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Absorption bands in the region $15500 - 30500 \text{ cm}^{-1}$ are observed in condensed phases of oxygen and are identified with optical transitions causing simultaneous excitation of two molecules by a single photon. The frequencies of the bands of such "double" transitions are approximately linear combinations of the frequencies of "single" transitions in the free molecule [1]. One of the most interesting features of the "double" transitions in the low temperature antiferromagnetic α -phase of oxygen ($T \leq 23.8^\circ\text{K}$), where the transitions are induced by exchange interaction [2,3], is the appreciable shift (up to 180 cm^{-1}) of the position of the absorption band from the frequencies corresponding to the gaseous oxygen. Such a shift (in the short-wave direction) is all the more surprising since an electron-vibrational analysis has shown that the molecular constants for crystalline oxygen (α -phase) and for the free molecule are practically identical [5].

To obtain experimental data which make it possible to interpret uniquely the difference between the calculated and observed frequencies in the α -oxygen spectrum, we investigated the dependence of the position of the absorption band on the temperature and on the concentration of the nonmagnetic impurity (nitrogen).

The investigation was made with a DFS-13 diffraction spectrograph having a linear dispersion 4 \AA/mm and a spectral slit width 0.4 \AA . The temperature was measured accurate to $\pm 0.5^\circ\text{K}$.

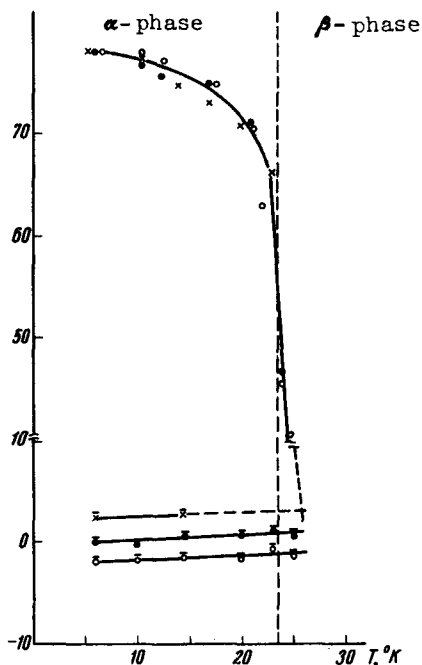


Fig. 1. Temperature dependence of the frequency shift of the bands of the transition $2^3\Sigma_g^- + 2^1\Sigma_g^+$: ∇ - ν_{00} ; \bullet, \circ - ν_{01}, ν'_{01} ; \square, \square' - ν_{02}, ν'_{02} ; \times, \times' - ν_{03}, ν'_{03} (the bar over the symbol and the prime of ν pertain to the mixture of 85% $\text{O}_2 + 15\% \text{N}_2$).

We investigated the behavior of four bands corresponding to the transition $2^3\Sigma_g^- \rightarrow 2^1\Sigma_g^+$ (purely electronic - $\nu_{00} = 26405 \text{ cm}^{-1}$, and electron vibrational $\nu_{01} = 27721 \text{ cm}^{-1}$, $\nu_{02} = 29095 \text{ cm}^{-1}$, and $\nu_{03} = 30437 \text{ cm}^{-1}$). Figure 1 shows the temperature dependence of the change in the frequencies. A characteristic feature is a shift of the bands into the long-wave region of the spectrum, which is slow at $T < 10^\circ\text{K}$ and accelerates with increasing temperature. The shift is particularly large in the region of the α - β transition, where a change takes place not only in the crystal structure but also in the magnetic structure of the oxygen.

Introduction of nonmagnetic nitrogen (the spin of the ground state of the N_2 molecule is zero) leads to a sharp decrease in the integrated intensity of the bands ν_{00} , ν_{01} , ν_{02} , and ν_{03} , accompanied by the occurrence of new bands $\nu'_{00} = 26251 \text{ cm}^{-1}$, $\nu'_{01} = 27645 \text{ cm}^{-1}$, $\nu'_{02} = 29017 \text{ cm}^{-1}$, and $\nu'_{03} = 30362 \text{ cm}^{-1}$ (Fig. 2).^{*} The frequencies of the maxima of the bands ν' coincide, within 1 to 10 cm^{-1} , with the frequencies calculated for the free molecules. The position of these bands does not depend on the temperature or on the concentration of the nitrogen and on the oxygen (Figs. 1 and 2).

