

Magnetic structure and dynamics in α - and β -phase solid oxygen

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We have carried out a polarized neutron scattering study of α - and β -phase solid oxygen. The diffuse quasielastic scattering in the β phase is suggestive of three-sublattice noncollinear short-range order with an in-plane correlation length of $9 \pm 1 \text{ \AA}$. α -phase oxygen exhibits strong inelastic magnetic scattering with the magnon density of states peaking at $10 \pm 1 \text{ meV}$. A two-dimensional model is shown to describe well the magnetic properties of both phases.

Solid O_2 is one of few magnetic insulators where the exchange results from the direct overlap of localized orbitals. In spite of this apparent simplicity, no consistent picture has yet emerged for the magnetic properties of solid O_2 .¹ This is evidently because of the complicated interplay between the magnetic and structural degrees of freedom. Recently, several different groups² have suggested that the α and β phases of oxygen could be understood using a two-dimensional (2D) model. In this paper we report the results of a quasielastic and polarized neutron study of the α and β phases of solid O_2 . The results are analyzed in the context of the 2D models of Ref 2.

We first discuss β oxygen, which is rhombohedral and is stable from 43.8 to 23.8 K. The structure is most simply thought of as being composed of triangular sheets stacked in an ABC sequence with the O_2 intramolecular axis perpendicular to the plane. The nearest-neighbor (NN) distance is 3.30 \AA while oxygen molecules in neighboring planes are separated by 4.21 \AA . As discussed by De Fotis,¹ the susceptibility of $\beta \text{ O}_2$ decreases with decreasing temperature suggesting antiferromagnetic (AF) behavior. Indeed, neutron scattering studies by Collins³ indicated at least short-range magnetic order, although little attention was paid to this feature.

We show in Fig. 1 the quasielastic neutron scattering in a polycrystalline sample of $\beta \text{ O}_2$ at 41 and 27 K. Evidently there is pronounced diffuse scattering centered about a wave vector of $\sim 1.3 \text{ \AA}^{-1}$ and this scattering is nearly temperature independent. Elastic scattering measurements with an energy resolution of 0.5 meV show no peak. Thus we conclude that the scattering near 1.3 \AA^{-1} is largely inelastic. In order to probe the dynamics further we have carried out an inelastic polarized neutron study at 25 K. The spectrometer utilized Heusler alloys as monochromator and analyzer together with a weak horizontal guide field of 0.2 T at the sample. The flipping ratio was 10 in this configuration. With the neutron spin resolved in the scattering plane, the coherent spin-flipped and unflipped cross sections are controlled purely by magnetic and nuclear scattering, respectively. Contour maps of the scattering are shown in Fig. 2. These results confirm that the diffuse scattering around 1.3 \AA^{-1} is indeed magnetic in origin; the characteristic energy is

about 3 meV . The scattering peaks at $E=0$, as one would expect in a paramagnet.

The diffuse scattering may be readily interpreted using the three-sublattice model of Loktev and of Stephens *et al.*² They have noted that for predominantly NN interactions, the mean-field interaction energy for a triangular XY magnet is minimized by the three-sublattice 120° configuration shown in Fig. 1. Here the spins are confined to the plane by the intramolecular crystal-field interaction. Further, the interaction between NN and next-nearest-neighbor (NNN) sheets vanishes by symmetry so that the structure is effectively 2D. Accordingly, we have fitted the data in Fig. 1 to a powder-averaged 2D Lorentzian centered about the $1/\sqrt{3}$ position ($1.27 \text{ \AA}^{-1}, 0, 0$). The results are shown as the solid

