PHYSICAL REVIEW VOLUME 109, NUMBER 3 FEBRUARY 1, 1958

Electronic Energy Bands in ZnS: Potential in Zincblende and Wurtzite

JOSEPH L. BIRMAN
Research Laboratories, Sylvania Electric Products, Incorporated, Bayside, New York

(Received July 23, 1957)

This paper reports on the calculation of the crystal potential in ZnS. Experimental evidence relating to the nature of the chemical bond is reviewed, and it is concluded that the bonding is a mixture of covalent and ionic with effective charges of $+\frac{1}{2}$ for Zn, $-\frac{1}{2}$ for S. Radially symmetric sp^3 valence electron densities are constructed for each ion and normalized within each equivalent volume sphere to the appropriate net ion charge. It is concluded that the same charge densities are appropriate for zincblende and wurtzite. Calculation using these charge densities then shows the crystal potential to be the same for both modifications in two corresponding prominent crystallographic directions. Hence, there is justification for using the same spherical potential for the cellular calculation of electronic energy bands in both structures. Finally, the close geometrical relationship of the two structures implies that many of the LCAO integrals which will arise in interpolating the band structures are identical.

1. INTRODUCTION

THIS is the first of several papers reporting on the cellular calculation of electronic energy bands in crystalline ZnS. In this paper the nature of the chemical bond in ZnS, and the calculation of the crystal potential, will be discussed. It will be shown that it is reasonable to use the same crystal potential for both ideal crystalline modifications of ZnS, in the approximation that the potential is spherically symmetric. The subsequent papers will report on the results for zinc blende, and for wurtzite.[1]

The cellular calculation can be conveniently carried through only at isolated points of high symmetry in the Brillouin zone (generally end points in prominent directions) and the main burden of the calculation is to obtain accurate eigenenergies at these points. When such eigenenergies are available, the method of Slater and Koster[2] can be used to obtain the values of certain "LCAO" (linear combination of atomic orbitals) integrals needed to interpolate the band structure at points of lower symmetry in the zone. As a consequence of the geometry of the two structures, many of the same LCAO integrals arise in the band calculation for zincblende and wurtzite. Hence the LCAO integrals determined from the two independent cellular calculations should agree closely. In fact, ZnS is well suited to test the LCAO approach in this manner because of the close relationship of its two ideal crystalline modifications. Since for ZnS, both of the ideal crystalline modifications exist, an experimental test can be made of the band structures predicted by the cellular calculations, and of the relationship between the wurtzite and zincblende band structures predicted from the appearance of common LCAO integrals.

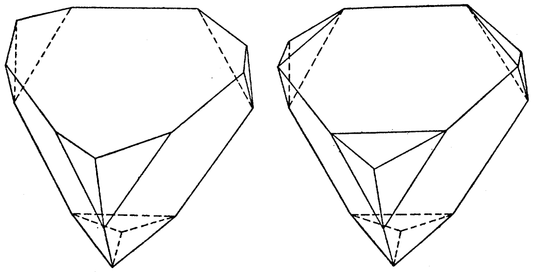

FIG. 1. Atomic polyhedra, zincblende (left-hand side) and wurtzite (right-hand side). The atoms are assumed equal in size. The polyhedron appropriate to zinc (or sulfur) is shown in each case. The wurtzite polyhedron is obtained from zincblende by rotating the three planes (110), (101), (011) into (100), (010), and (001), i.e., by 60° about the [111] direction. (All directions are given in a Cartesian system.)

2. GEOMETRY OF ZINCBLENDE AND WURTZITE

Zincblende belongs to space group T_d^2, with the atomic positions fixed by symmetry.[3] The structure may be considered as two cubic close-packed arrays, one of sulfur atoms, the other of zinc atoms, translated with respect to one another by $\frac{1}{4}$ the body diagonal of the usual cubic cell (i.e., along a threefold axis). Each atom has 4 first neighbors of the other kind at the corners of a regular tetrahedron, and 12 second neighbors of the same kind. Six of the second neighbors are in the same plane as the original atom, at the corners of a regular hexagon; the remaining six are distributed three above, and three below at the corners of a trigonal antiprism. Crystallographic data are summarized in Table I.

Wurtzite belongs to space group C_{6v}^4.[3] This space group allows the introduction of a parameter.[3] The structure may be considered as composed of two interpenetrating hexagonal close packed arrays of zinc and sulfur atoms displaced with respect to one another along their common threefold axis. The parameter in this space group is a measure of the relative separation of the two close packed arrays. In the *ideal* wurtzite structure, the ratio $c/a=(8/3)^{\frac{1}{2}}$ and the parameter $u=\frac{3}{8}$. For this ideal structure, each atom has 4 first

---

[1] In what follows, zincblende and wurtzite will refer to the *actual* ZnS cubic and hexagonal structures, which are to a good approximation "ideal."

[2] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[3] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951), Chap. III, p. 19; *International Tables for X-Ray Crystallography* (Kynoch Press, Birmingham, 1952), pp. 325, 293.

neighbors of the other kind at the corners of a regular tetrahedron, and 12 second neighbors of the same kind. Six of these are in the same plane as the original atom, at the corners of a regular hexagon, the remaining six are three above and three below this plane at the corners of a trigonal prism. For the appropriate crystallographic data see Table I.

Although the ZnS wurtzite structure is not ideal ($c/a \neq 1.633$), for purposes of this calculation it can be considered ideal. In addition the first and second neighbor spacings are, to within 2%, identical for both zinc blende and wurtzite. Hence, in comparing the two structures we see that first neighbors are in identical locations, as are 9 of the 12 second neighbors, the other 3 being rotated by 60° just as in the difference between a trigonal prism and a trigonal antiprism. It is necessary then, to go to third neighbors of a given atom in order to find significant differences between the two modifications (see also von Hippel[4]).

