TEMPERATURE DEPENDENCE OF THE INTENSITY OF THE BANDS OF "COOPERATIVE" LIGHT ABSORPTION BY CRYSTALLINE OXYGEN

V. V. EREMENKO, Yu. G. LITVINENKO, and É. M. OGNEVA

Physico-technical Institute of Low Temperatures, Academy of Sciences, Ukr. S.S.R.

The optical absorption spectra of crystalline oxygen were investigated in the temperature interval 4.2–25°K, which includes the low-temperature phase transition point (23.9°K). A detailed investigation of the narrow bands at 20,233 and 23,814 cm^{-1}, which are connected respectively with the double optical transitions $2^3\Sigma \to 2^1\Delta$ and $2^3\Sigma \to {}^1\Sigma + {}^1\Delta$, has shown that their integral intensity varies abruptly in the investigated temperature interval. To explain this fact, it is assumed that the "cooperative" transitions in oxygen are induced by the exchange interaction of the O_2 molecules. This interaction increases because of the change in the character of the rotation of the O_2 molecules on going from the β to the α modification of crystalline oxygen.

INTRODUCTION

SOLID oxygen has many interesting properties. This is the only molecular crystal, made up of molecules of uncompensated spins, and this causes the paramagnetism of its high temperature crystalline γ phase and apparently also the antiferromagnetism of the low temperature β and α phases.[1] The structure of solid oxygen was investigated by x-ray diffraction[2,3] and by neutron diffraction.[3,4] It must be assumed as a result of these investigations that the γ phase of crystalline oxygen, which is in equilibrium in the temperature interval from the triple point (54.1°K) to 43.8°K, has a cubic face-centered structure (T_h^6; a = 6.83 Å), the β phase (43.8–23.9°K) has a rhombohedral lattice (a = 6.19 Å, α = 99.1°),[3,5] and the low-temperature α phase has a nearly rhombohedral lattice.[2]

Investigations of the temperature dependence of the specific heat and of the magnetic susceptibility[1] have provided evidence that at the phase-transition points there takes place a rearrangement not only of the crystallographic but possibly also of the magnetic structure. At any rate, the magnetic susceptibility of the β and α phases decreases with decreasing temperature, a behavior characteristic of antiferromagnets. Neutron diffraction investigations do not contradict the assumption of antiferromagnetism of the β and α phases,[4,5] but whereas the α phase of oxygen has, according to the neutron diffraction data, uniaxial antiferromagnetism, the β phase has tri-axial antiferromagnetism, with a special form of exchange interaction between the vibrating molecules.[5]

At the same time, the spectrum of absorption of light by the crystalline oxygen has many interesting features.[6,7] This spectrum consists of five series of absorption bands:

1) $^3\Sigma \to {}^1\Delta$ (12 000—7300 Å),
2) $^3\Sigma \to {}^1\Sigma$ (7600 — 5700 Å),
3) $2^3\Sigma \to 2^1\Delta$
4) $2^3\Sigma \to {}^1\Sigma + {}^1\Delta$ (5500 — 3000 Å).
5) $2^3\Sigma \to 2^1\Sigma$

The frequencies of the bands of series 3—5 can be written as combination frequencies of the first and second series with each other and with the vibrational frequencies,[7] and the intensity of these bands in gas[8] and in liquid[9] depends much more strongly than linearly on the density. Usually the various singularities of combination bands in the absorption light by oxygen are regarded as proving the existence of quasi-stable complexes, namely $(O_2)_2$ dimers.[7,10] Such an explanation, however, cannot be regarded as the only one, since simultaneous optical transitions in two molecules can also occur without formation of dimers. Thus, for example, the appearance of additional absorption bands, with frequencies that are expressed by linear combinations of the frequencies of the electronic transitions of the individual ions, were recently observed in the spectra of crystals containing large amounts of rare-earth ions.[11]
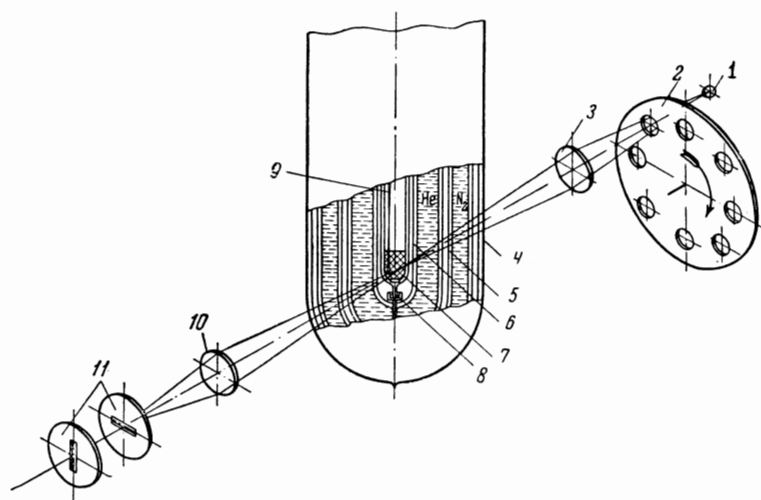
FIG. 1. Diagram of the experimental setup. 1 – Light source (DKSSh-1000), 2 – rotating perforated disc (intensity attenuator), 3 – focusing lens, 4 – flat windows, 5 – helium Dewar, 6 – Dewar container for oxygen, 7 – sample (solid oxygen), 8 – molybdenum rod (cold finger) and miniature heater, 9 – thermocouple, 10 – focusing lens, 11 – diaphragm with stepped wedge and entrance slit of spectrograph.

