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## The magnetic properties of $\gamma$ -phase and liquid oxygen

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**Abstract.** It is shown that the magnetic properties of  $\gamma$ -O<sub>2</sub> are mainly determined by the intra-chain exchange interaction, i.e.  $\gamma$ -O<sub>2</sub> is a quasi-one-dimensional magnetic material. On the basis of the analysis of magnetic susceptibility, it was suggested that in liquid oxygen the  $\gamma$ -phase-like structure persists as a short-range order.

### 1. Introduction

At equilibrium vapour pressure, oxygen exists in three crystalline modifications. The monoclinic low-temperature  $\alpha$ -phase is a quasi-two-dimensional antiferromagnet (Burakhovich *et al* 1977, Krupskii *et al* 1979). In the rhombohedral  $\beta$ -phase ( $T_{\alpha-\beta} = 23.8$  K), there is no long-range magnetic order, but quasi-two-dimensional three-sublattice antiferromagnetic short-range order persists in the whole range of existence of the phase. The high-temperature paramagnetic  $\gamma$ -phase ( $T_{\beta-\gamma} = 43.8$  K) is a quite exotic structure (Jordan *et al* 1964, Cox *et al* 1973, Krupskii *et al* 1979, Brodyanskii and Freiman 1985a, Stephens 1985); in an eight-molecule cubic unit cell the molecules exist in two non-equivalent orientational states, as shown in figure 1. Two molecules occupying the body-centred-cubic positions are orientationally disordered ('spherical'); the other molecules precess under 90° to  $\langle 100 \rangle$  axes and therefore have a disc-like distribution of the electron density. The 'disc-like' molecules form linear chains running along the  $\langle 100 \rangle$  directions. The intra-molecular spacing in the chains is shortest in the crystal.

In this paper, it is shown that the magnetic properties of  $\gamma$ -O<sub>2</sub> are mainly determined by the intra-chain exchange interaction, i.e.  $\gamma$ -O<sub>2</sub> is a quasi-one-dimensional magnetic material. Thus, we arrive at the conclusion that at the  $\beta$ -to- $\gamma$  phase transition the magnetic subsystem of the crystal transforms from a quasi-two-dimensional to a quasi-one-dimensional one.

### 2. Discussion and conclusions

The magnetic subsystem of  $\gamma$ -O<sub>2</sub> is described by the Hamiltonian

$$\mathcal{H} = \sum_f D(S_f^z)^2 + \frac{1}{2} \sum_{ff'} J_{ff'} S_f S_{f'} \quad (1)$$

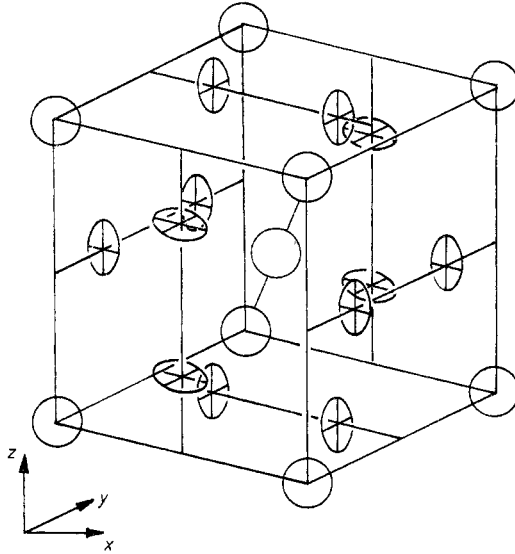


Figure 1. Structure of  $\gamma$ -O<sub>2</sub>.

where  $D$  is a spin-figure coupling constant which represents an anisotropy energy for the spins  $S = 1$ . For a free molecule,  $D_0 = 5.71$  K (Tinkham and Strandberg 1955). For a molecule in the crystal the constant  $D$  is renormalised by the spin-libron interaction (Freiman and Jeżowski 1984) resulting in  $D$  being equal to  $D_0\eta$  where  $\eta$  is a orientational order parameter calculated for the  $\gamma$ -phase by Brodyanskii and Freiman (1985a).

