Low-frequency Raman spectra of β- and α-oxygen single crystals

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A spectral study of the Raman effect in β- and α-oxygen single crystals unambiguously reveals the symmetry of their librations.

The Raman spectrum of the solid phases of oxygen was first studied by Cahill and Leroi.[1] In the low-frequency part of the Raman spectrum, β-O_2, they found a single broad band, while in α-O_2 they found two bands (Fig. 1a). A group-theory analysis linked these bands with intermolecular vibrations of a libration type in the crystal: of symmetry E_g in β-O_2 and of symmetry A_g and B_g in α-O_2. The latter vibrations were caused by a splitting of E_g due to a lowering of the symmetry of the crystal at the β-α transition. The large value of this splitting (nearly 40 cm^{-1}) and the difference in the widths and intensities of the bands of α-O_2, however, have caused several investiga-

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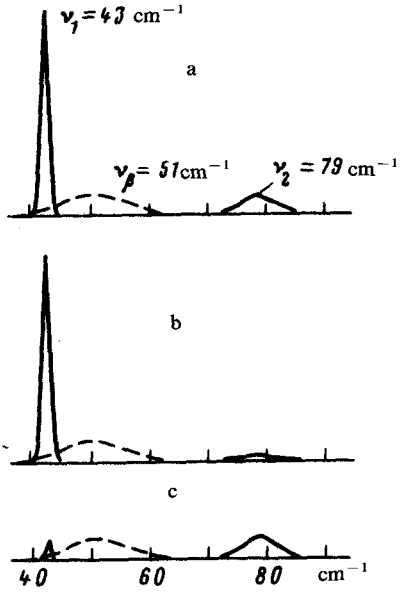

FIG. 1. Dashed line—Low-frequency Raman spectrum of β-O_2 at $T = 25$ K; solid line—Raman spectrum of α-O_2 at $T = 4.2$ K. a) Unpolarized light; b) $\mathbf{E}_1 \| \mathbf{c}'$, $\mathbf{E}_2 \| \mathbf{b}$ (the axes of the α-O_2 crystal); c) $\mathbf{E}_1 \| \mathbf{c}'$, $\mathbf{E}_2 \| \mathbf{a}$.

tors[2,3] to express doubt regarding the validity of this explanation of the bands. According to these other investigators, the splitting of the E_g vibration into A_g and B_g at the β-α transition should be very small. It has accordingly been suggested that the band ν_1 consists of the sum of components A_g and B_g which are not resolved experimentally. The band ν_2 is linked with the simultaneous scattering of light by two excitations: a libron and a magnon[2] or two phonons.[3]

The Raman spectra of oxygen were also studied in several later experiments.[4,5] All these other experiments, however, were carried out with polycrystalline samples, and they did not make it possible to unambiguously link the observed bands with vibrations of a definite symmetry and thereby resolve the difference of opinion regarding the nature of the Raman bands of α-O_2.

In this letter we report a study of single crystals of β and α oxygen. The β-O_2 single crystals are of rhombohedral symmetry, D_{3d}^5. At the β-α transition (23.9 K), their structure changes to monoclinic,[2] C_{2h}^3. The phase transition results from a deformation of the close-packed layers of the β crystal: a slight displacement of the centers of the molecules with no change in the directions of their axes.[2] The isotropic plane of close packing of the rhombohedron, (111), converts into the (ab) plane of α-O_2: the (001) plane. It was pointed out in Ref. 6 that α-O_2 single crystals grow predominantly with developed faces parallel to the (110) and ($1\bar{1}0$) diagonal planes. By using an external manipulator to rotate the crystal, one can change the orientation of the crystal with respect to the directions of the incident and scattered light and thus alter the experimental geometry. The principal directions in the single crystal are determined experimentally and monitored on the basis of the polarization of the absorption bands of the crystal.[6] The light source is a copper-vapor laser ($\lambda = 510.5$ nm).

