PHYSICAL REVIEW VOLUME 121, NUMBER 2 JANUARY 15, 1961

Optical Absorption of Cuprous Oxide*

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(Received July 19, 1960)

The relative optical absorption coefficient α of polycrystalline slabs of cuprous oxide was measured at 295°K, 77°K, and 4.2°K. At 4.2°K, α is proportional to $[\sigma - E_0]^{\frac{1}{2}}$ for $16\,510\ \mathrm{cm}^{-1} \leqslant \sigma \leqslant 16\,900\ \mathrm{cm}^{-1}$, where σ is the wave number. At 77°K an additional component appears, so that $\alpha = \alpha_1 + \alpha_2$, with $\alpha_1 \propto [\sigma - E_1]^{\frac{1}{2}}$ and $\alpha_2 \propto [\sigma - E_2]^{\frac{1}{2}}$. This is attributed to indirect transitions to exciton levels, in agreement with a theory by Elliott. The ratio of the integrated absorption coefficient of the first two exciton lines, after corrections for the background were applied, is also in satisfactory agreement with the Elliott theory.

INTRODUCTION

NEARLY a decade ago Hayashi[1,2] observed a series of hydrogen-like lines in the absorption spectrum of solid cuprous oxide which was cooled below room temperature. Subsequently investigators in Leningrad[3–5] and Strasbourg[6–10] made more accurate measurements of the wavelengths of these lines over a wide range of temperatures. The Russian group also observed the shift in energy and splittings of the absorption lines caused by magnetic and electric fields. A comprehensive review of the Russian work is found in reference 5. A summary of the work of Nikitine and his coworkers is given in reference 10.

It was not until recently, however, that serious attempts were made to measure the optical absorption coefficient as a function of photon energy. Data on the energy dependence of the optical absorption coefficient is quite useful. For example, it can indicate whether the optical absorption can be attributed to direct or indirect transitions and thus furnish useful information about the energy band structure of the crystal.[11–13] A theory has been proposed by Elliott[14] which gives the intensity of the exciton absorption lines which should apply to a semiconductor like cuprous oxide. Measurements of the relative intensity of the exciton lines could furnish a check on this theory. The present work was undertaken to measure the energy dependence of the optical absorption coefficient of cuprous oxide.

EXPERIMENTAL PROCEDURE

The apparatus which was used to measure the optical absorption is shown in Fig. 1. The sample was illuminated by a ribbon-filament lamp and was imaged on the entrance slit of a recording spectrophotometer, which was a three-meter concave grating in an Eagle mounting. Continuous photoelectric recording of the light intensity was made with a 1P-21 photomultiplier tube which was located behind a pair of adjustable slits and could move on a track along the Rowland circle. The slits were usually set so that the spectral bandwidth of the instrument was about one angstrom. In order to measure the absolute absorption coefficient, it is necessary to measure the intensity with the sample both in and out of the beam. Due to astigmatism of the concave diffraction grating, the light flux collected by the photomultiplier depends upon the way the slit is illuminated. It was never certain that the entrance slit was illuminated in the same way with the sample in and out of the beam and hence only the relative absorption coefficient could be measured with any degree of confidence.

The Dewar which held the refrigerated sample was the usual "double Dewar" design and had a glass bottom

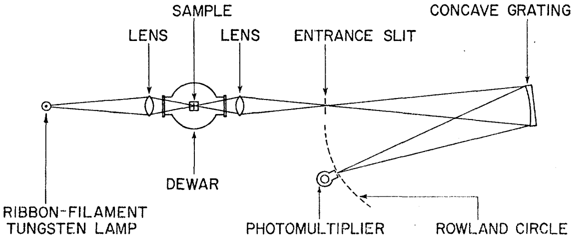

FIG. 1. Apparatus which was used to measure the relative absorption coefficients.

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[*] This work was supported in part by a grant from the National Science Foundation.

