order of reaction. Each of these requirements must be met by suitably planned sets of annealings or combinations of annealings over the whole of the temperature range to be investigated. The writer is not familiar with any investigation sufficiently detailed to meet these requirements. Since much of the complexity commonly results from the fact that the properties which are studied do not identify particular chemical species in particular environments (an analogy which could be taken in chemical kinetics would be the measurement of pressure in the pyrolysis of a gaseous mixture of organic compounds which was not simultaneously subjected to chemical analysis), it may be hoped that when suitable properties or combination of properties are studied much of the complexity of a particular system can be removed.

Exciton Absorption in Cuprous Oxide

J. H. Apfel, *Department of Physics, University of California, Berkeley, California*

AND

L. N. Hadley,* *Wilder Laboratory of Physics, Darmouth College, Hanover, New Hampshire, and Department of Physics, University of California, Berkeley, California*

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The exciton absorption spectrum of Cu_2O has been measured at low temperatures. As reported by Gross, the observed lines fit a hydrogen-like series formula. The wavelength shift of the position of the optical absorption band edge has also been measured as a function of temperature. The dependence is approximately quadratic.

INTRODUCTION

IN a series of papers, Gross and his collaborators[1] have reported on the exciton absorption in crystals of Cu_2O. This absorption appears as a series of lines near the main optical absorption edge which occurs in the red end of the visible region. The observation is made at low temperatures (77°K or lower) and with thin crystal slabs (of the order of 10 to 50 microns thickness). The observed lines may be empirically fitted to a hydrogen-like series formula with astonishing accuracy.

Wannier,[2] in 1937, postulated the existence of the corresponding energy levels, and proposed the following as a model. When an electron in an otherwise perfect dielectric crystal is raised to an excited state, it may be thought of as belonging to the crystal as a whole rather than to any particular atom. If its energy is insufficient to raise it to the conduction band, then it will remain within the Coulomb influence of the positive hole which it has left behind in the lattice. This electron-hole system may exist in stationary states, and will behave with respect to the remainder of the crystal as if embedded in a dielectric medium. The system is, however, free to migrate within the crystal.

The expected energy levels, measured from the ionization continuum (the conduction band), will be given by the Bohr expression:

$$W_k = -\mu e^4/4\pi\epsilon^2 k^2 c\hbar^3,$$

where $\mu = m_h^* m_e^*/(m_h^*+m_e^*)$, the reduced mass of the electron-hole system; ϵ is the dielectric constant of the dielectric material; k is the ordinal number of the level and takes on integral values. The other symbols have their usual meaning. The radii of the Bohr orbits will be given by

$$a = k^2\epsilon\hbar/\mu e^2.$$

These expressions for the energy and the radius differ from those obtained in the Bohr theory for atomic hydrogen only in that the value for the reduced mass is much different, and that a dielectric constant has been introduced into the force equation. It should be noted also that the "ground state" for this system is the recombined state in which the electron has collapsed into its hole. This occurs at an energy W_g (the width of the forbidden energy gap) below the conduction band. Consequently the series formula for the expected lines will be given by

$$\nu = W_g - W_k/k^2, \quad k = 1, 2, 3, \cdots.$$

EXPERIMENTAL

We have repeated the earlier measurements of Gross *et al.*, using the apparatus shown diagrammatically in Fig. 1. The spectrograph was a three-meter concave grating machine having a dispersion of roughly five angstroms per millimeter. The source was a tungsten filament. A water cell was placed between source and

* Now at Department of Physics, Colorado Agricultural and Mechanical College, Ft. Collins, Colorado.
[1] Ye. F. Gross and N. A. Karryev, Doklady Akad. Nauk S.S.S.R. 84, 261 (1952); 84, 471 (1952); Ye. F. Gross and B. P. Zakharchenya Doklady Akad. Nauk S.S.S.R. 90, 745 (1953); Gross, Zakharchenya, and Reinov, Doklady Akad Nauk S.S.S.R. 92, 265 (1953).
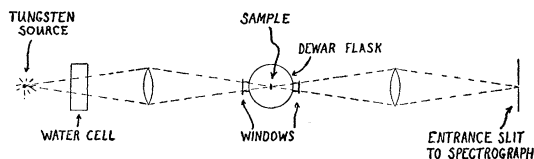[2] G. Wannier, Phys. Rev. 52, 191 (1937).

