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# Theory of the Valence Band Splittings at $\mathbf{k}=0$ in Zinc-Blende and Wurtzite Structures

STEPHEN L. ADLER*
*General Telephone & Electronics Laboratories, Inc., Bayside Laboratories, Bayside, New York*

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A theory of the valence band splittings at $\mathbf{k}=0$ in zinc-blende and wurtzite structures is proposed, in which the wurtzite levels are treated as perturbations of those in zinc blende. Starting from one-electron Hamiltonians for the two structures, the two-parameter formulas originally derived by Hopfield are obtained, with a minimum of approximations, along with explicit expressions for the parameters in terms of Hamiltonian matrix elements. The two-parameter formulas are compared with experimental data and agreement is found to be good. A simple tight-binding (linear combination of atomic orbitals), $3p$ valence band, point-ion lattice model is used to calculate an effective charge for ZnS from the known valence band splittings in the wurtzite and zinc-blende dimorphs; a value of $2.3e$ is obtained.

## 1. INTRODUCTION

THE object of this paper is to explore a theory of the $\mathbf{k}=0$ valence band energy splittings and wave functions in zinc-blende and wurtzite structures. This is of interest because recent experimental work on hexagonal (wurtzite) and cubic (zinc blende) ZnS,[1] hexagonal CdS,[1] CdSe,[2] and ZnO,[3] cubic ZnSe,[4] and other II–VI semiconductors has made available data on their valence band energy splittings and wave function symmetries.

Previous theoretical work on wurtzite and zinc-blende valence band splittings has been reported by Birman[5] and by Hopfield.[6] Birman's theory did not include the spin-orbit interaction. Hopfield's work, based on a quasi-cubic model of the wurtzite structure, gave useful formulas for the wurtzite and zinc-blende valence band splittings, which fit experimental data obtained for ZnS to within 10%. The theory presented below starts from the rigorous one-electron Hamiltonians for wurtzite and zinc blende and yields, with a minimum of approximations, the formulas proposed by Hopfield. In addition, the crystal field and spin-orbit parameters are expressed in terms of matrix elements of the wurtzite and zinc-blende Hamiltonians.

Although the anion and cation are for the sake of definiteness assumed to be S and Zn, this does not enter into the derivation. The two-parameter formulas should be valid in other substances than ZnS crystallizing in zinc-blende and wurtzite dimorphs, provided that the approximations made in the derivation still hold.

## 2. THEORY

Some details of the zinc-blende and wurtzite geometries will be needed.[7] In zinc blende there are two atoms per unit cell, and in wurtzite, four. Call the two sulfur atoms in the wurtzite basis sulfur 1 and 2, respectively. The nearest-neighbor configurations in zinc blende and ideal wurtzite are identical and the second-nearest-neighbor (nearest like ion) configurations are nearly so (Fig. 1). This local structural similarity will be exploited by using axis systems for the two structures in which the nearest neighbors of the sulfur 1 site in the wurtzite basis and the sulfur site in the zinc blende basis have identical coordinates. The axis systems which will be used throughout the rest of this paper, unless explicitly stated otherwise, are illustrated in Fig. 2. Note that the axes for zinc blende are not the usual Cartesian axes employed for this structure.[5]

The Hamiltonians for band-theoretic treatment of wurtzite and zinc blende, including in each the spin-orbit interaction term, are

$$H_{\mathrm{ZB}}=\mathbf{p}^2/2m+V_{\mathrm{ZB}}(\mathbf{r})+(\hbar/4m^2c^2)(\nabla V_{\mathrm{ZB}}\times\mathbf{p})\cdot\boldsymbol{\sigma},$$
$$H_{\mathrm{W}}=\mathbf{p}^2/2m+V_{\mathrm{W}}(\mathbf{r})+(\hbar/4m^2c^2)(\nabla V_{\mathrm{W}}\times\mathbf{p})\cdot\boldsymbol{\sigma},$$

