Polarization of absorption bands in crystals of α-oxygen

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The first polarized-light measurements of oxygen single crystals have been made in the two-exciton spectrum region, the results of which confirm the possibility of the existence of bi-excitons in this crystal.

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1. Studies of α-O_2, an antiferromagnetic modification of the molecular oxygen crystal (three modifications γ, β and α exist with the phase transition points $T_{\gamma\cdot\beta} = 43.8$ K and $T_{\beta\to\alpha} = 23.8$ K), have shown that its spectrum is determined by a set of collective excitations -- excitons, vibrons, magnons, librons.[1] In order to ascribe

the spectral lines to a given excitation it is necessary to know their polarization. However, in the $\gamma \rightarrow \beta$ transformation (a transition of the first kind) a multitude of seeds of the new phase appear and β-O_2 grows in the form of a polycrystal. A large change in the volume, by 6–8%, leads to strains and stresses, which can impede the development of the β-crystals and affect the spectra in an undesirable manner. The $\beta \rightarrow \alpha$ does not change this much -- the α-O_2 remains a polycrystal. Since it is impossible, under usual crystallization conditions, to avoid phase transitions, all studies of the low-temperature modifications of oxygen, including spectral, are carried out with polycrystals.

The crystallization conditions, however, can be improved by replacing the "hard" quartz cell, in which the oxygen is crystallized, by a "soft" one. This cell is metallic with a thickness of 0.2–0.4 mm. Its windows are closed with a vacuum-tight Lavsan film, which remains elastic at low temperatures. After crystallization of the γ-O_2, the film is removed and the effect of strains is greatly reduced. Then, by lowering the temperature for 5–6 hours to the narrow $\gamma \rightarrow \beta$ region, it is possible to grow relatively large β-O_2 single crystals up to 1 mm in size; this is adequate for the spectral studies. With a lowering of the temperature the β-O_2 single crystals are transformed into α-O_2 single crystals, with no disturbance of their shape and type. The transition occurs by means of the easy rearrangement of the rhombohedral lattice to monoclinic through a slight displacement of the centers of the molecules while the parallelism and direction of their axes are unchanged.[2]

In this case the C_3 axis in β-O_2 becomes the c' axis in α-O_2 ($c' \perp ab$ plane), and the plane, perpendicular to C_3 is replaced by the $(001)_\alpha$ plane (ab). Optically, the β-O_2 crystals are uniaxial while the α-O_2 are biaxial. As light propagates along the C_3 axis, the isotropic absorption of β-O_2 becomes anisotropic in α-O_2 after the $\beta \rightarrow \alpha$ transformation. This fact is used to determine the developed planes in β- and α-O_2. According to our observations the diagonal $(110, 110)_\alpha$ planes develop most often, but crystals also grow with a developed $(001)_\alpha$ plane.

The spectra of the α-O_2 single crystals were investigated in polarized light at 1.5 K with a dispersion of 2 Å/mm. The DFS-3 spectrograph was equipped with an FEU-79 connected to TA-1024 for analyzing the pulses N; the last instrument operated in the multichannel counting mode. The analyzer output goes to a computer, which controls the experiment and is used to analyze the data.

2. We investigated the two-exciton absorption region of oxygen 15,000-34,000 cm^{-1}, due to transitions into the bimolecular ($\Delta\Delta$), ($\Sigma\Sigma$) and ($\Delta\Sigma$) states from the ground ($^3\Sigma_g^-$) state. The states are caused by simultaneous excitation of two molecules into the $^1\Delta_g$ and $^1\Sigma_g^+$ levels from the $^3\Sigma_g^-$. In the crystal the two excitons Δ and Σ, interacting with each other, produce a new quasiparticle -- the bi-exciton -- characterized by the wave vector **K**, common to both. The creation of the bi-exciton is indicated in the spectrum by mulitplet splitting,[3] and in the case of oxygen -- by a doublet splitting of the electron and vibron lines.[4] The magnitudes of the bi-exciton splittings are of the order of the widths of the exciton Δ and Σ bands in the electron members and half that in the vibron. The components of the bi-exciton doublets should be polarized along the monoclinic b axis and perpendicularly to it.[4]

Actually, the lines, corresponding to purely bi-exciton transitions, are split into

