

Symmetry of Excitons in  $\text{Cu}_2\text{O}$ <sup>†</sup>

R. J. ELLIOTT\*

*Department of Physics, University of California, Berkeley 4, California*

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The anisotropy of the absorption of the  $1s$  exciton line in  $\text{Cu}_2\text{O}$  which is observed by quadrupole radiation shows that this exciton is of type  $\Gamma_{25}^+$ . The details of the anisotropic absorption properties of the Zeeman and Stark effect are predicted and compared with experiment. The anisotropy of the indirect absorption edges allows the symmetry of the phonon involved to be determined. From this symmetry identification it is possible to speculate about the nature of the valence and conduction bands in this substance. The results appear to be in agreement with a spin-orbit split valence band of Cu  $3d$  functions and a conduction band of Cu  $4s$  functions. Estimates of the ortho-para exciton splitting and Stark strain splitting on this model are of the right order of magnitude but smaller than those observed.

GROSS and Kaplyanskii<sup>1</sup> have shown that the weak  $n=1$  line ( $\lambda=6125 \text{ \AA}$ ) of the yellow exciton series of  $\text{Cu}_2\text{O}$  has characteristics which indicate that the transition is electric quadrupole. The absence of this line in an intensity appropriate to dipole absorption was earlier pointed out to be explained if the Bloch states at either side of the direct gap had the same parity,<sup>2</sup> so that transitions are forbidden between them. Quadrupole absorption in a cubic crystal is not isotropic and from the nature of this asymmetry it is possible to deduce the symmetry properties of the exciton state (i.e., the irreducible representation like which it transforms). It is then possible to predict the anisotropy of the various lines into which the exciton line is split under the action of electric and magnetic fields. Gross and Zakhartcherna<sup>3</sup> have observed the Zeeman effect and Gross and Kaplyanskii<sup>4</sup> the Stark splittings induced by strain.

After this paper was first submitted, further work of Gross and Kaplyanskii<sup>5</sup> appeared, giving a more detailed account of the Stark splitting of the  $1s$  line and of the associated absorption edges. These edges are due to indirect absorption to the  $1s$  exciton band<sup>6</sup> utilizing the creation or destruction of a single phonon of energy  $105 \text{ cm}^{-1}$ . From the asymmetry of this absorption it is possible to identify the symmetry nature of this phonon.

With these symmetry properties and other information about the spectrum of  $\text{Cu}_2\text{O}$  it is possible to speculate about the properties of the one-electron energy bands, although with so complicated a crystal structure it is difficult to draw definite conclusions. One picture of the bands which appears to fit the facts will be presented, and some other possibilities discussed. Various

experiments are suggested which might clarify the situation.

## LINE INTENSITIES

The dipole matrix elements are proportional to those of the operator  $\mathbf{e} \cdot \mathbf{p}$ , where  $\mathbf{e}$  is a vector in the direction of the electric field of the light and  $\mathbf{p}$  is a momentum matrix element. This can also be written  $m(\mathbf{e} \cdot \mathbf{r})2\pi\nu$ , where  $\nu$  is the frequency of the radiation. The quadrupole matrix elements are therefore proportional to those of

$$(m2\pi\nu)(\mathbf{e} \cdot \mathbf{r})(\mathbf{k} \cdot \mathbf{r}), \quad (1)$$

where  $\mathbf{k}$  is the wave vector of the radiation. If the direction of  $\mathbf{e}$  is  $(l_1, m_1, n_1)$  and  $\mathbf{k}$  is  $(l_2, m_2, n_2)$ , the angular dependence of (1) may be expanded in spherical harmonics of order two as

$$\frac{1}{2}n_1n_2(2z^2-x^2-y^2)+\frac{1}{2}(l_1l_2-m_1m_2)(x^2-y^2)+\lambda yz+\mu zx+\nu xy, \quad (2)$$

using the fact that  $\mathbf{e} \perp \mathbf{k}$ . For convenience we define

$$\lambda=(m_1n_2+m_2n_1), \quad \mu=(n_1l_2+l_1n_2), \quad \nu=(l_1m_2+l_2m_1). \quad (3)$$

The matrix element can also be written in terms of  $\mathbf{M}$ ,<sup>7</sup> using the relation between  $\mathbf{r}$  and  $\mathbf{p}$ , where

$$\mathbf{M}=\frac{1}{m}\sum_i\left[\frac{\mathbf{p}_{ci}(\mathbf{e} \cdot \mathbf{p}_{iv})}{E_c-E_i}-\frac{\mathbf{p}_{vi}(\mathbf{e} \cdot \mathbf{p}_{ic})}{E_i-E_v}\right]. \quad (4)$$

The sum is over all bands, other than the conduction and valence bands,  $c$  and  $v$ , respectively, and the  $E_i$  are the energies of the band edges.

