition temperature has been reduced from 23.9 to 11.8 K. The 2D β phase appears to melt in a broad transition between 36 and 44 K. McTague and Nielsen's phase diagram also shows a region of coexisting δ and β 2D solids, and a region of coexisting δ and α 2D solids.

Recently, Gregory[5] has measured the magnetic susceptibility of O_2 adsorbed on Grafoil. His measurements overlap the density range investigated by McTague and Nielsen plus selected coverages up to several layers where 3D effects are present. They show that on the first layer for $T > T_{\text{melting}}$ the adsorbed film is paramagnetic, while for $T < T_m$ the susceptibility varies with T as in an antiferromagnetic phase. When some second layer is present, there seems to be some form of magnetic order below 4 K, but no evidence is seen (probably due to lack of sensitivity) of the α-β transition. After about three layers are deposited, a magnetic transition becomes apparent at the 3D α-β transition.

Dericbourg has measured adsorption isotherms of O_2 adsorbed on exfoliated natural graphite in the liquid-N_2 temperature range. The isotherms show what appears to be the 2D liquid-vapor coexistence regions, giving a 2D critical point at 66 K. Adsorption isotherm measurements by Gilquin[7] show a lower critical temperature of about 60 K.

We present heat-capacity measurements of O_2 adsorbed on Grafoil, beginning at about 0.2-layer coverage and going up to the equivalent of several layers. Our measurements show for the first time the triple line of 2D O_2, the detail of the two-layer α-β transitions, the melting of β-O_2 as two distinct transitions, the disappearance of the 2D α-β transition with the building of a third layer, the appearance of the 3D α-β transition at a lower temperature than for a bulk sample, and the appearance of bulk melting. Extremely poor sensitivity at high temperature prevented us from surveying the liquid-vapor coexistence on the first layer.

II. EXPERIMENTAL

The adsorption cell consisted of 17.3 g of Grafoil disks tightly fitted into a 24-mm-o.d. × 55-mm long quartz cell. The cell was suspended with nylon threads from brass rods extending down from a copper block that could be cooled to 4.2 K or heated to any desired temperature. The cell was connected to a gas-dosing system via a $\frac{1}{32}$-in.-o.d. Cu-Ni tubing running from the cell to the copper block, and by a larger tubing from the copper block to the outside.

Heat-capacity points were taken by the usual method of supplying a known amount of heat ΔQ with an electric heater, and measuring the change in temperature ΔT. The thermometer used was an Allen-Bradley carbon resistor of room-temperature resistance of 1098 Ω. In addition to this resistor, a Rosemount model 146MA platinum thermometer was glued to the cell at all times, and for several of the measurements at the lower temperatures a Cryo-Cal germanium resistor was also attached to the cell. The carbon resistor was thus checked in every run against at least one of the other two thermometers. The carbon-thermometer resistance was fitted for every run to the Clement and Quinell's formula[8] and this fit was used to reduce the obtained data. In spite of this procedure, some ambiguity (of at most 0.3 K above 25 K) still exists in our knowledge of the absolute temperature, mainly because of discrepancies in the stated calibrations of the platinum and germanium thermometers. The O_2 gas used was 99.99% pure (research grade) supplied by Airco Industrial Products.

In a typical run a known amount of O_2 was admitted to the cell while at liquid-N_2 temperature. After several hours, usually overnight, equilibrium was achieved. The equilibrium pressure and temperature were recorded. All external volumes were then closed off, and helium was transferred into the cryostat with helium exchange gas in the container housing the calorimeter cell. In several runs, particularly those at low coverages, care was taken in cooling the cell very slowly in order to keep the cell fill line open.

III. RESULTS

A. Isotherms

An approximate value was obtained for the adsorption area of our cell by measuring an Ar-adsorption isotherm at liquid-N_2 temperature. The isotherm is shown in Fig. 1(a). Using the point "*B*" method (135 cm^3 STP in our cell) and an Ar area of 11.5 $Å^2$ per atom, we obtain 417 m^2 for the total adsorption area. We also used the known ratio of Ar to ^{4}He monolayer capacities from cells *A* and *B* of Bretz *et al.*[9] (see also Goellner, Daunt, and Lerner[10]) to estimate the adsorption area. We obtain total areas of 443 m^2 (from cell *A*) or 420 m^2 (from cell *B*). With the three methods giving comparable results, we have used for our calculations of areal density 427 m^2, the average of all the above determinations.