The experimental results are shown in Fig. 1. In the scattering of unpolarized

light (Fig. 1a) at frequencies up to 100 cm^{-1} we observe a single broad band in the Raman spectrum of β-O_2 at $T = 25$ K. This band peaks at the frequency $\nu_\beta = 51$ cm^{-1} and has a half-width ~ 14 cm^{-1}. In α-O_2 at $T = 4.2$ K we see two bands: an intense narrow band with $\nu_1 = 43$ cm^{-1} and with a half-width of about 1 cm^{-1} and a band $\nu_2 = 79$ cm^{-1} with a half-width ~ 7 cm^{-1}. The first of these bands is about 2.8 times as intense as the second. As the temperature is raised within the α phase, this intensity ratio remains the same within the experimental error (20%). The spectrum in Fig. 1a is similar to that which has been observed previously in a study of polycrystalline samples.[1,5] We do not observe lines due to a scattering of light by magnons (α-O_2 is an antiferromagnet), possibly because of the small thickness of the single crystal. It can, on the other hand, be asserted that the intensity of these lines with respect to that of the ν_1 band is at least an order of magnitude lower than reported in Ref. 4.

Figures 1b and 1c correspond to an experimental geometry in which the scattered light propagates nearly perpendicular to the (ab) plane of α-O_2 and is polarized ($\mathbf{E}_2$) along the **a** and **b** axes of the crystal. The electric vector of the incident light, $\mathbf{E}_1$, is directed near the **c**′ axis in the crystal [**c**′ is perpendicular to the (ab) plane of α-O_2].[1)] It can be seen from these figures that in the case $\mathbf{E}_2 \| \mathbf{b}$ the intensity of the band at $\nu_2 = 79$ cm^{-1} decreases sharply, while in the case $\mathbf{E}_2 \| \mathbf{a}$, in contrast, the intensity of the $\nu_1 = 43$ cm^{-1} band is nearly zero. The slight "residue" of band intensity which is observed (incomplete polarization), which is comparable in magnitude to corresponding residues in the absorption spectrum of polarized light, can be explained on the basis of the imperfections of the crystal and the inexact orientation of $\mathbf{E}_1$ and $\mathbf{E}_2$ with respect to the axes. In the β-O_2 spectrum, the band intensity does not change as the polarization of a beam scattered through 90° is changed, as can be seen from the figure. The reason is that the (ab) plane of α-O_2 corresponds to an isotropic (111) plane of β-O_2.

Comparison of these experimental results with the known Raman-scattering tensors[7] of the C_{2h} group shows that the band at $\nu_1 = 43$ cm^{-1} has a symmetry B_g, while that at $\nu_2 = 79$ cm^{-1} has A_g; these bands correspond to the same components of the tensor as in the case of the degenerate E_g vibration of the β phase. The experiments do not support the suggestion in Refs. 2 and 3 regarding the nature of the bands observed in the Raman spectrum of α-O_2. Specifically, if the ν_1 band were the sum of A_g and B_g components which are not resolved experimentally, then the intensity of this band would not vary as sharply upon a change in the polarization of the scattered light ($\mathbf{E}_2$) from the **b** direction to the **a** direction. It may thus be assumed that the ν_1 band corresponds exclusively to a B_g vibration. The ν_2 band must then be attributed to an A_g librational vibration. Its intensity is comparable to that of ν_1. The suggestion that it is associated with a two-particle excitation in the crystal[2,3] during light scattering is thus dubious.

In summary, this study unambiguously establishes that the $\nu_1 = 43$ cm^{-1} and $\nu_2 = 79$ cm^{-1} bands observed in the Raman spectrum of α-O_2 are in fact consequences of vibrations in the crystal, with symmetry B_g (librations around the a axis) and A_g (librations around the b axis), respectively, caused by a splitting of the E_g vibration at the β-α transition, as suggested in Ref. 1. As for the splitting between the A_g and B_g vibrations at the β-α transition, we note that, as was shown in Ref. 8, this splitting can

in fact be large when we take into account the exchange interactions between the molecules executing the librations. The different widths of the bands apparently stem from different couplings of the A_g and B_g librations with acoustic vibrations in the crystal.

[1)]Comparison of the theoretical and experimental results for other versions of the experimental geometry shows that the components α_{aa}, α_{bb}, $\alpha_{c'c'}$, α_{ab} of the α-O_2 scattering tensor and the corresponding components for β-O_2 are very nearly zero. Only $\alpha_{c'a}$ and $\alpha_{c'b}$ have values of significant magnitude.

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