The probability of transitions to the exciton level may be calculated by the method used in reference 2. It is again proportional to the probability that the electron-hole pair is to be found on the same atom; i.e., to  $|\phi(0)|^2$ , where  $\phi(\mathbf{r})$  is the wave function of relative electron-hole motion. The actual result for the  $f$  value is, per unit cell,

$$f=(B\hbar Z/\pi\nu m)|\phi(0)|^2(\mathbf{k} \cdot \mathbf{M})^2. \quad (5)$$

<sup>7</sup> R. J. Elliott and R. Loudon, *J. Phys. Chem. Solids* **8**, 382 (1959).

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\* Permanent address, Clarendon Laboratory, Oxford, England.

<sup>1</sup> A. F. Gross and A. A. Kaplyanskii, *Doklady Acad. Nauk* **132**, 98 (1960); *Soviet Phys.—Solid State* **2**, 353 (1960).

<sup>2</sup> R. J. Elliott, *Phys. Rev.* **108**, 1384 (1957).

<sup>3</sup> A. F. Gross and B. P. Zakhartcherna, *J. Phys. Radium* **18**, 68 (1957).

<sup>4</sup> A. F. Gross and A. A. Kaplyanskii, *Soviet Phys.—Solid State* **2**, 1518 (1961).

<sup>5</sup> A. F. Gross and A. A. Kaplyanskii, *Soviet Phys.—Solid State* **2**, 2637 (1961).

<sup>6</sup> R. J. Elliott, *Proceedings of the Prague Conference on Semiconductors, 1961* [Czech J. Phys. (to be published)].

TABLE I. Typical wave functions of the form  $\alpha\phi_{yz} + \beta\phi_{zx} + \gamma\phi_{xy}$  of a  $\Gamma_{25}^+$  level as split by magnetic fields and symmetrical strains—see text.

Symmetry	$\alpha$	$\beta$	$\gamma$	Line variation	Energy
$M=1$	$[\frac{1}{2}(m^2+n^2)]^{\frac{1}{2}}$	$(-lm+in)/[2(m^2+n^2)]^{\frac{1}{2}}$	$(-ln-im)/[2(m^2+n^2)]^{\frac{1}{2}}$	$\frac{1}{2}[\Sigma\lambda^2 - (\Sigma l\lambda)^2]$	$\frac{1}{2}(g_1+g_2)\beta H$
$M=0$	$l$	$m$	$n$	$(\Sigma l\lambda)^2$	0
$M=-1$	$[\frac{1}{2}(m^2+n^2)]^{\frac{1}{2}}$	$(-lm-in)/[2(m^2+n^2)]^{\frac{1}{2}}$	$(-ln+im)/[2(m^2+n^2)]^{\frac{1}{2}}$	$\frac{1}{2}[\Sigma\lambda^2 - (\Sigma l\lambda)^2]$	$-\frac{1}{2}(g_1+g_2)\beta H$
$M_4^+$	0	0	1	$\nu^2$	$-2a_4$
$M_5^+$	$\begin{Bmatrix} 1 \\ 0 \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ 1 \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ 0 \end{Bmatrix}$	$\lambda^2 + \mu^2$	$a_4$
$\Delta_1$	$1/\sqrt{3}$	$1/\sqrt{3}$	$1/\sqrt{3}$	$\frac{1}{3}(\Sigma\lambda)^2$	$2a_3$
$\Delta_3$	$\begin{Bmatrix} 1/\sqrt{3} \\ 1/\sqrt{3} \end{Bmatrix}$	$\begin{Bmatrix} \omega/\sqrt{3} \\ \omega^2/\sqrt{3} \end{Bmatrix}$	$\begin{Bmatrix} \omega^2/\sqrt{3} \\ \omega/\sqrt{3} \end{Bmatrix}$	$\Sigma\lambda^2 - \frac{1}{3}(\Sigma\lambda)^2$	$-a_3$
$\Delta_1$	0	0	1	$\nu^2$	$2b$
$\Delta_3$	$1/\sqrt{2}$	$1/\sqrt{2}$	0	$\frac{1}{2}(\lambda+\mu)^2$	$a_2-b$
$\Delta_4$	$1/\sqrt{2}$	$-1/\sqrt{2}$	0	$\frac{1}{2}(\lambda-\mu)^2$	$-a_2-b$

Here  $Z$  is the angle-dependent factor, and  $B$  is the volume of the unit cell. This may be compared to the intensity of the dipole allowed  $n \geq 2$  lines which are given by

$$f_n = B\hbar(n^2-1)|\mathbf{M}|^2/3\pi^2 m\nu n^5 a_0^5, \quad (6)$$

where  $a_0$  is the Bohr radius of the exciton series. Thus the ratio of the intensities of the  $n=1$  and  $n=2$  lines in  $\text{Cu}_2\text{O}$  should be  $2^5 Z(ka_0)^2$ . For unpolarized radiation on a polycrystal, later work [Eq. (7)] gives  $8/25$  as the average value of  $Z$ .