where $V_{\mathrm{ZB}}$ and $V_{\mathrm{W}}$ are the respective crystal potentials in the two substances. A modification of the linear combination of atomic orbitals (LCAO) procedure will be used to find expressions for the valence band energy splittings and wave functions at $\mathbf{k}=0$ in the Brillouin zone. In the usual LCAO formalism,[8] the Hamiltonian at $\mathbf{k}=0$ is diagonalized in a space spanned by the cell periodic functions $\Psi_n{}^{\beta}=N^{-\frac{1}{2}}\sum_j\psi_n(\mathbf{r}-\mathbf{R}_j{}^{\beta})$. Here $\psi_n$ is a free-ion orbital, $n$ denotes a complete set of quantum numbers and $\mathbf{R}_j{}^{\beta}$ is the position of the $\beta$th basis atom in the $j$th unit cell. In the modification used in this paper, the rigorous zinc-blende (ZB) Bloch functions at $\mathbf{k}=0$ are expanded in Wannier functions,

$$\Psi_n{}^{\mathrm{ZB}}=N^{-\frac{1}{2}}\sum_j\chi_n(\mathbf{r}-\mathbf{R}_j{}^1),$$

where $\mathbf{R}_j{}^1$ is the coordinate of the sulfur atom in the

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* Summer visitor, 1960; now at Physics Department, Princeton University, Princeton, New Jersey.

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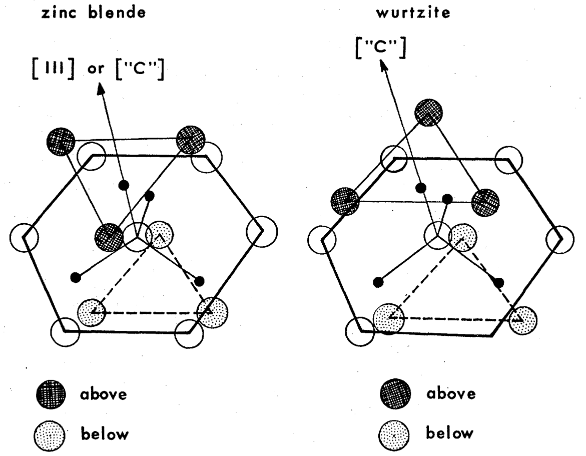

FIG. 1. First and second neighbors in zinc blende and wurtzite. Large circles are S atoms, small ones Zn. Open circles are in the same plane. Comparing the two structures, we note that only three of the twelve second neighbors differ, and even these are disposed symmetrically. These are shown as the 3 atoms "above" and are rotated by $\pi/3$ in zinc blende with respect to their positions in wurtzite.

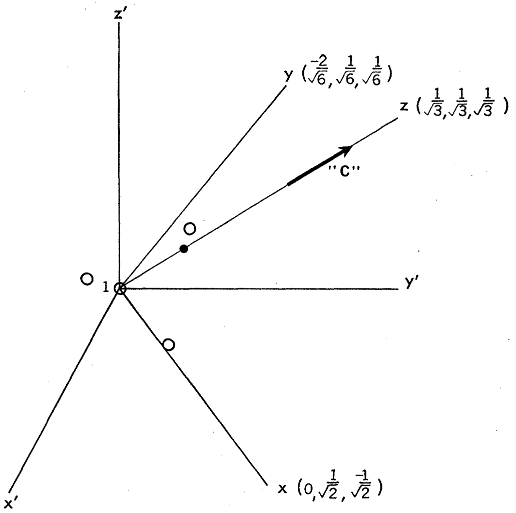

FIG. 2. Axes for zinc blende and wurtzite. The axes $x$, $y$, $z$ are the ones used in this paper. These are the axes usually employed for the wurtzite structure. The axes $x'$, $y'$, $z'$ are the conventional axes for the zinc-blende structure. The open and blackened circles represent sulfur and zinc sites, respectively.