TABLE I. Crystallographic data for ZnS.[a]

	Zincblende	Wurtzite
Primitive vector set[b]	$\mathbf{a}_1=\alpha(1,1,0)$ $\mathbf{a}_2=\alpha(1,0,1)$ $\mathbf{a}_3=\alpha(0,1,1)$	$\mathbf{a}_1=a(\sqrt{3}/2, -\frac{1}{2}, 0)$ $\mathbf{a}_2=a(0,1,0)$ $\mathbf{a}_3=c(0,0,1)$
Basis	$(0,0,0), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(0,0,0), (\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ $(0,0,u), (\frac{1}{3}, \frac{2}{3}, \frac{1}{2}+u)$
First neighbor distance	2.36 A	2.33 A
Second neighbor distance	3.82 A	3.81 A
c/a[c]		1.636
u[c]		0.375
r_{EVS}[d,e]	3.18 a.u.	3.17 a.u.

[a] Data from R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948), Vol. 1.

[b] Referenced on Cartesian coordinate axes. α = like atom separation; a and c: hexagonal cell sides.

[c] The value of u has been assumed $= \frac{3}{8}$. For the *ideal* wurtzite structure $c/a = 1.633$, which is sufficiently close to the observed value to consider it ideal.

[d] Radius of the equivalent-volume sphere (EVS), i.e., a sphere whose volume equals the volume per atom (atoms are assumed of equal size in each structure). (In atomic units: 1 a.u. = 0.528 A.)

[e] We shall take the r_{EVS} for wurtzite to be 3.18 a.u. in the calculation, even though this introduces an error of 0.01 a.u.

The geometrical relationship of the two structures is conveniently seen by constructing the atomic and cellular polyhedra which are appropriate.[5] An atomic polyhedron for a given structure may be defined as that region closer to the atom at its center than to any other atom in the structure. If there is more than one atom in the base, the cell polyhedron is formed by taking together the polyhedra for all the atoms of the base. (The concept of cell polyhedra or "fundamental bereiche" of the structure was earlier discussed by Schönfliess.[6]) To construct the atomic polyhedron the atom is imagined shrunk down to a point, and then the planes perpendicularly bisecting the radius vectors from the atom to its first and second neighbors are erected; these bound the polyhedron. In Fig. 1 the atomic polyhedron for zinc in zincblende and wurtzite are shown. Note the close similarity of the two figures; both polyhedra enclose the same volume, and the perpendicular distance from the center of each to corresponding planes is identical. For zincblende the bounding planes of the zinc polyhedron are (111), $(\bar{1}\bar{1}1)$, $(\bar{1}1\bar{1})$, $(1\bar{1}\bar{1})$ and the 12 {110} planes. If wurtzite is referenced on cubic axes, the corresponding bounding planes are (111), $(\bar{1}\bar{1}1)$, $(\bar{1}1\bar{1})$, $(1\bar{1}\bar{1})$, the 9 {110} planes with one or both indices negative, and (100), (010), (001). By this construction then, the cell polyhedron for zincblende, Fig. 2, is identical to that for diamond, O_h^7, and that for wurtzite, obtained by superimposing 4 polyhedra like the right-hand side of Fig. 1, to a D_{6h}^4 structure.

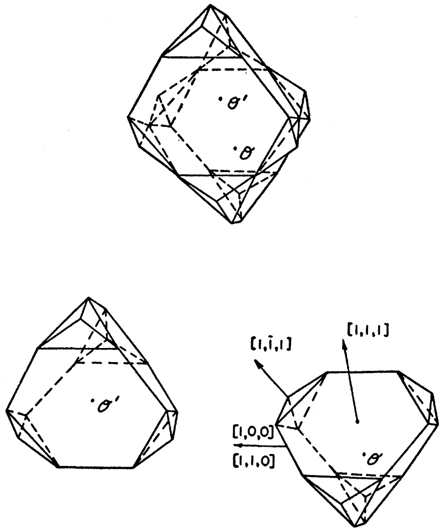

FIG. 2. Cell polyhedron, zincblende structure. Atoms are assumed equal in size. $\mathcal{O}$ is a zinc atom, $\mathcal{O}'$ a sulfur.

Clearly, if the zinc and sulfur atoms were the same size it would be reasonable to assign to each the same size polyhedron, and then Fig. 1 would be a valid representation of the region in space belonging to each atom, in the particular structure. Hence a decision as to the appropriate atomic or cell polyhedra in a given structure depends upon assigning sizes to the atoms, and this in turn depends upon our conception of the bonding.

3. CHEMICAL BOND IN ZnS

The evidence indicating that ZnS is characterized by a type of bonding intermediate between the extremes of pure covalent and pure ionic will be reviewed in this section.

If ZnS were pure ionic, one would picture closed-shell configurations of Zn^{+2}, S^{-2}, resulting from a transfer of two zinc 4s electrons to the sulfur M shell. The very first conception of the bonding in ZnS was that it was

---

[4] A. von Hippel, Z. Physik **133**, 158 (1952).

[5] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 329.

[6] A. Schönfliess, *Theorie der Kristallstruktur* (Gebruder Borntrager, Berlin, 1923), p. 513.

