

Elementary-excitation spectrum and phase transitions of solid oxygen

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(Submitted November 30, 1976)

Pis'ma Zh. Eksp. Teor. Fiz. **25**, No. 1, 37-40 (5 January 1977)

The spectra of the magnon and libration excitations of solid oxygen are calculated. It is shown that α -O₂ is a quasi-two-dimensional antiferromagnet.

PACS numbers: 75.30.Ds, 75.30.Et, 75.40.-s, 75.50.Et

The aggregate of its properties make solid oxygen one of the most peculiar molecular crystals. This is due to a considerable degree to the fact that the O₂ molecule in the electronic ground state has a spin $S=1$. As a result, solid oxygen combines the properties of a molecular crystal and of a magnet.

At equilibrium vapor pressure, oxygen exists in three crystalline modifications. The $\gamma \rightarrow \beta$ transition from the high-temperature cubic to the intermediate rhombohedral phase ($T_{\gamma\beta}=43.8$ K) is due to the appearance of long-range orientational order in the rotator system. The low-temperature transition to the monoclinic α phase ($T_{\beta\alpha}=23.8$ K), as follows from neutron-diffraction investigations,^[1] is connected with antiferromagnetic ordering. Despite the absence of long-range magnetic order, in β -O₂ the temperature dependence of

the magnetic susceptibility of β -O₂ is more readily typical of antiferromagnets than of paramagnetic crystals.^[2] Investigations of the spectra of α -O₂ in the far-infrared region^[3,4] have revealed two absorption peaks at 27.5 and 6.4 cm⁻¹; these peaks are sensitive to the magnetic field. Using the indicated AFMR frequencies and the estimated energy 37.5 cm⁻¹ of the spin excitations at the boundary of the Brillouin zone, the magnon spectrum was calculated in^[4] within the framework of a model with an isotropic exchange interaction.

Our analysis of the heat capacity of α -O₂ shows that at $T < 10$ °K, when the contribution of the molecule librations can be neglected, the sum of the lattice component of the heat capacity and the magnon component calculated from the spectrum^[4] exceeds the experimental values. We propose that the main shortcoming of^[4] is the assumption that the exchange interaction is isotropic. Indeed, both α -O₂ and β -O₂ have a layered structure with a collinear arrangement of the molecules. Since the molecules in the crystal are oriented perpendicular to the plane of the layers, and the π orbitals that cause the exchange interaction are perpendicular to the molecule axes,^[5] one should expect the interaction in the layer to predominate.

Consider the spectrum of the spin waves of α -O₂ with allowance for the anisotropy of the exchange interaction. The Hamiltonian of the magnetic subsystem is given by^[6]

$$\mathcal{H} = \sum_{f, \delta} [A(S_f^x)^2 + B(S_f^y)^2 + J_\delta S_f S_{f+\delta}],$$

where S_f is the spin operator, and A and B are the constants of the single-molecule anisotropy. Neglecting the exchange within the sublattices, the Hamiltonian contains two exchange constants, namely $J_0 = J_{11}$ for the four nearest neighbors and $J_2 = J_1$ for the neighbors from the two nearest layers. Analysis shows that introduction of two types of exchange interaction into the Hamiltonian should lead to the appearance (in place of a single end-point frequency for all directions of the wave vector k) of a band whose width is determined by the ratio of J_{11} and J_1 . Assuming that the value 37.5 cm⁻¹ used in^[4] really pertains to its lower edge, we arrived at the conclusion that the position of the upper edge is at the frequency 75 cm⁻¹ observed in the optical spectra of α -O₂.^[6,7] By specifying four characteristic frequencies we can obtain all the constants that enter in \mathcal{H} ($A = 5.71$ cm⁻¹, $B = 0.99$ cm⁻¹, $J_{11} = 17.15$ cm⁻¹, $J_1 = 0.94$ cm⁻¹) and reconstruct the magnon spectrum of α -O₂. As seen from Fig. 1, allowance for

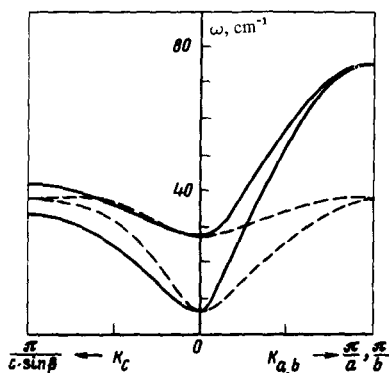


FIG. 1. Dependence of the energy of the spin waves of α -O₂ on the wave vector k ($k_{a,b}$ are the projections of k on the principal directions in the plane of the close-packed layers, k_c is the projection perpendicular to the layers). Solid-curves—our present results, dashed—results of^[4].

the anisotropy of the exchange interaction greatly influences the form of the magnon spectrum, and, in particular, leads to the presence of a gap between the two branches of the spectrum at the boundary of the Brillouin zone. A gap is missing only for the magnons with vectors k lying in the planes of the close-packed layers. For magnons propagating in a direction normal to the layers, the gap reaches 8.5 cm^{-1} . The doublet character of the exciton-magnon absorption lines, observed in^[6], is apparently due to the indicated character of the magnon spectrum of $\alpha\text{-O}_2$.

