

is expected to be reduced relative to the ionic case due to charge transfer from the  $\text{Cr}^{3+}$  ion to  $\pi$  bonds with the neighboring cyanide groups.<sup>24,25</sup> Since the effective cubic electric field component is larger in the cyanide and the spin-orbit coupling reduced  $|\Delta g|$  is expected to be appreciably smaller for  $[\text{Cr}(\text{CN})_6]^{3-}$  than for  $(\text{Cr}\cdot 6\text{H}_2\text{O})^{3+}$ . This difference is indeed observed, the  $g$ -shift for the chromicyanide at  $20^\circ\text{K}$  being only  $\sim 40\%$  of that found in the dilute alum. The distinction is less manifest in our room temperature cyanide data, however, where  $|\Delta g|$  is about  $80\%$  of the alum value.

The percentage variations of the cyanide  $g$ -shift with pressure and temperature are considerably larger than would be expected from simple ionic volume dependence of the cubic crystalline field component. This suggests that the spin-orbit coupling may vary quite rapidly with volume. However, a decrease of  $|\Delta g|$  upon volume reduction should result from either of these mechanisms whereas the opposite effect is observed up to  $7300 \text{ kg/cm}^2$ . A qualitative explanation of this anomaly may be that the cyanide octahedron is relatively incompressible but "intermolecular hybridization" or bond sharing increases with decreasing volume due to the decreasing distance between the chromium and its *next*-nearest neighbors. This would tend to make the  $\text{Cr}^{3+}$  ion see more isotropic surroundings, i.e., reduce the effective cubic electric field. Nuclear quadrupole resonance experiments indicate just such an effect in the case of the covalent C-Cl bond in *para*-dichlorobenzene.<sup>16</sup> The decrease of  $|\Delta g|$

with volume above  $7300 \text{ kg/cm}^2$  could be attributed to reduced spin-orbit coupling since this interaction might vary sufficiently rapidly with interatomic distance to eventually dominate the bond sharing mechanism.

It is surprising that the pressure and temperature variations of  $D$  and  $E$  are markedly smaller than the corresponding changes of  $\Delta g$  since both  $D$  and  $E$  are proportional to  $(\Delta g)^2$  in the equivalent crystalline field model. Since  $D$  and  $E$  are also proportional to the axial and rhombic electric field components, respectively, it appears that changes in these components roughly compensate for the variations of  $(\Delta g)^2$ . Such a high degree of correlation is unlikely, though not impossible, and suggests that the equivalent crystalline electric field representation of the  $[\text{Cr}(\text{CN})_6]^{3-}$  complex may not be valid.

#### CONCLUSION

The PMR experiments on dilute ammonium chrome alum demonstrate that the crystalline field splitting is a sensitive probe for determining variations of the average electric field at the  $\text{Cr}^{3+}$  sites. Detailed interpretation of the results is difficult, however, since the equation of state does not provide sufficient information concerning the positions of all ions within the unit cell.

The chromicyanide results show that the orbital contribution to the magnetic moment is a more sensitive function of stress and temperature than are the crystalline field splitting parameters. It is difficult to reconcile such behavior with the equivalent crystalline field model of the covalently bonded cyanide complex.

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<sup>24</sup> K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 542 (1953).

<sup>25</sup> It should be noticed that spin-orbit interaction is quite strongly reduced in nominally ionic iron-group complexes relative to free ion values (see Sec. V.A of I). While such an effect might be attributed to partially covalent bonding detailed considerations indicate that this cannot be the case in iron group oxides, for example. A theoretical treatment of the problem will be given in a paper to be published by Dr. W. Marshall.

## Some Selection Rules for Band-Band Transitions in Wurtzite Structure

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Optical selection rules at  $\mathbf{k}=(0,0,0)$  in the wurtzite structure are discussed. These rules suggest an interpretation of recently reported work on CdS by Dutton and Lempicki on reflection spectra, and the excitation spectrum of edge emission in polarized light. Assuming band-band transitions at  $\mathbf{k}=(0,0,0)$  are involved, a valence band spin-orbit splitting of  $0.0167 \text{ eV}$  and crystal field splitting of about  $0.070 \text{ eV}$  (at liquid  $\text{N}_2$  temperature) are obtained for CdS. Other predictions of the model and other possible interpretations of the data are discussed.

WITH the increasing attention being given to optical and other properties of compounds with wurtzite structure, e.g., ZnO, ZnS, CdS, it is of importance to have available the proper optical selection rules for this structure. These rules may help in the

identification of the levels involved in optical transitions in the pure, or activated materials. A recently published paper<sup>1</sup> correctly drew attention to the importance

<sup>1</sup> G. Dresselhaus, Phys. Rev. **105**, 135 (1957).

TABLE I. Base functions<sup>a</sup> for certain irreducible representations of  $C_{6v}$ .