FIG. 1. Optical arrangement used to observe exciton absorption.

sample to remove extraneous heat radiation. The light passing through the sample was focused onto the slit of the spectrograph. The sample was placed within a metal Dewar flask with quartz windows. The cuprous oxide samples were prepared either by grinding or etching to a thickness of 10 to 50 microns from slabs which were originally approximately one millimeter thick.

Figure 2 shows a typical spectrum. The sample was etched in this case to a thickness of about 25 microns. The two mercury yellow lines ($\lambda = 5769.60$ and $\lambda = 5790.66$) are also shown for wavelength calibration and to give some notion of line widths of the exciton lines as compared to instrumental line widths. The lines of ordinal number $k = 2$, 3, 4, and 5 are clearly shown above the background noise. For wavelength measurements in this particular case, the mercury source was turned off while sweeping through the line $k = 2$, in order to avoid distortion of the line.

Several observations were made at temperatures of 4°K and 77°K. In addition, one run was made at a temperature of 2°K and one at 195°K. The position of the absorption edge at room temperature was observed in a small constant deviation spectroscope. For the 2°K run, both the positions and the line widths were not appreciably changed from their values at 4°K within the limit of our observations. At the temperature of 195°K, the only lines seen were those of ordinal number $k = 2$ and $k = 3$ which were barely distinguishable above noise. At room temperature, no structure which could be interpreted as line structure was observed.

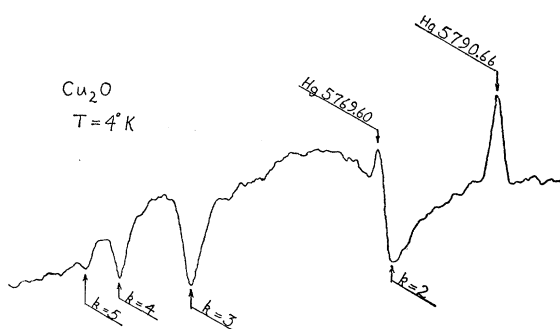Table I shows the results obtained at 77°K. Column (1) gives the ordinal number of the lines. Column (2)

FIG. 2. Spectrometer record of exciton series in Cu₂O at a temperature of 4°K. The lines whose ordinal numbers are $k = 2$, 3, 4, and 5 are shown. The two mercury yellow lines are shown in emission for the purposes of calibration and to indicate instrumental band width.

gives the average value of the measured wavelengths. Column (3) shows the corresponding wave numbers. Column (4) shows the wave numbers obtained from the formula

$$\nu = 17460 - 843/k^2,$$

in which the two constants have been adjusted to give the best fit for the lines $k = 3$, 4, and 5. The measured position of the line $k = 2$ thus deviates by about three angstroms from its computed value. Column (5) shows the corresponding wavelengths measured by the Russian group. It will be noticed that at this temperature our values are somewhat higher than theirs, while at 4°K (see Table II) our values are lower than theirs.

Table II shows the corresponding values at liquid helium temperature. These are best expressed by the following formula:

$$\nu = 17521 - 786/k^2.$$

TABLE I. $T = 77$°K. Ordinal number, wavelength, and frequency of the exciton absorption lines in Cu₂O. The last column quotes values obtained by Gross.

k	λ_{exp}	ν_{exp}	ν_{theor}	λ_{Russ}
2	5794.4	17258	17249	5792.7
3	5758.3	17366	17366	5756.6
4	5744.9	17407	17407	5743.8
5	5738.7	17426	17426	5738.1

TABLE II. $T = 4$°K. Otherwise same as Table I.

k	λ_{exp}	ν_{exp}	ν_{theor}	λ_{Russ}
2	5771.6	17326	17325	5775.8
3	5736.2	17433	17434	5740.2
4	5723.4	17472	17472	5727.4
5	5717.2	17491	17490	5721.7