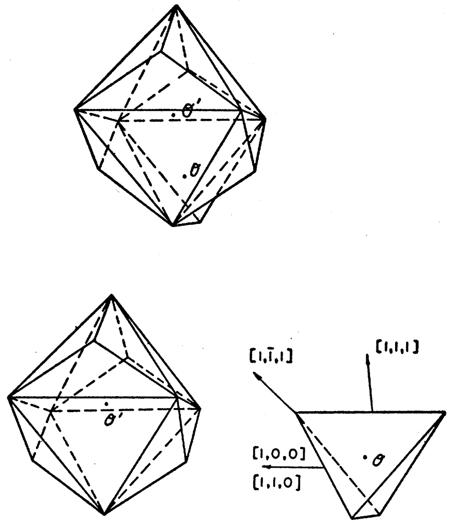

FIG. 3. Cell polyhedron for zincblende, assuming ions. Faces in the sulfur polyhedron are more developed; see text for details of construction. This cell would be appropriate for cellular-type band calculations in a pure ionic model. Θ is a zinc ion, Θ' a sulfur ion.

purely ionic, and this followed from the assumed ease of creating closed shell ions Zn^{+2}, S^{-2} by complete electron transfer. The fair agreement of (a) the theoretical and experimental (Born-Haber) binding energies, (b) the sum of ionic radii and the observed lattice spacing, and also (c) the large electronegativity difference which is consistent with this model, led support to this belief. In fact, as recently as 1940 Seitz included ZnS among the "ionic solids."[7] One then expects the two ions to differ markedly in size, as is reflected in the Pauling or Goldschmidt ionic radii, so that in defining the region about one ion "belonging" to that ion it would be natural to modify the construction which led to the atomic polyhedra. Figure 3 shows such a modified polyhedron constructed for zincblende by erecting planes perpendicular to the radius vectors from each atom, which divide the lines to first neighbors in the ratio of the ionic radii.[8] Crystallographically, the polyhedra shown in Fig. 3 are similar to those of Fig. 2 except that certain faces are more "developed." Similar polyhedra could be constructed for wurtzite by developing the appropriate faces of zinc and sulfur polyhedra.

The belief that ZnS is a purely covalent material stems essentially from the tetrahedral surroundings of each atom, which imply directed valence bonds of sp^3 character[9] for each atom. These are the strongest[10] covalent bonds which can be formed from the available s and p valence orbitals of both zinc and sulfur. Since the eight valence electrons per atom pair are shared equally, the effective formal charges would be Zn^{-2} and S^{+2}. Equal sharing also implies that equal regions of space belong to each ion and hence the polyhedra shown in Figs. 1 and 2 would be appropriate. However, because of the closer fit of the sum of ionic radii to the observed internuclear spacing, and the unlikelihood of occurrence of Zn^{-2}, it was early realized that the covalency must have a considerable admixture of ionic binding.[11]

Clearly, in order to proceed with a calculation, it is necessary to estimate the departure of the bond type from either extreme. One method of characterizing the bond is by means of the effective charge per ion, and so we need to estimate these charges from the available evidence. The first quantitative indications of the departure of ZnS from pure ionic binding were obtained by Born and Bormann in 1920 when they estimated the effective zinc charge as $+0.3$, using the Born lattice theory and the measured values of elastic, dielectric, and piezoelectric constants.[12] A more recent attempt, to obtain the ionic charges from the piezoelectric constant alone,[13] has been shown to be incorrect.[14] (It may be possible to use a model proposed by von Hippel[4] in this connection but this calculation has not yet been concluded.[14]) Vasileff, in a recent paper on thermal ionization of impurities has obtained a value of $+0.51$ for the zinc effective ionic charge, using measured values of the Reststrahl frequency and the dielectric constants.[15] Another indication of the departure of the bond in ZnS from pure ionic is obtained from the photoelastic constants[16] although the quantitative interpretation of the measured constants is not a simple matter, and the existing theory is incomplete for ZnS due to neglect of the inner displacements.[17] Studies based on hardness and the cleavage in ZnS[18] have also indicated a mixture of about $\frac{2}{3}$ ionic and $\frac{1}{3}$ covalent binding, hence effective charges of $+0.7$ for zinc. From considerations of the electronegativity coefficients for Zn and S,[19] one is led to an assignment of an effective charge of about $+0.5$ for zinc. Paramagnetic resonance experiments on ZnS:Mn also indicate the mixed bonding through the magnitude of the hyperfine splitting constant A.[20] A decreases in a systematic fashion with increasing covalency between Mn^{++} and its neighboring anion in a series of Mn^{++} substituted compounds.[21] A rough estimate indi-

---

[7] Reference 5, p. 53.

[8] A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, New York, 1950), p. 70.

[9] Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944), Chap. XII.

[10] Reference 8, p. 48.

[11] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1945), p. 178.

[12] M. Born and E. Bormann, Ann. Physik **62**, 218 (1920).

[13] B. D. Saksena, Phys. Rev. **81**, 1012 (1951).

[14] J. Birman, Phys. Rev. **98**, 1567(A) (1955).

[15] H. D. Vasileff, Phys. Rev. **97**, 896 (1955).

[16] E. Burstein and P. Smith, Phys. Rev. **74**, 229 (1948).

[17] H. Mueller, Phys. Rev. **47**, 947 (1935), especially footnote 18, p. 951.

[18] G. A. Wolff, Signal Corps Laboratories (private communication). I am indebted to Dr. Wolff for a discussion of his work.

[19] Reference 8, p. 37.

[20] W. D. Hershberger and H. N. Leifer, Phys. Rev. **88**, 714 (1952).

