

SPECTRUM OF ALPHA OXYGEN IN A STRONG MAGNETIC FIELD

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The effect of a 170 kOe magnetic field on the light absorption bands of the α modification of oxygen is investigated at a temperature of 4.2°K. The spectral range from 6300 to 3200 Å in which the "double" optical transitions $2^3\Sigma_g^- \rightarrow 2^1\Delta_g$; $2^3\Sigma_g^- \rightarrow ^1\Delta_g + ^1\Sigma_g^+$ and $2^3\Sigma_g^- \rightarrow 2^1\Sigma_g^+$ are located is investigated. Triplet splitting of the electron-vibrational bands of the first ($2^3\Sigma_g^- \rightarrow 2^1\Delta_g$) transition is observed. In the range of magnetic field intensities investigated the magnitude of the Zeeman splitting $\Delta\nu$ is directly proportional to the field intensity H . The magnetic field does not affect the bands of the second and third transitions. This indicates that the $2^3\Sigma_g^-$ ground state is not split in a magnetic field as one should expect if α -oxygen is antiferromagnetic.

INTRODUCTION

THE general features of the spectrum of solid oxygen can be considered as having been interpreted. The absorption bands common to all the states of condensed oxygen are located in the region of 12,600–3000 Å. Of these the "single" optical $^3\Sigma_g^- \rightarrow ^1\Delta_g$ and $^3\Sigma_g^- \rightarrow ^1\Sigma_g^+$ transitions occur in the red and near infrared region, whereas the "double" transitions whose frequencies are linear combinations of the "single"-transition frequencies occur in the visible and near ultraviolet region.^[1-4] However, it is still not possible to interpret uniquely the fine features of the optical absorption spectrum of solid oxygen, particularly those of its antiferromagnetic α modification. Moreover, the interaction mechanism between the molecules causing the appreciable intensity of the "double" bimolecular transitions is so far not clear.

Mashkevich^[5] has proposed that the exchange interaction which lifts the intercombinational forbiddenness is such a mechanism. His estimates of the intensities agree with those observed experimentally. In this work we have made an attempt to check Mashkevich's assumptions by investigating the oxygen spectrum in a strong magnetic field. We studied experimentally the effect of a magnetic field on the absorption bands of α -oxygen belonging to the "double" transitions

$$2^3\Sigma_g^- \rightarrow 2^1\Delta_g, \quad 2^3\Sigma_g^- \rightarrow ^1\Delta_g + ^1\Sigma_g^+, \quad 2^3\Sigma_g^- \rightarrow 2^1\Sigma_g^+, \quad (1)$$

located in the 5760–5315, 4460–4200, and 3600–3430 Å regions respectively.

EXPERIMENTAL PROCEDURE

The investigation was carried out on a high-luminosity STE-1 spectrograph and on high-resolution DFS-13 spectrograph. Magnetic fields with intensities up to 170 kOe were obtained by a pulse technique. The method of the magneto-optic investigations in pulsed magnetic fields and at low temperatures was close to that described previously in^[6].

A special cryostat shown schematically in Fig. 1 was employed to obtain thin films of polycrystalline α -oxygen. Gaseous oxygen was injected into the vacuum

jacket of the cryostat along a previously evacuated pipe through a movable spur 7 mounted in the bellows 8. The oxygen stream fell upon the helium-cooled quartz substrate 5, and condensed on it in the form of a thin, matte film 6. The quartz substrate and consequently also the oxygen sample were located inside a pulse solenoid 4. The rate of oxygen condensation was regulated by means of a needle valve placed between the pipe and the spur. The thickness of the condensed layer was determined by the rate and time of condensation. After completion of the condensation the movable spur was withdrawn from the optical path. In order to relax strains, the sample was annealed for 10–15 minutes at a temperature of 35–40°K. The investigated samples were about 0.3 mm thick. Only intense, comparatively narrow bands without weak satellites that would complicate the spectrum in a magnetic field are observed in the light absorption spectra of samples of such thickness at 4.2°K.

