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Deep energy levels of defects in the wurtzite semiconductors AlN, CdS, CdSe, ZnS, and ZnO

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The major chemical trends in the energy levels of sp^3-bonded substitutional deep impurities in the wurtzite semiconductors AlN, CdS, CdSe, ZnS, and ZnO are predicted. N impurities (deposited on the anion site by ion implantation) appear to be candidates for producing shallow p-type dopants in these materials.

I. INTRODUCTION

The II-VI semiconductors, most of which crystallize with the wurtzite structure, tend to have large direct band gaps, and so are prime candidates for blue and ultraviolet light-emitting diodes and lasers. However, the development of such optoelectronic devices has been impeded by the fact that p-n junctions have proven virtually impossible to fabricate in these materials: Most wurtzite II-VI compounds occur naturally as n-type semiconductors and have proven to be difficult to dope p-type. The currently accepted explanation of the resistance to p-type doping is the "self-compensation" of shallow acceptors by various naturally occurring or spontaneously generated donor defects such as vacancies or interstitials.[1] However, in certain cases, the expected shallow acceptors (e.g., P and As on the S site in CdS) have been reported to produce deep traps instead of shallow levels.[2] Thus there appear to be at least two possible mechanisms by which II-VI semiconductors can resist p-type doping: (i) native donor defects (e.g., interstitials or anion vacancies) are produced either thermally or in response to the doping, which then compensate the shallow acceptors, or (ii) the anticipated "shallow" group-V acceptors in reality yield "deep levels" so deep within the gap that the trapped holes cannot easily be thermally ionized. A first step toward understanding the "self-compensation problem" is to develop a theory of defect energy levels in II-VI semiconductors.[3,4]

In this paper we study the chemical trends in the defect energy levels of substitutional impurities in a number of semiconductors which have the wurtzite structure. We seek to determine which impurities are likely to produce deep levels and which are likely to form the shallow effective-mass-like levels. Our results have implications for the second point above, and indicate that, in some cases, defects expected to be shallow acceptors may in fact produce deep levels.

Our approach to the substitutional-impurity problem in wurtzite semiconductors is similar to that employed for defects in zinc-blende materials by Hjalmarson *et al.*[5] We first obtain a host crystal Hamiltonian H_0 by parametrizing the host band structure with a nearest-neighbor empirical tight-binding theory,[6] following the general ideas of Vogl *et al.*,[7] Harrison,[8] and Chadi.[9] Then we construct the defect potential matrix V in the empirical tight-binding basis. V has nonzero matrix elements at the impurity site only; these are related to the differences between the free-atom orbital energies of the impurity and the host atom it replaces. The off-site matrix elements of V between orbitals on near-neighbor sites are taken to be zero, because lattice relaxation and changes in the bond length d around the defect are neglected, and the off-site matrix elements of the host Hamiltonian H_0 for these semiconductors depend only on bond length d (according to Harrison's d^{-2} rule[8]). Thus the model includes only the central-cell potential of the defect, and the long-ranged Coulomb potential of a nonisoelectronic defect is neglected. This approximation introduces ~ 0.1-eV errors into the theory, but reduces the problem of a defect-level calculation to a multiband, single-site Koster-Slater[10] impurity problem—which is readily solved. In this model (which uses only the central-cell potential), shallow effective-mass-like impurity levels have zero binding energy, and a level that falls within the band gap is deep, by our definition.[5] If the central-cell potential is not strong enough to produce a level in the gap, "deep" resonant levels may occur within a band, but these generally have not been detected. The long-ranged Coulomb potential can then be added *a posteriori* to the defect potential, causing heterovalent impurities to yield shallow levels in the band gap.

Following earlier work,[5] the charge-state splittings of the levels (e.g., the energy difference between the levels of the neutral and the charged defect) are also omitted from the model, in its present simple form. The motivation for these omissions is that one obtains a simple global view of the chemical trends in the energy levels. The lattice relaxation and charge-state splittings can also be added to the theory *a posteriori* (they tend to be small ~0.1-eV effects), but may not follow precisely the same chemical trends as the energy levels themselves; thus a more complete theory would be reduced to treating each specific impurity level, for each charge state, and for the specific local environment individually—with a loss of the global picture we seek. The simple global theory we present here is likely to be quite accurate, with uncertainties of only a few tenths of an eV in its level predictions.[11]

This global defect theory is especially well-suited to exploring the questions concerning chemical trends that especially interest us. (i) What are the defect levels of the impurities one might expect to be chalcogen-site acceptors (viz., N, P, Sb, and Bi)—will these impurities produce deep or shallow levels? and (ii) how do the impurity levels depend on the host: Why are the II-VI hosts more difficult to dope *p*-type than III-V compounds?

