Magnetic Susceptibility of Oxygen Adsorbed on Graphite

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The susceptibility of oxygen adsorbed on graphite indicates that magnetic transitions are present even in films of submonolayer thickness. This result contrasts with previous work on amorphous oxygen films and strongly supports the supposition that antiferromagnetic order can only be present simultaneously with configurational order.

Susceptibility measurements on oxygen films adsorbed on Vycor porous glass[1] show behavior characteristic of amorphous antiferromagnetic systems. That is, at least for the case of submonolayer films, the susceptibility rises monotonically with decreasing temperature. However, it reaches values at low temperatures which are in excess of those predicted by a Curie-Weiss law evaluated with a mean value of the paramagnetic Curie temperature. The amorphous nature of the oxygen film is attributed to the glassy nature of the Vycor substrate. Hence, one might expect that films in which the substrate does not prevent configurational ordering would show considerably different magnetic properties.

Grafoil,[2] an exfoliated graphite substrate, is known to be very homogeneous and has a sufficiently large specific adsorption area to be usable in susceptibility measurements. A Grafoil sheet was cut into small ~2 mm squares and packed with (purposely) random orientations in a glass cell. This type of packing was chosen in order to facilitate a closer comparison with Vycor, in which there certainly is an isotropic distribution of substrate surface orientations. As in the Vycor work, susceptibility data were taken at 155 Hz with an rms field of 1.9 G. It should be borne in mind that, because of the smaller specific adsorption area of the Grafoil, the resolution of the present measurements is an order of magnitude poorer than that for the Vycor substrate. With use of the mutual-inductance bridge technique for measuring susceptibilities the data obtained are certainly adequate for the qualitative analysis to be given in this Letter. They do not, however, allow the kind of quantitative assessment which was possible with data obtained by the same measuring technique in the Vycor work.

McTague and Nielsen[3] have obtained neutron-scattering data for oxygen adsorbed on Grafoil. They find evidence for both configurational and magnetic order at all coverages. However, for submonolayer films, neither kind of order is truly of long range.[4] The tentative phase diagram proposed by McTague and Nielsen[3] is shown in Fig. 1. Coverages are re-expressed, for my purposes, in terms of the total mass of gas adsorbed in the present experimental cell (with Grafoil surface area of 20.1 m^2) by using[2] 12.9 Å as the oxygen molecule adsorption area. (This value is of precise quantitative significance only in maintaining consistency with the Vycor work.[1])

In Fig. 2 the total susceptibility of various coverages of oxygen is shown as a function of tem-

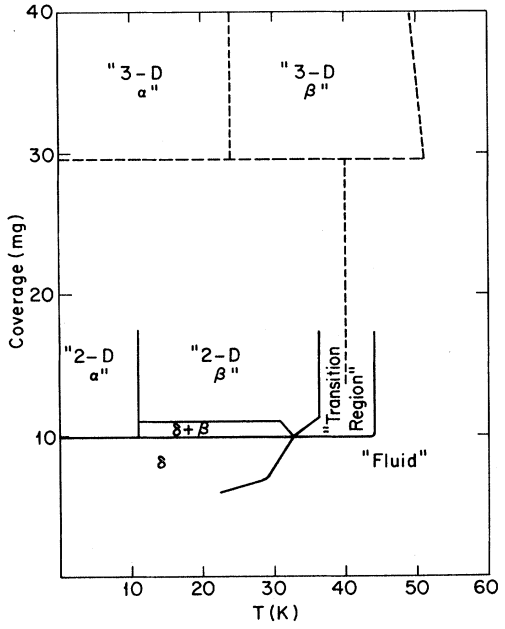

FIG. 1. Tentative phase diagram for oxygen adsorbed on Grafoil suggested by McTague and Nielsen (Ref. 3). The phase boundary between the δ and the α and $\delta+\beta$ phases occurs at a coverage corresponding to a monolayer of oxygen with a triangular lattice about 60% denser than the "$\sqrt{3}\times\sqrt{3}$" *registered* lattice for species adsorbed on graphite. The β lattice is very similar to the α lattice, being only 0.3% less dense. [Recent analysis indicates that a $\delta+\alpha$ phase exists below 11 K at the same coverages as the $\delta+\beta$ phase (J. P. McTague, private communication).] Additional phase boundaries suggested by the present work are shown by broken lines.