Nikitine *et al.*<sup>8</sup> measured  $f_2 = 2.7 \times 10^{-6}$ . With a value of  $a_0 \sim 10$  Å this gives  $M = 0.12$  per cell, and predicts  $f_1 \sim 10^{-9}$ .

$\text{Cu}_2\text{O}$  has over-all cubic symmetry and at the center of the zone, where direct exciton transitions take place, the group of  $\mathbf{k}$  is isomorphous with the point group  $O_h$ . The ground state of the crystal is, of course, completely symmetric, transforming like  $\Gamma_1^+$ .<sup>9</sup> The quadrupole matrix elements (2) contain functions which span  $D_2$  of the rotation group, and which in the cubic group are either from irreducible representation  $\Gamma_{12}^+$  like  $3z^2 - r^2$  and  $x^2 - y^2$ , or  $\Gamma_{25}^+$  like  $2yz$ ,  $2zx$  and  $2xy$ . Thus the only exciton states to which quadrupole transitions are possible are of types  $\Gamma_{25}^+$  and  $\Gamma_{12}^+$ . The intensity of such transitions are proportional to

$$\Gamma_{25}^+ = \Sigma\lambda^2 = 1 - 2\Sigma l_1^2 l_2^2, \quad (7)$$

$$\Gamma_{12}^+ = 3n_1^2 n_2^2 + (l_1 l_2 - m_1 m_2)^2 = 2\Sigma l_1^2 l_2^2 = 1 - \Sigma\lambda^2. \quad (8)$$

$Z$  in Eq. (5) is given by (7) or (8) multiplied by a numerical factor which depends on the actual exciton wave functions: if normalized second-order spherical harmonics are used, this number is  $8/15$ .

The results of Gross and Kaplyanskii<sup>4</sup> agree exactly with the anisotropy of Eq. (7), and we deduce that the  $n=1$  yellow exciton state is of type  $\Gamma_{25}^+$ . The splitting

of the absorption line in electric and magnetic fields confirms that it is triply degenerate. It also shows that there is no extra accidental degeneracy due to spin, but that this triple degeneracy includes the spin degeneracy, i.e., that it is an orthoexciton. It further shows that there must be considerable spin-spin forces present in this exciton, since without them the  $s$  exciton would be fourfold degenerate because of the two time-reversed states of the electron band, and two of the hole band. The origin and magnitude of these exchange forces will be discussed later. Because of the sphericity of the bands which is reflected in the extremely good hydrogenic properties of the yellow series, it seems likely that both the valence and conduction bands from which the yellow excitons are built have no more than double Kramers degeneracy. This means the types  $\Gamma_6$ ,  $\Gamma_7$  must be  $\Gamma_6^\pm$  or  $\Gamma_7^\pm$ . But the  $s$ -exciton relative motion is  $\Gamma_1^+$ , so that the  $1s$  excitons are  $\Gamma_6 \times \Gamma_7 \times \Gamma_1^+$ . The only combinations which give  $\Gamma_{25}^+$  are if one band is  $\Gamma_6$  and the other  $\Gamma_7$  of the same parity. In this case the singlet paraexciton also present is  $\Gamma_2^+$ , which will not be observable by quadrupole radiation.

The splitting of the  $\Gamma_{25}^+$  triplet by magnetic and symmetrical electric fields is most simply considered if the possible proximity of the  $\Gamma_2^+$  is neglected for the moment. In the presence of a magnetic field  $\mathbf{H}$  along  $(l, m, n)$  the triplet will split into three levels which correspond to values of the component of the "fictitious" spin  $S=1$  of  $M=\pm 1, 0$  along  $\mathbf{H}$ . The energies of these will be  $\pm(g_1+g_2)\beta H$  and 0, if  $g_1$  and  $g_2$  are the spectroscopic splitting factors of the electrons in the conduction and valence bands.

A typical set of wave functions describing the exciton will be  $\phi_{yz}$ ,  $\phi_{zx}$ ,  $\phi_{xy}$ , having transformation properties like  $yz$ ,  $zx$ , and  $xy$ , respectively. In the presence of  $\mathbf{H}$  each level will be described by a linear combination of these, say

$$\alpha\phi_{yz} + \beta\phi_{zx} + \gamma\phi_{xy}. \quad (9)$$

The intensity of absorption is such that a level is using (2) proportional to

$$(\lambda\alpha + \mu\beta + \nu\gamma)^2 = (\Sigma\lambda\alpha)^2. \quad (10)$$

<sup>8</sup> S. Nikitine, J. B. Grun, and M. Sieskind, J. Phys. Chem. Solids 17, 292 (1961).