A dependence of the exchange coupling parameter on the inter-molecular distance can be written in the form (Sumarokov *et al* 1980, Slyusarev *et al* 1981, Meier *et al* 1982)

$$J(R) = J_0 \exp[-\alpha(R/R_0 - 1)] \quad (2)$$

where  $\alpha = 12$  (Sumarokov *et al* 1980, Slyusarev *et al* 1981),  $R_0 = 3.187$  Å (Burakhovich *et al* 1977, Krupskii *et al* 1979);  $J_0$  is an effective exchange coupling constant averaged over orientational and translational vibrations. In the numerical calculations we used  $J_0 = 41$  K (Brodyanskii and Freiman 1985b), a value which is in fair agreement with the value obtained by Slyusarev *et al* (1980) from the data on antiferromagnetic resonance and magnetic susceptibility of  $\alpha$ -O<sub>2</sub>. This value exceeds the value which results from *ab initio* calculations (Wormer and van der Avoird 1984) by a factor of 2.

The thermodynamic functions of the magnetic subsystem of  $\gamma$ -O<sub>2</sub> have been calculated by means of a high-temperature expansion of the partition function up to the  $T^{-4}$  terms (see, e.g., Mattis 1965). In the numerical calculations, we have used the Padé approximation of the truncated sums.

Because of the presence in the Hamiltonian (1) of the anisotropy energy term the expansions obtained have the following form:

$$\sum_{i+j+k+l=n} \frac{D^i J_1^j J_2^k J_3^l}{T^n} \quad (3)$$

where  $J_1$ ,  $J_2$  and  $J_3$  are the exchange coupling constants between the nearest, next-nearest and third neighbours. As follows from equation (2) the main magnetic interaction

is between two nearest disc-like molecules ( $J_1 \approx 20$  K); a much smaller indirect inter-chain coupling is realised by means of disc–sphere coupling ( $J_2/J_1 \approx 0.2$ ), and a direct inter-chain coupling is negligible ( $J_3/J_1 \approx 0.05$ ). For inter-molecular spacings in the  $\gamma$ -O<sub>2</sub> lattice the above-mentioned  $J_i$ -values correspond to upper-bound estimates for all the possible mutual orientations of oxygen molecules (Slyusarev *et al* 1981).

On the basis of an analysis of the magnetic susceptibility of  $\gamma$ -O<sub>2</sub>, Brodyanskii and Freiman (1985b) suggested that  $\gamma$ -O<sub>2</sub> is a quasi-one-dimensional antiferromagnet. The existence of strong one-dimensional antiferromagnet correlations was found in  $\gamma$ -O<sub>2</sub> by polarised neutron scattering (Dunstetter *et al* 1985)†.

We have calculated the double-spin correlation functions

$$\Gamma_{ij} = \text{Sp}[S_i S_j \exp(-\mathcal{H}/T)] / \text{Sp}[\exp(-\mathcal{H}/T)] \quad (4)$$

by means of the high-temperature expansions (3). Leading terms in the expansions for two nearest spins in a chain (disc–disc correlation function  $\Gamma_{dd}$ ), two next-nearest neighbours (disc–sphere correlation function  $\Gamma_{ds}$ ) and next-nearest neighbours ( $\Gamma_{dd'}$ ) are

$$\begin{aligned} \Gamma_{dd} &= -\frac{4}{3}(J_1/T) \{1 + \frac{4}{3}[1 - \frac{16}{9}(J_2/J_1)^2 - \frac{32}{9}(J_3/J_1)^2](J_1/T) - \dots\} \\ \Gamma_{ds} &= -\frac{4}{3}(J_2/T) [1 - \frac{2}{3}(1 - \frac{3}{8}J_2/J_1 + 4J_3/J_1)(J_1/T) - \dots] \\ \Gamma_{dd'} &= -\frac{4}{3}(J_3/T) [1 - \frac{4}{3}(1 + J_2^2/J_1J_3 + \frac{5}{16}J_3/J_1)(J_1/T) - \dots]. \end{aligned} \quad (5)$$