$j$th cell in zinc blende. These functions form an orthonormal set ($\langle\Psi_n^{\mathrm{ZB}}|\Psi_{n'}^{\mathrm{ZB}}\rangle=\delta_{nn'}$) and are a complete cell-periodic set in zinc blende. In wurtzite (W), the Hamiltonian matrix at $\mathbf{k}=0$ will be computed using as basis functions the linear combinations of zinc-blende Wannier functions,

$$\Psi_n^{\mathrm{W}\pm}=(2N)^{-\frac{1}{2}}\sum_j[\chi_n(\mathbf{r}-\mathbf{R}_j^1)\pm\chi_n(\mathbf{r}-\mathbf{R}_j^2)],$$

where $\mathbf{R}_j^1$ and $\mathbf{R}_j^2$ are the coordinates of the two sulfur atoms in the cell in wurtzite. We remark that $\langle\Psi_n^{\mathrm{W}+}|\Psi_{n'}^{\mathrm{W}-}\rangle=\langle\Psi_n^{\mathrm{W}+}|H_{\mathrm{W}}|\Psi_{n'}^{\mathrm{W}-}\rangle=0$; in other words, the wurtzite Hamiltonian matrix breaks up into two submatrices spanned, respectively, by the functions $\Psi_n^{\mathrm{W}+}$ and $\Psi_n^{\mathrm{W}-}$. This is proved by noting that the symmetry operation $C_2$, the twofold screw axis in wurtzite, which interchanges type-1 and type-2 sites, leaves $H_{\mathrm{W}}$ and the $\Psi_n^{\mathrm{W}+}$ functions invariant while changing the sign of the $\Psi_n^{\mathrm{W}-}$ functions. Furthermore, the functions $\Psi_n^{\mathrm{W}+}$ and $\Psi_n^{\mathrm{W}-}$ are similar in form, respectively, to the zinc-blende valence band wave functions $\Psi_{n\mathbf{k}}^{\mathrm{ZB}}=N^{-\frac{1}{2}}\sum_j\exp(i\mathbf{k}\cdot\mathbf{R}_j)\chi_n(\mathbf{r}-\mathbf{R}_j)$ at the points $\mathbf{k}=(0,0,0)$ and $\mathbf{k}=(0,0,2\pi/c)$ in the zinc-blende Brillouin zone. Consequently, the wurtzite energy eigenvalues determined by the submatrix $\langle\Psi_n^{\mathrm{W}+}|H_{\mathrm{W}}|\Psi_{n'}^{\mathrm{W}+}\rangle$ correspond to levels at $\mathbf{k}=(0,0,0)$ in zinc blende, while those determined by the submatrix $\langle\Psi_n^{\mathrm{W}-}|H_{\mathrm{W}}|\Psi_{n'}^{\mathrm{W}-}\rangle$ correspond to levels at $\mathbf{k}=(0,0,2\pi/c)$, which is the point $\Lambda$ at the Brillouin zone edge in zinc blende. Only the wurtzite levels corresponding to those at $\mathbf{k}=(0,0,0)$ in zinc blende will be considered.

To a good approximation, the functions $\Psi_n^{\mathrm{W}+}$ are an orthonormal set. The reason is that the nearest *like ion* (second-nearest neighbor) configurations in wurtzite and zinc blende are almost identical, and consequently nearest-like-ion overlaps can be expected to give roughly equal contributions to $\langle\Psi_n^{\mathrm{ZB}}|\Psi_{n'}^{\mathrm{ZB}}\rangle$ and $\langle\Psi_n^{\mathrm{W}+}|\Psi_{n'}^{\mathrm{W}+}\rangle$. Assuming higher overlaps can be neglected, we have $\langle\Psi_n^{\mathrm{W}+}|\Psi_{n'}^{\mathrm{W}+}\rangle\approx\langle\Psi_n^{\mathrm{ZB}}|\Psi_{n'}^{\mathrm{ZB}}\rangle=\delta_{nn'}$. Thus, by means of a linear combination of zinc-blende Wannier functions one can construct a nearly orthonormal set of basis functions for the wurtzite structure, suitable for a comparison of the energy levels in the two structures at $\mathbf{k}=(0,0,0)$.