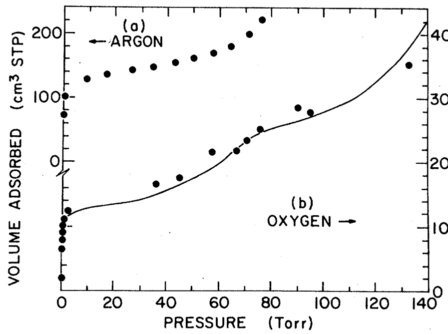

FIG. 1. Adsorption isotherms at liquid-N_2 temperature. (a) Argon, left-margin scale. (b) Oxygen, right-margin scale. Solid line, Brown and Hall's isotherm on graphitized carbon black (Ref. 11).

We also obtained an O_2 "quasi"-isotherm for reference and comparison. Every time an O_2 dosage was adsorbed and before closing the external volumes, the equilibrium pressure at approximately 78 K was measured. Since the experiment was done over a several-month period the liquid-N_2 temperature was not always exactly the same but fluctuated within 0.5 K. Figure 1(b) shows the isotherm for the first two to three layers. The solid line is the O_2 isotherm measured by Brown and Hall[11] on graphitized carbon black. We have scaled Brown and Hall's isotherm to our cell by using their ratio of O_2 to Ar capacities at 10 Torr (1.02) and our Ar capacity at that pressure (129.5 cm^3 STP). The agreement is fair and continues into the (not shown) higher-coverage region.

B. Heat capacity

We show in Fig. 2 the location of heat-capacity peaks found in our measurements, with several

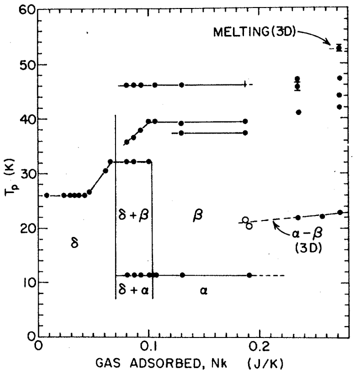

FIG. 2. The temperatures at which heat-capacity peaks are observed as a function of the amount of gas adsorbed. Particular regions are identified from this study and from Nielsen and McTague (Refs. 1–3).

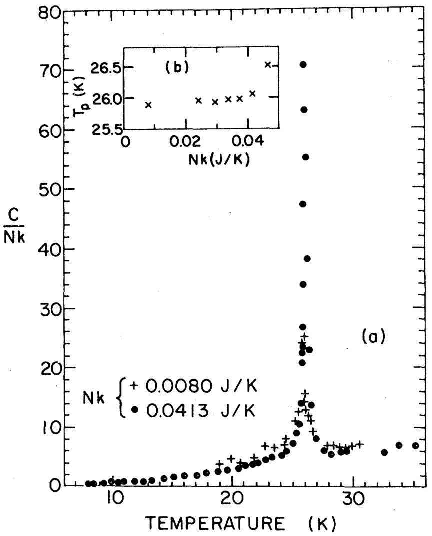

FIG. 3. (a) Heat-capacity peaks at the beginning and end of the triple-line melting. (b) Expanded T_{peak} vs adsorbed-gas region corresponding to the peaks of Fig. 3(a).

features (α, β, δ, etc.) named by comparison with Nielsen and McTague's measurements. Results are shown as a function of the amount of gas adsorbed in units of N (number of atoms adsorbed) times k (Boltzmann's constant). If our cell has 427 m^2 of area as described in Sec. III A, then a monolayer that would perfectly occupy $\frac{1}{3}$ of the graphite lattice sites ($\rho=1$ of Ref. 1 or $n=0.0637$ Å^{-2}, n being the areal density) corresponds to $Nk = 0.0375$ J/K.

1. First layer

The dominant feature in our measurements is the appearance of a very large and narrow heat-capacity peak occurring at essentially constant temperature over two-thirds of the first layer at densities below those explored in previous measurements. Figure 3 shows the two runs at about the beginning and end of this constant-temperature transition line, the insert being a very expanded portion of the phase diagram. This melting is reminiscent of triple line melting in 3D and is consistent with Dericbourg's and Gilquin's vapor-pressure determination of the 2D critical point and their fluid-vapor coexistence region. Our film-to-background heat capacity ratio is poor for the single layer so no accurate measurements could be made at high temperatures to check this agreement.

For densities larger than the one at the end of the triple line ($Nk \cong 0.0406$ J/K, $n \cong 0.0689$ Å^{-2}) a compression of the 2D solid O_2 produces a shift of the melting line to higher temperatures, in qualitative (but not quantitative) agreement with the neutron scattering and susceptibility data.