[21] J. S. van Wieringen, Discussions Faraday Soc. No. 19, 121 (1955); L. M. Matarrese and C. Kikuchi, J. Phys. Chem. Solids **1**, 117 (1956).

cates about 30% covalent character for the Mn—S bond, and if this is characteristic of the bonding of sulfur to zinc, too, then the zinc effective charge is about +0.8. In summary, the evidence cited in the foregoing paragraph indicates effective charges in the neighborhood of ±0.5 for zinc and sulfur, respectively.

Evidence indicating higher effective charges is provided by Asano and Tomishima[22] and Jumpertz.[23] The former is a theoretical paper in which the cohesive energy of zincblende is calculated by a variational method due to Schmid,[24] and effective charges of about ±1.7 are deduced for zinc and sulfur, respectively. These authors use interpolated atomic wave functions for sulfur, and for the zinc $4p$ state, which may introduce an error in computing necessary exchange and overlap integrals; these are particularly sensitive to the wave function.[25] This treatment is of value in illustrating the different contributions to the binding energy, and their relative magnitudes. The second paper, an experimental determination of the total electron density distribution in zincblende by Fourier x-ray methods, clearly shows the departure of the total electron density between the atoms from values presumably characteristic of either pure ionic or pure covalent binding. By means of an integration of the (assumed) spherically symmetric charge density Jumpertz finds an effective charge for Zn of +1.29. However, to determine the net charge of each ion precisely, requires values of $\mathfrak{F}(\sin\theta/\lambda)$ at small values of $(\sin\theta/\lambda)$. There are no experimental points at sufficiently small values (Jumpertz; Fig. 4) to allow an accurate extrapolation. Hence the net charge determined in this manner may be in error.[26]

Although the evidence is by no means conclusive, the writer feels that a choice of effective charges of $+\frac{1}{2}$ for zinc, $-\frac{1}{2}$ for sulfur is reasonable, and these effective charges will be used in the calculation. Since these charges imply a sizable $(\sim\frac{1}{3})$ covalent character for the bond, it is felt that the polyhedra of Fig. 1 which assign *equal volumes to each of the atoms in each structure* are appropriate. Of course in principle one should strive for self-consistency in the band calculation, i.e., the charge density $\rho(r)$ used in calculating wave functions ψ_k, should have the property $\rho=\sum_k|\psi_k|^2$ and further, at each stage of such a self-consistent calculation, the appropriate polyhedra should be constructed and used for normalization and boundary conditions. However, the work involved in such a program is probably greater than is justified by our lack of really precise and convincing knowledge of the nature of the bond. It is hoped that the energy band structures calculated here from the assumed charges and charge densities will at least be qualitatively correct. In discussing the uniformly-charged-sphere approximation, a method will be suggested for using fairly realistic potentials in which the effective ion charge and size could be carried through the band calculation as a parameter and varied to see its effect on the location of the calculated eigenenergies.

Although most of the evidence presented above relates to zincblende, the close similarity of the geometry and properties of zincblende and wurtzite lends strong support to using the same effective ionic charges and charge densities for the ions in both structures, and this will in fact be done.

4. CHARGE DENSITIES

In what follows we shall assume spherically symmetrical charge densities centered at each atom's site (in agreement with Jumpertz). The equivalent-volume sphere (EVS), whose volume equals the volume per atom, will be used for normalization and for integration of the radial equation.

From the Hartree calculation[27] for atomic Zn we can obtain charge densities for all zinc electrons up to and including $4s$. For the zinc $4p$ function we use a Slater orbital with constants so determined that the $4p$ function has its maximum at 3.15 a.u. just within the EVS.[28] Self-consistent-field calculations for K^+, A, Cl^- (a series isoelectronic with S^{-2}) are available[29] and have been extrapolated to obtain the charge densities of the sulfur atomic states $1s$ through $3p$. The actual extrapolation was carried out on Z_{nl} (the effective charge for potential[30] in state nl) as this is the most suitable quantity for an extrapolation (i.e., most smoothly varying as a function of atomic number). The extrapolation procedure used, described in the Appendix, was tested by "predicting" the $Z_{nl}(r)$ for Cl^- from those for argon. The agreement was excellent. (As distinct from reference 22 we are extrapolating essentially charge densities, rather than wave functions, so we hope a smaller error is thereby made.) From the extrapolated $Z_{nl}(r)$, the corresponding radial charge densities P_{nl} were obtained by a numerical differentiation. Thus we have obtained the "working" radial charge densities P_{nl} for zinc and sulfur, for all core states, and for the valence states: respectively, $4s$, $4p$ for Zn and $3s$, $3p$ for S. Although little can be said quantitatively about the accuracy of the interpolated densities, it is believed that the accuracy of the crystal potential determined from these densities is no less than the over-all accuracy with which the cellular calculation can be carried out.

The crystal charge density will consist of a core charge density for each atom plus a valence electron density for each. At the observed internuclear spacing,

---

[22] S. Asano and Y. Tomishima, J. Phys. Soc. Japan **11**, 644 (1956).

[23] E. A. Jumpertz, Z. Elektrochem. **59**, 425 (1955).

[24] L. A. Schmid, thesis, Princeton University, July, 1953 (unpublished); Phys. Rev. **92**, 1373 (1953).

[25] Reference 24, p. 2.

[26] J. M. Bijvoet and K. Lonsdale, Phil. Mag. **44**, 204 (1953).

[27] Hartree, Hartree, and Manning, Phys. Rev. **59**, 299 (1941).

[28] Reference 9, p. 163.

[29] D. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938); **156**, 45 (1936).