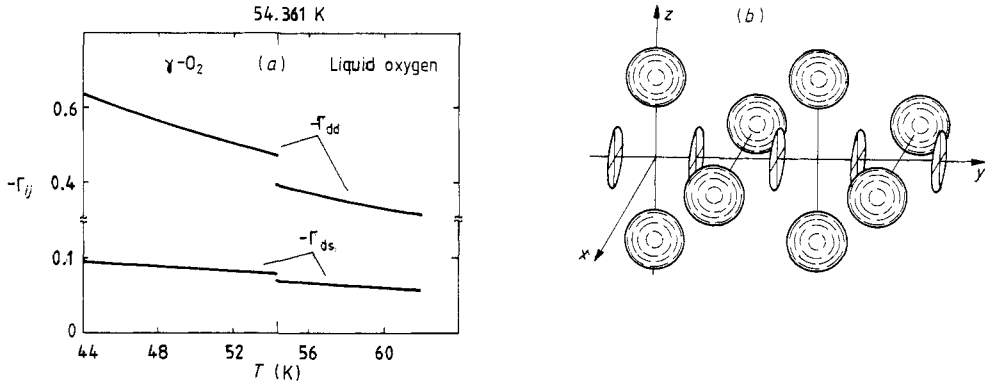
A rapid decrease in the values of successive terms in the expansions (5) is ensured not only by the parameter  $J_1/T$  but also by the numerical smallness of the corresponding coefficients, which results from the lattice structure of  $\gamma$ -O<sub>2</sub>‡. As a result, with good accuracy,  $\Gamma_{dd} : \Gamma_{ds} : \Gamma_{dd'} \approx J_1 : J_2 : J_3$ . The temperature dependences of  $\Gamma_{dd}$  and  $\Gamma_{ds}$  taking into account equation (2) and the lattice thermal expansion are shown in figure 2(a). The theoretical results agree with neutron data (Dunstetter *et al* 1985). Since  $J_3 \ll J_1$ ,  $J_3 \ll T$ ,  $\Gamma_{dd'}$  is negligible. Thus, a real structural quasi-one-dimensional unit is a chain of disc-like molecules alternated by pairs of spherical-like molecules (figure 2(b)).

The calculated magnetic susceptibility  $\chi(T)$  of  $\gamma$ -O<sub>2</sub> at equilibrium vapour pressure as a function of temperature is shown in figure 3 in comparison with the experimental data (Borovik-Romanov *et al* 1954, De Fotis 1981). In the same figure the calculated magnetic susceptibility  $\chi(p)$  of  $\gamma$ -O<sub>2</sub> along the equilibrium curve between the  $\beta$ - and  $\gamma$ -phases as a function of pressure is shown in comparison with the experimental data of Meier *et al* (1982). When calculating  $\chi(p)$  the values used for the inter-molecular distance were obtained by extrapolation of the dependence of the molar volume (Stevenson 1957).

The data obtained can be represented in the form of the Curie–Weiss law, where the Curie–Weiss temperature  $\Theta(T)$  is a decreasing function of temperature with  $\Theta(44.5 \text{ K}) = 61.4 \text{ K}$  and  $\Theta(54 \text{ K}) = 50.2 \text{ K}$ . The paramagnetic susceptibility  $\chi_0(T)$  of non-interacting molecules equals  $C/T$ , exceeding the value of  $\chi$  by a factor of 2. The difference between the values of  $\chi_0(T)$  and  $\chi$  is characteristic of the effect of the exchange interaction in the chains shown in figure 2(b), the contribution from the inter-chain interaction to the value of  $\chi_0 - \chi$  being less than 4%.

† Three groups arrived independently at the conclusion (Brodyanskii and Freiman 1985b, Dunstetter *et al* 1985, Uyeda *et al* 1985).

‡ Anisotropy terms appear in the expression for  $\Gamma_{ij}$  beginning with terms of the form  $(D/T)^2 (J_i/T)$ , and this is why they were omitted from equation (5). As follows from calculations, the statement on the absence of the lowest anisotropy term which is approximately  $DJ_1/T^2$  is valid for arbitrary spin, but we failed to find any general proof of this fact.



**Figure 2.** (a) Plots of  $\Gamma_{dd}$  and  $\Gamma_{ds}$  against temperature; (b) quasi-one-dimensional structural unit of  $\gamma$ - $O_2$ .

An additional confirmation of the quasi-one-dimensional nature of the magnetic subsystem of  $\gamma$ - $O_2$  can be obtained from the calculation of the magnetic heat capacity

$$C_H = C_J + C_D + C_{DJ} \quad (6)$$

where

$$C_J/R = (J_1/T)^2 [1 + 4(J_2/J_1)^2 + 4(J_3/J_1)^2 + \dots] \quad (6a)$$

$$C_D/R = \frac{1}{6}(D/T)^2 [1 + \frac{1}{3}(D/T) - \frac{1}{6}(D/T)^2 + \dots] \quad (6b)$$

