

Magnetic properties of solid oxygen

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In this work we show that quasi-two-dimensional nature of the magnetic subsystem of solid oxygen can explain the discontinuity of the magnetic susceptibility as a result of the α - β transition and the anomalous temperature dependence of the β phase.

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Solid oxygen, which occurs in three crystallographic modifications, combines the properties of a molecular crystal and a magnetic substance. The $\gamma \rightarrow \beta$ transition from the high-temperature cubic phase to the intermediate rhombohedral phase ($T_{\gamma\beta} = 43.8$ K) is due to the appearance of long-range orientational order in the system of rotators. Despite the absence of long-range magnetic order in β -O₂, the temperature dependence of the magnetic susceptibility of β -O₂ is more typical of an antiferromagnet than of a paramagnetic crystal.¹¹ The transition to the monoclinic α -phase ($T_{\beta\alpha} = 23.8$ K), which takes place without a noticeable change in volume and latent heat of transition, is accompanied by a sharp decrease in the magnetic susceptibility (by a factor of 1.5). According to the neutron-diffraction data,¹²¹ α -O₂ is a collinear antiferromagnetic substance with two magnetically nonequivalent molecules in the unit cell.

In this paper we show that allowance for the quasi-two-dimensional nature of the

magnetic subsystem of solid oxygen makes it possible to explain these anomalies of the magnetic susceptibility and to remove the difficulties connected with the attempt to correlate the data for the AFMR frequencies, the Néel temperature, the magnetic susceptibility, and the magnetic specific heat.^{1,3,4)}

The magnetic subsystem of solid O₂ is described by the Hamiltonian^{15,6)}

$$\mathcal{H} = \sum_f \left[A(S_f^z)^2 + B(S_f^y)^2 \right] + \frac{1}{2} \sum_{f, f'} J_{ff'} S_f S_{f'}, \quad (1)$$

where $J_{ff'}$ is the exchange integral between the molecules at the points f and f' , S_f is the spin operator, $A > 0$ is the anisotropy constant due to the intramolecular spin-spin dipole interaction, $B > 0$ is the anisotropy constant connected with a small deviation of the structure of α -O₂ from the rhombohedral structure, and the z axis coincides with the axis of the molecule. At low temperatures the magnetic subsystem of α -O₂ has a collinear structure (or close to it) and the magnon spectrum is described by the equation

$$\Omega^2(\mathbf{k}) = \frac{\eta [J(\mathbf{k}) + J(0)] - (2\xi A/\eta) \gamma(\mathbf{k})}{2 - \gamma^2(\mathbf{k})} \left\{ \eta \left[J(\mathbf{k}) - J(0) \right] + \frac{2\xi B}{\eta} \gamma(\mathbf{k}) \right\}, \quad (2)$$

$$J(\mathbf{k}) = \sum_{\vec{\delta}} J(\vec{\delta}) e^{i\mathbf{k}\vec{\delta}}; \quad J(0) = 4(J_1 + J_2); \quad \gamma(\mathbf{k}) = \frac{J(\mathbf{k})}{J(0)}.$$

Here J_1 and J_2 are respectively, the exchange interaction constants of the two closest molecules from the same and from the adjoining planes, $\eta = \langle S^x \rangle$, and $\xi = \langle (S^x)^2 - (S^y)^2 \rangle$. In deriving Eq. (2) we used the condition $J(0) \gg A, B$. The AFMR frequencies Ω_1 and Ω_2 and the magnon frequency at the boundary of the Brillouin zone Ω_3 are

$$\Omega_1 = \sqrt{4B\xi J(0)}, \quad \Omega_2 = \sqrt{4A\xi J(0)}, \quad \Omega_3 = 2\sqrt{\alpha\eta J(0)}, \quad (3)$$

where $\alpha = J_2/J_1$.

At zero temperature the anisotropy is large only at the edges and in the center of the Brillouin zone, which greatly simplifies the calculation of the ξ and η parameters in terms of the random-phase approximation. As a result, in the two-dimensional case, we obtain $\eta = 0.78$ and $\xi = 0.29$ and in the three-dimensional case $\eta = 0.82$ and $\xi = 0.35$. Using the experimental data for the corresponding frequencies ($\Omega_1 = 6.4 \text{ cm}^{-1}$, $\Omega_2 = 27.5 \text{ cm}^{-1}$, $\Omega_3 = 37.5 \text{ cm}^{-1}$ ^{15,7)}) and assuming that the constant A coincides with its value for a free molecule ($A = 5.14 \text{ K}$), we obtain the values for all the parameters characterizing the behavior of the α -phase at $T = 0$: $B = 0.194 \text{ cm}^{-1}$, $J(0) = 180 \text{ cm}^{-1}$, and $\alpha \approx 10^{-2}$. Since the obtained value $\alpha \ll 1$ is insensitive to the alternative values of η and ξ , we can use these parameters in numerical calculations of the two-dimensional case.