EXPERIMENTAL RESULTS

The direction of the magnetic field always coincided with the direction of propagation of the light, i.e., we were investigating the longitudinal Zeeman effect. We investigated the strongest electron-vibrational (0–1,

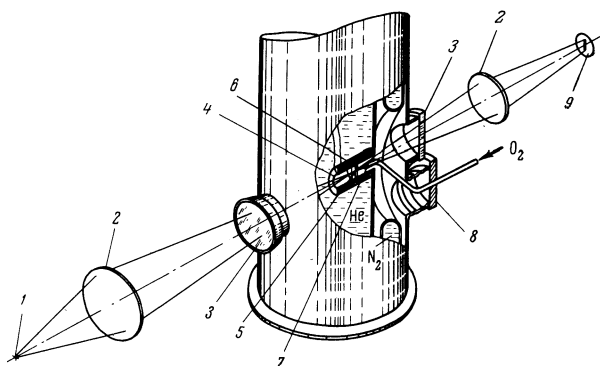


FIG. 1. Schematic diagram of the experimental setup: 1 – pulsed light source, 2 – lenses, 3 – quartz glass windows, 4 – pulse solenoid, 5 – quartz substrate, 6 – sample, 7 – spur, 8 – sylphon, 9 – spectrograph slit.

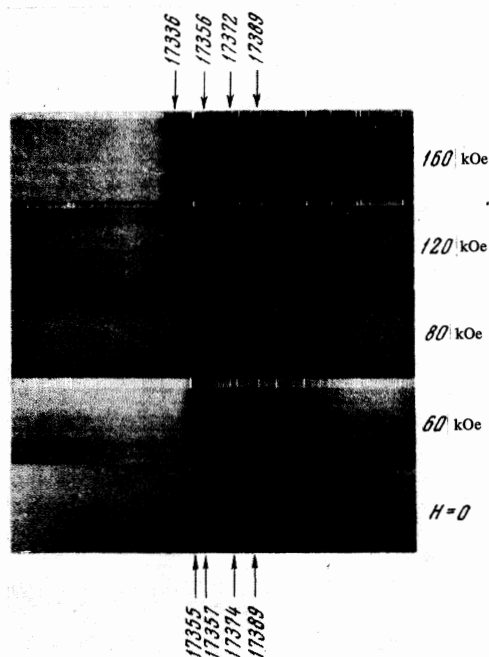


FIG. 2. Record of a section of the absorption spectrum of α -oxygen in the region of the 0-1 band of the $2^3\Sigma_g^- \rightarrow 2^1\Delta_g$ transition in various magnetic fields; $T = 4.2^\circ\text{K}$.

0-2) bands of the "double" transitions (1). The purely electron (0-0) bands of these series are rather broad, which rendered the investigation of the effect of a magnetic field upon them difficult and did not yield clear results.

Figures 2-4 show the spectrograms and microphotometer curves which illustrate the effect of a magnetic field on the electron-vibrational 0-1 ($\nu_0' = 17,356\text{ cm}^{-1}$) and 0-2 ($\nu_0'' = 18,811\text{ cm}^{-1}$) bands of the $2^3\Sigma_g^- \rightarrow 2^1\Delta_g$ transition. The behavior of these bands in a magnetic field is identical. Each is split by the magnetic field into a triplet. The shift of the long-wavelength component of the Zeeman triplet is directly proportional to magnetic field intensity ($\nu_1 = \nu_0 - \alpha H$, $\alpha = 12.2 \times 10^{-5}\text{ cm}^{-1}\text{ Oe}^{-1}$). Within experimental accuracy the central component does not shift with increasing field. The short-wavelength component is clearly observed only in a field $H = 120\text{ kOe}$. The dependence of its wavelength on the field cannot be investigated in detail, but one can state with confidence that it is not linear. This is apparently due to the proximity of the $17,356\text{ cm}^{-1}$ band to its short-wavelength $17,374\text{ cm}^{-1}$ satellite. In a field of 160 kOe this satellite becomes more intense and shifts towards longer wavelengths, this being obviously related to its coalescence with the short-wavelength Zeeman components of the $17,356\text{ cm}^{-1}$ band.

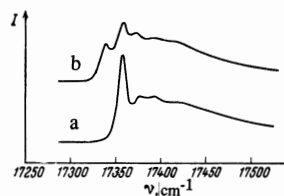


FIG. 3. Magnetic splitting of the 0-1 band of the $2^3\Sigma_g^- \rightarrow 2^1\Delta_g$ transition in the spectrum of α -oxygen: a - $H = 0$, b - $H = 160\text{ kOe}$; $T = 4.2^\circ\text{K}$.