We have integrated the area under the δ-phase melting peaks to obtain a heat of transformation $\Delta Q = 290$ J/mole. The heat of transformation of γ-O_2 in 3D at 54.4 K (triple point) is $\Delta Q \cong 445$ J/mole. Since the 2D transition occurs at about half the temperature of the 3D one, the entropy changes are about equal. We use our first-layer ΔQ results in the following section to look at the α-β transformation.

2. The two- to four-layer regime

The run at $Nk = 0.0801$ J/K (Figs. 4 and 5) is our lowest-coverage run to show a heat-capacity peak at 11.4 K indicating the α to β transformation in the adsorbed phase. In addition, the heat capacity shows a narrow sharp peak at 32 K ($C_{\text{peak}}/Nk = 46$), a rounded anomaly at 35.5 K, and a peak at 46 K. These last two features can be identified with the beginning and end of the continuous melting region of Ref. 1 while the 32-K peak indicates the end of the β-δ coexistence region. All these features, where measured (some runs only concentrated on the α-β transition), are indicated in Fig. 2. We show in Fig. 5 several runs for coverages from the beginning to the end of the α to β 2D transition, plus runs at higher coverages showing the onset of the α to β 3D transition.

The results shown in Fig. 5 confirm the neutron measurements finding that the α-β transition in the physisorbed system occurs essentially at constant temperature, independent of coverage. Even at higher coverages, when it fades away, the transition still occurs at constant T. Our data indicate that the 3D α-β transition does not evolve from the 2D one, but that it appears on its own at

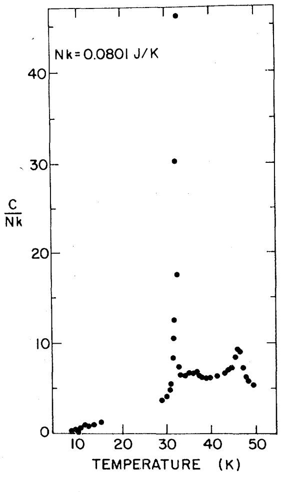

FIG. 4. Specific heat at $Nk = 0.0801$ J/K.

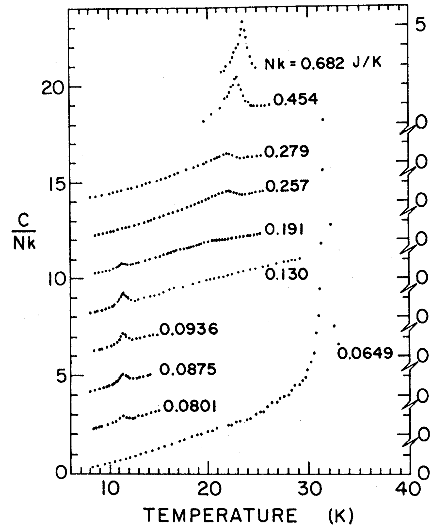

FIG. 5. Specific heat as a function of temperature for increasing amounts of adsorbed O_2 at the α-β 2D and 3D transitions. Numbers in figure indicate coverage Nk in J/K. Not all runs are shown. For clarity the zero on each run has been shifted by two units of C/Nk. The lowest density shown has a very narrow and large heat-capacity peak that goes to $C/Nk = 63.8$ at $T = 31.9$ K.

a lower temperature than in bulk. Our run at $Nk = 0.191$ J/K shows both a disappearing 2D transition at 11.4 K and a break in C/Nk at 20.5 K.

We have calculated the heat of transformation at the α-β transition with results shown in Fig. 6 together with the heats of transformation at the δ-phase melting from the first-layer data. The straight lines through the various sets of points have been drawn to estimate the heats of transformation. They also show that the amount of δ phase at melting grows proportionally to the total number of atoms over the first layer, while the α (or β) phase appears for our cell at $Nk \cong 0.070$ J/K and then grows proportionally to the number of atoms added past this amount. The two-phase coexistence region (α-δ or β-δ) is indicated by the overlap of δ melting and α-β heats of transformation between $Nk = 0.070$ J/K and $Nk \cong 0.104$ J/K.

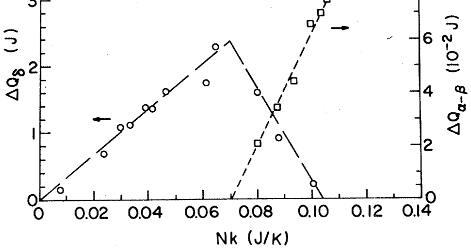

FIG. 6. Areas under heat-capacity peaks (heat of transformation) at the δ-phase melting and α- to β-phase transition as a function of coverage.