Representation	Function
$\Gamma_1$	$as \alpha\rangle + bz \alpha\rangle$ $as \beta\rangle + bz \beta\rangle$
$\Gamma_5$	$x \alpha\rangle$ $x \beta\rangle$ $y \alpha\rangle$ $y \beta\rangle$
$\Gamma_7$	$as \beta\rangle + bz \beta\rangle + \frac{1}{2}c(x+iy) \alpha\rangle$ $as \alpha\rangle + bz \alpha\rangle + \frac{1}{2}c(-x+iy) \beta\rangle$
$\Gamma_9$	$\frac{1}{2}(x-iy) \alpha\rangle$ $-\frac{1}{2}(x+iy) \beta\rangle$

<sup>a</sup> These are LCAO "s" and "p" functions which transform according to the indicated irreducible representations of  $C_{6v}$ , the group of  $\mathbf{k}=(0,0,0)$  in wurtzite. (Note that the base functions for  $\Gamma_7$  mix spin up and spin down functions.) To obtain a crystal LCAO function from these, which are to be understood as centered on one site, a sum over the four base sites is required. In the functions,  $a$ ,  $b$ ,  $c$  are constants.

of the crystal anisotropy in giving rise to anisotropy of optical absorption. However, in certain important details, the application of the theory was not correct giving rise to an error in the results so that these do not apply to the wurtzite structure. This has been independently recognized by Casella,<sup>2</sup> while a number of other workers<sup>3</sup> have (also independently) studied the group theory of the wurtzite structure and from their work one could also have obtained the correct results. In this note we shall give the correct  $\mathbf{k}=(0,0,0)$  selection rules for the wurtzite structure and list the appropriate spinor wave functions which may be useful in discussions of the cyclotron resonance experiments (our emphasis is on compounds with "s"- and "p"-like valence and conduction bands), and propose an identification of the absorption and reflection lines in CdS. Some other consequences of the proposed identification will be pointed out, as well as some alternate explanations of the experiments.

At  $\mathbf{k}=(0,0,0)$  in wurtzite (space group  $C_{6v}^4$ ) the wave functions transform irreducibly under the point group  $C_{6v}$ , the group of the wave vector. When spin-orbit effect is included, one must use the double group representation.<sup>4</sup> To obtain the character table for the double group of  $C_{6v}$  from the table already published<sup>5</sup> (which applies to the isomorphic group  $D_6$ ) one makes

<sup>2</sup> R. C. Casella, this issue [Phys. Rev. 114, 1514 (1959)]. I am indebted to Dr. Casella for a preprint of his work.

<sup>3</sup> W. J. O'Sullivan, J. Chem. Phys. 30, 379 (1959); M. L. Glasser, J. Phys. Chem. Solids (to be published); R. Parmenter (private communication); F. W. Quella, Jr., Quarterly Progress Report, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts, July 15, 1958 (unpublished), p. 28.

<sup>4</sup> R. J. Elliott, Phys. Rev. 96, 280 (1954); W. Opechowski, Physica 7, 556 (1940).

<sup>5</sup> See reference 1, Table I.

the following class substitutions<sup>6</sup>

for  $C_2'$  substitute  $\sigma_d$ ;

for  $C_2''$  substitute  $\sigma_v$ .

Of most importance is the new assignment of  $z$ , which in  $C_{6v}$  transforms like  $\Gamma_1$  while  $(x,y)$  transform like  $\Gamma_5$ . Aside from these changes, Tables I and II of reference 1 may be taken over. [In particular one may verify the fact that each of  $\sigma_d$ ,  $\sigma_v$ , and  $C_2=(C_6)^3$  is in *one* class in the double group, from the general theory.]<sup>4</sup> Hence for the band-band selection rules in the wurtzite structure which would apply at  $\mathbf{k}=(0,0,0)$  to "s"- and "p"-type compounds, we find

(a) no spin-orbit effect:

$$E(\parallel c): \Gamma_1 \leftrightarrow \Gamma_1,$$

$$E(\perp c): \Gamma_1 \leftrightarrow \Gamma_5;$$

(b) including spin-orbit effect:

$$E(\parallel c): \Gamma_7 \leftrightarrow \Gamma_7,$$

$$E(\perp c): \left\{ \begin{array}{l} \Gamma_7 \leftrightarrow \Gamma_9 \\ \Gamma_7 \leftrightarrow \Gamma_7 \end{array} \right\}.$$

