Adsorbed Oxygen as an Amorphous Antiferromagnetic System

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Oxygen adsorbed on porous Vycor glass, a heterogeneous substrate, displays properties of an amorphous antiferromagnet. However, no antiferromagnetic ordering transition is seen for submonolayer coverages in the temperature range studied (1.9–95 K) although these coverages have paramagnetic Curie temperatures as large as – 50 K.

There is considerable current interest in the properties of amorphous magnetic systems. In particular, it is intriguing that, while ferromagnetically ordered amorphous systems are encountered, there does not seem to be any clear evidence for an ordering transition in an amorphous system with purely antiferromagnetic interactions. Mindful of the many problems involved in fabricating an amorphous antiferromagnet with a selectable high density of spins, I decided that physisorption of the antiferromagnetic gas, oxygen, on a heterogeneous, amorphous substrate, should provide a uniquely convenient system for study. (I believe that the present work is, as it happens, the first investigation of the susceptibility of physisorbed oxygen on *any* substrate in the interesting temperature range below 100 K). The data give strong indication of amorphous antiferromagnetic behavior.

Measurements of the heat of adsorption of various gases on porous Vycor glass show quite clearly that this substrate presents a distribution of site binding energies with a width typically of the order of 5000 J mole^{-1} (600 K) (e.g., see Horiguchi, Hudgins, and Silveston[1]). The heat of fusion of oxygen is 445 J mole^{-1} (Giauque and Johnston[2]). One sees, therefore, that it should be possible to adsorb oxygen at a fairly high temperature (say, 100 K) and expect the adsorbate molecules to distribute themselves on preferred sites in an array whose configurational randomness reflects that of the substrate itself. When cooled, the molecules are restrained from undergoing configuration ordering, but interact magnetically as a "quenched" amorphous antiferromagnetic system. As to the dimensionality of this system, one need only assert, for present purposes, that it is of order two or greater.

Recent neutron-scattering work[3] has been performed on oxygen adsorbed on Grafoil, an exfoliated graphite substrate. Typical binding-energy distribution for gases adsorbed on Grafoil are very narrow (width ~ 50 J mole^{-1}).[4] That is, Grafoil is a very homogeneous substrate, and, in fact, oxygen does not even register with the graphite surface, forming instead lattice phases at low temperatures which are quite similar to single planes of α and β bulk oxygen. Below 10 K a magnetic superlattice is seen, indicating that both configurational and antiferromagnetic order are present. One can therefore say that magnetic phase transitons occur in both two- and three-dimensional crystalline oxygen systems. Measurements of the susceptibility of oxygen adsorbed on Grafoil which support this picture will be presented elsewhere.

In the present work, oxygen was adsorbed on 1.8 g of crushed Vycor contained in a glass cell. A bundle of copper wires connected the copper thermometry block to the inside of the cell. Improved thermal contact was obtained by adding a small quantity of helium as exchange gas—a necessary precaution at temperatures where the vapor pressure of the oxygen becomes very low. ac susceptibility measurements were performed at 155 Hz, with an rms field of 1.9 g, over a temperature range of 4.2–95 K. (One data run was extended down to 1.9 K, further confirming the absence of evidence for a magnetic transition, but experimental difficulties precluded doing this on a regular basis.)

Figure 1 shows the gram susceptibility of oxygen on Vycor for a series of coverages. (Data from different series of runs are not so identified because there did not appear to be any significant series-dependent properties. The data are, for clarity of presentation, a representative subset of a considerably larger set of data.) For low coverages (i.e., those less than one monolayer), no obvious evidence for a magnetic phase transition is seen. What is seen, however, is that, at low temperatures, there is considerable deviation of the susceptibility from a simple Curie-Weiss law, $\chi = C/(T - \theta)$, where χ is the sus-