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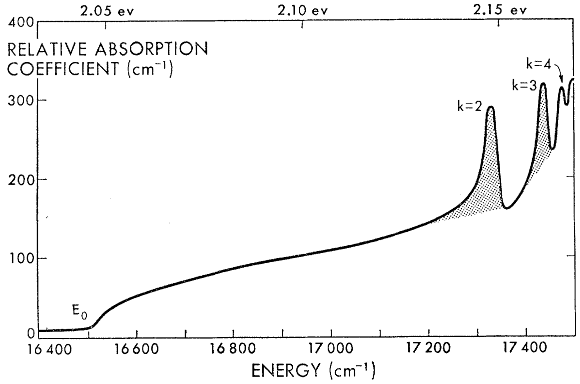

FIG. 2. Relative absorption coefficient as a function of photon energy in cm^{-1} of Cu_2O at 4.2°K.

so that the optical transmission of the sample could be measured while the sample itself was immersed directly either in liquid nitrogen or liquid helium. This meant that the sample was definitely at the temperature of the surrounding liquid and also that it was possible to measure the transmission of unbacked samples. Other workers have found that samples which are cemented to a substrate are strained when they cool. These strains distort the crystal lattice and thus influence the optical absorption spectrum.[15]

Walter H. Brattain of Bell Telephone Laboratories supplied the samples of cuprous oxide, which were polycrystalline slabs about 0.5 mm thick. They were prepared by oxidizing strips of high-purity copper.[16,17] and showed p-type conductivity with a specific resistivity of about 10 ohm-cm. The slabs were quite opaque and had to be ground to a thickness of less than 150 microns before they became appreciably transparent. This grinding damages the crystal lattice near the surface, but should have little effect on the optical transmission, which is largely determined by the bulk material. There is always a question what other impurities, such as CuO, Cu, etc., are present in such samples. A powder x-ray analysis which was made of one of these cuprous oxide samples merely showed that the crystals were strongly preferentially oriented. A powder x-ray analysis could be made of a sample which has been ground up, but the results would be questionable because the grinding process often changes the stoichiometry of the sample.

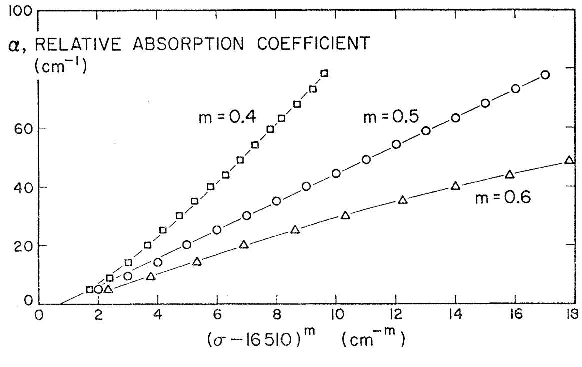

FIG. 3. The data of Fig. 2 plotted as a function of $(\sigma-E_0)^m$ on the abscissa for various values of the exponent m.

The relative absorption coefficient was computed from the logarithm of the transmission. This procedure is valid provided that the sample is quite opaque and the reflectivity is constant with wavelength. The reflectivity of optically polished samples of cuprous oxide was measured at room temperature and it was found that it changed only 2% in the region from 5600 to 6600 A.

RESULTS

Relative Absorption Coefficients in the Region of Continuous Absorption

The relative absorption coefficient as a function of photon energy is shown in Figs. 2, 4, and 5. These data were all obtained from an unbacked Cu_2O slab which was 0.0042 ± 0.0002 in. thick.

