

Far-Infrared Properties of Cuprous Oxide

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The transmission and reflectance of cuprous oxide has been measured from 6 to 250 μ and analyzed by classical dispersion theory. The two infrared-active vibrational frequencies are given by $\nu_1=613$ cm^{-1} and $\nu_2=146.0$ cm^{-1} with corresponding longitudinal-mode frequencies of 638 and 149 cm^{-1} . The maximum values of the extinction coefficient are calculated to be 2.7 and 4.0, respectively, for the two modes; both are higher than the literature values. The high-frequency and static dielectric constants are found to be $\epsilon_\infty=6.6$ and $\epsilon_0=7.6$, respectively.

INTRODUCTION

CUPROUS oxide has a cubic symmetry known as the cuprite structure. Elliott¹ and Huang² have shown there should be two isotropic, infrared-active, lattice-vibrational modes. Absorption measurements by Pasterniak³ and by Bouster *et al.*⁴ have enabled the latter to specify all of the observed bands and in particular the two infrared-active modes as $\nu_1=610$ cm^{-1} (16.4 μ) and $\nu_2=147$ cm^{-1} (68 μ). O'Keefe⁵ has measured the reflectivity of single crystals of Cu_2O in the region of ν_1 ; his results are included in the discussion below. The present work is an extension of these measurements to obtain a description of the second vibrational mode at $\nu_2=147$ cm^{-1} .

EXPERIMENTAL DETAILS

The polycrystalline samples used in these experiments were prepared by oxidizing and then annealing copper sheets⁶ which were subsequently ground and mechanically polished. Transmission and spectral-reflectance measurements were made on two of the samples at room temperature with a Perkin Elmer Model 301 spectrophotometer in double beam mode from 6 to 250 μ . These samples had areas of approximately 3.5 and 1.7 cm^2 with average thicknesses of 0.085 and 0.025 cm, respectively. Neither sample had perfectly flat parallel faces and the thicknesses varied by about 6 and 10%, respectively, from the above values. When the samples were etched in HNO_3 solutions they showed single-crystal grains of 1 to 10 mm^2 . There was no appreciable difference in reflectance spectra taken before and after a slight etch, although stronger etching reduced the reflectance, presumably because of preferential etching at grain boundaries which roughened the surface.

The reflectance measurements were made at an incident angle of 9° and compared to the reflectance of an aluminum-coated mirror which was taken to be 99%

reflecting.^{7,8} The surface reflectivity R_0 and absorption coefficient α were determined from the relations⁹

$$T = (1 - R_0)^2 e^{-\alpha d} / (1 - R_0^2 e^{-2\alpha d}) \quad (1)$$

and

$$R = [R_0 + R_0(1 - 2R_0)e^{-2\alpha d}] / (1 - R_0^2 e^{-2\alpha d}), \quad (2)$$

where T and R are the measured transmission and reflectance, and d is the thickness of the sample. R_0 and α are related to the optical constants by

$$R_0 = [(n-1)^2 + k^2] / [(n+1)^2 + k^2] \quad (3)$$

and

$$\alpha = 4\pi k / \lambda, \quad (4)$$

where n and k are the real and imaginary parts of the index of refraction (k is also called the extinction coefficient). The dielectric constant is also related to the above by

$$\epsilon = (n + ik)^2. \quad (5)$$

Interference effects were not observed in these measurements, and in view of the nonuniformity of d as noted above, would not be expected except perhaps at the longest wavelengths for the thinner sample. Because of the relatively thick samples used, the absorption coefficient could not be determined from Eqs. (1) and (2) in regions of strong absorption where the transmission became too small.

DISPERSION THEORY

The classical oscillator dispersion theory has been presented by several authors^{10,11} and will not be reproduced here. The result is an expression for the dielectric constant

$$\epsilon = \epsilon_\infty + \sum_j S_j \omega_j^2 / (\omega_j^2 - \omega^2 - i\omega\gamma_j) \quad (6)$$

in terms of a strength S_j , frequency ω_j , and damping constant γ_j of the j th mode, and the high-frequency

⁷ P. W. Kruse, L. D. McGlauchlin, and R. B. McQuistan, *Elements of Infrared Technology* (John Wiley & Sons, Inc., New York, 1962), p. 122.

⁸ Several mirrors were also compared with each other and no difference in their reflectivities could be detected.

⁹ These relations can be readily obtained by ray tracing or by solving the appropriate boundary-value problem and eliminating interference effects. See, e.g., Ref. 10, p. 124.

¹⁰ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954), Chap. II.

¹¹ A. S. Barker, Jr., *Phys. Rev.* **136**, A1290 (1964).

¹ R. J. Elliott, *Phys. Rev.* **124**, 340 (1961).

² K. Huang, *Z. Physik* **171**, 213 (1963).

³ I. Pasterniak, *Opt. Spectry.* **6**, 64 (1959).

⁴ C. Bouster, J. Claudel, X. Gerbaux, and A. Hadni, *Ann. Phys. (Paris)* **8**, 299 (1963).

⁵ M. O'Keefe, *J. Chem. Phys.* **39**, 1789 (1963).