A theoretical analysis shows that the appearance of combination bands, connected with the "cooperative" simultaneous optical transitions in pairs of ions (molecules), is due to the rather weak interaction between the ions (molecules).

Inasmuch as the mechanism that induces combined or double transitions in the oxygen spectrum still remains unclear, further experimental investigation is necessary for the purpose of clarifying the new peculiarities of the "cooperative" absorption of light, due to these transitions. In particular, additional information can be gained, apparently, from investigations of the temperature dependence of the spectral position of the "cooperative" absorption bands, their form, and especially their integral intensity. In this paper such an investigation was made in the low-temperature region (5—25°K), using as an example two isolated narrow bands at 20,233 cm^{-1} ($2^3\Sigma \rightarrow 2^1\Delta$) and 23,814 cm^{-1} ($2^3\Sigma \rightarrow {}^1\Sigma + {}^1\Delta$).

METHODOLOGICAL REMARKS

The samples were grown from oxygen obtained by decomposition of $KMnO_4$. The oxygen obtained in this manner was accumulated in an ampoule cooled with liquid nitrogen, liquefied, and then redistilled. Such a procedure made it possible to obtain oxygen with a high degree of purity.[6]

The growing of polycrystalline samples of the α phase of oxygen and the investigation of the optical absorption spectra were carried out with the aid of the apparatus shown schematically in Fig. 1. Confining ourselves to an investigation of the visible region of the spectrum, we carried out the measurements in ordinary glass Dewars with transmitted light. The oxygen was condensed in Dewar ampoule 6 with thick plane-parallel walls

underneath. The inside dimensions of the ampoule were such that a 5 ± 0.5 mm layer of solid oxygen 7 could be obtained. A dismountable molybdenum rod 8 passed through the vacuum jacket of the Dewar ampoule.[13] one end of this rod was immersed in liquid helium, and the other secured to the internal part of the ampoule, in which the oxygen first condensed and then crystallized. The temperature of the sample, the rate of crystallization, etc. were varied with the aid of a miniature oven 8, wound on the molybdenum rod, which served as a cold finger, and by varying the vacuum in the jacket of the measuring ampoule (by pumping on a regulated amount of gaseous helium). It is very convenient to vary the temperature of the sample by varying the power incident on it by radiation from a gas-discharge xenon lamp DKSSh-1000 (1), with the aid of which the absorption spectrum of the light by the solid oxygen was photographed. To regulate the averaged intensity of the radiation incident on the sample 7, a rapidly rotating perforated disc 2 was placed between the sample and the light source 1. The number of holes in the disc governed the average attenuation of the intensity of the radiation incident on the sample. By combining all the foregoing methods, we could vary the temperature of the sample over a wide range from 12.2°K to the melting point (54.1°K).

The measurement of the temperature was made by a differential copper-constantan thermocouple 9, one end of which was in the oxygen sample and the other in the liquid helium. The accuracy of measurement in the investigated temperature interval was ±1°K.

Prolonged attempts to grow a single-crystal α-phase oxygen sample were unsuccessful, in spite of the possibility of varying the rate of cooling of the oxygen over a very wide range. In the case of very

slow cooling (for 3—5 hours) it is possible to obtain samples which scatter light less than the samples obtained by fast cooling, but even in this case the polycrystals obtained are semitransparent and dull. At a thickness of approximately 5 mm, to obtain sufficiently distinct spectrograms of the described samples, the required exposure time is on the order of 30 minutes with well focused and unattenuated light from the DKSSh-1000 lamp incident on the sample, and using the highly sensitive film RF-3.

