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FAR-INFRARED ABSORPTION IN SOLID ALPHA OXYGEN

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The far-infrared absorption spectrum of crystalline alpha oxygen (α-O_2) has been measured in annealed samples up to 20 mm thick. The prominent feature of the spectrum is a temperature-dependent absorption near 27 cm^{-1} which appears to be an antiferromagnetic resonance mode, the first such collective excitation to be observed in a molecular solid.

We report here the first far-infrared (10- to 100-cm^{-1}) spectrum of solid polycrystalline oxygen in the antiferromagnetic α phase[1,2] which is stable from 0 to 23°K. The main feature of the α-O_2 spectrum is a pronounced absorption peak near 27 cm^{-1} at 4.2°K with a linewidth of about 1.4 cm^{-1}. This peak shifts to lower frequencies and diminishes in amplitude with increasing temperature and is unobserved above the $\alpha \rightarrow \beta$ transition (23.8°K).

Carefully annealed[3] samples up to 20 mm thick were prepared in situ on a wedge-shaped sapphire window mounted on the end of a special lightpipe section equipped with heaters and temperature sensors to control the sample preparation. Standard Fourier-transform spectroscopy techniques[4] were employed using a commerical Michelson-type interferometer modified for low-temperature investigations.

Figure 1 compares a representative spectrum (sample thickness = 6 mm) of the antiferromagnetic α phase at 5°K with the β and γ phases (see below) and the background. The spectra have the same transmission-maximum normalization and are displaced vertically for clarity. The irregular structure on top of the main beam-splitter mode is due to the channel spectra[4] of the windows in front of the detector element.[5] For γ-O_2, the total signal level at the detector is the same as that of the background, but decreases upon cooling to the β phase due to increased absorption of short-wavelength radiation. There was no significant change in the signal level upon cooling to the α phase. This result is consistent with the fact that the α and β structures have about the same density.[2]

Figure 2 illustrates the striking temperature dependence of the main absorption in the α-O_2 spectrum. The frequencies of maximum absorption extracted from these data are plotted versus temperature in Fig. 3. The points at 68 and 150 GHz were obtained in an earlier attempt[6] to observe antiferromagnetic resonance in solid alpha oxygen using the fixed-frequency, variable-temperature method[7] appropriate to polycrystalline samples in zero applied field. These points have been included for completeness since they are consistent with a cooperative magnetic mode interpretation to be discussed below.

The oxygen molecule is of great interest since its ground state has a nonzero spin $S = 1$ and the study of the magnetic properties of its condensed phases should give information on the nature of "direct" p-electron exchange and the dependence of exchange on molecular rotational quantum states. The details of the low-lying, spin-rotational energy-level structure of the free molecule are well known from accurate measurements in the microwave range[8] and more recently in the far infrared.[9] On the other hand, there is

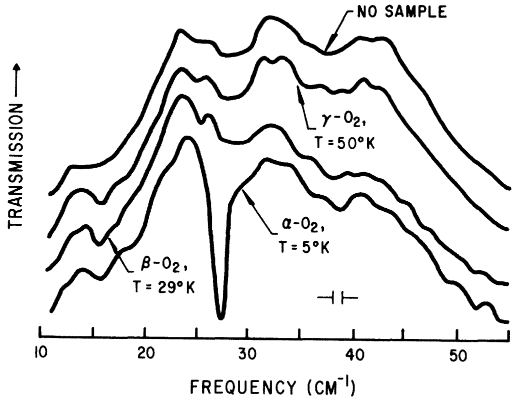

FIG. 1. Far-infrared absorption in solid phases of oxygen.

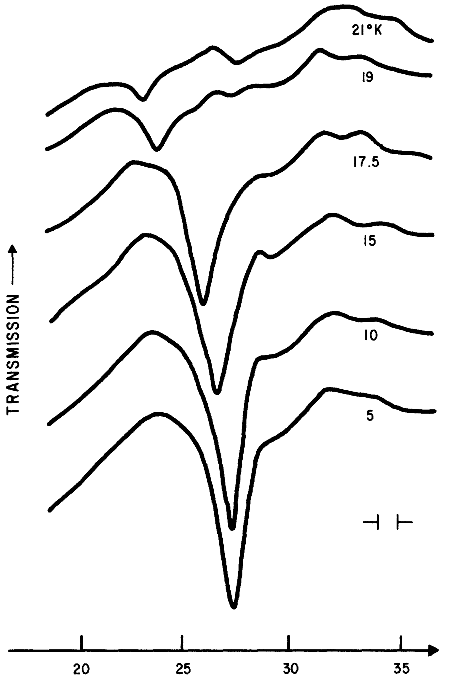

FIG. 2. Far-infrared absorption in alpha oxygen.

