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Magnetic structure of β -oxygen

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Treating the spins classically, we show that for β -O₂ the two-dimensional three-sublattice structure is unstable with respect to interlayer exchange couplings. The energetically most favorable structure is found to be incommensurate. Quantum-mechanical spin-wave calculations agree with the conclusions from the classical magnetic-structure calculations.

I. INTRODUCTION

The combination of magnetic and molecular properties makes solid oxygen a unique system. Although it has been studied for a long time, much remains unexplained. One of the unsolved problems is the magnetic structure of the β phase. This phase consists of stacked triangular layers forming a structure with space group $R\bar{3}m$ (see Fig. 1).¹

Magnetic susceptibility measurements^{2,3} indicate that β -O₂ is a triangular antiferromagnet. The main feature of triangular antiferromagnets is an intrinsic frustration effect. If only intralayer nearest-neighbor exchange interactions are taken into account, we already have a complex system. If the spins are treated classically, it can be

proved that they adopt a three-sublattice structure, i.e., the nearest-neighbor spins make angles of 120°. ^{4,5} However, a quantum-mechanical treatment of $S = \frac{1}{2}$ spins on such lattice has shown that there are other structures, which are energetically more favorable.⁶ This may be true for β -O₂ ($S=1$) also. Actually, the situation is more complex because of the interlayer exchange interactions. In most papers it is assumed that the layers adopt the three-sublattice structure, and that there is no interaction between the layers.^{7,8} The latter assumption follows from the former in this sense, that if the spins are treated classically, then the field for a given spin due to the spins in other layers vanishes exactly. The first assumption of a perfect three-sublattice structure is, however, in contradiction with neutron diffraction, which shows only short-range but no long-range order.⁹

In a recent paper¹⁰ a magnetic-structure calculation was done for a system with a comparable lattice (i.e., C₆Eu). It was shown, using a model worked out by Nagamiya,¹¹ that the three-sublattice structure lost its long-range order due to the interlayer exchange coupling. In this paper we determine the magnetic structure of β -O₂, using the same model. We check whether β -O₂ shows the same distortion of the three-sublattice structure as C₆Eu, thus explaining the neutron-diffraction experiment. Moreover, we compare the results of this classical model with those from quantum-mechanical spin-wave calculations.

II. THEORY

As we have shown in a previous paper,¹² the spin-dependent part of the Hamiltonian of solid oxygen can be written as a sum of three terms:

$$H = H_{\text{ex}} + H_{\text{s.o.}} + H_{\text{dip}}. \quad (2.1)$$

The first term is the well-known Heisenberg exchange term, the second term is due to the intramolecular spin-spin and spin-orbit coupling, which couples the spin to the molecular axis, and the third term describes the magnetic dipole-dipole coupling between the spin momenta. Wormer and van der Avoird¹³ have shown that the exchange-coupling constant J in

$$H_{\text{ex}} = -2 \sum_{\langle n, m \rangle} J_{n-m} \mathbf{S}_n \cdot \mathbf{S}_m \quad (2.2)$$

FIG. 1. Structure of β -O₂.

strongly depends on the positions and the orientations of the molecules. In this equation the sum runs over all spin pairs. The composite index $\mathbf{n} = \{n_1, n_2, n_3\}$ denotes the spin at $\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$, $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ being primitive translations (see Fig. 1). Also, the other two terms contain position- and orientation-dependent factors.¹² However, in a mean-field (MF) sense we can take statistical averages over the lattice vibrations and make the Hamiltonian of Eq. (2.1) only spin dependent. The Heisenberg term then remains formally the same, with the coupling parameter J replaced by its average value. The second term $H_{s.o.}$ for the β phase simplifies further if we assume that the librations of the molecules are small so that effectively the molecular axes are fixed along the crystallographic c axis, which we take as the z axis (see Fig. 1). This leads to the form in which this term is normally used:¹⁴

$$H_{s.o.} = A \sum_{\mathbf{n}} S_{nz}^2 \quad (A > 0). \quad (2.3)$$

As the dipole-dipole term is much smaller than the other two, we neglect it altogether (usually, instead of the dipole-dipole term, one takes an in-plane anisotropy term, which is zero in β -O₂).¹⁵