The investigation was carried out with a DFS-8 diffraction spectrograph with linear dispersion 6 Å/mm at a spectral width of the instrument slit of 0.6 Å. The measurements of the intensity were by the usual method of photographic photometry.[14] Using a nine-step wedge, and using good homogeneity of illumination of the input slit of the spectrograph, and exercising caution in the spectrogram development, the main error in the measurement of the absorption coefficient of the bands is due to the inaccuracy of determination of the thickness of the sample and the errors due to separating the absorption connected with the investigated band and the background of the band. The first of these sources of error is largely removed by carrying out all the measurements in the same ampoule, whose inside diameter determines the thickness of the sample. The second source of error introduces in the integral intensity of the 20,233 cm^{-1} band an error of 30% and in the 23,814 cm^{-1} band an error of 10%.

EXPERIMENTAL RESULTS

The α phase of solid oxygen has a whole series of absorption bands in the visible region of the spectrum.[6,7] They are all due to optical double transitions but differ appreciably in their intensity and width. Even a spectrograph of a rather narrow portion of the spectrum (Fig. 2) illustrates the abundance of absorption bands of α oxygen.

However, from all this multiplicity of lines we chose two for a detailed analysis: 23,814 cm^{-1} and 20,223 cm^{-1}. These bands are identified with different transitions (see Fig. 2), a fact which makes it possible to compare the temperature dependence of their intensity, and they are single, sufficiently far from other bands, which facilitates their separation from the background. It is also important that at a sample thickness of 5 mm, the chosen bands are observed and can be easily processed (by photometry) in a sufficiently broad temperature interval (5—25°K), which covers the α-β phase transition point.
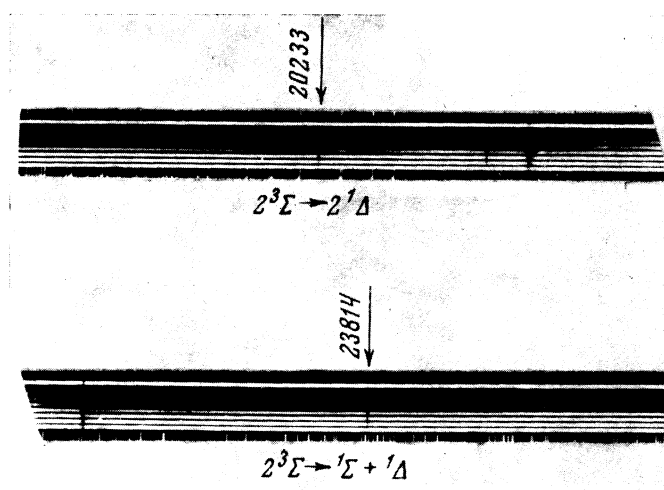

FIG. 2. Light absorption spectrum — oxygen modifications. T = 4.2°K, d = 5 mm.

Figure 3 shows spectrograms which cover a very narrow section of the spectrum near the 20,233 cm^{-1} band, and curves of the spectral distribution of the coefficient of absorption of light near this band, obtained at five different temperatures (9.5—22°K). The value of the absorption coefficient at the maximum of the band at 9.5°K (and lower) reaches k = 0.064 cm^{-1} (the coefficient is given by the following relation: $I = I_0 e^{-kd}$, where I_0 and I are the intensities of the light incident on the sample and transmitted through it; d is the sample thickness in centimeters).

The first striking fact is the stable position of the band in the frequency scale: when the temperature varies from 4.2 to 25°K, the position of the band remains unchanged, within the limits of experimental accuracy. This result agrees with the data of Prikhot'ko et al.,[6] according to which the frequency of this line is the same in the α and in the β phase of oxygen (20,231 cm^{-1}). The half-width of the 20,233 cm^{-1} line likewise does not change noticeably in the investigated temperature interval.

The absorption coefficient at the maximum of the band, and consequently also the integral intensity of the band, decrease strongly with increasing temperature. If we subtract the intensity of the background, as shown dashed in Fig. 3, then the integral intensity of the 20,233 cm^{-1} band is determined by the remaining area under the curve. The temperature dependence of this integral intensity S (in relative units) is shown in Fig. 4. A characteristic feature is the constancy of the intensity of the 20,233 cm^{-1} band below 10°K and its sharp weakening when heated above 12°K. When the temperature changes from 12 to 22°K (region of existence of the α phase), the intensity of the