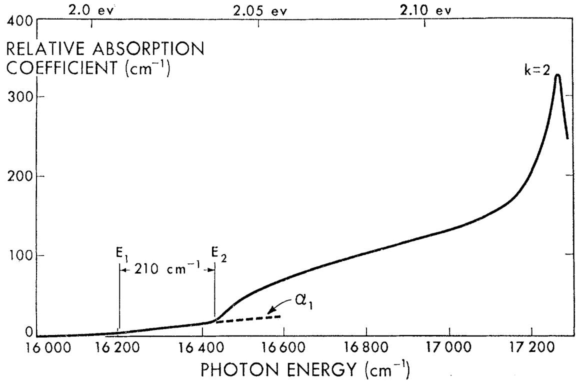

FIG. 4. Relative absorption coefficient as a function of photon energy in cm^{-1} of Cu_2O at 77°K. The dashed line is an extension of the absorption component α_1.

The relative absorption coefficient α at 4.2°K as a function of wave number is shown in Fig. 2. The relative absorption coefficient was constant from 16 100 cm^{-1} to 16 400 cm^{-1}. It was assumed that in this region the absorption coefficient was zero and that the opacity of the sample was due to scattering and reflection from the surfaces. The scale of the ordinate was determined from the thickness of the sample. From Fig. 2, it is seen that at 16 510 cm^{-1} the absorption rises as $\epsilon^{\frac{1}{2}}$, where $\epsilon=h\nu-E_0$. This $\epsilon^{\frac{1}{2}}$ dependence is better shown in Fig. 3, which depicts the relative absorption coefficient as a function of ϵ^m. It is seen that the experimental points lie on a fairly good straight line for $m=0.5$. The plots for $m=0.4$ and $m=0.6$ show some curvature and certainly do not fit a straight line as well as the $m=0.5$ plot. This gives an indication of the precision with which the exponent m can be determined from the experimental data.

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In the region starting at 16 900 cm^{-1} the absorption increases more rapidly due to the long "tail" of the $K=2$ excitation line. Finally, in the region starting at 17 300 cm^{-1} the absorption is due to a series of excitation lines superimposed in a background which is also rapidly rising.

The absorption at 77°K is shown in Fig. 4. The absorption was nearly constant for energies less than 16 000 cm^{-1}; this was taken as the reference point for the relative absorption coefficient. The absorption rises slowly at E_1 as $\alpha_1 \propto \epsilon_1^{\frac{1}{2}}$, where $\epsilon_1 = h\nu - E_1$. The absorption rises more rapidly at E_2; the absorption for energies greater than E_2 can be expressed as $\alpha = \alpha_1 + \alpha_2$, where $\alpha_2 = \epsilon_2^{\frac{1}{2}}$ and $\epsilon_2 = h\nu - E_2$. The component α_2 may be attributed to a transition involving the emission of a phonon and α_1 to the absorption of a phonon. The extrapolation of α_1 is shown as a dashed line in Fig. 4.

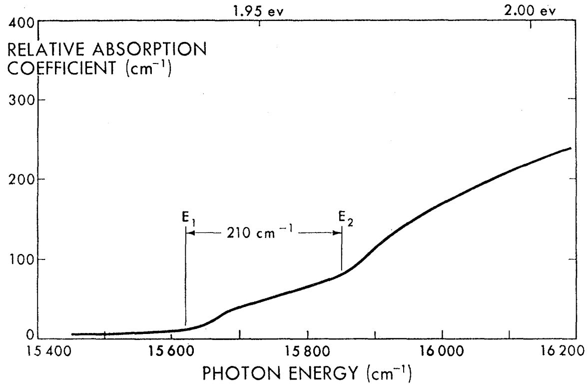

FIG. 5. Relative absorption coefficient as a function of photon energy in cm^{-1} of Cu$_2$O at 295°K.

The relative amplitudes of the two contributions of the absorption at an absolute temperature T should be given by the Boltzmann factor,

$$\alpha_1(E_1+\delta E)/\alpha_2(E_2+\delta E) = \exp(-\theta/T), \qquad (1)$$

where δE is an energy increment and θ is the temperature of the phonon involved in the transition. From Eq. (1), θ was calculated to be 130°±10°K. The separation of the two "knees" should be twice the energy of the phonon: $E_2 - E_1 = 2k\theta$, where k is Boltzmann's constant. From the separation of 210 cm^{-1} from Fig. 4, θ is 150°K. There is, of course, some uncertainty as to where E_1 is actually located; this introduces an uncertainty of at least 10% into this result.