## Zinc Blende

Let us consider in more detail the zinc-blende Bloch functions at the top of the valence band. If we omit the spin-orbit interaction term in the zinc-blende Hamiltonian, the top of the valence band will be sixfold degenerate, with state vectors $(|X\rangle,|Y\rangle,|Z\rangle)\cdot(|+\rangle,|-\rangle)$ where $|X\rangle$, $|Y\rangle$, $|Z\rangle$ are Bloch states transforming like $x$, $y$, $z$ under the operations of the zinc-blende symmetry group $T_d$. The zinc-blende Hamiltonian with the spin-orbit interaction term is diagonal in the manifold spanned by

$$\Gamma_8\begin{cases}|1\rangle=|\Pi\rangle|+\rangle,\\ |2\rangle=(1/\sqrt{6})[\sqrt{2}|\Pi\rangle|-\rangle-2|Z\rangle|+\rangle],\\ |3\rangle=(1/\sqrt{6})[\sqrt{2}|\bar{\Pi}\rangle|+\rangle+2|Z\rangle|-\rangle],\\ |4\rangle=|\bar{\Pi}\rangle|-\rangle,\end{cases}\tag{1}$$

$$\Gamma_7\begin{cases}|5\rangle=(1/\sqrt{3})[\sqrt{2}|\Pi\rangle|-\rangle+|Z\rangle|+\rangle],\\ |6\rangle=(1/\sqrt{3})[\sqrt{2}|\bar{\Pi}\rangle|+\rangle-|Z\rangle|-\rangle],\end{cases}$$

$$|\Pi\rangle=(1/\sqrt{2})(|X\rangle+i|Y\rangle),\quad|\bar{\Pi}\rangle=(1/\sqrt{2})(|X\rangle-i|Y\rangle).$$

The first group of states transforms as a basis for the irreducible representation $\Gamma_8$ of the double group of $T_d$; the second set is a basis for $\Gamma_7$. Use of the finite basis, Eq. (1), to diagonalize the Hamiltonian is equivalent to treating the spin-orbit term by first-order perturbation theory. Thus, the error in the energies made by the neglect of admixtures of wave functions from other bands is of the order $\delta^2/E_g$, where $\delta$ is the zinc-blende spin-orbit splitting and $E_g$ is the band gap. Since $\delta^2/E_g \approx 0.067\delta/3.6$, the fractional error made in the valence band splitting is small. The prediction that the zinc-blende valence band is split into a $\Gamma_8$ level and a $\Gamma_7$ level agrees with experiment.[1]

### Wurtzite

The basis functions in wurtzite are taken as sums of zinc-blende Wannier functions. Consider in particular those constructed from the zinc-blende valence band wave functions, using for these the approximate forms Eqs. (1). Since the threefold rotation operation and the reflection plane parallel to its axis are symmetry operations in *both* zinc blende and wurtzite, the behavior of the sets of states $|1\rangle, \cdots, |6\rangle$; $|1^+\rangle, \cdots, |6^+\rangle$ under these operations will be identical. It is thus possible to show, by using characters of the double group of $C_{3v}$, that the states $|1^+\rangle, \cdots, |6^+\rangle$ transform according to representations of the double group of $C_{3v}$ as follows[9]

$$\begin{array}{lll} \begin{array}{ll}\Lambda_4 & (1/\sqrt{2})[|1^+\rangle+|4^+\rangle] \\ \Lambda_5 & (1/\sqrt{2})[|1^+\rangle-|4^+\rangle]\end{array} & \Lambda_6\begin{cases}|2^+\rangle \\ |3^+\rangle\end{cases} & \Lambda_6\begin{cases}|5^+\rangle \\ |6^+\rangle\end{cases} \\ (\Gamma_9) & (\Gamma_7) & (\Gamma_7) \end{array} .$$

This permits a simplification of the submatrix of the wurtzite Hamiltonian spanned by $|1^+\rangle, \cdots, |6^+\rangle$, to

$$\begin{array}{c|cccccc} & 1^+ & 4^+ & 2^+ & 5^+ & 3^+ & 6^+ \\ \hline 1^+ & a & 0 & 0 & 0 & 0 & 0 \\ 4^+ & 0 & a & 0 & 0 & 0 & 0 \\ 2^+ & 0 & 0 & b & c & 0 & 0 \\ 5^+ & 0 & 0 & c^* & d & 0 & 0 \\ 3^+ & 0 & 0 & 0 & 0 & b & c \\ 6^+ & 0 & 0 & 0 & 0 & c^* & d \end{array}$$

The prediction that the wurtzite valence band consists of a $\Gamma_9$ level and two $\Gamma_7$ levels agrees with experiment.