[30] J. C. Slater, *Quantum Theory of Matter* (McGraw-Hill Book Company, Inc., New York, 1951), p. 137.

the core densities do not overlap, hence atomic core densities are taken over for the crystal. For the valence density we construct for each atom, an sp^3 hybrid consisting of the radial parts of the appropriate atomic densities, i.e., $\rho_{\text{val}}=N(\rho_s+3\rho_p)$ using $4s$, $4p$ for zinc and $3s$,$3p$ for sulfur. The normalization constant N is so chosen that the net charge in the equivalent-volume sphere is $+\frac{1}{2}$ and $-\frac{1}{2}$ for zinc and sulfur, respectively. Effectively then, we create a smeared-out covalent-like spherical charge density for each atom, so normalized as to yield ions at the sites. This is the basic crystal charge density for both wurtzite and zincblende.

5. CRYSTAL POTENTIAL

The crystal potential consists of a classical part, and a quantum-mechanical part; these will be discussed in order.

The classical or Coulomb potential consists of an inner potential and an exciting potential. The *inner potential* is the Coulomb potential within the equivalent-volume sphere, due to the point charge nucleus, the core electrons, and the valence density contained therein. The charge densities are spherically symmetric so the classical inner potential is too, and is easily calculated by Gauss's theorem. Clearly, the inner potential is the same, for the same ion in each of the two structures.

The *exciting potential*[31] is the potential within one EVS due to all the ions in the crystal except the one in that EVS. Clearly, the exciting potential is not spherically symmetric in zincblende or wurtzite, and, since it must show the crystallographic symmetry T_d^2 or C_{6v}^4, respectively, may be expected to differ in the two structures. First we discuss the calculation of the exciting potential in zincblende and then in wurtzite. In the following two paragraphs crystallographic directions in zincblende and wurtzite will be indicated by affixing a subscript z or w to the bracket: thus $[hkl]_z$, $[hkl]_w$, respectively, for zincblende and wurtzite. (For the former, directions will be referred to Cartesian axes, while for the latter, directions will be referred to the vector set $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ defined for wurtzite in Table I.)

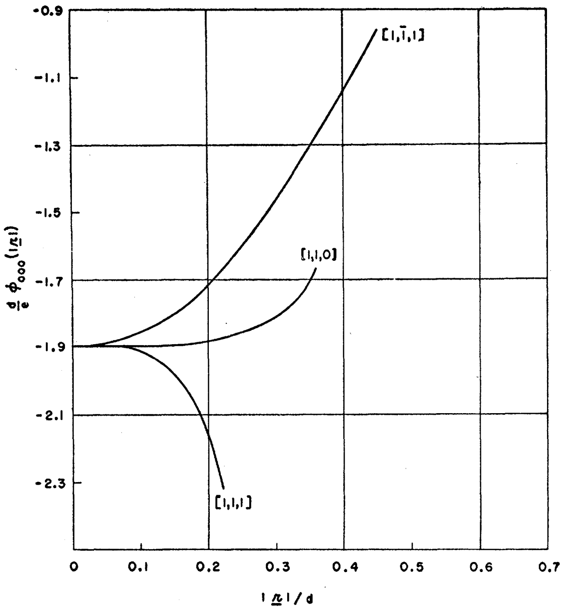

FIG. 4. Exciting potential in ZnS. Ordinate gives the value of the exciting potential, abscissa the distance along the specified direction in fractions of the cubic cell edge. Directions indicated are for zincblende; however, the potential is the same to first and second neighbors in wurtzite. Results from a sulfur ion are negative of those illustrated.

TABLE II. Exciting potential in ZnS.[a]

1. Self-potential (Madelung constant)
$\phi_{000}(000)=-1.8914$

2. [b] $[111]_z=[001]_w=[1/3, 2/3, -1/8]_w$
$\phi_{000}(1/24, 1/24, 1/24)=-1.8984$
$\phi_{000}(1/12, 1/12, 1/12)=-1.9902$
$\phi_{000}(1/8, 1/8, 1/8)=-2.3094$

3. [b] $[110]_z=[010]_w$
$\phi_{000}(1/8, 1/8, 0)=-1.8961$
$\phi_{000}(1/4, 1/4, 0)=-1.6579$

4. $[1\bar{1}1]_z$
$\phi_{000}(1/12, -1/12, 1/12)=-1.8105$
$\phi_{000}(1/8, -1/8, 1/8)=-1.6739$
$\phi_{000}(1/4, -1/4, 1/4)=-1.0108$
$\phi_{000}(3/8, -3/8, 3/8)=-0.7698$
$\phi_{000}(1/2, -1/2, 1/2)=-0.72125$

[a] The ions are assumed to have net charges of $\pm\frac{1}{2}$ for zinc and sulfur, respectively. All potentials are given in units of $|e|/d$, where $|e|$ is the magnitude of the electron charge and d is the cubic cell side. The subscript on the direction bracket indicates either zincblende (z) or wurtzite (w), the latter in terms of the usual hexagonal coordinate system. (See Table I.) The directions indicated are from a zinc ion, assumed at 000. The results in corresponding directions from a sulfur ion are the negative of those listed.

[b] Coordinates of points refer to zincblende. The potential is identical at corresponding points in wurtzite (see text), to 5%.