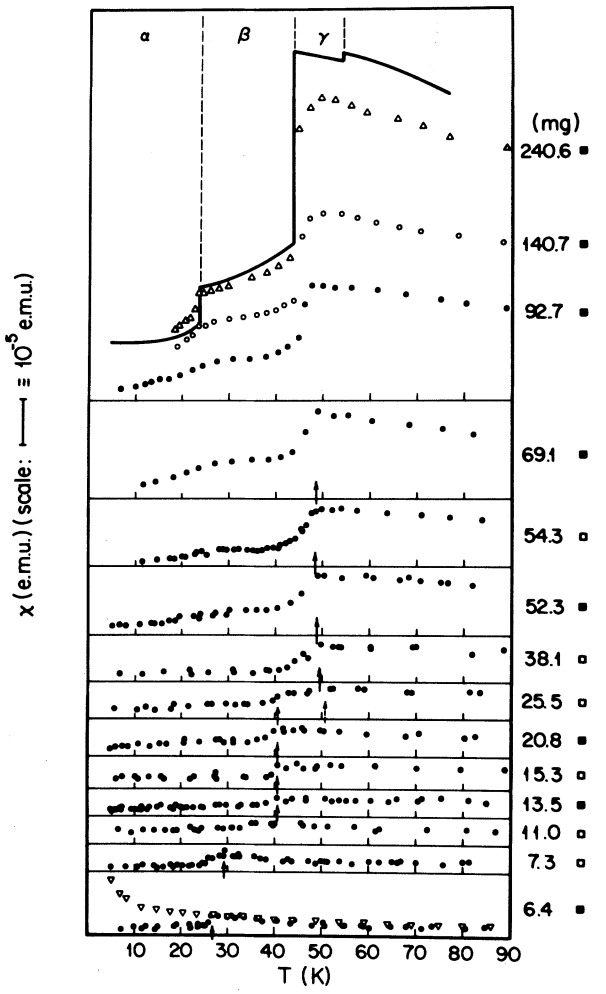

FIG. 2. Susceptibility of oxygen films as a function of temperature for fourteen coverages. One monolayer of the triangular phases α and β corresponds to a coverage of 9.9 mg. Thus, the one-to-three monolayer "two-dimensional" regime ends at about 30 mg and higher coverages manifest "three-dimensional" behavior. The code of open or closed squares (found on the figure next to the coverage) identifies data obtained during two different sets of runs. Open circles and triangles are used for the two highest-coverage data sets in order to avoid confusion. The solid curve is the susceptibility curve of 250.1 mg of bulk oxygen, measured by the author and data shown by inverted triangles are those for a Vycor coverage 22% lower than that of the lowest Grafoil coverage (see text). Arrows suggesting transition locations are included as a guide to the eye.

perature. No distinction is made between data points obtained during warming and those obtained during cooling, because, in contrast to the oxygen-Vycor data, no noticeable hysteresis effects were observed at any coverage. To avoid crowding, the data for all but the three highest coverages are plotted separately, though with the same temperature scale. All the data sets exhibit one or more transitions below which the susceptibility falls with decreasing temperature. This behavior is radically different to that for the oxygen-Vycor system. To illustrate this difference, oxygen-Vycor data for a coverage comparable to (22% lower than) that of the lowest oxygen-Grafoil data are plotted in Fig. 2.

Agreement between the neutron-scattering and susceptibility data as to the location of the fluid-δ transition is very good—perhaps somewhat fortuitously so, in view of the fact that coverage comparisons between experiments depend on the determination of surface area. As the coverage is increased above one monolayer, there is a region in which the susceptibility falls only very little with decreasing temperature below a poorly defined maximum at 35–45 K. A further increase in coverage brings a transition into visibility in the vicinity of 40 K. There is, however, no evidence for the 11-K transition which is clearly identified by neutron scattering. (This 11-K transition is also seen in specific-heat measurements by Stoltenberg and Vilches.[5]) As the pore size of Grafoil is several hundred angstroms, one can attain film thicknesses for which the susceptibility might be expected to approach bulk behavior. Indeed, one does see the emergence of bulk α-β and β-γ transitions at the highest coverages. (The susceptibility of bulk oxygen is shown in Fig. 2 for comparison.)