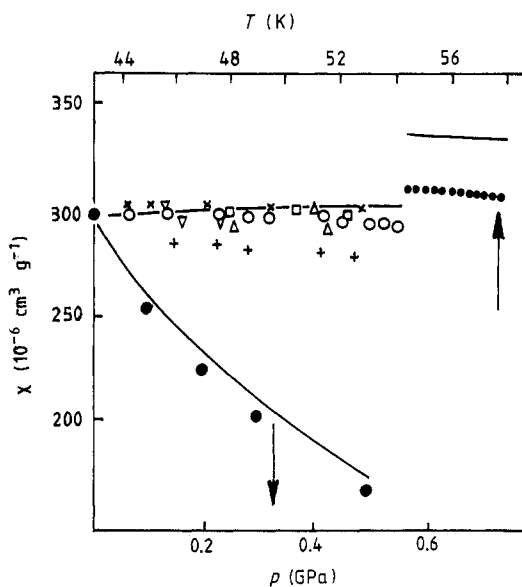
$$C_{DJ}/R = \frac{1}{3} (\sqrt{DJ_1}/T)^4 [1 + \frac{20}{11}(J_2/J_1)^2 + \dots]. \quad (6c)$$

Here  $C_J$ ,  $C_D$  and  $C_{DJ}$  are the contributions to the magnetic heat capacity from the exchange and spin-figure interactions, and magnetic anisotropy energy, respectively. The leading contribution to the magnetic heat capacity is introduced by the exchange interaction ( $C_{DJ}/C_J \approx 10^{-2}$ ,  $C_D/C_J \approx 2 \times 10^{-3}$ ), where the main part results from the intra-chain exchange interaction. As is seen from equation (6a) the contribution to  $C_J$  from the direct inter-chain interaction is about equal to  $(J_3/J_1)^2$ .

The small value of the jump in magnetic susceptibility at the melting point (figure 3) indicates that in liquid oxygen the  $\gamma$ -phase-like structure persists as a short-range order. The values of  $\chi(T)$  calculated under this assumption (figure 3) are described by the Curie-Weiss law with  $\Theta_{liq}^{calc} \approx 40$  K, the experimental value  $\Theta_{liq}^{exp}$  being about 46 K (Meier *et al* 1982). At the same time a rearrangement during melting into a close-packed structure typical for simple liquids, taking into account the experimental jump in molar volume, results in a sharp increase in the inter-molecular distance ( $R \approx 3.9$  Å) and, as a consequence, in a significant decrease in the exchange interaction which will not be compensated by the increase in the coordination number. The Curie-Weiss temperature for such a system would be about 27 K†.

The conclusion about the  $\gamma$ -phase-like pattern of the short range in liquid oxygen is

† At first sight, this conclusion seems to be in contradiction to the results of Uyeda *et al* (1985) where they managed to describe the experimental dependences  $\chi(T)$  for the liquid and  $\gamma$ -phases assuming a close-packed structure for the former and a quasi-one-dimensional structure for the latter. This agreement, however, is the result of a certain inconsistency: the contribution from spherical-like molecules into the exchange field has not been taken into account nor has the change in  $J$  because of an increase in volume at the melting point.



**Figure 3.** Magnetic susceptibility as a function of temperature and pressure: +,  $\chi(T)$   $\gamma$ -O<sub>2</sub>, experimental results of Borovik-Romanov *et al* (1954); ○, □, △, ▽, ◇,  $\chi(T)$ ,  $\gamma$ -O<sub>2</sub>, experimental results of DeFotis (1981) (—, corresponding theoretical results); ●,  $\chi(p)$ ,  $\gamma$ -O<sub>2</sub>, experimental results of Meier *et al* (1982) (—, corresponding theoretical results); ····, liquid oxygen, experimental results (—, corresponding theoretical results).

supported by the similarity in the Raman spectra of  $\gamma$ -phase and liquid oxygen (Cahill and Leroi 1969). The same conclusion was implicit in the work of Dunstetter *et al* (1985) on the basis of near coincidence in the polarised neutron spectra. The suggestion of the persistence in liquid oxygen near the melting line and quasi-one-dimensional chains permits us to explain the anomalously low values of volume change under melting, entropy of melting and saturated vapour pressure at the triple point (Brodyanskii and Freiman 1986).

The existence of one-dimensional and two-dimensional phases in one substance is unique and, apparently, impossible in the usual low-dimensional compounds where strong covalent forces act inside low-dimensional complexes (chains or planes) and there are weak van der Waals forces between them. Implementation of such structures in solid oxygen is possible owing to the peculiarities of the inter-molecular potential, i.e. the proximity of the energy minima for a pair of collinear molecules and a pair of disc-like molecules (Brodyanskii and Freiman 1985a). The former is realised in the collinear orientational structure of  $\alpha$ - and  $\beta$ -phases and the latter in the  $\gamma$ -phase. The quasi-two-dimensional magnetic structure corresponds to the collinear orientational molecules and the quasi-one-dimensional orientation structure of  $\gamma$ -O<sub>2</sub> imposes quasi-one-dimensionality on the magnetic subsystem.

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