Consistency of the obtained parameters can be checked by using the data on magnetic susceptibility. The transverse components of the magnetic-susceptibility tensor are

$$\chi_{yy} = \frac{1}{2J(0) + A\xi/\eta} ; \quad \chi_{zz} = \frac{1}{2J(0) + B\xi/\eta} . \quad (4)$$

In the same approximation $\chi_{xx} = 0$. Taking into account that $J(0) \gg A, B$, for the susceptibility of the polycrystal at zero temperature we obtain

$$\chi(0) = \frac{1}{3} (\chi_{yy} + \chi_{zz}) = \frac{1}{3J(0)} . \quad (5)$$

Using the experimental data for the magnetic susceptibility,^(1,8) we obtain $J(0) = 200 \text{ cm}^{-1}$. Taking into account the interpolation nature of the approximation, we can see that the values of $J(0)$ obtained from the data for the AFMR frequencies are in good agreement with those obtained from the data on susceptibility.

An independent estimate of α can be obtained from an analysis of the data on low-temperature magnon specific heat. At $T \lesssim J_2$ the magnon heat capacity has a "three-dimensional" nature

$$C_V = \frac{2}{(2\pi)^{3/2}} \left(\frac{\Omega_1}{\eta J(0)} \right)^3 \left(\frac{\Omega_1}{T} \right)^{1/2} \exp \left(- \frac{\Omega_1}{T} \right) . \quad (6)$$

At $\alpha \ll 1$, the specific heat approaches "two-dimensional" asymptotic form

$$C_V = \frac{1}{\pi} \left(\frac{\Omega_1}{\eta J(0)} \right)^2 \left(\frac{\Omega_1}{T} \right) \exp \left(- \frac{\Omega_1}{T} \right) . \quad (7)$$

A comparison of the theoretical and experimental values of the specific heat also agrees with the value $\alpha \sim 10^{-2}$.

A strong anisotropy of thermal expansion is observed in the narrow temperature range near the temperature of the α - β transition; as a result, the monoclinicity of the α -O₂ lattice decreases and the molecules attempt to occupy positions corresponding to the nondeformed hexagonal plane.⁽⁴⁾ The constant B tends to zero, which is accompanied by a conversion of the collinear antiferromagnetic structure to a triple-sublattice structure in which in the limit $B = 0$ the angles between the spins of the nearest neighbors are equal to $2\pi/3$.⁽¹⁾

The magnetic susceptibility in the paramagnetic β phase is

$$\chi_P = \frac{1}{3} (\chi_{xx} + \chi_{yy} + \chi_{zz}) = \frac{20}{27J(0)} . \quad (8)$$

Thus, the ratio of the magnetic susceptibility of the β phase near the α - β transition

point to that at zero temperature is $\chi_p(T_{\alpha\beta})/\chi(0) = 20/9$. The experimentally observed value of this ratio^(1,8) agrees with this value. The main temperature dependence of the susceptibility of the α phase fits that region near the α - β transition in which, according to thermal-expansion data,⁽⁴⁾ a sharp decrease of the monoclinic distortion of the lattice occurs. Since this temperature region is very narrow, the susceptibility changes abruptly as a result of the α - β transition. The hypothesis of quasi-two-dimensional nature explains the anomalous behavior of the magnetic susceptibility. A breakdown of long-range order in quasi-two-dimensional systems is attributable to long-range correlations, whereas the susceptibility (and the average energy) is connected with the spin correlations at short distances. Since $J(0) \gg T$, a high degree of short-range order, which has a triple-sublattice structure, is preserved in the entire region of the β phase. The aforementioned factors indicate that the temperature dependence of the susceptibility of the α phase is the same as that of the β phase of oxygen. The observed temperature dependence of the β phase, according to our estimates, can be explained by the anomalously high thermal expansion coefficient in the plane of the closely-packed layers ($\sim 10^{-3} \text{ K}^{-1}$) and by the variation of the exchange integrals associated with it.

The low temperature of the antiferromagnetic transition compared with the value of T_N^0 , which is determined by the self-consistent field approximation and which is equal to $J(0)$ in order of magnitude, is also attributable to the quasi-two-dimensional magnetic subsystem of solid oxygen. In fact, as the group-renormalization analysis shows,⁽¹⁰⁾ the transition temperature of the quasi-two-dimensional system is determined by the relation

$$T_N \sim J(0)/\ln |a| . \quad (9)$$

Thus, the data on the behavior of solid oxygen can be explained consistently if it is assumed that its magnetic subsystem is a quasi-two-dimensional Heisenberg magnet, whose magnetic structure is characterized as follows. In the α phase, it is a quasi-two-dimensional, collinear, antiferromagnetic structure; in the narrow temperature region near the α - β transition, it is a quasi-two-dimensional, triple-sublattice structure, which remained as a short-range order in the entire region of the paramagnetic β phase.

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¹The possibility for the existence of this structure in solid oxygen was indicated for the first time in Ref. 9.

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