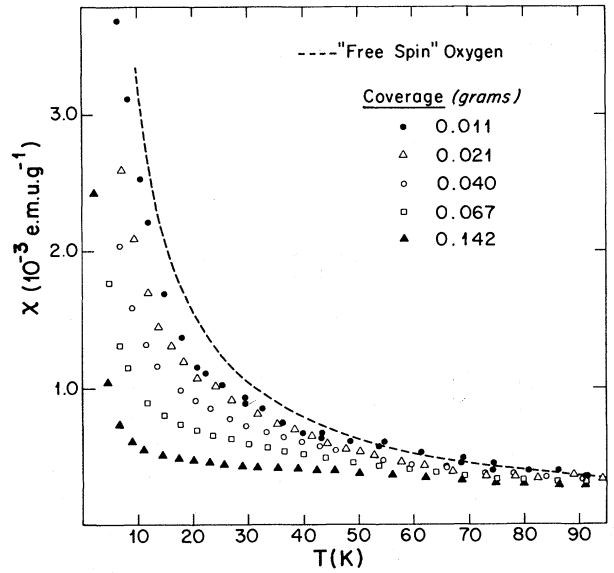

FIG. 1. Susceptibility vs temperature for a series of coverages. (One monolayer corresponds to 0.097 g assuming an oxygen adsorption area of 12.9 Å^2 per molecule.) The "free-spin" susceptibility is given by $\chi = 0.0313T(\mathrm{K})^{-1}$ emu g^{-1}.

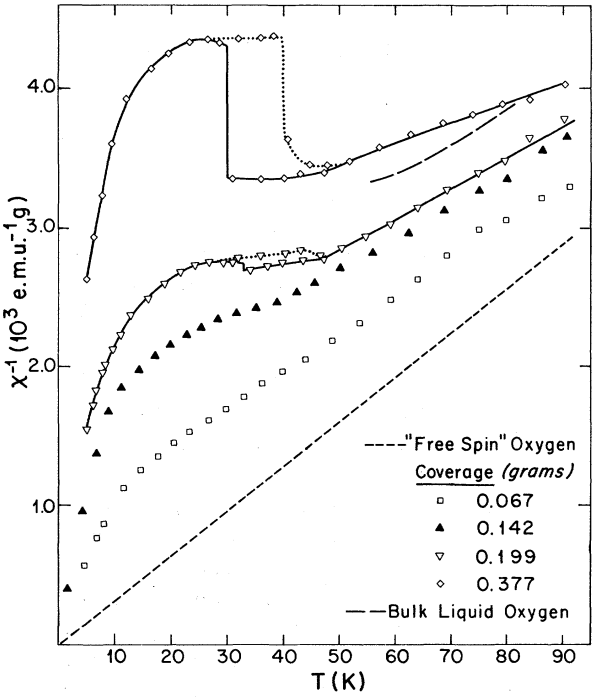

FIG. 2. Inverse susceptibility vs temperature for a series of high coverages. Solid lines are cooling curves and broken lines are warming curves. Pore filling occurs at 0.404 g. Bulk liquid data were obtained in an earlier phase of the present work.

ceptibility, C is the Curie constant, and θ (<0) is the paramagnetic Curie temperature. This deviation is most easily seen in Fig. 2, which is an inverse susceptibility plot of some of the higher-coverage data. (Two sets of data are included which are also represented in Fig. 1.)

Before discussing the low-temperature behavior, it is instructive to extract rough values of $\hat{\theta}$, the characteristic "average" value of the paramagnetic Curie temperature, and $\hat{C}$, the "average" Curie constant. Although these quantities can only be approximately obtained from the high-temperature region, they are of significance. In Fig. 3 they are plotted as a function of coverage. $\hat{\theta}$ rises from zero to a value greater than that for bulk liquid oxygen—a not surprising result in view of the fact that the mean density of the adsorbate will be higher than that of the bulk liquid. It should be noted that $\hat{\theta}$ would be a constant for a crystalline form of oxygen. $\hat{C}$, which is proportional to the effective magnetic moment, is also a function of coverage. Neither curve shows any structure which could be interpreted as a consequence of monolayer formation. It is to be expected that, at sufficiently high coverages, both $\hat{\theta}$ and $\hat{C}$ should approach bulk values. In Vycor, however, this asymptotic situation obviously never obtains. It will be very interesting to ascertain how much larger than the mean pore size of the present adsorbent (~ 65 Å diam) the pores must be before bulk properties are recovered.