<sup>9</sup> The notation for irreducible representations is taken from Koster [G. Koster, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 174], except that instead of primes, the parity is denoted by + or - superscripts.

The values of  $\alpha$ ,  $\beta$ ,  $\gamma$  together with the value of (10) are given in the table for arbitrary directions of  $\mathbf{H}$ ,  $\mathbf{E}$ , and  $\mathbf{k}$ .

When the crystal is compressed, there is a Stark splitting whose symmetry properties can be determined from the symmetry properties of the point group which is isomorphous with the group at  $\mathbf{k}=0$ . For compression along a fourfold axis [001] reduces the symmetry from cubic  $O_h$  to tetragonal  $D_{4h}$ , compression along a threefold axis [111] to trigonal  $C_{3v}$ , and along a twofold axis [110] to rhombic  $C_{2v}$ . The representations of these groups into which  $\Gamma_{25}^+$  decomposes, together with the anisotropy of the absorption, are given in the table. The energies are given in terms of arbitrary parameters which should be linear in the deformation. There should be, in addition, an over-all shift of the center of gravity of the lines due to the uniform compression. The experimental results<sup>5</sup> show a shift which is very small compared to that which might be expected from the large temperature dependence of the energy gap.

The resulting formulas are in agreement with the experimental results<sup>3-5</sup> in that they predict the correct number of lines. The identification with the experimental lines is as follows.  $\lambda_1^{(4)} = M_5^+$ ,  $\lambda_2^{(4)} = M_4^+$ ,  $\lambda_1^{(3)} = \Delta_1$ ,  $\lambda_2^{(3)} = \Delta_3$ ,  $\lambda_1^{(2)} = \Delta_1$ ,  $\lambda_2^{(2)} = \Delta_4$ ,  $\lambda_3^{(2)} = \Delta_3$ . In their latest paper Gross and Kaplyanskii<sup>5</sup> make a similar analysis of these results. They feel, however, from the expected sign of the strain splitting that the symmetries of the line pairs  $\lambda_1^{(3)} \leftrightarrow \lambda_2^{(3)}$  and  $\lambda_2^{(2)} \leftrightarrow \lambda_3^{(2)}$  are interchanged. There is no obvious theoretical reason for this, although as will be shown later, the overall picture would be somewhat more satisfactory if this were the case. The simplest check on whether or not this theory of quadrupole absorption has broken down would be to subject a crystal already strained along [111] to a small perpendicular stress or magnetic field. For the theory says that the line always observed in this geometry is the doublet  $\Delta_3$  and such an experiment should split the line. One possible origin of a breakdown in the theory of quadrupole absorption could arise from the fact that under strains along the threefold and twofold axes the unit cell loses its center of symmetry. Thus the

exciton could have a dipole moment induced by the strain and this moment would not be parallel to  $\mathbf{k}$ . However, such strain-induced absorption does not seem to have exactly the characteristics required.

The relative intensities of the lines do not show up very clearly in the published data, and it is difficult to say whether these are in agreement. For example, for the case of deformation  $\mathbf{P}$  along [110] and light  $\mathbf{k}$  along [111] the absorption  $\Delta_3$  is found only if  $\mathbf{E} \parallel \mathbf{P}$  with intensity  $3K$ , say; when  $\mathbf{E} \perp \mathbf{P}$ ,  $\Delta_1$  and  $\Delta_4$  are found, with intensity  $2K$  and  $K$ , respectively. For unpolarized radiation in this case the three lines should be in the ratio 3:2:1.

If the separation in energy to the singlet para-exciton  $\Gamma_2^+$  is comparable to these splittings, it is possible that a fourth absorption line could be visible. In a magnetic field it becomes an  $M=0$  state and mixes with the  $M=0$  state of the triplet causing a shift in energy of that state. Thus a fourth line could appear with  $M=0$  angular dependence as given in the table. In the limit where the magnetic field effects are much larger than the ortho-para splitting, these two  $M=0$  states have energies  $\pm \frac{1}{2}(g_1 - g_2)\beta H$  and equal intensities  $\frac{1}{2}(\sum \lambda)^2$ . The trigonal distortion changes  $\Gamma_2^+ \rightarrow M_3^+$  which is not observable, and this is also true for the tetragonal distortion which changes  $\Gamma_2^+ \rightarrow \Delta_2^+$  and for the rhombic distortion which changes  $\Gamma_2^+ \rightarrow \Delta_2$ . Thus the para-exciton will only be observable in magnetic fields or strains of lower symmetry.