For zincblende the exciting potential has been computed in the three inequivalent directions from a zinc atom (assumed at 000): $[111]_z$, $[110]_z$, and $[1\bar{1}1]_z$. There are four equivalent $[111]_z$, and twelve $[110]_z$ directions going to first and second neighbors, respectively. These are the prominent directions of interest in choosing a spherical potential. The $[1\bar{1}1]_z$ directions lead to "holes" in the structure, and may be of importance in calculating activation energies for diffusion of ions; results in this direction will not be used in the band calculation, but are appended for illustrative purposes. The calculated exciting potentials are tabulated in Table II and illustrated in Fig. 4. From the figure we note that the exciting potential is equal in $[111]_z$ and $[110]_z$ directions, and essentially constant to $(|\mathbf{r}|)/d=0.1$. When $(|\mathbf{r}|)/d>0.1$, the two potentials differ, and this difference increases as we go to the edge of the EVS $(|\mathbf{r}|/d=0.31)$. To proceed with a cellular calculation we need to create a spherically symmetric exciting potential. This is often done by simply adding the constant Madelung potential to the Coulomb inner potential, but we feel this gives too much weight to the

---

[31] M. Born and M. G. Mayer, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), second edition, Vol. 24, Part 2, p. 712.

potential at the origin, which is a nonrepresentative point. Instead we multiply the computed exciting potential in the $[111]_z$ direction by a constant so chosen that the total classical potential (inner plus exciting) is zero at the edge of the zinc EVS. This has the effect of normalizing the results in the most important covalent direction (that to nearest neighbors) in such a way that the classical potential obeys an ionic-like condition: namely is zero midway between nearest neighbors. [The edge of the EVS corresponds in this sense, to the point $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$.] A similar procedure is applied in the sulfur EVS. In Fig. 5 we plot the potential in each EVS due to the *net core* charge (+2 for zinc, +6 for sulfur), plus the assumed valence electron density, as the dashed curve; and then this potential plus the sphericalized exciting potential as the solid curve. It will be noted that the latter is continuous and smooth across the surface of the EVS, which corresponds to the midpoint between the ions. (The true classical potential, including the proper contribution from core states, is included in Table III).

The exciting potential was computed in wurtzite in the directions $[001]_w$, $[\frac{1}{3}, \frac{2}{3}, -\frac{1}{8}]_w$ which are inequivalent directions to first neighbors (there are three equivalent directions $[\frac{1}{3}, \frac{2}{3}, -\frac{1}{8}]_w$, $[\frac{1}{3}, -\frac{1}{3}, -\frac{1}{8}]_w$, $[-\frac{2}{3}, -\frac{1}{3}, -\frac{1}{8}]_w$, and the unique $[001]_w$ direction to first neighbors), and in the direction $[010]_w$, to second neighbors. It was necessary to interpolate the available Ewald potentials[32] in order to make the calculation, and hence the results are accurate to only about 5%. To this accuracy we find: (1) exciting potential in $[\frac{1}{3}, \frac{2}{3}, -\frac{1}{8}]_w$ is the same as in $[001]_w$, i.e., *along the line* to first neighbors the potential has tetrahedral symmetry; (2) this first neighbor exciting potential in wurtzite is the same as the $[111]_z$ exciting potential in zincblende; (3) the $[010]_w$ exciting potential is the same as that for $[110]_z$. Hence along two prominent crystallographic directions (to first and second neighbors) the potential in zincblende and wurtzite is the same. We therefore feel it reasonable to construct a spherical exciting potential in wurtzite in the same manner as was done for zincblende (the midpoint between first neighbors should be at zero potential for an ionic wurtzite, too). Hence the results illustrated in Fig. 5 apply for wurtzite as well as zincblende.

TABLE III. Effective charge for potential in ZnS.

r	$2Z_p$ zinc	$2Z_p$ sulfur	r	$2Z_p$ zinc	$2Z_p$ sulfur
0	60.00	32.00	0.30	28.16	16.20
0.005	58.86		0.35	26.01	14.86
0.01	57.70		0.40	24.34	13.68
0.015	56.55		0.45	22.82	12.69
0.02	55.44		0.50	21.39	11.79
0.025	54.40		0.55	19.96	11.01
0.03	53.43	29.53	0.60	18.75	10.30
0.035	52.47		0.70	16.54	9.082
0.04	51.60	28.73	0.80	14.69	8.038
0.05	50.02	28.08	0.90	13.14	7.211
0.06	48.55	27.21	1.00	11.85	6.540
0.07	47.23	26.51	1.10	10.76	5.976
0.08	46.12	25.83	1.20	10.32	5.468
0.09	44.79	25.19	1.30	8.944	
0.10	43.64	24.57	1.40	8.337	4.472
0.12	41.47	24.59	1.60	7.128	3.790
0.14	39.43	22.31	1.80	6.208	3.229
0.16	37.54	21.36	2.00	5.334	2.784
0.18	35.77	20.42	2.20	4.783	2.464
0.20	34.16	19.58	2.40	4.202	2.261
0.22	32.68	18.81	2.60	3.697	2.089
0.24	31.34	18.09	2.80	3.318	2.059
0.26	30.16	17.43	3.00	2.954	2.050
0.28	29.07	16.79	3.18	2.676	2.098

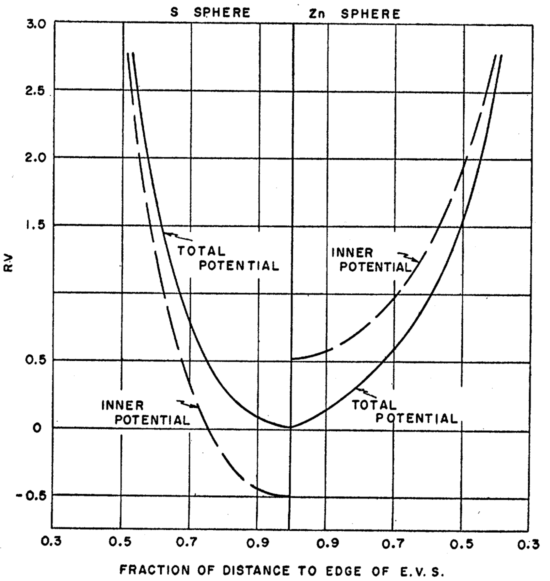

FIG. 5. Classical potential in ZnS. Dashed curve: inner potential due to core charge (+2 or +6 for zinc and sulfur, respectively) plus valence electron density (normalized sp^3 density); full curve: dashed curve plus the sphericalized exciting potential. Potential is normalized and plotted against fraction of the distance to the edge of the EVS.