⁶ R. S. Toth, R. Kilkson, and D. Trivich, *J. Appl. Phys.* **31**, 1117 (1960).

dielectric constant ϵ_∞ (i.e., at frequencies high compared to the lattice vibrational modes but below the frequencies of electronic motion). The sum in Eq. (6) extends over all of the infrared active modes of the lattice (i.e., $j=1, 2$ for Cu_2O). The static dielectric constant is found by setting $\omega=0$ in Eq. (6),

$$\epsilon_0 = \epsilon_\infty + \sum_j S_j. \quad (7)$$

For a given set of dispersion parameters, one can calculate R_0 from Eqs. (3), (5), and (6) with the aid of a computer. The best choice of parameters is found by comparing R_0 with the measured values and adjusting the parameters until the best fit is obtained.

RESULTS AND DISCUSSION

O'Keeffe⁵ has performed this analysis for the ν_1 mode of cuprous oxide. Our results are in reasonably good agreement with his and only the parameters of the calculation are reproduced here. Table I lists these parameters together with O'Keeffe's for comparison. Our value of the high frequency dielectric constant, $\epsilon_\infty=6.6$, is determined from the high-frequency side of the reflectivity spectrum where $R_0=0.195\pm 0.010$. From Eqs. (3) and (5) (with $k=0$) one can see that an error of 0.01 in R_0 shows up as an error of 5% in ϵ . O'Keeffe's value, $\epsilon_\infty=6.46$, was determined from interference fringes in the transmission of thin films and is probably more reliable.

Frequencies are known in general to better than 1% and have been checked by measuring known water vapor absorption lines.^{12,13} The quoted uncertainties in the other parameters are the minimum deviations which produced a noticeably poorer fit to the data. Since they do not include experimental errors (which are difficult to determine) and since these parameters are interdependent, not too much significance can be attached to the uncertainties.

Figure 1 shows the measured and calculated values of R_0 for the ν_2 mode. The solid and dashed curves are obtained from the measurements on the two samples and serve as an indication of the uncertainty in the

TABLE I. Dispersion Parameters of Cu_2O .

	O'Keeffe ν_1 mode	Present work	
		ν_1 mode	ν_2 mode
Frequency ν_j (cm^{-1})	609	613 ± 3	146.0 ± 0.7
Wavelength λ_j (μ)	16.4	16.3	68.5
Strength S_j	0.65 ± 0.03	0.70 ± 0.05	0.30 ± 0.03
Damping constant γ_j (cm^{-1})	15	21 ± 3	1.3 ± 0.2
(Dielectric constants)			
ϵ_∞	6.46 ± 0.10	6.6 ± 0.4	7.6 ± 0.4
ϵ_0			

¹² H. Szymanski, *Theory and Practice of Infrared Spectroscopy* (Plenum Press, Inc., New York, 1964), p. 54.

¹³ R. Narahari Rao, R. V. de Vore, and E. K. Plyler, J. Res. Natl. Bur. Std., Phys. and Chem. **67A**, 351 (1963).

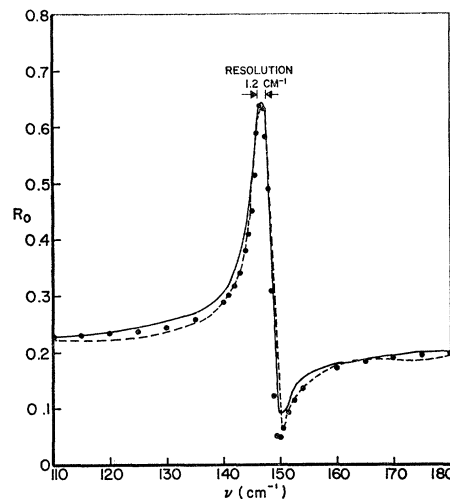


FIG. 1. Reflectivity of cuprous oxide in the region of $\nu_2=146.0$ cm^{-1} . The measured values for two samples are given by the solid and dashed curves while the circles represent values calculated from classical dispersion theory.

data. The reflectivity values on the long-wavelength side are estimated to be accurate to ± 0.015 , so that there is no significant difference between the two curves. Since the resolution is comparable to the bandwidth, the height of the band is somewhat more in doubt. The circles are values calculated from Eqs. (3), (5), and (6) with the parameters listed in Table I. The uncertainties in these parameters are found in the same way as noted above.

Our value for the dispersion frequency, $\nu_2=146$ cm^{-1} , compares favorably with the value given by Bouster *et al.*,⁴ $\nu_2=147$ cm^{-1} , from the position of the maximum absorption. As has been pointed out by several authors,¹⁴ the dispersion frequency is given by the maximum of $nk\nu$ rather than the maximum value of k which occurs at a somewhat higher frequency. In the present case, this difference amounts to only about 0.5 cm^{-1} . From Eq. (7) we can now find $\epsilon_0=7.6$ which is identical to the value given by Frank,¹⁵ and close to the value given by Gross and Pastriak,¹⁶ $\epsilon_0=7.5$ (at $T=77^\circ\text{K}$). In view of the rather large uncertainty in ϵ_∞ , this agreement must be considered fortuitous. O'Keeffe's value for ϵ_0 is too low since it does not include the contribution from S_2 .