### EDGE INTENSITIES

The continuous absorption edges appearing in the red 105  $\text{cm}^{-1}$  above and below the 1s line<sup>10</sup> have been shown to be consistent<sup>6</sup> with the theory of indirect transitions involving a phonon. The absorption coefficient is proportional to the density of states in the 1s exciton band and to

$$\left| \frac{\langle 0 | \mathbf{e} \cdot \mathbf{p} | i, 0 \rangle \langle i, 0 | \mathcal{H}_e | 1s, \mathbf{K}; n_K \pm 1 \rangle}{E(i, 0) - E(1s, \mathbf{K}) \mp E_p(\mathbf{K})} \right|^2. \quad (11)$$

The first matrix element represents the interaction of the electric field of the light raising the crystal from its ground state to an excited state  $i$ , where the small wave vector of the light has been neglected, i.e.,  $\mathbf{k}=0$ . The second matrix element represents the electron-phonon interaction transferring the crystal from the intermediate state to the  $|1s, \mathbf{K}\rangle$  exciton state. Momentum is conserved by simultaneously creating or destroying a phonon of wave vector  $\mathbf{K}$ , and energy  $E_p(\mathbf{K})$ . The experimental results indicate that this second matrix element is independent of  $\mathbf{K}$  at small  $\mathbf{K}$  and its proper-

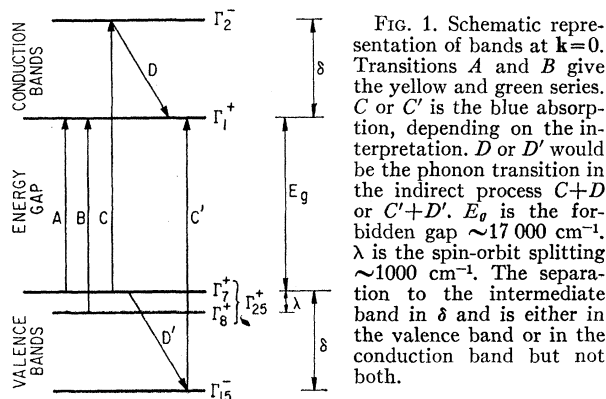


FIG. 1. Schematic representation of bands at  $\mathbf{k}=0$ . Transitions A and B give the yellow and green series. C or C' is the blue absorption, depending on the interpretation. D or D' would be the phonon transition in the indirect process C+D or C'+D'.  $E_g$  is the forbidden gap  $\sim 17\,000\text{ cm}^{-1}$ .  $\lambda$  is the spin-orbit splitting  $\sim 1000\text{ cm}^{-1}$ . The separation to the intermediate band is  $\delta$  and is either in the valence band or in the conduction band but not both.

<sup>10</sup> I. Pastrnyak, Soviet Phys.—Solid State 1, 888 (1959); P. W. Baumeister, Phys. Rev. 121, 359 (1961); S. Nikitine, J. B. Grun, and M. Sieskind, Proceedings of the Prague Conference Proceedings on Semiconductors, 1961 [Czech. J. Phys. (to be published)], J. Phys. Chem. Solids 19, 189 (1961).

ties may therefore be discussed in terms of the transition to  $|1s,0\rangle$  exciton using a  $K=0$  phonon.

From the properties of  $\mathbf{p}$  the intermediate state must have symmetry  $\Gamma_{15}^-$ , since the ground state is  $\Gamma_1^+$ . Since the  $|1s,0\rangle$  state is  $\Gamma_{25}^+$ , the phonon involved in the transition must be

$$\Gamma_{15}^- \times \Gamma_{25}^+ = \Gamma_{15}^- + \Gamma_{25}^- + \Gamma_{12}^- + \Gamma_2^- \quad (12)$$

Typical angular dependences of such symmetries can be obtained from tables of cubic harmonics.<sup>11</sup> For  $\mathbf{e}$  along  $[111]$  the transition probability (11) to a final exciton state of form (9) is for the various phonon types in (12) proportional to

$$\begin{aligned} \Gamma_{15}^- & \quad \sum (n_1\beta + m_1\gamma)^2 = 1 + (\sum l\alpha)^2 - 2 \sum l^2\alpha^2, \\ \Gamma_{25}^- & \quad \sum (n_1\beta - m_1\gamma)^2 = 1 - (\sum l\alpha)^2, \\ \Gamma_{12}^- & \quad \frac{3}{2}(\alpha\beta + m\beta)^2 + \frac{1}{2}(2n\gamma - l\alpha - m\beta)^2 \\ & \quad = [3 \sum l^2\alpha^2 - (\sum l\alpha)^2], \\ \Gamma_2^- & \quad (\sum l\alpha)^2. \end{aligned} \quad (13)$$

Strictly speaking, these selection rules hold only at  $\mathbf{K}=0$  and will be relaxed where the density of states becomes appreciable—particularly close to other band edges. However, they should indicate which edges begin sharply  $[\kappa \sim (\hbar\nu - E_g)^{1/2}]$ .