To explain the differences in the frequencies of the transitions in gaseous oxygen and in the α -phase of the crystal, it was assumed earlier [4] that the structure of the absorption band in α -oxygen is a superposition of electron-vibrational overtones, with the

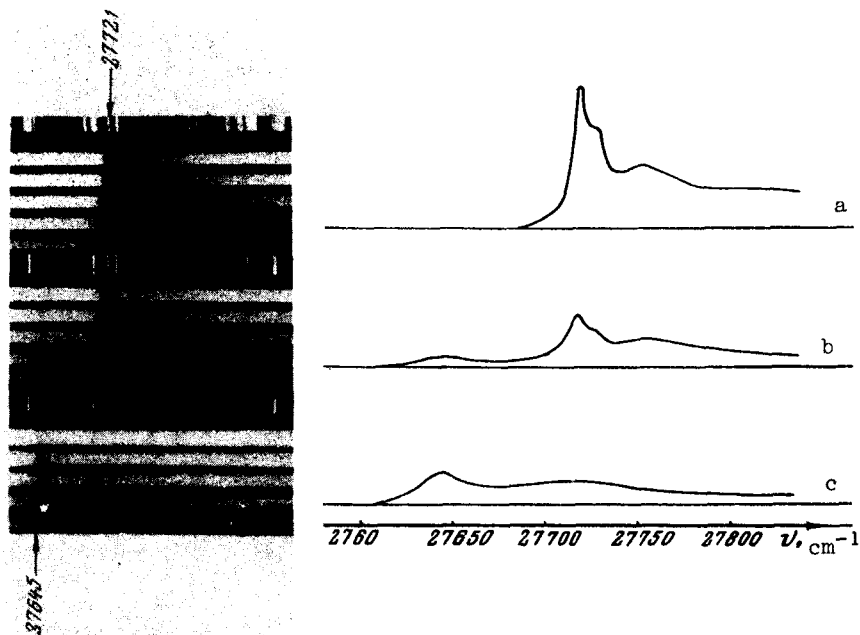


Fig. 2. Contour of the absorption bands in the region of the transition $2^3\Sigma_g^- \rightarrow 2^1\Sigma_g^+$ (0 - 1) at the different nitrogen concentrations in an oxygen crystal: a - 100% O_2 , b - 90% O_2 + 10% N_2 , c - 80% O_2 + 20% N_2 . $T = 5^\circ\text{K}$.

^{*} The error in the determination of the frequencies was $\pm 7 \text{ cm}^{-1}$ for the pure electronic band and $\pm 5 \text{ cm}^{-1}$ for all the remaining electron-vibrational bands.

intramolecular-vibrations frequency ν_m , on the continuous distribution of the lattice frequencies, wherein the frequencies of the maxima of the absorption bands are determined by the relation $\nu = \nu_m + n\nu_D$ (where ν_D is the Debye frequency of the solid oxygen, and $n = 1, 2, 3, \dots$). However, inasmuch as α -oxygen is antiferromagnetic, it can be assumed with equal justification that the cause of the discussed singularity lies not in the excitation of phonons but in the excitation of magnons (the possibility of observing the electron-magnon bands was demonstrated theoretically and experimentally with a number of antiferromagnetic crystals as examples [6]).

The foregoing experimental facts favor the hypothesis of magnon excitation. Indeed, this hypothesis explains in natural fashion the temperature dependence of the spectral position of the absorption bands. With increasing temperature, the antiferromagnetic order in the α -oxygen becomes destroyed, and the exchange energy (or else the maximum magnon energy) decreases, leading to a gradual shift of the maxima of the bands towards lower energies. In the β -phase, which has only short-range antiferromagnetic order [7], the energy required for magnon excitation is quite low and therefore the positions of the bands almost coincide with those calculated for free molecules. On the other hand, from the phonon-excitation hypothesis it follows that the spectral position of the band should duplicate the variation of the Debye temperature (θ_D). But a comparison of the change in the Debye temperature of oxygen [8] with the experimentally observed shift of the absorption bands shows that in the region of the α - β transition the shift of the bands is much greater than the change in θ_D . Moreover, in the β -phase at 26°K the frequencies of the maxima of the bands practically coincide with the frequencies calculated from the molecular constants of the free molecule, whereas on the basis of the phonon hypothesis one should expect the interval between the calculated and measured frequencies to amount to approximately 70 cm^{-1} ($\theta_D \approx 100^\circ\text{K}$). Thus a qualitative disparity is observed between experiment and the interpretation based on the excitation of acoustic phonons.