In Table I of this paper we list spinor wave functions which transform like  $\Gamma_1$ ,  $\Gamma_5$ ,  $\Gamma_7$ , and  $\Gamma_9$  at  $\mathbf{k}=(0,0,0)$ , in the Jones or energy zone.<sup>7</sup> The function centered around one site is listed; in order to obtain the full LCAO (linear combination of atomic orbitals) type function it is necessary to sum over the four sites in the base<sup>7</sup> [since we are at  $\mathbf{k}=(0,0,0)$  no phase factor will arise in the sum]. By inspecting these functions we can gain insight into why the selection rules change when spin-orbit effect is included. Thus when  $\Gamma_1$  becomes  $\Gamma_7$  the effect of the spin-orbit perturbation is to mix  $x$  and  $y$  orbital parts into what was previously only  $s$  and  $z$ , allowing a transition to another  $\Gamma_7$  for  $E(\perp c)$ , where this was previously forbidden. Similarly, for the  $\Gamma_7$  derived from  $\Gamma_5$ ,  $s$  and  $z$  orbital functions have been mixed into what previously was only  $x$ ,  $y$ , thus allowing a transition to  $\Gamma_7$  for  $E(\parallel c)$ , where this was previously forbidden. While we thus naively expect that the  $\Gamma_7$  derived from  $\Gamma_5$  will be predominantly  $x$ ,  $y$ , and the  $\Gamma_7$  derived from  $\Gamma_1$ , predominantly  $s+z$ , only the solution of the appropriate secular equation would give valid values for the coefficients of the terms in the wave function of each state. In Fig. 1 we give the correspondence and order of states which were recently illustrated, in a somewhat different connection,<sup>8</sup> and were obtained using a combination of "simplified

<sup>6</sup> H. Margenau and G. M. Murphy, *Mathematics of Physics and Chemistry* (Van Nostrand and Company, New York, 1943), p. 558, Table 7.

<sup>7</sup> J. L. Birman, Phys. Rev. (to be published). In the energy zone, the points  $\mathbf{k}=(0,0,0)$  and  $\mathbf{k}=(0,0,2\pi/c)$  ( $c$  is the repeat distance along the  $z$  axis) are considered as distinct, so that no phase factor will arise, in summing over the base sites.

<sup>8</sup> J. L. Birman, Phys. Rev. Letters 2, 157 (1959), J. Phys. Chem. Solids 8, 35 (1959).

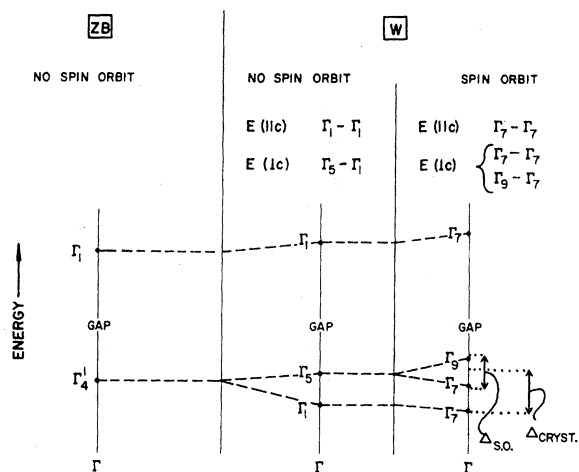


FIG. 1. Selection rules at  $\mathbf{k} = (0, 0, 0)$  in wurtzite (*W*) structures, assuming a normal order of states in valence and conduction bands. Corresponding zinc blende (*ZB*) states are shown at the left side of the figure. Crystal and spin orbit splittings are defined in the text. We have indicated the  $\mathbf{k} = (0, 0, 0)$  gap in wurtzite structure to be greater than in the zinc blende, as seems true for ZnS, and SiC. Also indicated are polarization rules for optical transitions in wurtzite structure, with and without inclusion of spin-orbit effect.

LCAO" theory and preliminary numerical results for ZnS. We expect at  $\mathbf{k} = (0, 0, 0)$  in a "normal" wurtzite material (listing the states in order of increasing binding energy) including spin-orbit effect, a  $\Gamma_7$  conduction band (derived from  $\Gamma_1$ ) followed by, in order (the energy gap and then)  $\Gamma_9$  valence band, an upper  $\Gamma_7$  valence band (derived from  $\Gamma_5$ ) and a lower  $\Gamma_7$  valence band (derived from  $\Gamma_1$ ). Again speaking naively, we expect the  $\Gamma_9$ -upper  $\Gamma_7$  valence band separation to be mainly due to spin orbit splitting while the  $\Gamma_9$ -lower  $\Gamma_7$  valence band separation would be mainly due to symmetry, or crystal field splitting. The actual situation must be more complicated, of course, since the two  $\Gamma_7$  valence levels will repel one another so that what is needed is, as before, the solution of the appropriate secular determinant. This order of states then allows us to predict that for optical transitions at  $\mathbf{k} = (0, 0, 0)$  there should be three characteristic wavelengths:

$$\lambda_1 > \lambda_2 > \lambda_3,$$

where  $\lambda_1$  is for the  $\Gamma_9 \rightarrow \Gamma_7$  transition and appears only for  $E(\perp c)$ ;  $\lambda_2$  and  $\lambda_3$  are  $\Gamma_7 \rightarrow \Gamma_7$  transitions and appear for  $E(\perp c)$  and  $E(\parallel c)$ .