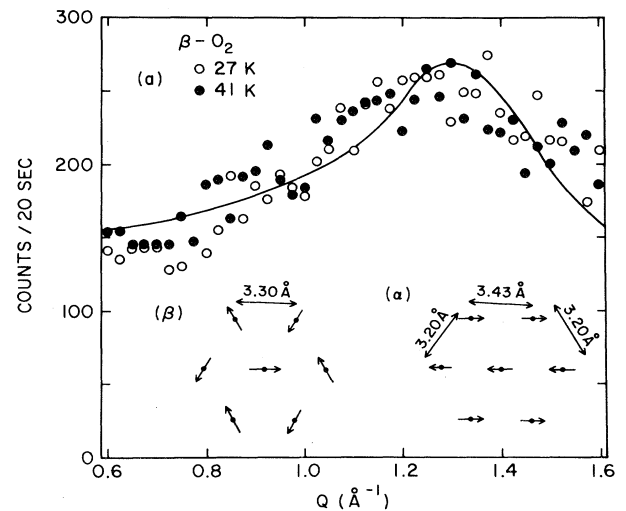


FIG. 1. Quasielastic scattering from $\beta \text{ O}_2$ in the region of the $(\sqrt{3} \times \sqrt{3})$ magnetic wave vector. The smooth curve is a fit to a powder-averaged 2D Lorentzian, discussed in text, with a background of 100 counts/20 sec. The insets show the 2D in-plane crystal and (proposed) magnetic structures of β - and α -phase oxygen.

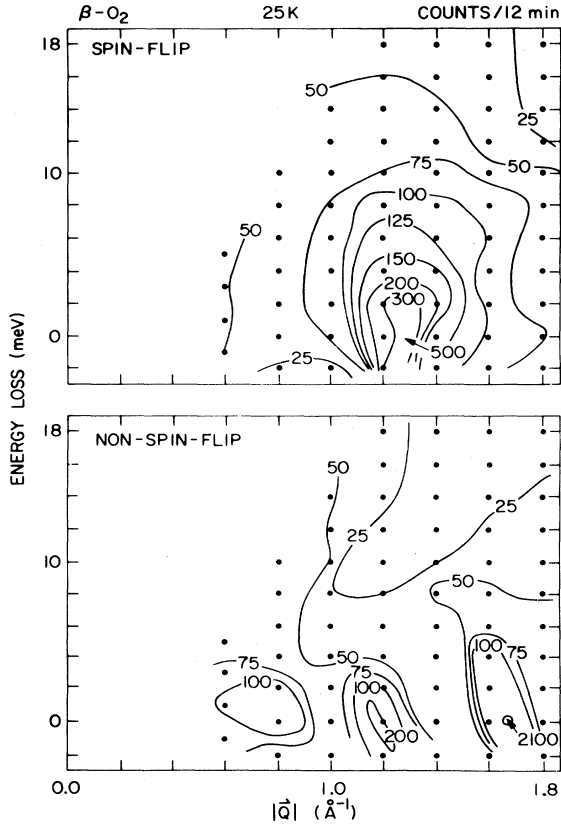


FIG. 2. Inelastic neutron spectra from powdered β O₂, corrected for a flipping ratio of 10. The spectrometer had collimation 40'-40'-open-40', with a constant final energy of 31.4 meV, and no filter. The elastic non-spin-flip intensity at 1.18 Å⁻¹ is second-order contamination; this also contributed to the spin-flip intensity.

line in Fig. 1. The correlation length so obtained is 9 ± 1 Å at both 41 and 27 K. We conclude, therefore, that β O₂ exhibits strong fluctuations into a 2D three-sublattice structure; this explains the susceptibility behavior. However, as we discuss below, any transition to long-range magnetic order in this phase is preempted by the bulk α - β transition.

The α phase of solid O₂ has been extensively studied¹; the structure is monoclinic, with two molecules in the conventional unit cell. Here we shall focus on the in-plane structure; as shown in the inset of Fig. 1, the in-plane structure is obtained by a simple distortion of the β -phase triangular array. This results in four NN molecules at 3.20 Å and two NNN at 3.43 Å. Further, from a comparison of x-ray and neutron^{3,4} results it is known that α O₂ is a two-sublattice antiferromagnet. The probable in-plane magnetic structure is also shown in Fig. 1. Infrared measurements⁵ indicate antiferromagnetic resonance modes at 0.79 and 3.4 meV. Little additional information is available on the magnetic excitations except for the fact that various optical studies¹ indicate characteristic energies between 10 and 20 meV.