In order to determine the magnetic structure, we follow a standard method that treats the spins classically.¹¹ We start by taking only the Heisenberg term into account. Defining

$$J(\mathbf{q}) = \sum_{\mathbf{n}} J_{\mathbf{n}} e^{i\mathbf{q} \cdot \mathbf{R}_{\mathbf{n}}} \quad (2.4a)$$

and

$$\mathbf{S}(\mathbf{q}) = N^{-1/2} \sum_{\mathbf{n}} \mathbf{S}_{\mathbf{n}} e^{i\mathbf{q} \cdot \mathbf{R}_{\mathbf{n}}}, \quad (2.4b)$$

the energy pertaining to the Heisenberg term can be written as

$$E_{ex} = - \sum_{\mathbf{q}} J(\mathbf{q}) \mathbf{S}(\mathbf{q}) \cdot \mathbf{S}(-\mathbf{q}). \quad (2.5)$$

The magnetic structure is obtained by minimizing this energy with the restriction that $\mathbf{S}_{\mathbf{n}}^2 = S^2 = 1$ for all $\mathbf{n}$. The minimum energy is given by

$$-NS^2 J(\mathbf{Q}). \quad (2.6)$$

Here $\mathbf{Q}$ is a vector that maximizes $J(\mathbf{q})$. The spin orientations are given by

$$\mathbf{S}_{\mathbf{n}} = N^{-1/2} [e^{-i\mathbf{Q} \cdot \mathbf{R}_{\mathbf{n}}} \mathbf{S}(\mathbf{Q}) + e^{i\mathbf{Q} \cdot \mathbf{R}_{\mathbf{n}}} \mathbf{S}(-\mathbf{Q})], \quad (2.7)$$

where $\mathbf{S}(\mathbf{Q}) [= \mathbf{S}(-\mathbf{Q})^*]$ is arbitrary with the restriction on $\mathbf{S}_{\mathbf{n}}^2$ mentioned above. We note that in the minimum-

energy configuration all spins lie in a plane. As the Heisenberg Hamiltonian is isotropic in spin space, it is clear that we can choose the plane we want the spins to lie in. If we interpret the operator S_{nz} classically as the z component of the spin $\mathbf{S}_{\mathbf{n}}$, we see that, as $A \sum_{\mathbf{n}} S_{nz}^2 \geq 0$, we can minimize this term if we put all spins parallel to the crystallographic a - b plane. The orientations of the spins then become

$$\begin{aligned} S_{nx} &= S \sin(\mathbf{Q} \cdot \mathbf{R}_{\mathbf{n}}), \\ S_{ny} &= S \cos(\mathbf{Q} \cdot \mathbf{R}_{\mathbf{n}}), \\ S_{nz} &= 0. \end{aligned} \quad (2.8)$$

The foregoing discussion shows that this structure minimizes the energy of the total Hamiltonian, and thus that Eqs. (2.8) denote the orientations that the spins will adopt in the ground state of the crystal.

In order to get further support for the results of these classical calculations, via a quantum-mechanical treatment of the spins, we have computed magnon frequencies using the MF formalism followed by the random-phase approximation (RPA), starting from the three-sublattice structure. If only the Heisenberg term is taken into account, MF yields the same magnetic ground state as the classical model.¹¹ However, we can impose the translational symmetry of the three-sublattice structure on the MF solution. MF then yields this structure and RPA yields the corresponding magnon frequencies. This method is well known; therefore, we just refer to Refs. 12, 16, and 17 for details. As we are interested in the stability of the three-sublattice structure, we have to scan reciprocal space to see if there are magnon modes with imaginary frequency.¹⁸ In that case it can be proved that the three-sublattice structure is not stable.¹⁹⁻²² From the $\mathbf{q}$ vectors of such modes and the solutions of the corresponding RPA equations one can deduce in what way the three-sublattice structure will distort.

III. RESULTS

As the exchange-coupling constants decrease very fast with increasing distance between the molecules, the summation in the definition of $J(\mathbf{q})$, Eq. (2.4a), can be truncated after a few terms. The dominant terms pertain to the nearest-neighbor pairs, with $J_{NN} < 0$. Although β -O₂ is often considered a two-dimensional system,^{7,8,15} we will show that this is not correct. For this purpose we have to take into account the coupling J' between neighboring molecules in different layers. Furthermore, also the intralayer next-nearest-neighbor constant J_{NNN} turns out to be important. The three interactions are indicated in Fig. 1. We can express $J(\mathbf{q})$ in terms of J_{NN} , J_{NNN} , and J' :