Just as in zinc blende, the admixture of other wave functions forming the basis will be neglected. Let us write

$$\langle n|H_0|n'\rangle = \langle\Psi_n{}^{\mathrm{ZB}}|H_{\mathrm{ZB}}|\Psi_{n'}{}^{\mathrm{ZB}}\rangle - \delta\delta_{nn'}\left(\sum_{k=1}^{4}\delta_{nk}\right),$$

$$\langle n|H_1|n'\rangle = \langle\Psi_n{}^{\mathrm{W}+}|H_{\mathrm{W}}|\Psi_{n'}{}^{\mathrm{W}+}\rangle - \langle\Psi_n{}^{\mathrm{ZB}}|H_{\mathrm{ZB}}|\Psi_{n'}{}^{\mathrm{ZB}}\rangle + \delta\delta_{nn'}\left(\sum_{k=1}^{4}\delta_{nk}\right),$$

where $\delta$, as before, is the zinc-blende spin-orbit splitting, and $\delta_{nn'}$ is the Kronecker delta. The near degeneracy of the valence band in zinc blende has been made a complete degeneracy in $H_0$ by subtraction of $\delta\delta_{nn'}(\sum_{k=1}^{4}\delta_{nk})$; this term has been included in the perturbation $H_1$. In this way we have defined a problem in degenerate perturbation theory. If the degenerate manifold is treated exactly, neglect of the admixture of other wave functions of the basis is equivalent to neglecting second- and higher order terms in a perturbation expansion, and results in an error $\approx|\langle|H_1|\rangle|^2/E_g$. Here $|\langle|H_1|\rangle|$ is the magnitude characteristic of matrix elements of the perturbation, which can be expected to be of the order of the valence band splittings in wurtzite $\approx 0.05$ ev. Thus, the fractional error made in the valence band splitting $\approx 0.05/3.6$, which is small.

### Two-Parameter Formulas

Because $H_1$ factors completely into $2\times 2$ submatrices, exact solution of the eigenvalue problem within the degenerate manifold is easy. The results for the wurtzite and zinc-blende valence band energy splittings and the wurtzite valence band eigenstates are:

$$\Delta E_{\mathrm{W}}:\quad \begin{cases} E_a - E_b = \dfrac{\alpha+\delta}{2} - \left[\left(\dfrac{\alpha+\delta}{2}\right)^2 - \dfrac{2\alpha\delta}{3}\right]^{\frac{1}{2}}, \\[2ex] E_b - E_c = 2\left[\left(\dfrac{\alpha+\delta}{2}\right)^2 - \dfrac{2\alpha\delta}{3}\right]^{\frac{1}{2}}, \end{cases} \tag{2}$$

$$\Delta E_{\mathrm{ZB}}:\qquad \delta = \langle 1|H_{\mathrm{ZB}}|1\rangle - \langle 5|H_{\mathrm{ZB}}|5\rangle;$$

$$\begin{aligned} |a\rangle &= |1^+\rangle, \\ N_b|b\rangle &= \frac{\sqrt{2}\alpha}{3}|5^+\rangle + \left\{\frac{\delta}{2} - \frac{\alpha}{6} + \left[\left(\frac{\alpha+\delta}{2}\right)^2 - \frac{2\alpha\delta}{3}\right]^{\frac{1}{2}}\right\}|2^+\rangle, \\ N_c|c\rangle &= \frac{\sqrt{2}\alpha}{3}|5^+\rangle + \left\{\frac{\delta}{2} - \frac{\alpha}{6} - \left[\left(\frac{\alpha+\delta}{2}\right)^2 - \frac{2\alpha\delta}{3}\right]^{\frac{1}{2}}\right\}|2^+\rangle. \end{aligned} \tag{3}$$

Here $N_b$ and $N_c$ are normalization constants and $\alpha$ is a crystal field parameter defined by

$$\alpha = [\langle\Pi^+|H_{\mathrm{W}}|\Pi^+\rangle - \langle\Pi|H_{\mathrm{ZB}}|\Pi\rangle] - [\langle Z^+|H_{\mathrm{W}}|Z^+\rangle - \langle Z|H_{\mathrm{ZB}}|Z\rangle].$$