The quantum-mechanical part of the potential which will be used for the band calculation is the exchange potential, which was computed by making use of the Slater free-electron approximation.[33]

In Table III the radially symmetric effective charge for potential including the Coulomb contributions from the point nuclei, the atomic core states, and the hybridized valence states, the sphericalized exciting potential, and the free electron exchange potential, is given for each ion, within its equivalent-volume sphere, as it will be used in the subsequent numerical integration of the radial equation, for both zincblende and wurtzite.

6. UNIFORMLY CHARGED SPHERE APPROXIMATION; ADDED TERM

Recent work on approximate molecular charge densities[34] makes it of some interest to examine a uniformly-

---

[32] F. Hund, Z. Physik 94, 11 (1935).

[33] J. C. Slater, Phys. Rev. 81, 385 (1951).

[34] Neumark, Westerman, Kleiss, and Birman, theses, Columbia University Chemistry Department, 1951–1952 (unpublished).

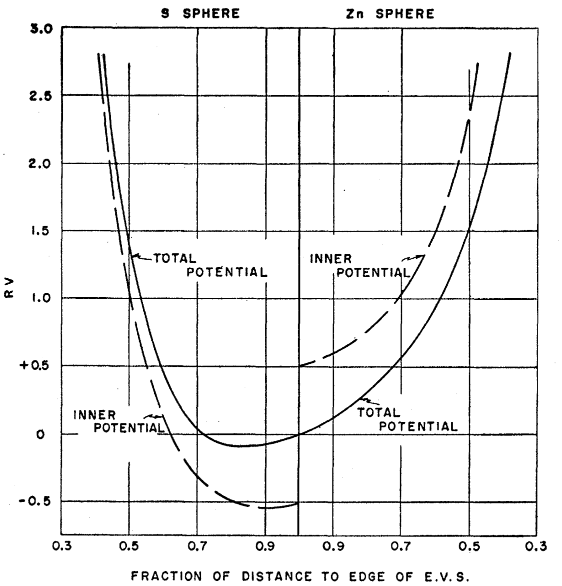

FIG. 6. Classical potential for the uniformly-charged-sphere model of ZnS. Dashed curve: inner potential due to both core charge (+2 or +6) and uniform valence electron density, normalized to −1.5 and −6.5, respectively; full curve: the dashed curve plus the exciting potential along the line of centers. Potential is normalized and plotted against fraction of the distance of the edge of the EVS.

charged-sphere approximation to the potential. This approximation leads to a simple analytical expression for the spherical inner potential, for which the radial Schrödinger equation is easily integrable. Further, it is a simple matter in this approximation to alter the effective charges of the ions, and to relate the ionic radius to the effective charge in any prescribed manner. One may thus obtain the solution of the Schrödinger radial equation with effective charge as a parameter, and examine the dependence of the location of band edges on effective charge. Consider two point charges +2 and +6 separated by a distance $2R$, each surrounded by a spherical cloud of uniform negative charge density, radius R, content −1.5 and −6.5, respectively. A simple calculation of the inner potential and the exciting potential along the line of centers, gives the result illustrated in Fig. 6. Aside from the location of the minimum in the inner potential of the S cell (the radius at which the net enclosed charge = 0), Fig. 5 and Fig. 6 are quite similar.

In principle, valence and conduction band electron wave functions should be orthogonalized to lower lying core wave functions. Gombas has pointed out[35] that the requirement of orthogonality is essentially a statement of the Pauli exclusion principle. That is, for a solid, valence and conduction band electrons are excluded