As shown by Barker,¹¹ the longitudinal mode frequencies can be obtained from the zeros of ϵ' , the real part of the dielectric constant. They are found to be $\nu_{l1}=638$ cm^{-1} and $\nu_{l2}=149$ cm^{-1} .

The extinction coefficient is shown in Fig. 2 as solid and dashed curves for the measured values and circles for the points calculated from Eqs. (5) and (6). The

¹⁴ T. S. Moss, *Optical Properties of Semiconductors* (Butterworths Scientific Publications Ltd., London, 1959), p. 16.

¹⁵ H. Frank, *Polovodice v teorii i praxi* (Státní Nakladatelství Technické Literatry, Prague, 1955), referred to in Ref. 16.

¹⁶ E. F. Gross and I. Pastriak, *Fiz. Tverd. Tela* **1**, 518 (1959) [English transl.: Soviet Phys.—Solid State **1**, 466 (1959)].

difference between the two measured curves is about as expected if transmission measurements are uncertain to 1% of full scale. As explained earlier, k could not be measured near the center of the band. The maximum calculated value of k is 4.0 (at $\nu=146.5 \text{ cm}^{-1}$) or $\alpha=7300 \text{ cm}^{-1}$ which is an order of magnitude bigger than the value given by Bouster *et al.* directly from absorption measurements on samples only as thin as 0.03 mm. In the case of the ν_1 mode, the maximum calculated absorption is $k=2.7$ or $\alpha=21000 \text{ cm}^{-1}$ which occurs at 617 cm^{-1} . This is also higher than the value given by Pastriak³ ($\alpha=10^3-10^4 \text{ cm}^{-1}$) from measurements on Cu_2O powder in a KBr pellet.

On either of the steep slopes of the band shown in Fig. 2, the measured values are lower than the calculated ones. The transmitted intensity in this region is approaching zero, so that inaccuracies of 1% (such as stray light) could almost account for the difference. A little farther to either side of the band, the measured

absorption is higher than that calculated, and well outside the experimental error. This is reasonable, however, because the theory only accounts for absorption from the fundamental lattice mode, and not from other mechanisms. Several very weak bands may be present on the short wavelength side of this lattice band at 163, 185, 197, and 211 cm^{-1} . These do not correspond to anything reported by Bouster *et al.* Another weak band, not known to have been reported previously, was observed at about 330 cm^{-1} (not shown in Fig. 2) which may well be a combination frequency between ν_2 and the Raman active mode⁸ at 182 cm^{-1} , i.e., $\nu=146+182=328 \text{ cm}^{-1}$. Other absorption maxima were also observed at shorter wavelengths, corresponding to those reported by Pastriak.

A Kramers-Kronig analysis¹⁷ of the reflectivity data was also attempted, but agreement with the present results could be obtained only for $k>1.0$. For smaller values of k , the agreement was extremely poor.

SUMMARY

We have shown that the infrared dispersion of cuprous oxide can be described by the classical theory with a single oscillator for each of the two infrared-active modes. The optical constants can be found by inserting the dispersion parameters into the appropriate formulas. These two bands were the only ones observed in the reflectivity spectrum, although others were observed in transmission. In particular, we observe a weak band near 330 cm^{-1} which is probably a combination frequency. A rough calculation of the integrated absorption of these bands indicates that they would not contribute appreciably to the dielectric constant. The maximum calculated absorption from either of the two fundamental lattice bands is higher than the published measured values.

ACKNOWLEDGMENTS

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¹⁷ See, e.g., W. G. Spitzer and D. A. Kleinman, *Phys. Rev.* **121**, 1324 (1961).

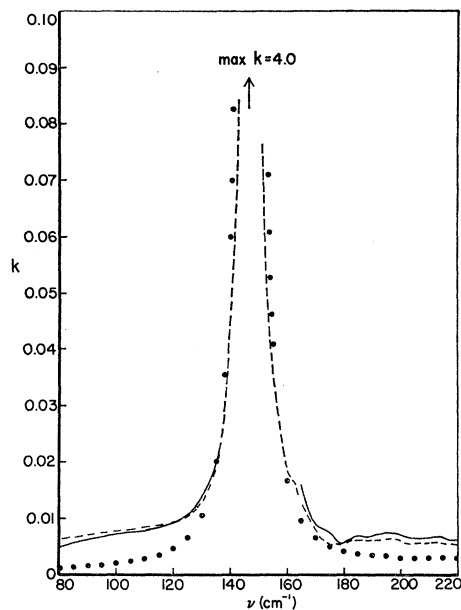


FIG. 2. The extinction coefficient of cuprous oxide in the region of $\nu_2=146.0 \text{ cm}^{-1}$. The measured values for two samples are given by the solid and dashed curves while the circles represent values calculated from classical dispersion theory. The maximum calculated value of k is 4.0 which occurs at 146.5 cm^{-1} .