In this expression $H_{\mathrm{W}}$ and $H_{\mathrm{ZB}}$ signify the Hamiltonians without the spin-orbit interaction terms.[10]

Equations (2) are the two-parameter formulas originally derived by Hopfield.[5] They have been obtained by making only three approximations:

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[9] The designation in parentheses refers to the representation of the double group of $C_{6v}$ according to which the functions approximately transform. The basis functions for wurtzite would transform exactly according to irreducible representations of $C_{6v}$ if we took the zinc-blende valence band Bloch functions to be linear combinations of ionic $3p$ orbitals. We have instead used the exact zinc-blende Bloch functions. Because the wurtzite Hamiltonian is diagonalized with respect to only a finite basis, and because the functions in the basis transform only approximately according to irreducible representations of $C_{6v}$, the wurtzite valence band wave functions obtained have only approximately the correct symmetry properties. Nevertheless, in the remainder of this paper the wurtzite functions will be labeled by the indicated representations of $C_{6v}$.

[10] It is easy to show that the fractional error resulting from neglect of these terms is of the order

$$\frac{|\langle 1^+|(\hbar/4m^2c^2)\nabla V_{\mathrm{W}}\times\mathbf{p}|1^+\rangle|}{|\langle 1^+|V_{\mathrm{W}}|1^+\rangle|} \approx \frac{\hbar^2}{m^2c^2\langle r^2\rangle} \approx 10^{-4},$$

where $\langle r^2\rangle$ is the mean square sulfur ion radius.

(1) Assumption of approximate orthonormality of the wurtzite basis;

(2) Neglect of energy terms $\approx\delta^2/E_g$;

(3) Neglect of energy terms $\approx|\langle|H_1|\rangle|^2/E_g$.

Note that the equations for the splittings in wurtzite are completely symmetric in $\alpha$ and $\delta$. This means that $\alpha$ and $\delta$ cannot be determined uniquely from the wurtzite splittings: if $(\alpha,\delta)=(a,b)$ is one solution consistent with the data, then $(\alpha,\delta)=(b,a)$ is another. The ambiguity just corresponds to the fact that solving (2) for $\alpha$ and $\delta$ in terms of $E_a-E_b$, $E_b-E_c$ leads to a quadratic equation, both roots of which are allowable solutions. This symmetry of the two-parameter formulas is not explicitly evident in the version of them given by Balkanski and Cloizeux.[11]

Finally, it is to be emphasized that the anion and cation have been assumed to be S and Zn in the above derivation purely for the sake of convenience in referring to them. The theory should be valid in other semiconductors with $p$-like valence bands and with spin-orbit and crystal field splittings which are small relative to the band gap.

## 3. APPLICATION TO ZnS, CdS, AND OTHER II–VI COMPOUNDS

The two-parameter formulas describe three splittings in terms of two parameters. They fit well the values given by Birman *et al.*[1] for the spin-orbit splitting of the zinc-blende form and the two valence band splittings of the wurtzite form of ZnS. From the data (Table I) at 77°K, $\delta=0.068$ ev and $E_a-E_b+\frac{1}{2}(E_b-E_c)=\frac{1}{2}(\alpha+\delta)=0.069$ ev, giving $\alpha=0.070$ ev. The theory then gives 0.080 ev and 0.029 ev for the wurtzite splittings, within 10% of the experimental values of 0.084 ev and 0.027 ev. The order of levels predicted is also correct.

A reasonable result is also obtained when Eqs. (2) are applied to data for CdS. Crystals of cubic CdS have not yet been grown. However, with data for hexagonal CdS, the formulas can be used to predict the value of the spin-orbit splitting which would be observed in cubic CdS. Two values are obtained as a result of the ambiguity discussed above: $\delta=0.065$ ev or $\delta=0.029$ ev (at 77°K). The first of these is close to the ZnS splitting and is probably the correct solution, since the valence band spin-orbit splitting should be determined primarily by the wave function and potential near the sulfur ion and should depend only weakly on the nature of the cation. Measurements on CdSe[2] and on ZnSe,[4] which show nearly the same spin-orbit splitting for both substances, are evidence for the validity of this type of argument.