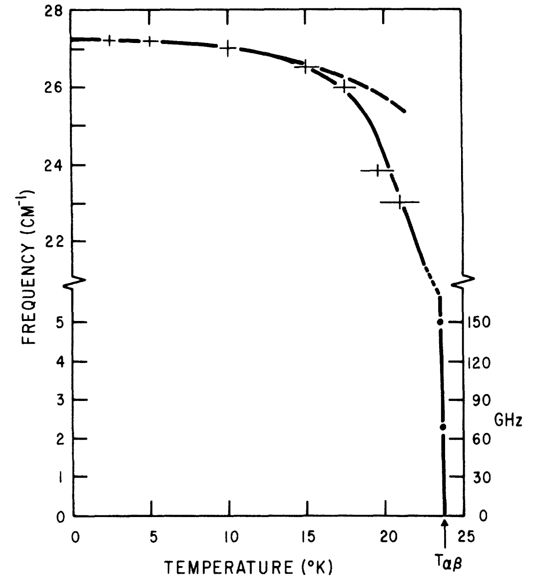

FIG. 3. Temperature dependence of far-infrared absorption in alpha oxygen. The points at 4- and 2-mm wavelengths were taken in this laboratory. The dashed curve is proportional to $(\gamma_e H_E)^{1/2}$ taken from optical data (Refs. 14 and 15) (see text).

very little information on the energy-level scheme in the condensed state. At least two important mechanisms for perturbing the low-lying levels are operable: rotational hindrance and the exchange interaction. The molecule's rotational degree of freedom will become hindered because of the close proximity of neighboring molecules. As a result, the free rotator states characterized by energy levels $E_K \sim B_K K(K+1)$ go over to two-dimensional harmonic oscillator or librational states $E_{n,m} \sim (n+m+1)\hbar\omega$. This effect has been observed[10-12] for oxygen molecules in a β-quinol clathrate matrix and can be described by adding an anisotropic term to the Hamiltonian of the form

$$D[S_z^2 - \tfrac{1}{3}S(S+1)].$$

For the case[11] where the molecular axis is completely pinned, $D/hc = 3.9$ cm^{-1}, which is essentially the energy separation of the free-molecule states $|K=1, J=0\rangle$ and $|K=1, J=1\rangle$.

The magnitude of the exchange interaction between oxygen molecules has been the subject of several studies[13-15] since neutron diffraction experiments[16] showed α-O$_2$ to be antiferromagnetic and the crystal structure of this low-temperature phase was determined.[1,17] Recently Eremenko and his coworkers[14,15] have observed a temperature-dependent shift attributed to magnetic-exchange interactions in the double[18] optical transition spectrum of alpha oxygen. The exchange energy, corresponding to magnons excited at the Brillouin-zone boundary, was measured to be $\gamma_e H_E \simeq 75$ cm^{-1} at 4.2°K (γ_e is the gyromagnetic ratio and H_E is the effective exchange field). The exchange energy, as measured[15] by the magnon shift, is constant from 5 to 10°K and then falls off smoothly with increasing temperature to about 85% of its low temperature value before falling rapidly to zero at $\alpha \rightarrow \beta$ transition.

One would expect the energy of a $k=0$ magnon (antiferromagnetic resonance mode) to be of order[19] $\gamma_e(2H_E H_A)^{1/2}$, where $\gamma_e H_A$ is the effective anisotropy energy. A large contribution to the anisotropy energy will come from the interaction between the spin and the figure axis of the molecule discussed above, and assuming that the molecular axis is completely pinned,[20] will amount to 3.9 cm^{-1}. This corresponds to an anisotropy field of $H_A \sim 50$ kOe which is large for most magnetic systems. Assuming that other contributions to the anisotropy are negligible[21] and using the value $\gamma_e H_E \simeq 75$ cm^{-1} from the optical data, we calculate the antiferromagnetic resonance energy at 4.2°K to be

$$\hbar\omega \simeq \gamma_e (2H_E H_A)^{1/2} = 24 \text{ cm}^{-1},$$

in reasonable agreement with the line reported here.

The dotted curve in Fig. 3 is proportional to $(\gamma_e H_E)^{1/2}$ taken from optical data.[14,15] If the above expression correctly describes our data, then the anisotropy must also decrease with increasing temperature.

Finally, we should mention that in the thickest samples we observed at 4.2°K additional weak absorption lines at 37 and 43 cm^{-1} with linewidths ~1 cm^{-1}. These may be spin-librational level transitions or transitions of cooperative magnetic origin. Any assignment would be premature without further study, however.

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[3] The annealing process involved (1) condensing an appropriate volume of the pure gas onto the liquid-helium–cooled sapphire window while maintaining the temperature of the lightpipe above the copper-sample holder (Fig. 1) above the melting point (55°K) and (2) raising the sample temperature to 50°K (γ phase), maintaining it there for some time, and then cooling it slowly through the $\gamma \leftrightarrow \beta$ (45°K) and $\beta \leftrightarrow \alpha$ (24°K) transitions. Unannealed samples deposited at 4.2°K showed only exponentially increasing absorption with increasing sample thickness and decreasing wavelength characteristic of an amorphous powder of fine particles. The annealing requirements and the necessity of using fairly thick specimens in order to observe the intrinsic spectra probably accounts for the absence up to now of any report on the far-infrared spectrum of solid oxygen. The oxygen used in these experiments was Matheson's research grade (99.999% pure).

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[19] This is an exact expression for the case of a two-sublattice antiferromagnet with uniaxial anisotropy in zero external field at 0°K.

[20] The α structure is a close-packed structure (see Ref. 2).

[21] An order of magnitude calculation of the spin dipole-dipole anisotropy yields $\sim 10^{-1}$ cm^{-1}.