Our elastic scattering studies of the α phase support previous results. At 23.5 K we observe a rather sluggish first-order transition from the β to the α phase. The (101) intensity jumps to $\sim 65\%$ of its saturation value at 23.5 K and then increases gradually with decreasing temperature, reach-

ing its limiting value around 10 K. In our later discussion, the associated second-order transition temperature for α O₂ will be important. Comparison of the temperature dependence of the sublattice magnetization in α O₂ with that of planar antiferromagnets of the K₂NiF₄ type⁶ suggests that if the α -phase structure were held rigid, the Néel temperature would be 31 ± 3 K. De Fotis¹ finds the same value using a different technique.

The spin dynamics of α O₂ are shown in Fig. 3; this is a contour map of the inelastically scattered polarized neutron intensity at 10 K. Aside from the Bragg peaks at zero energy transfer, the only strong feature is a pronounced peak in the spin-flip scattering at 10 ± 1 meV for $|Q|$ ranging between 1.1 and 1.4 Å⁻¹.

The spin Hamiltonian in the α phase may be written

$$H = -2 \sum_{i>j} J_{ij} \vec{S}_i \cdot \vec{S}_j - D \sum_i S_i^z{}^2 - D' \sum_i (S_i^y{}^2 - S_i^x{}^2) \quad (1)$$

where the X and Z axes are in the spin (\vec{b}^*) and molecular (\vec{c}^*) directions, respectively; here $D > D' > 0$. In our analysis we assume that only in-plane NN and NNN exchange interactions are important; this makes the model 2D. The Néel state for this Hamiltonian is unstable to the formation of a long-wavelength modulation along b^* if $J_{NN}/J_{NNN} < 2$, neglecting anisotropy.⁷ Using standard spin-wave theory,⁸ the antiferromagnetic resonance frequencies may be shown to be

$$[1 + i(0)][-16J_{NN}(D \pm D')]^{1/2} = (0.8, 3.4) \text{ meV} \quad (2)$$

Here $i(0)$ represents the zero-point spin-deviation correction. Calculations with a range of plausible exchange and

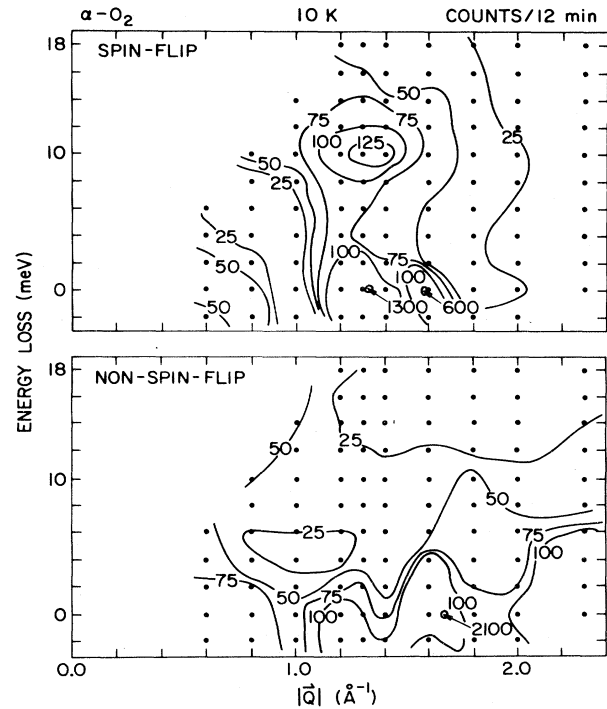


FIG. 3. Inelastic neutron spectra from powdered α O₂. Note magnetic Bragg peaks at 1.32 and 1.58 Å⁻¹ and a nuclear Bragg peak at 1.68 Å⁻¹.

anisotropy parameters show that the peak energy in the magnon density of states is strongly dominated by the $\bar{b}^*/2$ zone-boundary van Hove singularity. We therefore identify the 10-meV feature in Fig. 1 with $E(\bar{b}^*/2)$. This yields

$$[1 + i(0)](8J_{\text{NNN}} - 8J_{\text{NN}} + D) = 10 \pm 1 \text{ meV} \quad (3)$$

In Eqs. (2) and (3), terms of order D^2 have been omitted. In spin-wave theory, the low-temperature transverse susceptibility is given by

$$\chi = \frac{N}{2} \frac{g^2 \mu_B^2}{8(-J_{\text{NN}})} \left[1 - \frac{\Delta S}{S} - i(0) \right], \quad (4)$$

where ΔS represents the zero-point spin deviation; to the accuracy required here we may take $\Delta S = 0.197$ and $i(0) = 0.08$, the values for a quadratic-layer antiferromagnet with $S = 1$. De Fotis estimates $\chi = 2.4 \pm 0.03 \text{ cm}^3/\text{mole}$.