The CdS edge emission excitation spectrum of Dutton,<sup>9</sup> may be interpreted by assuming we are dealing with band-band transitions and assigning  $\lambda_1 = 4874 \text{ \AA}$ ,  $\lambda_2 = 4844 \text{ \AA}$ , and similarly for the  $90^\circ\text{K}$  reflection spectrum measured by him.<sup>10</sup> Lempicki's recent measurement indicates a third reflection anomaly in CdS and

<sup>9</sup> D. Dutton, J. Phys. Chem. Solids **6**, 101 (1958).

<sup>10</sup> D. Dutton, Phys. Rev. **112**, 785 (1958).

using his values<sup>11</sup> under the assumption that we are dealing with band-band transitions, we obtain  $\lambda_1 = 4877 \text{ \AA}$ ,  $\lambda_2 = 4845 \text{ \AA}$ ,  $\lambda_3 = 4731 \text{ \AA}$ . Hence, we are led to assign 0.0167 eV as the (liquid  $\text{N}_2$  temperature) spin-orbit splitting:  $\Delta_{s.o.}$  (see Fig. 1). If we define the crystal splitting:  $\Delta_{\text{cryst}}$  (see Fig. 1) as the downward displacement of the lower  $\Gamma_7$  level from the mean of the  $\Gamma_9$  and upper  $\Gamma_7$  [i.e.,  $\Delta_{\text{cryst}} = \frac{1}{2}(\Gamma_9 - \Gamma_7) + (\Gamma_7 - \Gamma_7)$ ], we obtain about 0.070 eV as the estimated crystal splitting in CdS. These values seem reasonable, although small. This "spin-orbit splitting" of 0.0167 eV may be compared with the 0.0227 eV separation of the two edge emission sequences at  $4^\circ\text{K}$  measured by Furlong.<sup>12</sup>

If these assignments are correct, the model predicts the existence of certain polarized infrared absorption lines, during simultaneous band edge irradiation. Thus, if holes are produced in the  $\Gamma_9$  valence band by 4877  $\text{\AA}$  irradiation, these can be promoted (down) to the upper  $\Gamma_7$  valence band by  $7.75 \mu$  infrared and to the lower  $\Gamma_7$  valence band by  $\sim 17.7 \mu$  infrared, both for  $E(\perp c)$ . The polarization of edge or 6200  $\text{\AA}$  center emission should diminish, with the optical depletion of the  $\Gamma_9$  hole population. A similar infrared absorption should occur during simultaneous 4845  $\text{\AA}$  irradiation. Note also that the reported quenching of 4877  $\text{\AA}$  absorption by pre-irradiation of a CdS sample with red or infrared light (Gross<sup>13</sup>) is consistent with our model. Thus, red or infrared light produces free holes (by emptying shallow hole traps) which congregate in the  $\Gamma_9$  level, and quench the absorption from this level to the conduction band.

The assignment of transitions in CdS as  $\mathbf{k} = (0, 0, 0)$  band-band transitions based on obedience to band-band selection rules does not, of course, rule out other possibilities. For example, exciton transitions may be playing a role particularly in view of the reported low-temperature complexity of the absorption.<sup>14</sup> Another possibility for  $\lambda_2$  and  $\lambda_3$  is that the  $\Gamma_7$  conduction band has [at  $\mathbf{k} \neq (0, 0, 0) \neq (0, 0, k_z)$ ] subsidiary minima, and/or the  $\Gamma_9$  valence band subsidiary maxima [ $\mathbf{k} \neq (0, 0, 0)$ ,  $\mathbf{k} \neq (0, 0, k_z)$ ], and some interband transitions involve only these two surfaces; perpendicular polarization may arise, also, along  $\Gamma$ - $A$ , at  $K$ , and at  $M$ , depending on whether or not spin orbit effect is included.<sup>2</sup> Hence the assignments made are equivocal, although in accord with available data on CdS.

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It is a great pleasure to thank Mr. A. Lempicki and Dr. G. Neumark for many discussions.

<sup>11</sup> A. Lempicki, Proc. Phys. Soc. (London) (to be published).

<sup>12</sup> L. R. Furlong, Phys. Rev. **95**, 1086 (1954).

<sup>13</sup> E. F. Gross *et al.*, Doklady Akad. Nauk S.S.S.R. **110**, 761 (1956).

<sup>14</sup> E. F. Gross and M. A. Iakobson, Doklady Akad. Nauk S.S.S.R. **102**, 485 (1955).