$$\begin{aligned} J(\mathbf{q}) &= 2J_{NN} \left[\cos(aq_x) + 2 \cos\left(\frac{aq_x}{2}\right) \cos\left(\frac{aq_y \sqrt{3}}{2}\right) \right] + 2J_{NNN} \left[\cos(aq_y \sqrt{3}) + 2 \cos\left(\frac{3aq_x}{2}\right) \cos\left(\frac{aq_y \sqrt{3}}{2}\right) \right] \\ &\quad + 2J' \left[\cos\left[-\frac{aq_y \sqrt{3}}{3} + \frac{cq_z}{3}\right] + 2 \cos\left(\frac{aq_x}{2}\right) \cos\left[\frac{aq_y \sqrt{3}}{6} + \frac{cq_z}{3}\right] \right]. \end{aligned} \quad (3.1)$$

180° on approaching the boundary with phase II.

The phase diagram for $J' > 0$ is identical to Fig. 2 if we put $-J'/J_{NN}$ on the horizontal axis. We can get the magnetic structures of the phases by reversing the small arrows and those of intermediate length in Fig. 3.

The magnon frequencies for the three-sublattice structure have been calculated with two (de)excitation operators per molecule, one for each excited state. Because of the second term, $H_{s.o.}$ of Eq. (2.1), the two excited states interact. This implies that there are six magnon modes for every $\mathbf{q}$ vector (there are three spins per unit cell of the three-sublattice structure).

We have found that there is always a mode with imaginary frequency with wave vector $\mathbf{Q}$, the vector that maximizes $J(\mathbf{q})$. This agrees with the magnetic-structure calculations, which predict a structure with wave vector $\mathbf{Q}$ that is more stable than the three-sublattice structure. However, the reverse statement, i.e., that the $\mathbf{q}$ vector of a mode with imaginary frequency maximizes $J(\mathbf{q})$, is not true. As there are no discontinuities in the dispersion curves, there is always a range in reciprocal space of modes with imaginary frequencies. So the vector $\mathbf{Q}$ may only be determined approximately from the spin-wave calculations. But there are also modes with imaginary frequencies with $\mathbf{q}$ vectors that yield small values for $J(\mathbf{q})$. This becomes clear if we realize that the Brillouin zone of the three-sublattice structure is smaller than the Brillouin zone corresponding to the unit cell of Fig. 1. Suppose that $\mathbf{Q}$ lies outside the Brillouin zone of the three-sublattice structure. Then there is a magnon with imaginary frequency with vector $\mathbf{Q}-\mathbf{K}$ in this Brillouin zone, where $\mathbf{K}$ is a primitive translation of the reciprocal lattice of the three-sublattice structure. However, $J(\mathbf{Q}-\mathbf{K})$ is, in general, much smaller than $J(\mathbf{Q})$.

IV. DISCUSSION AND CONCLUSION

The results of the magnetic-structure calculations show that the three-sublattice structure is not the structure with the lowest energy if $J' \neq 0$ and $J_{NNN} \neq 0$. The instability is primarily caused by the interlayer exchange coupling (if $J' = 0$ and $J_{NNN}/J_{NN} < \frac{1}{8}$, then the three-sublattice structure is still stable). The intralayer next-nearest-neighbor exchange coupling also has an important influence, however, as Fig. 2 clearly shows.

It is well known that the nearest-neighbor exchange coupling dominates the system. This means that β -O₂ adopts the structure of phase IV, V, or, if $J' > 0$, the corresponding phases with reversed spins in alternating

layers, which we denote by IV' and V'. Thus, according to the classical model and MF, we can conclude that β -O₂ has an incommensurate magnetic structure. No other magnetic-structure calculation^{4,5,24} has yet led to this conclusion. In a recent paper Meier²⁴ pointed out that a nonzero interlayer exchange coupling might lead to a distortion of the three-sublattice structure. However, his model was too crude to draw any definite conclusions concerning the magnetic structure. Moreover, he did not realize the importance of the intralayer next-nearest-neighbor exchange coupling. Loktev⁴ and Kuchta⁵ included only nearest-neighbor interactions in their calculations and thus concluded that the three-sublattice structure was most stable. Kuchta's generalized MF theory excluded incommensurate structures. So his results would probably not change if the interlayer exchange would be included.