On the basis of the identification of the lines made in the last section the angular dependence of the absorption in the edges corresponding to the lines<sup>5</sup> are in agreement only if the  $105 \text{ cm}^{-1}$  phonon is  $\Gamma_{12}^-$ . If, however, the symmetries of  $\lambda_1^{(3)} \leftrightarrow \lambda_2^{(3)}$  and  $\lambda_2^{(2)} \leftrightarrow \lambda_3^{(2)}$  are reversed for some unknown reason, the edge selection rules would indicate that the phonon is  $\Gamma_2^-$ .

### SYMMETRY OF $\text{Cu}_2\text{O}$

The translation group of the  $\text{Cu}_2\text{O}$  lattice is simple cubic. The unit cell is a cube with O at the body center (0,0,0) and the corners  $\frac{1}{2}a(1,1,1)$  and Cu in a tetrahedron about the central O at  $\frac{1}{4}a(1,1,1)$ ,  $\frac{1}{4}a(1,-1,-1)$ ,  $\frac{1}{4}a(-1,1,-1)$ ,  $\frac{1}{4}a(-1,-1,1)$ . The rotation elements of the group are isomorphous with those of the diamond lattice,<sup>7</sup> since those elements which are in the tetrahedral group  $T_d$  appear as point operators, while the other elements in  $O_h$  appear with the translation  $\frac{1}{2}a(1,1,1)$ . The point symmetry at O is  $T_d$  and at Cu is  $D_{3d}$  with a large axial component from the two nearest O's forming linear O-Cu-O arrangements in the  $[111]$  directions.

The symmetries of the phonons and bands are readily obtained by the method of Moskalenko.<sup>12</sup> Placing displacement vectors on the atoms and examining their transformation properties under the group,<sup>13</sup> it is found that the Cu motions give rise to  $2\Gamma_{15}^- + \Gamma_{25}^- + \Gamma_{12}^- + \Gamma_2^-$

and the O motions, rather like in diamond, to  $\Gamma_{15}^-$  and  $\Gamma_{25}^+$  phonons. With some knowledge of the normal modes of tetrahedral molecules<sup>13</sup> it is easy to obtain a crude picture of the nature of these phonons.

- (1)  $\Gamma_{15}^-$ —the acoustical modes.
- (2)  $\Gamma_{15}^-$ —relative motion of the  $\text{Cu}^+$  and  $\text{O}^-$  lattices.
- (3)  $\Gamma_{15}^-$ —rhombic distortions of cell along  $[110]$  directions; central O atom moves along  $[001]$ .
- (4)  $\Gamma_{25}^-$ —rotation of tetrahedron of Cu, causing bending of O-Cu-O bonds.
- (5)  $\Gamma_{12}^-$ —compression of tetrahedron along opposite edges.
- (6)  $\Gamma_2^-$ —dilation mode of Cu tetrahedron—causing displacement of Cu in O-Cu-O bonds.
- (7)  $\Gamma_{25}^+$ —relative motion of the O lattices.

As noted by Pastrnyak,<sup>14</sup> two of these are optically active and one [probably type (2)] was observed by him at about  $600 \text{ cm}^{-1}$ . Hradny (private communication from S. Nikitine) has observed the infrared absorption around  $100 \text{ cm}^{-1}$  and finds no absorption corresponding to the phonon seen in the indirect absorption in agreement with the symmetry assigned to it in the last section.

The symmetries of the band states can also be similarly determined. The point symmetries of the Cu  $3d$  functions are  $L_1^+$  and  $2L_3^+$ . The over-all cell symmetry of the combinations are

$$4L_1^+ \rightarrow \Gamma_{25}^+ + \Gamma_1^+, \quad 4L_3^+ \rightarrow \Gamma_{12}^+ + \Gamma_{15}^+ + \Gamma_{25}^+.$$

The point symmetries of the O  $2p$  functions are  $P_4$  and the over-all cell symmetry of combinations

$$2P_4 \rightarrow \Gamma_{15}^- + \Gamma_{25}^+.$$

Thus there are 10 valence bands at  $\Gamma$  of which all are even except one. The conduction bands for the Cu  $4s$  functions are

$$4L_1^+ \rightarrow \Gamma_{25}^+ + \Gamma_1^+,$$

and those from the O  $3s$  functions

$$2P_1 \rightarrow \Gamma_1^+ + \Gamma_2^-,$$

so that of the four conduction bands only one is odd.