TABLE I. Valence band splittings in ZnS and CdS.

| Temperature (°K) | $\delta$ (ev) | $E_a-E_b$ (ev) | $E_b-E_c$ (ev) |
|---|---|---|---|
| | Cubic ZnS | | |
| 77 | 0.068 | | |
| 14 | 0.065 | | |
| | Hexagonal ZnS | | |
| 77 | | 0.027 | 0.084 |
| 14 | | 0.026 | 0.082 |
| | Hexagonal CdS | | |
| 77 | | 0.016 | 0.062 |

From the formulas, Eqs. (3), the parentage of the lines in wurtzite ZnS can be determined. Taking $\alpha=0.070$ ev, one obtains

$$|b\rangle=0.48|5^+\rangle+0.88|2^+\rangle,$$
$$|c\rangle=0.88|5^+\rangle-0.48|2^+\rangle.$$

These can also be written

$$|b\rangle=0.90|\Pi^+\rangle|-\rangle-0.44|Z^+\rangle|+\rangle,$$
$$|c\rangle=0.44|\Pi^+\rangle|-\rangle+0.90|Z^+\rangle|+\rangle.$$

These expressions have a simple interpretation (see the splitting diagram, Fig. 3). The states $|5\rangle$ and $|2\rangle$ transform according to the irreducible representations $\Gamma_5$ and $\Gamma_1$, respectively, of the double group of the wave vector at $\mathbf{k}=(0,0,0)$ in zinc blende. These states are zinc-blende valence band eigenstates which differ in energy by $\delta$, the spin-orbit energy. Equations (3) indicate how these zinc-blende levels mix when the crystal field perturbation is "turned on." The states $|\Pi^+\rangle|-\rangle$ and $|Z^+\rangle|+\rangle$ transform, respectively, according to the irreducible representations $\Gamma_5$ and $\Gamma_1$ of the single group $C_{6v}$, the

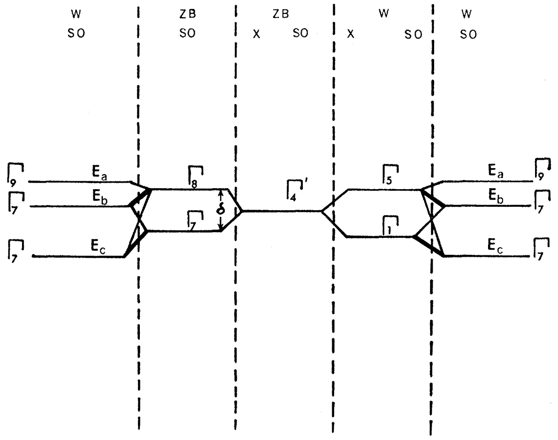

FIG. 3. Splitting diagram indicating the mixings and splittings of the valence band levels as the perturbations, the spin-orbit interaction, and the crystal field, $V_{\mathrm{W}}-V_{\mathrm{ZB}}$, are turned on in opposite orders. As in the text, W means wurtzite and ZB means zinc blende; SO and XSO mean, respectively, *with* and *without* the spin-orbit interaction. At the right of the figure, the lowest $\Gamma_7$ level in the W SO column is joined by a double line to the $\Gamma_1$ level and by a single line to the $\Gamma_5$ level. This signifies that the wave function of the lowest $\Gamma_7$ level is a mixture of functions which transform according to $\Gamma_5$ and $\Gamma_1$ of the single group $C_{6v}$, and that the coefficient of the $\Gamma_1$ wave function is larger than the coefficient of the $\Gamma_5$ wave function. The other single and double lines have a similar significance.