Neutron-diffraction experiments show only diffuse magnetic scattering.⁹ No long-range order is observed. However, the observed and calculated magnetic peaks are weak. Therefore, we think that an incommensurate magnetic structure is compatible with the neutron-diffraction experiments. It would be interesting to take a closer look at the magnetic scattering to see if there are indications of an incommensurate structure.

To determine the actual magnetic structure we have to know the values of the exchange-coupling constants. Using the Wormer-van der Avoird potential¹³ and putting the molecules parallel to the crystallographic c axis, we have found $J_{NN} = -9.6$ K, $J_{NNN} = -2.3 \times 10^{-3}$ K, and $J' = 0.49$ K. This means that the magnetic structure of β -O₂ is given by phase V' with $\alpha = 121.7^\circ$. Neutron diffraction has shown, however, that J' is negative and small.⁹ So β -O₂ most probably adopts phase V. The angle α can be calculated from the relation

$$12 \frac{J_{NNN}}{J_{NN}} \cos^2 \alpha + 2 \cos \alpha + 1 - 3 \frac{J_{NNN}}{J_{NN}} + \frac{J'}{J_{NN}} = 0. \quad (4.1)$$

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¹I. N. Krupskii, A. I. Prokhvatilov, Yu. A. Freiman, and A. I. Erenburg, *Fiz. Nizk. Temp.* **5**, 271 (1979) [*Sov. J. Low Temp. Phys.* **5**, 130 (1979)].

²G. C. DeFotis, *Phys. Rev. B* **23**, 4714 (1981), and references therein.

³R. J. Meier, C. J. Schinkel, and A. de Visser, *J. Phys. C* **15**, 1015 (1982).

⁴V. M. Loktev, *Fiz. Nizk. Temp.* **5**, 295 (1979) [*Sov. J. Low Temp. Phys.* **5**, 142 (1979)].

⁵B. Kuchta, *Phys. Lett.* **103A**, 202 (1984).

⁶P. Fazekas and P. W. Anderson, *Philos. Mag.* **30**, 423 (1974).

⁷V. A. Slyusarev, Yu. A. Freiman, and R. P. Yankelevich, *Fiz. Nizk. Temp.* **6**, 219 (1980) [*Sov. J. Low Temp. Phys.* **6**, 105 (1980)].

⁸R. D. Ethers, A. A. Helmy, and K. Kobashi, *Phys. Rev. B* **28**, 2166 (1983).

⁹R. J. Meier and R. B. Helmholtz, *Phys. Rev. B* **29**, 1387 (1984).

¹⁰T. Sakakibara, *J. Phys. Soc. Jpn.* **53**, 3607 (1984).

¹¹T. Nagamiya, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1967), Vol. 20, p. 305.

- ¹²A. P. J. Jansen and A. van der Avoird, *Phys. Rev. B* **31**, 7500 (1985).
- ¹³P. E. S. Wormer and A. van der Avoird, *J. Chem. Phys.* **81**, 1929 (1984).
- ¹⁴E. J. Wachtel and R. G. Wheeler, *Phys. Rev. Lett.* **24**, 233 (1970).
- ¹⁵V. A. Slyusarev, Yu. A. Freiman, and R. P. Yankelevich, *Fiz. Nizk. Temp.* **7**, 536 (1981) [*Sov. J. Low Temp. Phys.* **7**, 265 (1981)].
- ¹⁶J. C. Raich and R. D. Etters, *Phys. Rev.* **168**, 425 (1968).
- ¹⁷A. P. J. Jansen, W. J. Briels, and A. van der Avoird, *J. Chem. Phys.* **81**, 3648 (1984).
- ¹⁸A. Lagendijk (private communication).
- ¹⁹D. R. Fredkin and N. R. Werthamer, *Phys. Rev.* **138**, A1527 (1965).
- ²⁰D. J. Thouless, *Nucl. Phys.* **21**, 225 (1960).
- ²¹J. Čížek and J. Paldus, *Phys. Rev. A* **3**, 525 (1971).
- ²²A. van der Avoird, W. J. Briels, and A. P. J. Jansen, *J. Chem. Phys.* **81**, 3658 (1984).
- ²³R. F. Churchhouse, *Numerical Methods*, Vol. III of *Handbook of Applicable Mathematics*, edited by W. Ledermann (Wiley, Chichester, 1981).
- ²⁴R. J. Meier, *Phys. Lett.* **107A**, 275 (1985).