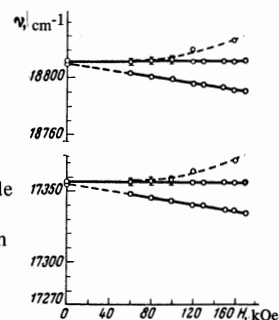


FIG. 4. Dependence of the magnitude of the magnetic splitting of the 0-1 and 0-2 bands of the $2^3\Sigma_g^- \rightarrow 2^1\Delta_g$ transition on the magnetic field intensity.

At magnetic field intensities smaller than 60 kOe the splitting could not be resolved on account of the appreciable widths of the bands at $T = 4.2^\circ\text{K}$, but a broadening of the $17,356$ and $18,811\text{ cm}^{-1}$ bands was observed which depended linearly on the field intensity. It is also interesting to note that the $17,356\text{ cm}^{-1}$ band is at 4.2°K even in the absence of an external field a close, poorly resolved doublet ($\Delta\nu \approx 2\text{ cm}^{-1}$).

None of the bands of the $2^3\Sigma_g^- \rightarrow 1^1\Delta_g + 1^1\Sigma_g^+$ and $2^3\Sigma_g^- \rightarrow 2^1\Sigma_g^+$ transitions exhibits splitting or appreciable broadening in magnetic fields up to 170 kOe . At the same time, the electron-vibrational 0-1 and 0-2 bands of these transitions are no broader than the corresponding bands of the $2^3\Sigma_g^- \rightarrow 2^1\Delta_g$ transition for which the splitting in a magnetic field has been described above.

Finally, it should be noted that the observed splitting of the 0-1 and 0-2 bands of the $2^3\Sigma_g^- \rightarrow 2^1\Delta_g$ transition is sensitive to the structure of the sample. Samples annealed at 40°K for at least 10 minutes exhibit large splitting illustrated in Figs. 2 and 3. Freshly deposited samples exhibit a considerably smaller splitting which retains however a linear dependence on the magnetic field intensity. Spectra of annealed and unannealed samples in a magnetic field $H = 120\text{ kOe}$ are compared in Fig. 5.

DISCUSSION OF RESULTS

Proceeding to the discussion, we estimate first of all how large the attained intensity of the magnetic field H is compared with the intensity of the effective

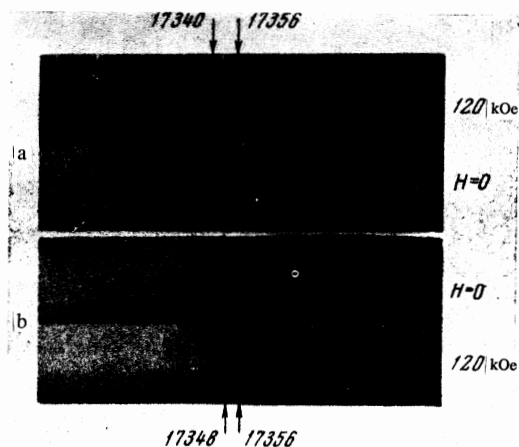


FIG. 5. Comparison of the effect of a magnetic field on the absorption spectra of annealed (a) and unannealed (b) samples of α -oxygen; $T = 4.2^\circ\text{K}$.

field of the exchange interaction in antiferromagnetic α -oxygen.^[7-9] The temperature of the transition from the β phase which has only short-range magnetic order^[9] to the antiferromagnetic α phase is 23.8°K. However, this transition is also accompanied by a change in the crystallographic structure.^[10, 11] Therefore for the crystal structure of the α modification the antiferromagnetic ordering could also be retained above 23.8°K ($T_N \geq T_{\alpha\beta}$). Thus from the temperature of the α - β transition one can only estimate the lower limit of the intensity of the exchange field:

$$H_E = \frac{3kT_N}{g\mu_B(S+1)} \geq \frac{3kT_{\alpha\beta}}{g\mu_B(S+1)}, \quad H_E \geq 2.7 \cdot 10^5 \text{ Oe.} \quad (2)$$

A more accurate estimate of H_E can be obtained by using the experimental data on χ_{\perp} . True, in^[7, 12] the measurements were of the magnetic susceptibility of a powder $\chi_p = (\chi_{\parallel} + 2\chi_{\perp})/3$, but since in the 4–15°K temperature range χ_p practically did not change, one may assume that here $\chi_{\parallel} \ll \chi_{\perp}$ and $\chi_{\perp} = \frac{3}{2}\chi_p$. Thus,

$$H_E = M_0/\chi_{\perp} = \frac{2}{3}M_0/\chi_p \quad (3)$$

where M_0 is the saturation magnetization. Such an estimate yields $H_E = 3 \times 10^6$ Oe which corresponds to $T_N \approx 250^\circ\text{K}$.