At room temperature (295°K) the same general features of the absorption curve are preserved, as is shown in Fig. 5. There are two "knees" in the absorption curve, at E_2 and at E_1, separated by 210 cm^{-1}. The absorption also rises as $\epsilon^{\frac{1}{2}}$. The knees of the curve no longer rise abruptly as they did at 4.2°K, indicating that more than one phonon is emitted or absorbed at higher temperatures, as one might expect. More information about the absorption at temperatures between 77°K and room temperature is necessary in order to interpret the behavior at room temperature. No exciton lines were seen at 295°K.

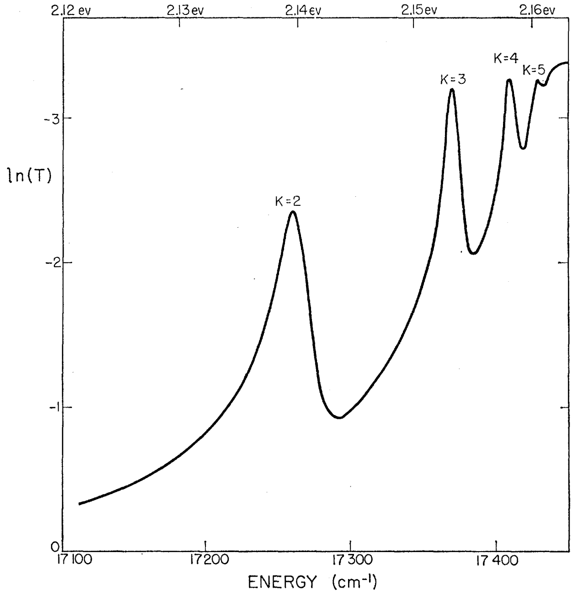

FIG. 6. The logarithm of the transmission as a function of photon energy of a Cu$_2$O sample at 77°K, showing the details of the yellow series of exciton lines.

Relative Intensity of the Exciton Lines

The exciton absorption lines at 4.2°K are shown in Fig. 2. Figure 4 shows the absorption edge at lower energies and one of the exciton absorption lines at 77°K, while Fig. 6 depicts the exciton lines at 77°K on an expanded ordinate scale which is proportional to the absorption coefficient. The exciton lines did not narrow appreciably as the temperature decreased from 77°K to 4.2°K.

From Figs. 2 and 6, it is seen that the $K=2$ line is broader than the others and has an asymetrical line shape showing a long tail extending toward lower energy. All of the lines are superimposed on a background due to other absorption processes which increases rapidly beyond the $K=2$ line. It is necessary to subtract off this background if the intensity ratios of the exciton lines are to be compared. The Elliott[14] theory gives the f value of the absorption lines, which is proportional to its area. The area of the lines cannot be simply determined from the widths at half intensity, due to their asymmetry.

The areas of the $K=2$ and $K=3$ lines, shown as a shaded region in Fig. 2, were integrated with a planimeter. The ratio of the areas of the lines is shown in Table I.

It should be emphasized that no high degree of accuracy is claimed for these results due to the uncertainty of estimating the background. However, the results are not in significant disagreement with the theoretical

TABLE I. Experimental and theoretical intensity ratios of exciton lines.

Experimentally observed area of the $K=3$ line, with the area of the $K=2$ normalized to one			Theoretical relative intensities from reference 14, normalized so $K=2$ line has intensity of 1.0	
Temperature				
77°K	4.2°K	K	Allowed transitions	Forbidden transitions
1.00	1.00	2	1.00	1.00
0.37	0.34	3	0.296	0.351

intensities for either allowed or forbidden transitions. The intensity for forbidden transitions is proportional to K^2-1, which means that the $K=1$ is missing. The fact that the $K=1$ line was not observed along with the data in Table I favors forbidden transitions.