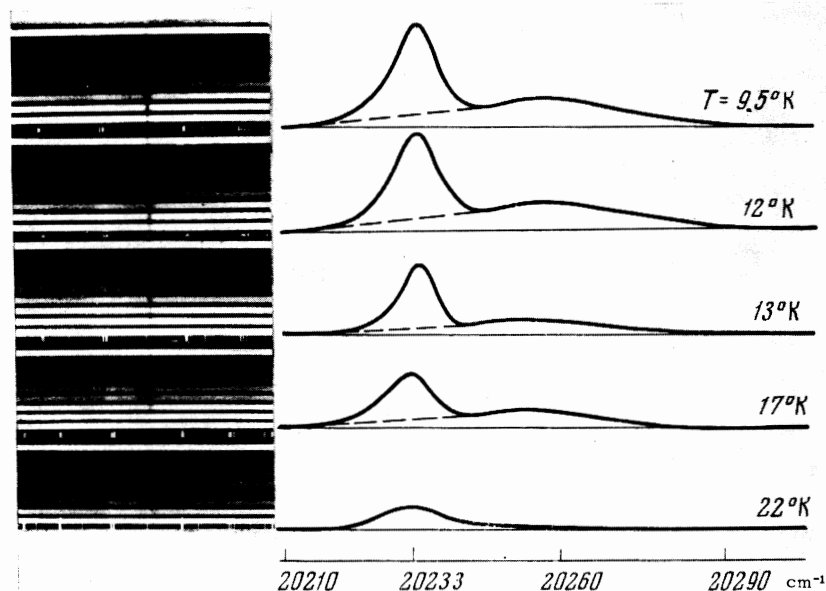FIG. 3. Contour of absorption band at 20,233 cm⁻¹ ($2^3\Sigma \to 2^1\Delta$) at various temperatures.

20,233 cm⁻¹ band (transition $2^3\Sigma \to 2^1\Delta$) is weakened by a factor of 5.

The 23,814 cm⁻¹ band behaves in similar fashion: the frequency of its maximum and its half-width do not change in the investigated temperature interval, but the intensity changes noticeably. Figure 4 shows the temperature dependence of the integral intensity of the 23,814 cm⁻¹ band, with account taken of the background in a fashion similar to what was done for the 20,233 cm⁻¹ band. A characteristic circumstance is the fact that the intensity of the 23,814 cm⁻¹ band ($2^3\Sigma \to {}^1\Sigma + {}^1\Delta$) remains constant up to 16°K, and begins to decrease rapidly with further heating. As a result it turns out that whereas the 20,233 cm⁻¹ band is more intense at 4.2°K, the 23,814 cm⁻¹ band becomes more intense above 12°K.

DISCUSSION OF RESULTS

The results of magnetic[1] and neutron diffraction[4,5] investigations confirm the assumption that the low-temperature α phase of oxygen is antiferromagnetic, and the same, with a lesser degree of reliability, for the β phase. We can therefore expect the phase transitions in crystalline oxygen to be accompanied by effects in the optical absorption spectrum, characteristic of antiferromagnetic ordering of crystals. As shown by spectral investigations of several antiferromagnetic compounds of transition metals,[15-18] among the most characteristic features is the frequency shift of the absorption spectra,[15,16] and their narrowing.[17,18] If the absorption bands are due to optical transitions accompanied by a change in

spin, as is the case for oxygen (for example, the transitions $2^3\Sigma \to 2^1\Delta$ and $2^3\Sigma \to {}^1\Sigma + {}^1\Delta$), then the frequency shift should be observed upon magnetic ordering, even if the electronic excitation is not accompanied by a change in the exchange integral. Indeed, the exchange energy $W_{exc} = 2J \sum_{k=1}^{z} s_r s_k$ [J is the exchange integral, z the number of nearest neighbors, and s_i and s_k are the spins of the chosen ion (molecule) and of the neighbors], has in the ground state a value $W_{exc} \sim kT_N$. In the excited states of oxygen, on the other hand, $s_i = 0$ and accordingly the energy of the exchange interaction between the excited molecule and the environment is equal to zero. Thus, inasmuch as the exchange energy reduces the energy of the ground state, and does not affect the levels of the excited states, upon ferromagnetic ordering the oxygen bands should shift towards the short-wave side by an amount $\sim kT_N$. If the temperature of the phase transition from the paramagnetic γ phase into the β phase (43.8°K) coincides with T_N, then we can expect in this transition the appearance of a frequency shift of the bands amounting to $\Delta\nu \approx 30 \, \text{cm}^{-1}$. Actually, however, a much larger shift is observed
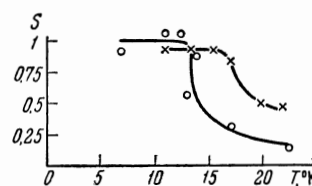

FIG. 4. Temperature dependence of integrated intensity: o — $\nu_{max} = 20{,}233$ cm⁻¹ ($2^3\Sigma \to 2^1\Delta$), × — $\nu_{max} = 23{,}814$ cm⁻¹ ($2^3\Sigma \to {}^1\Sigma + {}^1\Delta$).

in this phase transition (for example, for the 20,233 cm^{-1} band the shift is $\Delta\nu_{\gamma\beta} \approx 715$ cm^{-1}[6]), connected apparently not so much with the magnetic ordering as with the considerable change in the parameters of the crystal lattice (from 6.83 to 6.19 Å).