The "excess susceptibility" seen at low temperatures is very much a characteristic of amorphous antiferromagnetic systems, but there appear to be two possible explanations for this behavior and from susceptibility measurements alone, one cannot presently choose between them. (Measurements which should resolve the issue will be mentioned at the end of the Letter.) The first explanation is very straightforward: An amorphous magnetic system cannot be characterized by a single value of θ. Inasmuch as one can talk about "effective internal fields," it is clear that a distribution of these must exist, which would manifest itself at low temperatures in an "excess susceptibility"—for, at low temperatures, spins in small internal fields contribute increasingly to the susceptibility. (The small-field spins need not be spatially isolated, but merely in an environment in which the arrangement of neighboring spins produces a small value of the local field.)

The second explanation invokes the concept of

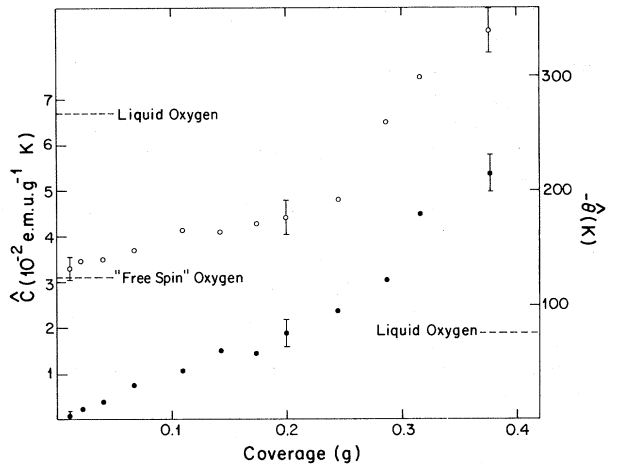

FIG. 3. Dependence of $\hat{C}$ (open circles) and $\hat{\theta}$ (closed circles) on coverage. Error bars are included as a rough guide to the uncertainties involved.

superparamagnetism. Verhelst *et al.*[5] obtained data for the susceptibility of transition-metal aluminosilicate glasses which are qualitatively very similar to those for adsorbed oxygen. These glasses are postulated to contain microscopic "clusters" of higher magnetic-ion concentration. Verhelst *et al.* stress that their clusters are amorphous; yet it is proposed that, below a certain transition temperature, a cluster acquires a large net magnetic moment because of imperfect antiferromagnetic spin cancellations and that the paramagnetic behavior of the cluster net moments can explain the observed excess susceptibility. Now, for adsorbed oxygen, it does not seem likely that actual clusters will form on the surface in view of the previously mentioned heterogeneous adsorption picture. Moreover, θ increases monotonically with coverage.[6] One would expect it to become constant when clusters of significant size form, as the mean interaction would not then depend on cluster size. Nonetheless, it is possible that the tortuosity of the Vycor substrate brings about an effective isolation of (actually contiguous) regions of adsorbed oxygen and the "clusters" thereby created may give rise to superparamagnetic properties.

The low-temperature behavior is most interesting for higher coverages, where evidence for ordering processes appears (see Fig. 2). We again interpret the behavior in terms of the alternative discussed above. For the first mechanism we might postulate the following:

At about 48 K one sees a "leveling off" which might be an indication of some sort of freezing process. It is well known that adsorbed multilayer films show specific-heat anomalies well below the bulk freezing temperature[7] (which is 54 K for oxygen). Although the nature of the process is not presently understood, we can say that the anomalies must accompany a phase change in which the adsorbate loses some degrees of freedom. A transition to a crystalline form is not necessarily implied.[8] When cooling, there is a discontinuity at about 32 K in the high-coverage curves. However, the warming curves do not have this discontinuity, but rise more gradually around the "leveling off" temperature, terminating the hysteric region. The behavior of the high-coverage curves below 32 K suggests the continued presence of amorphous magnetism. Therefore, one can postulate that the first layer of oxygen molecules always remains amorphous and that higher layers, being subject to greatly reduced substrate forces, can order. The large reduction in susceptibility at 32 K very probably accompanies a transition to magnetic and configuration order in these layers.