One line at 5493 A of the green exciton series was observed in the 0.004-in. thick sample at 77°K. This presumably is the $K=2$ line which Gross observed at 5496 A. The spectrum of much thinner samples failed to show any more lines in the green series.

DISCUSSION

The results at 4.2°K indicate that the absorption initially rises at $\epsilon^{\frac{1}{2}}$, which is in substantial agreement with the Elliott[14] theory which predicts this dependence for indirect transitions from the valence band to exciton levels for each phonon contribution. Direct band-to-band transitions would also show an $\epsilon^{\frac{1}{2}}$ dependence,[11] but the absorption coefficient would be much larger, thousands of cm^{-1}, instead of the few hundred cm^{-1} which was observed.

At higher temperatures, two "knees" in the absorption curve were observed which could be attributed to the emission and absorption of a phonon. The phonon temperature of 150°K is the more reliable of the two values which were calculated by different means. At room temperature, the detailed shape of the absorption curve was found to be more complicated and it was not possible to interpret the shape of the absorption curve on the basis of a simple model of the absorption and emission on a single phonon. This is not surprising, inasmuch as more than one type of phonon must be excited at higher temperatures. Even the most simple model of a solid would predict that both optical and acoustical phonons are present.

Gross and Pastrnyak[18,19] have recently measured the optical absorption coefficient in the temperature range of 77°K to 295°K. They also found an $\epsilon^{\frac{1}{2}}$ energy dependence for the absorption coefficient and two "steps" in the absorption separated by 220 cm^{-1} at room temperature, which is in reasonable agreement with the results of this paper. However, Gross found that the steps varied with temperature as n^{-2} and n^{-1}, where $n=\exp(\theta/T)-1$. In the present investigation it was found that the ratio of the absorption of the two steps was proportional to $\exp(\theta/T)$, rather than $\exp(\theta/T)-1$ as Gross found. The difference is that Gross's results predict that at absolute zero both absorption components vanish, because n vanishes. The absorption data at 4.2°K, depicted in Fig. 2, indicate very definitely that the higher energy component does not go to zero and thus is in disagreement with Gross's results.

The results of this investigation also differ from the results of other workers in two other respects. The $K=1$ line of the yellow series was not observed and the width of the absorption lines did not narrow appreciably at liquid helium temperatures so that the higher members of the yellow exciton series with $K=5, 6, \cdots$ could not be observed. Other investigators have also failed to see the absorption lines which Nikitine[9] reported observing in the red. The fact that the exciton lines did not narrow appreciably between 77°K and 4.2°K indicates that the residual linewidth can be attributed to strains in the crystal lattice which could be removed by proper annealing.

It has been tacitly assumed in this discussion that the hydrogen-like series of lines could be attributed to direct transitions from the valence band to exciton levels, rather than to impurity levels. The fact that these absorption lines have been observed in cuprous oxide samples of varying composition which have been prepared by a variety of different methods is strong, though not conclusive, evidence that they are an intrinsic property of the crystal itself.

Various workers have shown that the electrical and optical properties can vary widely depending upon the temperature and partial pressure of the oxygen during the oxidation of copper to Cu_2O which in turn influence the density of copper and oxygen vacancies in the lattice.[20] Whether the method of preparation of Cu_2O influences the intensity and width of the exciton lines could well be the subject of another investigation.

ACKNOWLEDGMENTS

The author appreciates the helpful counsel of Professor C. Kittel and Professor F. A. Jenkins. M. Rao at the University of Rochester measured the reflectivity. The author is indebted to Dr. A. F. Turner of Bausch & Lomb Optical Company for the use of an x-ray machine to perform the powder analysis. Dr. W. H. Brattain of Bell Telephone Laboratories generously supplied the cuprous oxide.

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