### SPECULATION ABOUT BAND STRUCTURE

The energy separations of the various bands enumerated in the last section are caused by overlap of the atomic functions and can only be explicitly determined by a band calculation; they will probably be of the order of eV. Of the predominantly Cu  $3d$ -wave functions, an  $L_3^+$  orbital will probably have highest energy in the dominantly axial environment, and it is suggested that the  $\Gamma_{25}^+$  combination forms the highest valence band. A  $\Gamma_1^+$  bonding combination of Cu  $4s$  and/or O  $3s$  functions probably forms the lowest conduction band.

<sup>11</sup> F. C. von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).

<sup>12</sup> S. A. Moskalenko, Soviet Phys.—Solid State Phys. **2**, 1587 (1961).

<sup>13</sup> E. B. Wilson, J. Chem. Phys. **2**, 432 (1934).

<sup>14</sup> I. Pastrnyak, Optika i Spectvos Kopya **4**, 64 (1959).

It is known that there is a near degeneracy in one of these bands with a second band which gives rise to the green series. Optical transitions in *p*-type material indicate that this is in the valence band.<sup>15</sup> This near degeneracy may be accidental, but its magnitude suggests a spin-orbit splitting arising from the Cu 3*d* functions. Some confirmation of this is provided by the fact that both bands move together relative to the conduction band as the forbidden gap changes with temperature. The  $\Gamma_{25}^+$  will split under spin-orbit coupling into  $\Gamma_7^+$  (higher) and  $\Gamma_8^+$ . A conduction band  $\Gamma_1^+$  ( $\rightarrow \Gamma_6^+$  with spin) gives, therefore, the combination  $\Gamma_6^+ \times \Gamma_7^+$  which was shown to give 1s yellow excitons of the right symmetry. Irrespective of the details of this picture, it can be said that if the valence band splitting is due to spin-orbit coupling, the green series must arise from a  $\Gamma_8$  state which has an extra degeneracy. Thus the green series should show a much larger strain splitting than the yellow.

The magnitude of the valence band splitting is largely determined by the atomic spin-orbit coupling; thus it will be appreciable only in those bands which arise from  $L_3$  atomic states which are themselves split by the spin-orbit coupling, and will be small in those bands which arise from  $L_1$  states.

It seems unlikely that the valence band which gives the yellow series has an extra degeneracy unresolved by spin-orbit coupling as suggested in reference 4; since there should always be a small splitting of a few  $\text{cm}^{-1}$  if the bands come from  $L_1$  Cu functions or O functions and these together with the ortho-para splitting and the extra spin degeneracy should show up in the experiments. The quantitative aspects of the strain energies in our interpretation will be treated in the next section.

In addition, some information is available about the bands of odd parity. It was proposed in reference 6 that the main intermediate state  $|i\rangle$  in the indirect process as given by (11) was from a band to which optical transitions are allowed. This has been confirmed by Grun *et al.*<sup>16</sup> who find a strong absorption roughly where it was expected in the blue. Since they find two absorption peaks separated by an amount equal to the difference between the green and yellow series, they suggest that this is a transition from the top valence band to an excited conduction band (transition *C* in figure) which, from the considerations of the last section, must be  $\Gamma_2^-$ . If this is so, the phonon transitions in (11) must come dominantly from electron scattering from  $\Gamma_2^-$  to  $\Gamma_1^+$  and must use a  $\Gamma_2^-$  phonon. This would fit in extremely well with the symmetry properties of the edges provided Gross is correct in his feeling that the quadrupole symmetries of some of the strain split 1s absorption lines are reversed. Furthermore the  $\Gamma_2^-$  phonon which displaces the Cu in the O-Cu-O bonds and

changes the size of the Cu tetrahedron would be expected to have a strong interaction with excitons mainly on the Cu and contribute to the extra binding energy of the 1s excitons.

On the other hand, it was shown that there was no need to assume a breakdown of the quadrupole selection rules to explain the anisotropies of the lines and edges so far reported. In this case the phonon must be  $\Gamma_{12}^-$  so that the intermediate state must arise because the  $\Gamma_{15}^-$  antibonding combination of O 2*p* functions is not far below the top valence band. If this is true, other phonons  $\Gamma_{15}^-$ ,  $\Gamma_{25}^-$ , and  $\Gamma_2^-$  will scatter the hole as well as  $\Gamma_{12}^-$ , and it is surprising that no edges corresponding to these phonons are observed. The question of which band gives the intermediate state could probably be settled by looking for the  $\Gamma_7^+ \rightarrow \Gamma_{15}^-$  absorption of holes in *p*-type material which should occur at  $\delta = 4500 \text{ cm}^{-1}$ .<sup>16</sup> This would be an optical transition like *D'* in the figure. In this case the blue absorption of reference 16 is transition *C'*.

