Electronic Energy Bands in ZnS: Preliminary Results

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(Received September 18, 1957)

Preliminary results of the cellular calculations of electronic energy bands in cubic ZnS have been obtained at three points in the Brillouin zone: Γ, X, Λ. These results indicate that there is a normal order of states in the valence band, and an energy gap of 6–8 volts at $\mathbf{k}=(0,0,0)$ corresponding to the $\Gamma_4' \to \Gamma_1$ transition.

WE are reporting some preliminary results that we have obtained in a cellular calculation of electronic energy bands in zincblende (cubic ZnS). In this work we used a potential that was spherically symmetric within the equivalent-volume sphere of each atom and which was derived from valence charge densities corresponding to a mixture of ionic and covalent bonding.[1] For both zinc and sulfur the valence electron density consisting of the radial part of an sp^3 hybrid was constructed, and normalized within each ion's equivalent-volume sphere to the assumed net charge of that ion: respectively, $+\frac{1}{2}$ for zinc and $-\frac{1}{2}$ for sulfur.

In the preliminary calculation reported here, the wave function of each of the states considered was expanded in a four-term series in each cell, as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_l \sum_\alpha A_{l\alpha} K_{l\alpha}(\theta\phi) R_l(|\mathbf{r}|,\epsilon). \qquad (1)$$

In (1), $K_{l\alpha}(\theta\phi)$ is a lattice harmonic completely specified by symmetry,[2] $R_l(|\mathbf{r}|,\epsilon)$ a solution of the radial equation for given l, depending upon the trial energy parameter ϵ, and $A_{l\alpha}$ is a constant. Both ϵ and $A_{l\alpha}$ can be determined from the boundary and normalization conditions. Boundary conditions have been applied at discrete match points on the bounding surface between a zinc polyhedron and its four neighboring sulfur polyhedra. At each match point P we obtain two equations of the form

$$\psi_{\mathrm{Zn}}(P) = +\gamma_{\mathbf{k}}\psi_{\mathrm{S}}(P),$$

$$\mathbf{n}\cdot\nabla\psi_{\mathrm{Zn}}(P) = -\gamma_{\mathbf{k}}\mathbf{n}\cdot\nabla\psi_{\mathrm{S}}(P), \qquad (2)$$

where $\gamma_{\mathbf{k}}$ is a phase factor, depending on wave vector $\mathbf{k}$, which includes the effects of the basis displacement and the Bloch condition.[3]
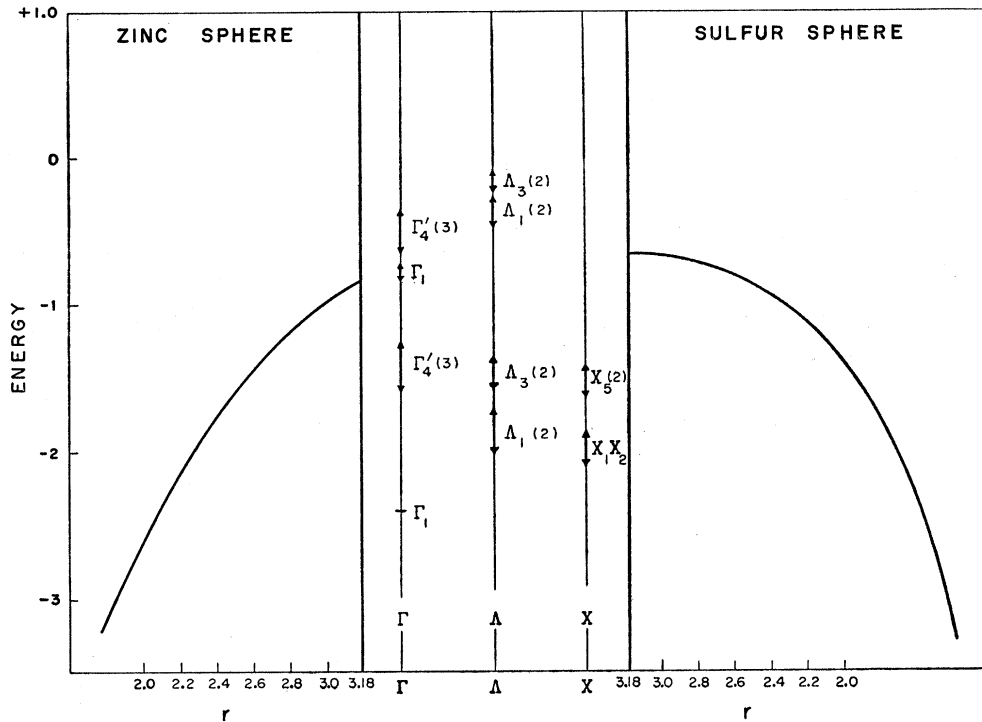

FIG. 1. Electronic potential energy near the edge of the zinc and sulfur equivalent volume spheres plotted *versus* distance from the center of each sphere, and cellular results for certain eigenenergies at three prominent points in the Brillouin zone: $\Gamma(0,0,0)$, $\Lambda(\pi/2a,\pi/2a,\pi/2a)$, and $X(\pi/a,0,0)$. Potential energy is discontinuous because of the contribution from exchange in each cell. The length of each arrow indicates approximately the range of variation of numerical results due to use of different sets of match points in matching zinc and sulfur wave functions. The number in parentheses indicates the degeneracy of the state so labeled, except for Λ_1, where the two independent Λ_1 states fell within the indicated range. Our present approximation is not sufficiently accurate to resolve the conduction band states at X. Energy is in rydbergs, and distance (r) in atomic units.

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The results we obtained for the location of the eigen-energies at the points Γ, X, and Λ in the Brillouin zone[4] are shown in Fig. 1, which also illustrates the variation of the spherically symmetric potential energy with distance near the edge of the equivalent-volume sphere. These results are taken from use of several sets of match points for each state. For all states except Γ_1, the numerical results were sensitive as to which set of match points was used. However we believe that certain conclusions can be drawn tentatively from the calculation at this time. They are:

(a) The valence and conduction band edges are at $\mathbf{k} = (0,0,0)$.

(b) The top of the valence band is triply degenerate Γ_4'.

(c) The bottom of the conduction band is non-degenerate Γ_1.

(d) The optical and thermal gaps both represent a vertical transition at $\mathbf{k} = (0,0,0)$, of about 6–8 volts.

(e) The states are in normal order in valence band ("s"-like lowest, "p"-like higher).

From the results illustrated in Fig. 1 we have determined the approximate values of certain LCAO (linear combination of atomic orbitals) integrals that may be used to interpolate the band structure by the Slater-Koster method.[5] In this we have used the nearest-neighbor approximation, assuming a linear combination of s and p orbitals for each atom. The integrals that arise correspond to diagonal s and p zinc and sulfur energies, and off-diagonal zinc and sulfur first-neighbor s and p interactions. The values we obtained seem reasonable, although because of the present uncertainty in the cellular results it seems better to wait until more precisely known eigenenergies are available before carrying out the interpolation.

In the improved calculation now in progress, the series expansion of the wave function (1) is terminated when all terms for each state up to and including $l = 6$ are included. The four-term expansion for Γ_1 already includes $l = 6$, and the results are not sensitive to the set of match points chosen. For this reason we believe the procedure described will result in an improvement in the precision of the calculation.

ACKNOWLEDGMENTS

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