The latter estimate indicates that the external field intensity attained is still far from the value of the effective field of the exchange interaction ($H \ll H_E$). Therefore the absence of appreciable effect of the external field H on the intensity of "double" transitions in the spectrum of α -oxygen is still no indication that the exchange interaction can be excluded as the mechanism inducing these transitions. Moreover, a comparison of the effect of the magnetic field on the bands of the three different "double" transitions (1) attests to the fact that the exchange interaction of the molecules in antiferromagnetic α -oxygen determines to a large extent the observed peculiarities.

This is simplest to illustrate by using as an example the $2^3\Sigma_g^- \rightarrow 2^1\Sigma_g^+$ transition, since the $2^1\Sigma_g^+$ excited state cannot be split (both the spin and the orbital angular momentum are zero). A splitting of the bands of this transition could occur because of the removal of the degeneracy in the spin of the ground state $2^3\Sigma_g^-$ in the magnetic field, and its value in a field $H = 170$ kOe would approximately be 16 cm^{-1} . Since in reality the bands of the $2^3\Sigma_g^- \rightarrow 2^1\Sigma_g^+$ transition do not split, it must be assumed that the two molecules participating in the "double" transition are nearest neighbors and belong to different magnetic sublattices. The total spin of such a pair is zero ($S_p = 0$) and as long as $H < H_E$ there should be no splitting of the bands of the transition under consideration. Consequently the absence of Zeeman splitting (or at least of a shift) of the bands of the $2^3\Sigma_g^- \rightarrow 2^1\Sigma_g^+$ transition in the spectrum of α -oxygen is in agreement with the assumption that it is antiferromagnetic.

Since the ground state $2^3\Sigma_g^-$ is common to all the investigated transitions and since, as the behavior of the $2^3\Sigma_g^- \rightarrow 2^1\Sigma_g^+$ transition indicates, it is not split, it follows that the magnetic splitting of the 0–1 and 0–2 bands of the $2^3\Sigma_g^- \rightarrow 2^1\Delta_g$ transition is apparently due to the orbital angular momentum of the excited state. However, a detailed interpretation of the ob-

served phenomenon is difficult. The splitting into a triplet is not surprising if one considers only transitions with $\Delta m_J = \pm 1, 0$. But the magnitude of the splitting (between the central and long-wave components, $\Delta\nu = 12.2 \times 10^{-5} \text{ cm}^{-1} \text{ Oe}^{-1}$) is unusually large. The sensitivity of the magnetic splitting of the light absorption bands to the structure of the sample is not trivial. The absence of splitting of the bands of the $2^3\Sigma_g^- \rightarrow 2^1\Delta_g + 2^1\Sigma_g^+$ transition which is sufficiently narrow for it to be observed is also altogether not obvious.

If the excited $\{2^1\Delta_g + 2^1\Sigma_g^+\}$ state were simply a superposition of the $2^1\Delta_g$ and $2^1\Sigma_g^+$ states, then one should expect splitting of the bands of this transition in a magnetic field. In one of the molecules in the excited state the orbital angular momentum is not zero, and the magnetic splitting of the bands of the $2^3\Sigma_g^- \rightarrow 2^1\Delta_g + 2^1\Sigma_g^+$ transition should only be smaller by a factor of 2 than in the bands of the $2^3\Sigma_g^- \rightarrow 2^1\Delta_g$ transition. But as has been noted above, the bands of the first transition are altogether not split in a magnetic field. This means that the "bimolecular" excited states must not be represented as a simple superposition of "monomolecular" states: the interaction of the molecules is large not only in the ground but also in the excited states. The results of the investigation of the temperature dependence of the intensity of "double" transitions^[13] indicate that the intermolecular interaction for different combinations of excited "monomolecular" states— $\{2^1\Sigma_g^+ + 2^1\Sigma_g^+\}$, $\{2^1\Delta_g + 2^1\Delta_g\}$, $\{2^1\Sigma_g^+ + 2^1\Delta_g\}$ —is different.

The sensitivity of the magnetic splitting to the structure of the sample can be understood if this splitting is partly due to magnetostriction which can be appreciable for an antiferromagnetic molecular crystal such as α -oxygen.

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