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[11] M. Balkanski and J. Cloizeux (to be published).

group of the wave vector at $\mathbf{k}=(0,0,0)$ in a wurtzite structure in which there is no spin-orbit interaction. According to Eqs. (3), when the spin-orbit interaction in wurtzite is "turned off" by setting $\delta=0$, the state $|b\rangle$ becomes $|\Pi^+\rangle|-\rangle$ (transforming according to $\Gamma_5$), the state $|c\rangle$ becomes $|Z^+\rangle|+\rangle$ (transforming according to $\Gamma_1$), and the $\Gamma_5$ state has the higher energy. The prediction that the $\Gamma_5$ level would exceed the $\Gamma_1$ level in energy in wurtzite ZnS if the spin-orbit interaction could be eliminated agrees with the observations showing that in hexagonal ZnO, in which the spin-orbit interaction is extremely weak due to the low anion atomic number, the $\Gamma_5$-like levels lie above a $\Gamma_1$-like level.[12]

## 4. ESTIMATION OF THE EFFECTIVE CHARGE

An attempt was made to make an *a priori* calculation of $\alpha$, and by this means to estimate an effective charge for ZnS. The zinc-blende Bloch states $|X\rangle$, $|Y\rangle$, $|Z\rangle$ were assumed to be LCAO states constructed from sulfur $3p$ ionic orbitals. Only zeroth and first-neighbor interaction integrals were retained, and a point-ion model of the zinc-blende and wurtzite lattices, with effective ionic charges $+\lambda e$ and $-\lambda e$ for zinc and sulfur ions, respectively, was used. This model gives $\alpha=-(3E/5)\times\int_0^\infty dr\, r^4(R_{3p})^2$, where $E$ is the coefficient of $r^2P_2(\cos\theta)$ in the expansion of $V_{\mathrm{W}}$ about a sulfur ion site and $R_{3p}$ is an ionic radial orbital. Evaluation of $E$ by an Ewald summation method[13] gives $\lambda=2.3$, clearly too large. Taking into account the effect of mixings of sulfur $3d$ states into the zinc-blende valence band wave function and the deviation of wurtzite ZnS from ideality was found to produce little change in the value of $\lambda$ obtained. (The expansions of $V_{\mathrm{W}}$ and $V_{\mathrm{ZB}}$ used are given in the Appendix.) Mixings of zinc $4p$ states into the zinc-blende wave function may have an important effect on $\lambda$, but the overlap integrals necessary to estimate this were not calculated.

## ACKNOWLEDGMENT

The author wishes to express his gratitude to Dr. J. L. Birman, who suggested the problem discussed in this paper and with whom the writer has had many valuable discussions.

## APPENDIX

We give here the first few terms of the expansion in solid harmonics of the potentials in ideal wurtzite and zinc-blende point-ion lattices. The nearest like-ion distance is $d_{SS}$ and the effective charge parameter is $\lambda$. The origin for the expansion is a sulfur site such as is at the orgin in Fig. 2; in other words, a sulfur site with nearest neighbors with direction cosines $(0,0,1)$; $(0,\ -2\sqrt{2}/3,\ -1/3)$; $(\sqrt{2}/\sqrt{3},\ \sqrt{2}/3,\ -1/3)$; $(-\sqrt{2}/\sqrt{3},\ \sqrt{2}/3,\ -1/3)$ on the unprimed axes. All sums were evaluated by an Ewald method and were checked to the number of places indicated by summing with two different values of the convergence parameter.

Zinc blende (conventional axes, i.e., primed axes in Fig. 2):

$$\frac{V_{\mathrm{ZB}}}{e^2\lambda/d_{SS}}=A_0+B_0\frac{x'y'z'}{d_{SS}^3}+\cdots,$$

$$B_0=76.8.$$

Wurtzite (unprimed axes in Fig. 2):

$$\frac{V_{\mathrm{W}}}{e^2\lambda/d_{SS}}=C_0+D_0\frac{z}{d_{SS}}+E_0\frac{\frac{1}{2}(2z^2-x^2-y^2)}{d_{SS}^2}+F_0\frac{\frac{1}{2}[2z^3-3(x^2+y^2)z]}{d_{SS}^3}+G_0\frac{(3x^2y-y^3)}{d_{SS}^3}+\cdots,$$

$$D_0=-0.0397,\quad F_0=14.43,$$

$$E_0=\ 0.142,\quad G_0=10.1.$$

Note that $E=(-e^2\lambda/d_{SS}^3)E_0$.

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[12] However, in ZnO, unlike ZnS, the order of levels is $\Gamma_7$, $\Gamma_9$, $\Gamma_7$; this is discussed by Hopfield[6] and by Thomas.[3]

[13] B. R. A. Nijboer and F. W. De Wette, Physica **23**, 309 (1957).