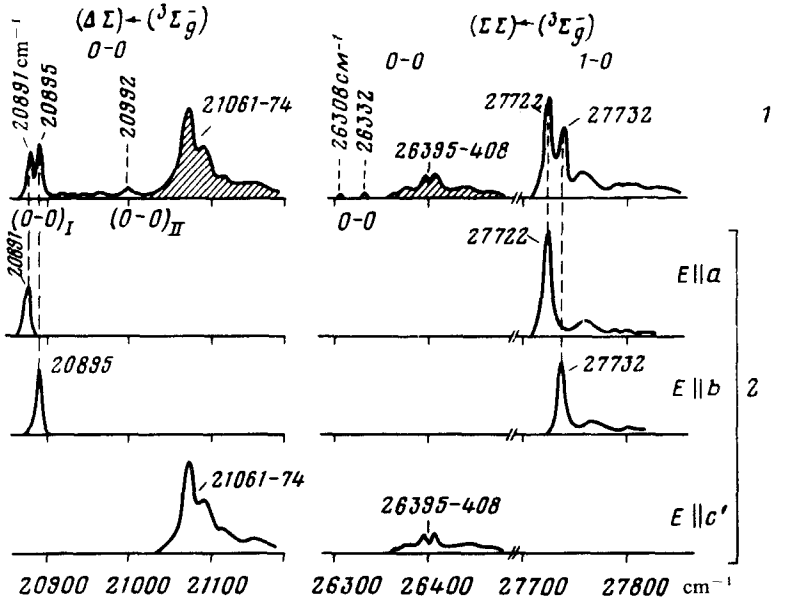

FIG. 1. Contours of α-O_2 absorption bands: 1—spectrum of polycrystal, 2—single crystal.

narrow doublets. The are weak and, with the exception of the one belonging to the $(\Delta\Sigma)_1$ excitation, are visible only in large absorbing layers of the polycrystal (see Fig. 1). The splitting of the nondegenerate $(\Sigma\Sigma)$-term is remarkable; it is hard to find other reasons for it besides interexciton interactions.

In polarized light the spectra, shown in the same Fig. 1, each decay into three components, along the *a*, *b* and *c'* axes of the monoclinic lattice. The 20,891 - 895 cm^{-1} bi-exciton doublet and all the vibron doublets of both transitions into the $(\Sigma\Sigma)$ and $(\Delta\Sigma)$ states have components along only the *a* and *b* axes; they are polarized in the (*ab*) plane. The bands of the complicated structure (shaded in the figure), associated with libration intervals of about 70 cm^{-1} with weak bi-exciton lines -- the exciton-libron lines -- are polarized along the *c'* direction. The exciton-libron band of the $(\Delta\Delta)\leftarrow(^3\Sigma_g^-)$ transition is an exception. The components of the doublets, forming its structure, are polarized along the *c'* and along the *b* axes of the lattice.

3.It can be assumed that for bi-exciton absorption the pairs of nearest molecules, arranged in the (*ab*) plane of the monoclinic lattice (Fig. 2), are excited with the highest probability. The symmetry of the free pair is D_{2h}. The dipole moments of the bimolecular electron and vibron transitions lie in a plane, perpendicular to the axes of the molecules in the (*ab*) plane[5]; the dipole moments of the transitions, associated with the librations of the pair, are directed perpendicularly to this plane. In the crystal the bimolecular absorption is transformed into two-exciton and exciton-vibron absorption. As follows from a group analysis[4] and is seen from Fig. 2, corresponding lines are polarized along the *b* and *a* axes of the crystal. It follows from a geometrical addition of the dipole moments of the pair that each of the lines, having different intensities,

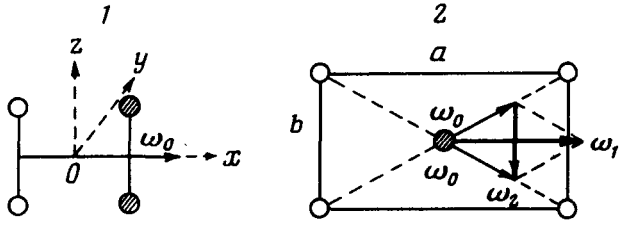

FIG. 2. 1—pair of absorbing molecules with D_{2h} symmetry, 2—scheme of dipole bi-exciton transitions in α-O_2. ω_0 is the dipole moment of transition in pair of molecules, ω_1, ω_2 are the dipole moments of the bi-exciton transitions. Open and shaded circles are molecules having different magnetic sublattices.

belong to the *b* and *a* directions. The exciton-libron bands are polarized along the *c* axis, perpendicularly to the (*ab*) plane. The doublet structure in them may belong to the two libration branches of the vibrations of the α-O_2 lattice. The polarization of these bands, unlike the polarization of the components of the bi-exciton and vibron doublets, confirms that they belong to the exciton-libron.[6]

Thus, the polarization of the two-exciton absorption bands in β: and α-O_2 single crystals, observed for the first time, permits correct assignment of the lines of the crystal spectrum to bi-exciton, exciton-vibron and exciton-libron absorption, distinguished by its strict polarization along the different directions of the lattice. The measurement results, in agreement with the theory developed earlier, confirm the collective nature of the states of the crystal and are an additional proof for the existence of bi-excitons in the molecular antiferromagnetic α-oxygen crystal.

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