In the low-temperature phase transition (23.9°K), both the lattice parameters and the exchange energy apparently change very little, for in this temperature interval one observes no noticeable frequency shift in the bands. This assumption does not contradict the results of neutron-diffraction investigations,[5] according to which both the α and the β phases are antiferromagnetic, differing only in the features of the magnetic structure.

At the same time, the observed temperature dependence of the integral intensity of the combination bands $2^3\Sigma \rightarrow {}^1\Sigma + {}^1\Delta$ (23,814 cm^{-1}) and $2^3\Sigma \rightarrow 2^1\Delta$ (20,233 cm^{-1}) can be understood qualitatively by assuming that in the investigated temperature region (5—25°K) there is a noticeable change in the interaction between the oxygen molecules, if the mechanism whereby the "cooperative," double transitions are induced is connected with this interaction.

In the β modification of crystalline oxygen, as shown by neutron diffraction investigations,[5] the O_2 molecules rotate about the center of gravity over a cone, and this leads to a special exchange interaction: interaction between the molecules and a varying overlap integral. If we assume that this is the interaction that induces the double, "cooperative" optical transitions, then the observed temperature dependence of their intensity is evidence of considerable change in the vertex angle of the rotation cone, occurring near the temperature of the low-temperature phase transition, this leading to some increase in the exchange interaction of the O_2 molecules.

This hypothesis, however, cannot explain the difference between the temperature dependence of the 20,233 and 23,814 cm^{-1} bands, or the absence of a frequency shift of the bands in this temperature interval. To clarify these questions it is necessary to investigate the temperature dependence of the frequencies and the intensity of a larger number of bands of solid oxygen. Such an investigation is now under way.

[1] Borovik-Romanov, Orlova, and Strelkov, DAN SSSR **99**, 699 (1954).

[2] L. Vegard, Nature **136**, 720 (1935).

[3] E. M. Hörl, Acta Cryst. **15**, 845 (1962).

[4] R. A. Alikhanov, JETP **45**, 812 (1963), Soviet Phys. JETP **18**, 556 (1964).

[5] R. A. Alikhanov, Tezisy dokladov XI Vsesoyuznogo soveshchaniya po fizike nizkikh temperatur (Abstracts of papers of Ninth All-union Conference on Low-temperature Physics), Minsk, Nauka i tekhnika, 1964, pp. 6—7.

[6] Prikhot'ko, Ruemann, and Federitenko, JETP **5**, 712 (1935); Phys. Z. Sowjetunion **7**, 410 (1935); A. F. Prikhot'ko and M. Ruemann, Phys. Z. Sowjetunion **8**, 294 (1935). A. F. Prikhot'ko, ibid **11**, 465 (1937).

[7] Landau, Allin, and Welsch, Spectrochimica Acta **18**, 1 (1962).

[8] J. W. Ellis and D. Kneser, Z. Physik **86**, 583, (1933). Publ. Astron. Soc. of the Pacific **56**, 106 (1934).

[9] J. Jansen, Compt. rend. **101**, 649 (1885).

[10] V. I. Dianov-Klokov, DAN SSSR **105**, 290 and 504 (1955).

[11] F. Varsanyi and G. H. Dicke, Phys. Rev. Letters **7**, 442 (1961).

[12] D. L. Dexter, Phys. Rev. **126**, 1962 (1962).

[13] V. G. Manzheliĭ and A. M. Tolkachev, FTT, 1965 (in press).

[14] E. F. Prokof'ev, Metody spektral'nogo analiza (Methods of Spectral Analysis), Gostekhizdat, 1950.

[15] I. Tsujikawa, J. Phys. Soc. Japan **13**, 315 (1958).

[16] J. W. Stout, J. Chem. Phys. **31**, 809 (1959).

[17] A. I. Belyaeva and V. V. Eremenko, JETP **44**, 469 (1963), Soviet Phys. JETP **17**, 319 (1963).

[18] V. V. Eremenko and A. I. Belyaeva, FTT **6**, 1967 (1964), Soviet Phys. Solid State **6**, 1553 (1964).