Alternatively, if superparamagnetism is considered, we might expect that, because this implies that magnetic transitions occur in the clusters at a temperature of the order of 50 K, the "leveling off" is a manifestation of the onset of a magnetically ordered state in thicker films, for which either the appearance of crystallinity or some other property gives a definite local anisotropy axis.

Future investigations must firstly be directed at distinguishing between the two alternative mechanism discussed above, particularly because one implies that there is antiferromagnetic order in the amorphous state, clustered though this state may be, and the other does not. Since the excess susceptibility is the most characteristic property of an amorphous antiferromagnetic system, it must be established whether this results *solely* from the random configuration of spins (as, indeed, it could) or from the less-fundamental property of clustering. Magnetization measurements would give a value for the effective magnetic moment below 48 K. If superparamagnetism has set in, then this quantity should have increased over the high-temperature value. Specific-heat data also could provide significant information through the whole region below 48 K and, of course, both x-ray and neutron scattering data should be obtained.

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[5]R. A. Verhelst, R. W. Kline, A. M. de Graaf, and H. O. Hooper, Phys. Rev. B 11, 4427 (1975).
[6]The glasses of Ref. 5 possessed θ values which varied from sample to sample, but did not depend in any straightforward way on the magnetic ion concentration.
[7]See, for example, J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975).
[8]Capillary condensation will also occur at high coverages in a microporous adsorbent such as Vycor. It should be possible to assess the effect of this on the susceptibility behavior by performing measurements on samples of porous glass which are commercially available in which the mean pore size can be as large as 3000 Å and in which capillarity effects are therefore much reduced.

Zero Dimensionality and Josephson Coupling in Granular Niobium Nitride

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Ultrathin granular niobium nitride films have been found to behave like an array of zero-dimensional superconducting grains coupled through grain boundaries by a Josephson-type interaction. The temperature dependence of the current at which a voltage first appears fits the Josephson-junction–like critical-current predictions remarkably well. The films exhibit a paraconductivity which extends to 24 K, more than twice the critical temperature, T_{cG}, of the grains and varying as $(T-T_{cG})^{-2}$.

In recent years, much attention has focused on the properties of granular films.[1-9] There has been speculation that some granular superconducting films can be characterized by two regimes of superconducting behavior. The first regime reflects the properties of zero-dimensional grains of superconducting material. The second type of behavior characterizes the coupling of these grains by a Josephson-type interaction. Previous studies have suggested the validity of this model[1-7] but none have unambiguously isolated these two characteristics. This Letter reports measurements of the superconducting properties of ultrathin niobium nitride films which have for the first time illustrated these distinct regimes with a remarkable clarity. Either current or temperature can switch the films from one regime to the other. Furthermore, the zero-dimensional character of the grains was unambiguously demonstrated by a paraconductivity observed in one film to temperatures as high as 30 K or more than twice the critical temperature, T_{cG}, of the grains themselves. This is the first time that paraconductivity, clearly characteristic of zero dimensionality, was observed over so large a temperature range.

Niobium nitride films, 170–1500 Å thick, were reactively sputtered onto heated substrates.[8] Films thinner than 170 Å were produced by anodic thinning of thicker films. A standard four-lead technique was used to measure the resistance of the films as a function of temperature, current, and magnetic field. The resistive transitions of films 240–1500 Å thick were quite sharp. The change from 99% of normal resistance to "zero" (undetectable) resistance generally occurred in less than 0.5 K. The 1500-Å film has a T_c (midpoint of transition) of 15.8 K. The T_c's of the thinner films decreased exponentially with inverse thickness reaching 13 K at 240 Å. This behavior is quite similar to results previously reported on thin Nb films.[10] The thicker NbN (>240 Å) films also exhibited typical metallic conduction above the transition temperature with a resistance that increased as the temperature was raised towards room temperature. However, the superconducting properties of the films changed markedly as the film thickness was decreased below about 120 Å. Since the expected grain size for these films is 100 Å,[8] we attribute this change in behavior to the production of a