The singularities of the exchange interaction in solid O_2 explain many anomalies of its properties. The relatively low temperature of the $\alpha \rightarrow \beta$ transition, in comparison with the Néel temperature calculated in the self-consistent field approximation,^[8] is due to the appreciable role played by the fluctuations in quasi-two-dimensional systems. The strong exchange interaction J_{\parallel} is the reason for the appreciable value of the correlation radius of $\beta\text{-O}_2$ in the plane of the close-packed layers. This obviously explains the antiferromagnetic character of the magnetic susceptibility^[2] and the recently observed^[9] anomaly in the temperature dependence of the sound velocities.

At $T > 10^\circ\text{K}$, an appreciable contribution to the thermodynamic properties of solid O_2 is made also by libration oscillations. The noncentral part of the intermolecular interaction, which forms the orientation structure and the spectrum of the librational vibrations, is determined by the electrostatic quadrupole-quadrupole interaction of the molecules and the anisotropic part of the dispersion and valent intermolecular forces. The smallness of the quadrupole moment of the O_2 molecules makes a collinear orientational structure, which is usually not realized in the simplest molecular crystals, more convenient in the α and β phases. The dispersion curves calculated by us for the two orientationally-ordered O_2 phases are shown in Fig. 2 for symmetrical directions of the wave vectors. The parameter characterizing the intermolecular valent interaction was chosen to satisfy the condition that the libration frequency $\omega(k=0)$ of $\beta\text{-O}_2$ agree with the value observed in the Raman-scattering spectra.^[10] It is seen from Fig. 2 that the libronic spectrum is only insignificantly altered in the $\beta \rightarrow \alpha$ transition. However, lowering the crystal symmetry lifts the twofold degeneracy of the frequency $\omega(k=0)$. Calculation yields for the splitting a value $\Delta\omega = 4.6 \text{ cm}^{-1}$. The data on the spectra of the spin and libronic excitations have made it possible to identify the upper frequency of the Raman-scattering spectra of $\alpha\text{-O}_2$ ^[10] as a combined libron-magnon mode.

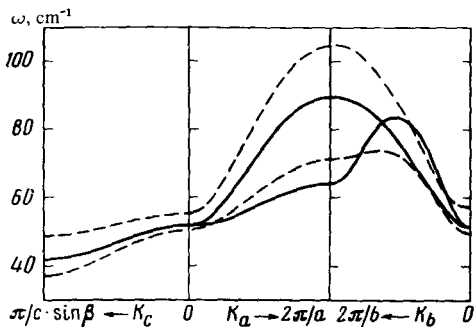


FIG. 2. Dispersion curves of libration excitations of orientationally-ordered phases of solid O_2 . Solid curves— $\beta\text{-O}_2$, dashed— $\alpha\text{-O}_2$.

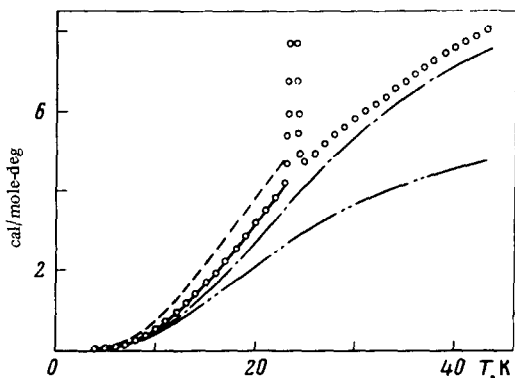


FIG. 3. Heat capacity of the α and β phases of O_2 at constant volume. Circles—experimental data, lower curve—phonon heat capacity, dash-dot—contribution of phonons and librations, solid curve—total heat capacity of the phonon, libron, and magnon subsystems, dashed—total heat capacity of α - O_2 with allowance for the spectrum of^[4].

The total heat capacity at constant volume $C_V = C_{ph} + C_m + C_{lib}$ calculated for α - O_2 is shown in Fig. 3 and is compared with the experimental C_V obtained from data on C_p ^[11] with allowance for the correction $C_p - C_v$. The contribution of the phonon subsystem C_{ph} was calculated in the Debye approximation with $\Theta_D = 104$ °K,^[2,11] while the contributions of the magnon and libron subsystems C_m and C_{lib} were calculated using the spectra obtained in the present study. It is seen that in the entire region of the existence of the α phase the calculated values are in good agreement with the experimental data. The difference between the experimental and calculated curves in the β phase is due to the decrease of the correlation contribution of the magnon subsystem with increasing temperature and the increasing contribution of the anharmonicity of the libration oscillations.

The quasi-two-dimensional character of the short-range magnetic order regions should lead to an excess interlayer "friability" of the β - O_2 structure, as is indicated by the negative coefficient of thermal expansion in a direction perpendicular to the plane of the layers.^[12] The anisotropy of the thermal expansion leads to an increase in the angle of the rhombohedron of the unit cell of β - O_2 . The libron spectrum then becomes unstable, and this determined ultimately the transition of the crystal into an orientationally-disordered state.

The authors are grateful to V. V. Eremenko and V. A. Slyusarev for a useful discussion and valuable advice, and to V. F. Manzhelii, A. F. Prihod'ko, and V. M. Loktev for a discussion of the results.

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