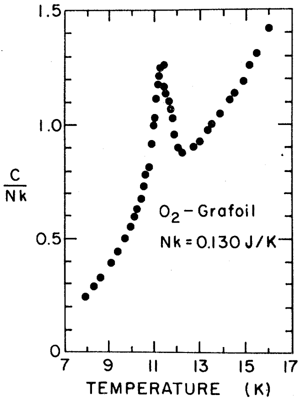

FIG. 7. The thin-film α-β transition specific heat.

An additional feature of the α-β transition in all our measurements is that the heat-capacity peaks appear to be slightly nonsymmetric (Fig. 7). The high-temperature side of the peak seems to be rounded as if the signal we are measuring was the superposition of two effects occurring half a degree apart. We do not know if this is an (unlikely) experimental problem, or some intrinsic feature of the system, like the double transition appearing in Domany and Riedel's calculated phase diagram.[12]

The α-β transition seems to disappear gradually, but we do not have enough data to make a quantitative analysis. Our single run at $Nk = 0.191$ J/K has an area under the peak of 3.1×10^{-2} J, compared with other runs in Fig. 6. Our run at $Nk = 0.235$ J/K has no trace of the transition.

3. *Multilayers*

We measured the heat capacity of several very thick "films" in order to look for the evolution of 3D properties. We did not look at all the features as a function of coverage and temperature but rather focused on three features: the α-β, the β-γ, and the melting transitions. Of the three signals, the β-γ one is the most complex, appearing at the lower coverages as multiple transitions occurring over a 10-K temperature interval. Only for the largest coverage we found essentially a single transition. The overall behavior is too complex to understand in terms of simple models, and probably originates in the rather large crystallographic changes occurring at that temperature.

A series of consecutive runs at the α-β and γ-liquid transitions is shown in detail in Figs. 8 and 9. Both figures show the appearance of the

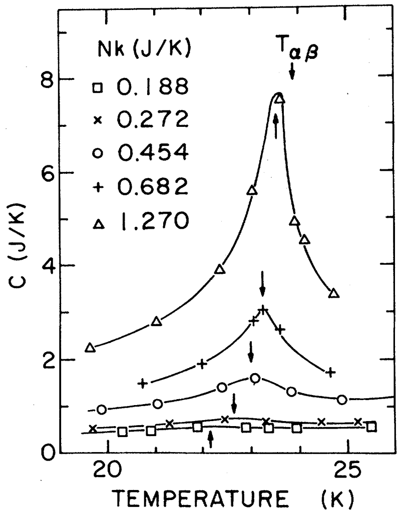

FIG. 8. The 3D oxygen α-β transition heat capacity as measured in our calorimeter cell as a function of temperature and coverage. The $T_{\alpha\beta}$ arrow indicates the transition temperature for a large sample (Ref. 17).

transition at a lower temperature than that measured in large samples. Chung and Dash[13] have observed a similar decrease in the melting temperature of thick N_2 films adsorbed on Grafoil, although in their case the melting occurred at an almost constant-temperature shift regardless of film thickness.

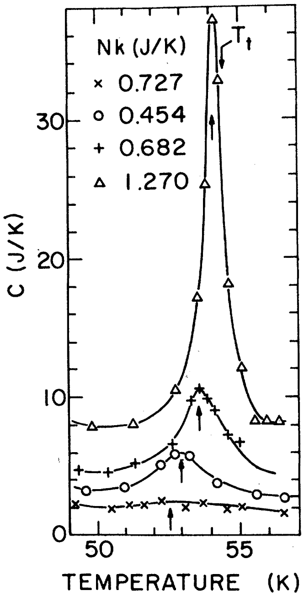

FIG. 9. The onset of the 3D triple-point melting in our calorimeter cell as a function of temperature and coverage. The T_t arrow indicates the bulk sample triple point.

IV. DISCUSSION

The location of heat-capacity peaks shown in Fig. 2 defines phase boundaries much like those described by Nielsen and McTague. In particular one should compare this figure to Fig. 4 of Ref. 1 and to the slightly modified Fig. 3 of Ref. 3 since our measurements indicate features existing in both phase diagrams. To the extent that Gregory's results agree with those of Nielsen and McTague at low density, in particular the first-layer melting line, our results are in agreement with his. We note that although we have identified the features following Refs. 1–3, we have a systematic 14% difference in the areal-density scale, our densities being larger. This difference may come from errors in isotherm comparisons and perhaps in differences between what is called "perfect registry" in heat-capacity and neutron scattering experiments.