It would seem that there is no gradual metamorphosis of "two-dimensional" α and β phases into their three-dimensional counterparts with increasing coverage. The data suggest that, between one and three monolayers, the only transition which can be identified in the present work is at about 40 K. Above three monolayers the visible transition is seen at about 50 K and it is this transition which one can identify as the three-dimensional β-γ transition. (This identification becomes clearer at the highest coverages where the transition is much sharper and localized at 45 K.) There is, in fact, some suggestion of the presence of the 50-K transition at 25.5-mg coverage indicating that the "two-dimensional" and "three-dimensional" behaviors overlap at this coverage. (The peak corresponding to the 11-K transition in the specific-heat data of Stoltenberg and Vilches[5] is observed at coverages between one and 2.4 monolayers. Above three monolayers a 22-K peak appears and this is the "three-

dimensional" α-β transition which the present work locates at the slightly higher temperature of 24 K.)

It thus seems probable that there exist three distinct coverage regimes: submonolayer, one-to-three layers, and more than three layers. Although the physics of the one-to-three monolayers regime *might* be straightforwardly determined by the proximity of the substrate, it seems more likely that this regime is exhibiting behavior determined specifically by low dimensionality. In further studies it would therefore be necessary to reconcile the existence of two kinds of "two dimensionality"—that of the submonolayer, which must surely require this description ***and*** that of the one-to-three monolayers regime. (The latter regime has, of course, already been labeled "two-dimensional" in both the present work and that of McTague and Nielsen.[3]) Among other possibilities, it is suggested that one should measure the dependence of the susceptibility on the graphite basal-plane orientation and study the effects of appreciable magnetic fields on the various transitions. When better understood, the oxygen-Grafoil system might well provide a very convenient experimental realization of more than one variation on the two-dimensional Heisenberg model.

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[1]S. Gregory, Phys. Rev. Lett. 39, 1035 (1977).

[2]See, for example, J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975).

[3]J. P. McTague and M. Nielsen, Phys. Rev. Lett. 37, 596 (1976).

[4]The range of the antiferromagnetic correlation in the δ phase is estimated to be appreciably shorter than the substrate coherence length of 125 Å (which is the bound on the long-range order in this system, and which is the low-temperature structural coherence length in both the δ and α phases). The magnetic order in the α phase is approximately of the range of the structural order at low temperature (J. P. McTague, private communication). None of the observed oxygen structures is registered with the substrate (Ref. 3). Therefore, as the substrate potential does not appear to play any symmetry-breaking role, it is not surprising that the δ phase lacks long-range magnetic order. This result is consistent with the theoretical argument of N. D. Mermin and H. Wagner [Phys. Rev. Lett. 17, 1133 (1966)] for such a two-dimensional Heisenberg system.

[5]J. Stoltenberg and O. E. Vilches, private communication.

Some Properties of a Cosmological Solution in the Brans-Dicke Theory

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Properties of a closed cosmological solution with the negative coupling parameter of the scalar field compatible with Mach's principle in the Brans-Dicke theory are summarized.

As a homogeneous isotropic dust model of the universe the Brans-Dicke theory[1] has a cosmological solution[2]

$$ds^2 = -dt^2 + a^2(t)[d\chi^2 + \sin^2\chi(d\theta^2 + \sin^2\theta\, d\varphi^2)],$$

$$a(t) = \left[-\frac{4M}{(3+2\eta)\pi c^2 D}\right]^{1/2} t \equiv \alpha t,$$

$$2\pi^2 a^3(t)\rho(t) = M, \tag{1}$$

$$a(t)\varphi(t) = D,$$

on the conditions that

$$\eta < -2,$$

$$M/c^2 D > \pi, \tag{2}$$

$$\eta/(3+2\eta) = 2 - 3\pi c^2 D/2M, \tag{3}$$

where the constant η is a coupling parameter of a scalar field φ, M and D are constants, and M can be regarded as the mass of the whole universe.

The behavior of the expansion of this universe is the same as that of the Milne universe[3] in kinematics. However, contrary to the Milne universe, this universe is closed and nonempty.