If we take the median values in Eqs. (2)–(4), the derived interaction parameters slightly violate the stability criterion. However, one can satisfy all of the requirements within the stated error bars, with

$$\begin{aligned} J_{\text{NN}} &= -2.2 \text{ meV}, \quad J_{\text{NNN}} = -1.1 \text{ meV}, \\ D + D' &= 0.28 \text{ meV}, \quad D - D' = 0.016 \text{ meV}, \end{aligned} \quad (5)$$

with 10% standard errors.

We now discuss the implications of this set of parameters. First, the ratio of $J_{\text{NNN}}^{\alpha}/J_{\text{NN}}^{\alpha}$ corresponds to r^{-10} power-law behavior, as has been observed in many magnetic insulators.⁹ The easy-plane anisotropy $D + D'$ is roughly half that of a free molecule while the in-plane anisotropy $D - D'$ is about a factor of 4 larger than the intraplanar dipole-dipole interaction. These differences presumably reflect intermolecular crystal-field effects.

The most important consequence of the interaction strengths is the predicted Néel temperature. As is well known, phase-transition temperatures are depressed in 2D because of fluctuation effects. Scaling the Stanley-Kaplan¹⁰ formula for a 2D Heisenberg AF by the ground-state energy to allow for intrasublattice interactions, we find

$$T_N^{\text{SK}} = \frac{9}{10} (-2J_{\text{NN}} + J_{\text{NNN}}) = 34 \text{ K}.$$

This predicted value may be compared with the empirical extrapolated value of $31 \pm 3 \text{ K}$. We regard this agreement as quite satisfactory. Bhandari and Falicov¹¹ have shown that exchange interactions of the order of Eq. (5) can pro-

vide a satisfactory description of the measured optical properties.

In β oxygen we have no direct measure of J_{NN}^{β} . However, if we simply interpolate from α O_2 we find $J_{\text{NN}}^{\beta} = 1.5 \pm 0.2 \text{ meV}$. For the three-sublattice 120° structure we estimate the temperature T_N^{β} at which the β O_2 structure would order utilizing the Stanley-Kaplan formula for 6 NN but with J_{NN}^{β} replaced by $J_{\text{NN}}^{\beta}/2$; this gives $T_N^{\text{SK}} = 26 \text{ K}$. The estimate may be compared with the actual α - β transition temperature of 23.5 K which represents an upper limit for T_N^{β} . Again the agreement is fair.

The mean-field magnetic ground-state energy of β O_2 is $\frac{3}{2} J_{\text{NN}}^{\beta} = -2.3 \text{ meV}$ per molecule compared with $2 J_{\text{NN}}^{\alpha} - J_{\text{NNN}}^{\alpha} = -3.3 \text{ meV}$ for α O_2 . The mechanism for the α - β transition is therefore that suggested by Stephens *et al.*² The system initially develops three-sublattice 120° short-range order. However, by breaking the triangular symmetry with its concomitant frustration the planes can develop a collinear two-sublattice structure with significantly lower magnetic energy. Because of the weak van der Waals binding the cost in elastic energy is slight.¹²

One potential difficulty with this interpretation is the fact that 2D films of O_2 on graphite magnetically order at a significantly lower temperature of 12 K.¹³ The low-temperature film ϵ phase has the in-plane structure of α O_2 ; however, the higher-temperature ζ and β phases do not correspond (Stephens *et al.*, Ref. 2). Thus the film ζ to ϵ transition does not have a simple connection with the bulk β to α transition, and correspondingly, there need be no simple relationship between the respective phase-transition temperatures.

In conclusion, we believe that a quasi-2D model is able to provide a satisfactory description of the magnetic properties of the α and β phases in solid O_2 as well as the transition between them. A final test of these ideas will require measurements of the magnon dispersion relations in a single crystal.

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