The calorimetric measurements combined with the high-temperature isotherm indicate for the first layer the existence of a triple line and first-order melting. For melting at constant area, the end of the triple line and the start of the melting-temperature shift to higher temperatures should correspond to the entire substrate area available for adsorption occupied by the solid. If this is the case in our system, the δ-phase density obtained from our measurements is 0.0689 $Å^{-2}$. This value is very different from the density obtained from the neutron scattering measurements.

The neutron data indicate, assuming a triangular structure for the δ phase, a nearest-neighbor distance $a_{NN} = 3.46$ Å for amounts of gas from $\rho = 0.7$ to $\rho = 1$ and an areal density of 0.097 $Å^{-2}$. The neutron measurements would imply that only 65% of the graphite surface is covered by O_2 at $\rho = 1$ (equivalent to $n = 0.0634$ $Å^{-2}$ if density were uniform). We want to point out, too, that in the neutron scattering measurements, completion of the first layer is estimated at $\rho \cong 1.6$ with a_{NN} for the triangular δ of 3.36 Å. The areal density now corresponds to 0.103 $Å^{-2}$. This implies that with a rather large change of the amount of gas adsorbed, from $\rho \cong 1$ to $\rho \cong 1.6$, a_{NN} changed by only 3%. Thus the triangular δ phase should have a large number of voids at $\rho \cong 1$ or higher average density to accommodate the additional O_2 with such a small lattice change.

While it is impossible to deduce structural information from thermodynamic data, we *conjecture* that some of the discrepancies between our interpretation and that of Nielsen and McTague could be resolved if the δ phase were actually not forming a triangular lattice. The following *speculation* could be explored by a careful reexam-

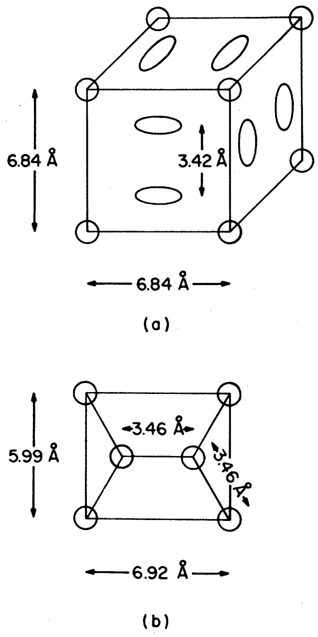

FIG. 10. (a) The unit cell of γ-O_2. (b) A hypothesized structure for adsorbed δ-O_2 derived from the (100) planes of γ-O_2, keeping all molecules equivalent and equidistant.

ination of the neutron data or additional scattering experiments.

In the 3D system, the solid O_2 phase that melts into a liquid is γ-O_2. Its unit cell[14,15] is shown in Fig. 10(a). The most compact plane (100) has an areal density of 0.0637 $Å^{-2}$, rather close to that observed at the end of our triple line. The 2D structure formed by the (100) planes will give additional neutron scattering peaks that are not experimentally observed. On the other hand, a small distortion of the square cell into a rectangular cell, making the distances between all O_2 molecules identical and conforming to the neutron scattering spectrum, will give a structure like Fig. 10(b), with $a_{NN}=3.46$ Å giving $n=0.072$ $Å^{-2}$. It is also possible to construct a honeycomb lattice with the same density and a_{NN}. The structure of Fig. 10(b) will give a few additional scattering peaks of very small amplitude and mostly at high wave vector in the range explored by Nielsen and McTague (1.6 $Å^{-1} < \tau < 2.3$ $Å^{-1}$). Given the scatter in the published neutron scans and the fact that at high wave-vector values the calculated fitted lines in general fall below the experimental points, those scattering peaks could exist. A careful low-energy electron diffraction (LEED) study could resolve this point.[16]

If our conjecture were correct, completion of the first layer would occur at the end of the triple line. This in itself would agree with the 77-K isotherm of Fig. 1(b). Further addition of O_2 would produce a small compression of the first-layer solid with a consequent shift in its melting temperature, and start to populate the second layer.