The assumption of "double" transitions accompanying the excitation of the magnons agrees well with the behavior of the spectrum of the α -oxygen following introduction of nitrogen. The presence of a nonmagnetic impurity changes the energy of the exchange interaction and leads to a local disturbance of the magnetic order, and consequently it is possible to observe simultaneously in the crystal bands characteristic of both the α -phase (ν) and the β -phase (ν'). At a 20% nitrogen content, when there is no long-range magnetic order at all, only the ν' bands are observed (Fig. 2c).

Notice should be taken of the difference between the electron band ν_{00} and its vibrational repetitions ν_{01} , ν_{02} , and ν_{03} . For electron-vibrational bands the interval $\nu - \nu'$ amounts to $75 - 78 \text{ cm}^{-1}$, whereas for the electron band it equals 154 cm^{-1} . This is obviously connected with the excitation of one magnon in the former case and two magnons in the latter.

By analogy with [6], we can expect the absorption of light to be accompanied by creation of a magnon on the edge of the Brillouin zone at $k = \pi/2$.

Thus we can conclude that in the antiferromagnetic α -phase of oxygen, in the spectral

region $26000 - 31000 \text{ cm}^{-1}$, the exchange interaction induces "double" electron-magnon ($\nu = 2\nu(0) + 2\nu_\mu$) and electron-vibrational magnon ($\nu = 2\nu(0) + \nu_m + \nu_\mu$) transitions, as the result of which the selection rules pertaining to the purely electron transition $2^3\Sigma_g^- \rightarrow 2^1\Sigma_g^+$ is violated and an appreciable intensity of this transition is ensured ($\nu(0)$ - frequency of the transition in the free molecule, ν_m - molecule vibration frequency, ν_μ - frequency of magnon excitation).

Similar results which offer evidence of the magnon origin of the bands were obtained by us also for other transitions ($2^3\Sigma_g^- \rightarrow 1^1\Lambda_g$ and $2^3\Sigma_g^- \rightarrow 1^1\Lambda_g + 1^1\Sigma_g^+$), but the appearance of a non-zero orbital angular momentum in the excited state makes the interpretation of these transitions complicated. Detailed data on the investigation of these transitions will be published later.

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EXCITATION OF FORBIDDEN AND ALLOWED RADIATIVE TRANSITIONS IN A $\text{CaF}_2:\text{Dy}^{2+}$ CRYSTAL IN A MAGNETIC FIELD

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The emission spectrum of a $\text{CaF}_2:\text{Dy}^{2+}$ crystal has in the 2.3μ region a group of lines due to magnetic dipole transitions between the Stark sublevels of the excited 5I_7 state and the ground state 5I_8 of the Dy^{2+} ion. The spectroscopic and magnetic-optical investigations of $\text{CaF}_2:\text{Dy}^{2+}$ [1,2] have made it possible to identify the scheme of the Stark sublevels and to identify the observed lines with different allowed transitions in a crystal of symmetry O_h (see the figure). A characteristic feature of the Stark structure of the states 5I_8 and 5I_7 is the fact that several components are close to one another. Particularly close are the components $^2\Gamma_3^{(2)}$ and $^3\Gamma_4^{(1)}$ of the state 5I_8 ($\Delta = 4.8 \text{ cm}^{-1}$) and the components $^2\Gamma_3$ and $^3\Gamma_5^{(2)}$ ($\Delta = 15.3 \text{ cm}^{-1}$) belonging to 5I_7 . The complicated splitting of the closely lying sublevels in the magnetic field is due to their interaction with one another. Contributing to the strong interaction is the fact that the g-factors of the Stark sublevels are large in the system under consideration. The interaction of the levels $^3\Gamma_4^{(1)}$ with $^2\Gamma_3^{(2)}$ of the ground state in a magnetic field leads, for example, to splitting of the latter [3].