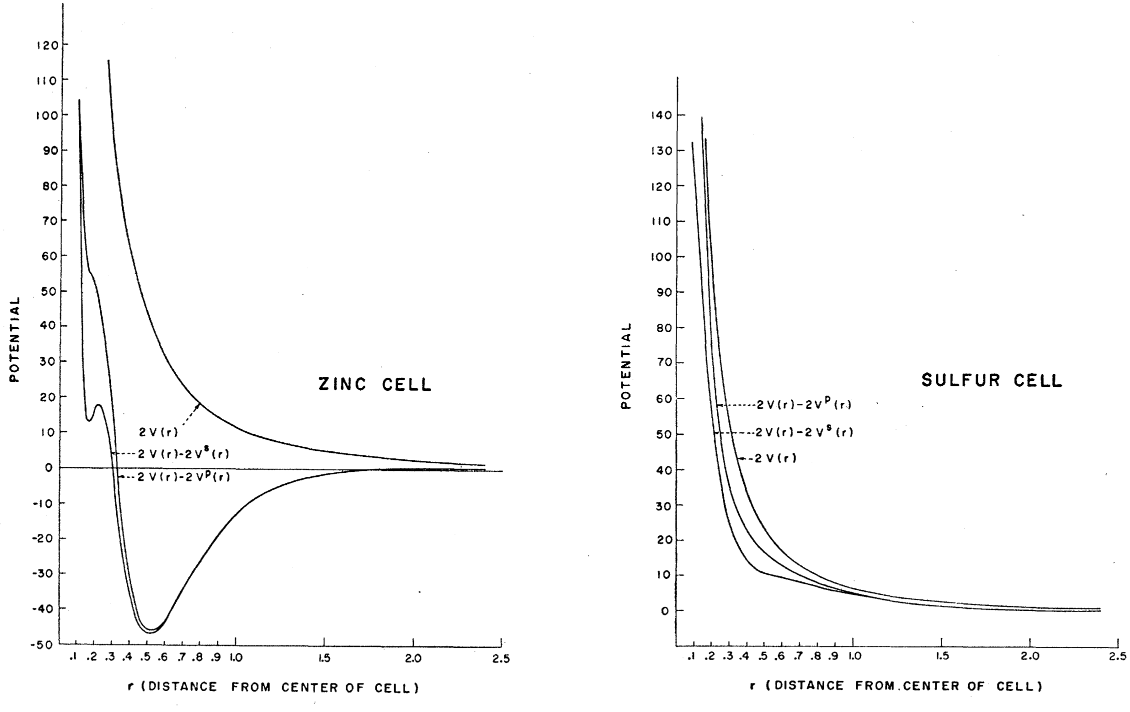

FIG. 7. Inner potential in zinc and sulfur cells without Gombas orthogonality term $2V(r)$; with the term for "s"-like states $2V(r)-2V^s(r)$; with the term for "p"-like states $2V(r)-2V^p(r)$. (Ordinate: potential; abscissa: distance from the origin of each EVS.) To emphasize the effect of the Gombas term, only the potential near the origin is plotted for each ion. For both zinc (left half of the figure) and sulfur (right half of the figure) the edge of the EVS is at 3.18, and from $r \cong 2.5$ to $r = 3.18$ the results with and without the Gombas term are essentially indistinguishable.

---

[35] P. Gombas, *Die Statistische Theorie des Atoms* (Springer-Verlag, Berlin, 1949), p. 150; *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 36, p. 168.

from states in phase space already occupied by core electrons, and this has the effect of repelling the outer electrons from regions in phase space densely occupied by core electrons. This "repulsion" can be formulated in the sense that the outer electrons do a certain amount of work to get into such regions. Gombas has shown how (in the free-electron approximation) to construct a potential to be added to the Schrödinger equation for a given state, incorporating the desired effect of repulsion of lower states with the same symmetry. At $\mathbf{k}=000$, in zinc blende, the valence and conduction states may be described as "*s*"- or "*p*"-like so that Gombas' procedure can be used directly to calculate the added potential for those states. To illustrate the added term, the total inner potential with and without this correction is plotted in Fig. 7. Although the added term was not used in integrating the radial equations, it may be used later as a perturbation.

It may well be that a simple uniformly-charged-sphere approximation, with free electron exchange (Slater) and orthogonality (Gombas) terms, will suffice to give a qualitative picture of the energy band structure of materials with mixed binding. However, further work will need to be done on this point before anything can be conclusively stated.

7. SUMMARY

The nature of the binding in ZnS has been discussed, and the evidence indicating mixed covalent and ionic binding reviewed. The effective ionic charges used in the calculation are $\pm\frac{1}{2}$ for zinc and sulfur, respectively. Radially symmetric valence charge densities of the form sp^3 have been set up, and normalized to the chosen effective charge within the equivalent-volume sphere of each ion (the ions are assumed of equal size). It has been shown that the same equivalent-volume sphere, and spherically symmetric potential is appropriate in both zincblende and wurtzite.[36] It has also been shown that a crude uniformly-charged-sphere model is a fair approximation to the calculated potential. Further work along the lines of such simple models may prove fruitful in elucidating the qualitative detail of band structures in solids with mixed bonding.

Finally, because of the great similarity in the geometry of first and second neighbors, in zincblende and wurtzite, it follows that many of the same LCAO parameters should arise in both band calculations. This will be discussed further in the later papers.

8. ACKNOWLEDGMENTS

It is a pleasure to thank Mrs. Marilyn Wurtzel Levine and Mr. Seymour Siegal for computational assistance, and my colleagues in the Research Laboratories for many stimulating and profitable discussions.

APPENDIX. INTERPOLATION PROCEDURE

Given $Z_{nl}^N(r)$, we want to find the radial scaling function $F_{nl}(r)$ such that $Z_{nl}^N(rF_{nl}(r))=Z_{nl}^{N'}(r)$ where $N'=N\pm1$ and the superscript refers to the atomic member of the ion. The two ions are assumed to be isoelectronic, e.g., Cl^- and A. Physically we wish to find the radius r of the sphere about ion N' which contains the same net charge as the sphere of radius $rF_{nl}(r)$ about the isoelectronic ion N. It is assumed that

$$F_{nl}(r)=\frac{N-S_{nl}(r)}{N'-S_{nl}(r)},$$

and the $S_{nl}(r)$ are determined numerically from the isoelectronic series K^+, A, Cl^- for use in extrapolating from Cl^- to S^{-2}.

---

[36] L. M. Matarrese and C. Kikuchi [J. Phys. Chem. Solids 1, 126 (1956)], have assumed that (a') (ground-state splitting parameter in zero magnetic field) is identical in zincblende and wurtzite, in computing a doublet splitting of 32 gauss for Mn^{++} in wurtzite. If the experimentally observed splitting is of this magnitude it will be a confirmation of our result and their assumption, on the equality of the potential in prominent directions in zincblende and wurtzite. I am indebted to Dr. Kikuchi for a discussion of this point.