In our cell, $Nk \cong 0.070$ J/K is the onset of the α-δ (or β-δ) coexistence region. This region, as indicated in our Fig. 2, appears to be somewhat wider than shown by the neutron measurements using either Grafoil or ZYX as the substrate. If we assume that the heat of melting of δ-O_2 is independent of the presence of β-O_2, then Fig. 6 indicates that with the addition of O_2 the δ phase disappears at about twice the rate at which it was built. The heat of transformation obtained for the α-β transition on the assumption that the linear growth of Fig. 6 is due to every molecule added participating in the new phase is 17.3 J per mole added ($\Delta S \cong 1.5$ J/mole K). If the δ-phase molecules were being converted to α- (or β-) phase molecules at the rate of two per each added, then the heat of transformation would be ~ 5.8 J/mole ($\Delta S \cong 0.5$ J/mole K). The entropy change at the α-β 3D transition, on the other hand, is much larger, of the order of 4.2 J/mole K.[17] Considering that the 2D α and β structures are essentially identical to planes of the α and β 3D structures, the large entropy difference between the 2D and 3D transitions points toward a more complex layer and phase structure in the adsorbed system than those assumed for the calculation above and to a much smaller number of O_2 molecules participating in the α-β transition. Further indication of this complexity is given by the heat-capacity peak at $Nk \cong 0.130$ J/K which should be in the pure α-β transition region with no δ phase to complicate the description. The heat of transformation for this run is 5.0 J/mole and the entropy change is $\Delta S \cong 0.44$ J/mole K, again small and more troublesome, not on a line through the origin in Fig. 6 like it should be if further addition of O_2 only made more α or β phases.

In retrospect, it would have been important to measure in as much detail as in the two-phase region the way in which the α-β 2D transition goes away with increasing coverage to help decide how many layers or molecules actually participate in such a transition.

For the multilayer films we have used the analysis of Chung and Dash for N_2 films to understand the decrease in the bulk melting temperature with reduced surface coverage for the O_2 films. They attributed the lower-temperature signal to solid clusters of N_2 with the decrease (δT) in melting temperature being related to the small size of the clusters by

$$\delta T/T_m = 2\sigma_{SL}/rL, \qquad (1)$$

where σ_{SL} is the solid-liquid interfacial energy, r is the radius of an (assumed) spherical cluster, L is the latent heat of fusion per volume, and T_m is the melting temperature of the infinite system.

If we use (1) for our O_2 samples we can see that we get clusters of increasing size with coverage, since the melting temperature shifts continuously. We estimated σ_{SL} from σ_{LG} (liquid-gas) using $\sigma_{SL} \cong (\rho_S - \rho_L)\sigma_{LG}/\rho_L$, , with ρ_S and ρ_L being the density of γ-O_2 (1.33 g/cm^3) and ρ_L that of liquid O_2 (1.28 g/cm^3) and $\sigma_{LG} = 22.7\times 10^3\ N/\mathrm{m}$ at the triple point. If we use $T_m \cong 54.4$ K, then the four runs of Fig. 8 give clusters of approximately 60, 70, 130, and 340 Å diameter. These values are within the range of Chung and Dash's results and the void size of the spaces between graphite-adsorbing surfaces in Grafoil.

If finite-size clusters exist in the multilayer O_2, it is not surprising that the α-β transition would show a similar shift to lower temperatures. It is presently known from model calculations[18] and experimental results that magnetic transitions will be shifted to lower temperatures with decreasing particle size. Theoretical treatments predict a shift in temperature from the one of the infinite system proportional to $d^{-1/\nu}$, where d is the size of the system and ν is the critical exponent of the correlation length (of order $\frac{2}{3}$). Our knowledge of the absolute temperature in this experiment is not good enough to check this relationship. Furthermore, a true check of the power dependence should be done with a system where one does not have to deal with void volumes and one can build an unrestricted amount of 3D solid O_2 to obtain the transition temperature of the infinite system.

Note added in proof. A heat-capacity measurement of two peaks at the first-layer δ melting in qualitative temperature agreement with these measurements have been reported recently [R. Marx and R. Braun, Solid State Commun. 33, 229 (1980)].

ACKNOWLEDGMENTS

We thank J. G. Dash for many discussions and the support and encouragement of E. Domany and E. K. Riedel. We acknowledge receipt of the Nielsen and McTague data and several of their manuscripts as well as S. Gregory's data prior to publication, and useful conversations with R. Birgeneau and P. Stephens. We thank E. A. Stern for explaining to us details of x-ray and neutron scattering data reduction and interpretation. This research was supported by the National Science Foundation, Grant No. DMR 78-22697.

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