### EXCITON FINE STRUCTURE

Within the framework of this particular model of the band structure the various splittings of the 1s exciton levels can be estimated. The ortho-para splitting arises from the exchange interaction between the electron and hole which is important only when the two particles are on the same atom. Using a method similar to that for obtaining the intensity of absorption,<sup>2</sup> the effective exchange interaction comes out to be

$$J_{\text{eff}} = B |\psi(0)|^2 J,$$

where *J* is the exchange interaction which would be obtained if the electron and hole were confined within the same cell. If it is further assumed that the band functions are like 3*d* and 4*s* atomic functions on the Cu,

$$J \sim \frac{1}{4} J_{sd},$$

where  $J_{sd}$  is an atomic exchange integral. Because of the particular combination of spin states in the  $\Gamma_7$  level, the  $J_{sd}$  will be only one-third of that which determines the singlet-triplet splitting in atoms. In  $\text{Cu}^+ 3d^9 4s$  the  $^3D-^1D$  splitting is about  $3000 \text{ cm}^{-1}$ .<sup>17</sup> From the Rydberg constant of the yellow series and an estimated dielectric constant  $\epsilon \sim 8$ , the radius of the 1s orbit would appear to be  $a_0 \sim 10 \text{ \AA}$ , although the greater binding energy of the 1s exciton showing a breakdown of the effective-mass theory indicates that perhaps a value of  $|\psi(0)|^2$  should be used which is about twice the hydrogenic value  $1/\pi a_0^3$ . This predicts a value of  $J'$ , the ortho-para splitting, of about  $15 \text{ cm}^{-1}$ , which is a reasonable order of magnitude.

The Stark strain splitting of the triplet<sup>5</sup> is about  $2 \text{ cm}^{-1}$  for a pressure of  $1 \text{ kg/mm}^2$ . Although the elastic

<sup>15</sup> M. P. Lisitsa and G. A. Kholodar, Soviet Phys.—Solid State 2, 1518 (1961).

<sup>16</sup> J. B. Grun, M. Sieskind, and S. Nikitine, J. Phys. Chem. Solids (to be published).

<sup>17</sup> C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. 2.

properties of  $\text{Cu}_2\text{O}$  do not seem to have been measured, this is considerably smaller than might be expected for a splitting arising because of orbital degeneracy in the valence or conduction band. For example, for the same pressure the degenerate valence band of Ge is split<sup>18</sup> by about  $50 \text{ cm}^{-1}$ . On the other hand, in lowest order one would not expect any strain splitting of a 1s exciton built from two bands without orbital degeneracy. The only source of such a splitting can be an anisotropy in the exchange splitting just discussed, if one of the component bands becomes anisotropic. This is possible in the valence band because of the proximity of the other degenerate band. Since the exciton binding energy is comparable to this spin-orbit splitting,  $\lambda$  say, there will be appreciable admixtures of states of this  $\Gamma_8$  band in the exciton. In order of magnitude the strain splitting will therefore be  $J'\Delta/\lambda$ , where  $\Delta$  is the strain splitting of the degenerate band, which will show as a splitting of the green series. Since the band positions are very temperature sensitive, it is possible that this splitting will be large, say  $100 \text{ cm}^{-1}/\text{kg mm}^{-2}$ , and since we have already found  $J' \sim 15 \text{ cm}^{-1}$ , the order of magnitude is satisfactory.

#### CONCLUSION

In conclusion, it may be said that this analysis indicates that the model of the energy bands previously put forward, in which the valence band is a spin-orbit-

split Cu 3d band and the conduction band a 4s band, agrees in broad outline with the new properties of the 1s yellow-exciton band recently measured. The exchange and strain splittings do, however, appear to be a factor of two or so larger than the theory predicts, and it would be interesting to check some of its other aspects. In particular, it would be useful to detect the para-exciton: using large strains of low symmetry, the para-exciton line should appear and the orthoexciton splitting should become nonlinear. The selection rules for the indirect edges indicate that the paraexciton edge is forbidden. Also the green exciton series should have a large strain splitting because of the degenerate valence band from which it is formed.

It may be reiterated that as far as the selection rules are concerned, the experimental results are all adequately explained on the basis of the identification given in the text and a  $\Gamma_{12}^-$  phonon. However, there are some slight indications that the quadrupole selection rules are in some aspects inadequate under certain strains, and if this were true, the results would agree with a  $\Gamma_2^-$  phonon which would make a better fit with the over-all picture. Further experiments are required to clear up this point.

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<sup>18</sup> L. Roth and W. Kleiner, *Phys. Rev. Letters* **2**, 334 (1959); W. Paul and D. M. Warschauer, *J. Phys. Chem. Solids* **5**, 89 (1958).