Table III shows a further series of values obtained from a ground crystal whose thickness was not determined but was probably close to 10 microns. The temperature was not accurately determined in this case but was intermediate between the temperatures of liquid helium and nitrogen. This series is shown only to indicate the greater number of lines observed in this case. These are fitted by the formula:

$$\nu = 17508 - 800/k^2.$$

The position of the band edge (interpreted as the series limit of the above series) shifts approximately quadratically with absolute temperature as it does with germanium and silicon.[3] Figure 3 shows the experimental values obtained at the various temperatures. The solid curve is the empirical equation,

$$\lambda = 0.0034T^2 + 5707.4 \text{ (in angstrom units)}.$$

DISCUSSION

While the energy W_g is essentially a property of the crystal, the energy W_k may be thought of as a property

[3] G. G. Macfarlane and V. Roberts, Phys. Rev. **98**, 1865 (1955).

of the exciton within the crystal environment. The actual values of the reduced mass and of the dielectric constant are not well known, but if reasonable values are taken for them, the constant W_k may be evaluated. Choosing the value for the reduced mass as half the free-electron mass, and taking the dielectric constant to be 10, the computed value of W_k is about 550 cm^{-1}. This is in fair agreement with the observed values at the various temperatures. The value is, of course, quite sensitive to the value of the index of refraction, and hence of dielectric constant, of the Cu_2O crystal.

The observed line widths do not seem to be particularly sensitive to temperature, at least in the range from 2°K to 77°K. The observed widths are of the order of a few angstroms, leading to lifetimes of the order of 10^{-12} second. An attempt was made to observe the lines in fluorescence emission at a temperature of 77°K with no success. Evidently other recombination processes compete too strongly to observe such radiation.

The line $k=1$ was not observed by us. Gross reports that it is somewhat weaker than the other lines, and that

TABLE III. Same as Table I except that the temperature is intermediate between 4° and 77°K. (A different crystal sample was used than that of Tables I and II.)

k	λ_{exp}	ν_{exp}	ν_{theor}
2	5777.7	17308	17308
3	5741.2	17418	17419
4	5728.2	17457	17458
5	5722.1	17476	17476
6	5718.9	17486	17486
7	5716.5	17493	17492

there is a considerably discrepancy between its observed position and that calculated from the series formula.

It is of some interest to calculate the size of the Bohr orbits for the exciton. Using the values given above for the reduced mass and for the dielectric constant, the first orbit has a radius of 10 angstroms, while that associated with the line $k=7$ in Table III would have a radius of approximately 500 angstroms. Thus,
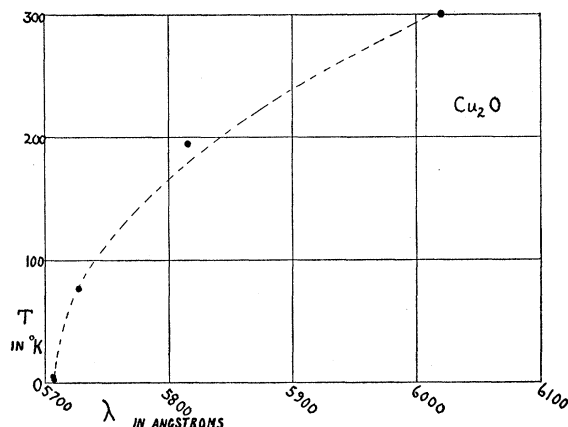

FIG. 3. Shift of the position of the absorption edge (series limit of the exciton series) as a function of absolute temperature.

from this picture, the electron is still able to feel the Coulomb influence of its hole at a distance of several hundred atomic spacings. It is conceivable that the reported misfit of the line $k=1$ by Gross, and our misfit for the line $k=2$ (Table I) may be due to the inability of the exciton to see the average value of the dielectric constant when so few atoms of the crystal lattice are contained within the orbit.

ACKNOWLEDGMENTS

[4] W. H. Brattain, Revs. Modern Phys. 23, 203 (1951).