II. THEORY

The common II-VI semiconductors CdS, CdSe, ZnO, and ZnS crystallize with the wurtzite structure, as does AlN, whose anion and cation have quite different electronegativities. The atoms of this structure are tetrahedrally bonded with the same nearest-neighbor environment as the zinc-blende structure but with a different second-neighbor geometry: Wurtzite is hexagonal-close-packed with an *ABAB*. . . stacking sequence of hexagon layers along the *c* axis, but zinc-blende is face-centered cubic with an *ABCABC*. . . sequence of hexagon layers along the [111] direction. The unit cell contains four atoms, two anions, and two cations, and is shown in Fig. 1(a). The basis vectors $\vec{t}_1$, $\vec{t}_2$, $\vec{t}_3$, and $\vec{t}_4$ are (0,0,0), $(a/\sqrt{3},\ 0,c/2)$, $(a/\sqrt{3},\ 0,c/8)$, and $(0,0,5c/8)$, respectively, and the direct lattice vectors are defined as $\vec{a}=((\sqrt{3}/2),\ a(-\frac{1}{2})a,0)$, $\vec{b}=(0,a,0)$, and $\vec{c}=(0,0,c)$ in Cartesian coordinates. Here a is the length of a hexagonal side, and c is the repeat distance along the z direction. The anions are at positions $\vec{t}_1$ and $\vec{t}_2$ while the cations are at $\vec{t}_3$ and $\vec{t}_4$. The reciprocal lattice, shown in Fig. 1(b), is hexagonal with basis vectors $\vec{b}_a=((4\pi/\sqrt{3})/a,0,0)$, $\vec{b}_b=((2\pi/\sqrt{3})/a,2\pi/a,0)$, and $\vec{b}_c=(0,0,2\pi/c)$.

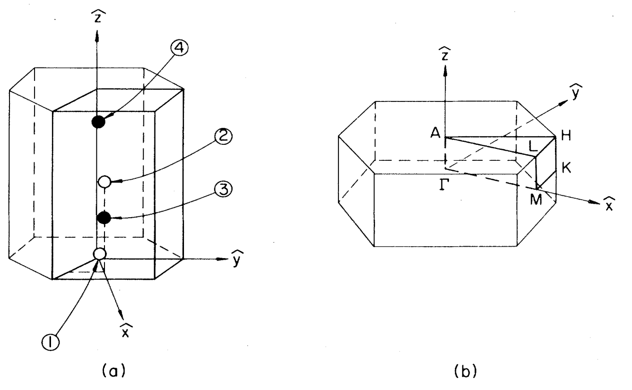

FIG. 1. (a) Hexagonal close-packed structure with four basis atoms, where 1 and 2 are anions, 3 and 4 are cations, with basis vectors, $\vec{t}_1=(0,0,0)$, $\vec{t}_2=(a/\sqrt{3},0,c/2)$, $\vec{t}_3=(a/\sqrt{3},0,c/8)$, and $\vec{t}_4=(0,0,5c/8)$, respectively. (b) The reciprocal lattice. The symmetry points of the Brillouin zone are $\Gamma=(0,0,0)$, $K=(2\pi/a)(1/\sqrt{3},1/3,0)$, $M=(2\pi/a)(1/\sqrt{3},0,0)$, $A=(2\pi/c)(0,0,\frac{1}{2})$, $H=(2\pi/a)(1/\sqrt{3},1/3,a/2c)$, $L=(2\pi/a)(1/\sqrt{3},0,a/2c)$.

The band-structure energy levels are computed in the empirical tight-binding approximation using the symmetry of the wurtzite crystal structure and a nearest-neighbor model with an sp^3 basis set similar to that of Vogl *et al.*[7] and Chadi.[9] We use the simplest possible parametrization of the tight-binding Hamiltonian H_0, namely the one-center and two-center approximation of Slater and Koster[12]; the on-site matrix elements are assumed to be one-center integrals and the nearest-neighbor matrix elements are assumed to be two-center integrals. This approximation treats the four nearest-neighbor atoms as equivalent, even though the crystal is not cubic. Thus the effects of the small crystal field, which splits the p_z orbital from the p_x and p_y, are neglected, and the local point symmetry is approximately tetrahedral (T_d rather than C_{3v}). There are four on-site matrix elements $E(s,a)$, $E(p,a)$, $E(s,c)$, and $E(p,c)$ (s and p refer to the sp^3 basis states, and a and c refer to the anion and cation) and five nearest-neighbor transfer-matrix elements $V(ss\sigma)$, $V(sp\sigma)$, $V(ps\sigma)$, $V(pp\sigma)$, and $V(pp\pi)$ (where σ and π refer to the orientation of p orbitals).

Bloch-type orbitals $|n,b,\vec{k})$ can be constructed as linear combinations of functions $|n,b,\vec{R})$ localized at each atomic site,

$$|n,b,\vec{k})=N^{-1/2}\sum_{\vec{R}}\exp[i\vec{k}\cdot(\vec{R}+\vec{t}_b)]\,|n,b,\vec{R})\ ,$$

where n is the orbital index (s,p_x,p_y,p_z), and b labels four basis atoms in the unit cell. In this Bloch-type basis, we have the 16×16 host Hamiltonian matrix

$$H_0(\vec{k})=\begin{array}{c|cccc} b\backslash b' & 1 & 2 & 3 & 4 \\ \hline 1 & E_a & 0 & H_{1,3} & H_{1,4} \\ 2 & 0 & E_a & H_{1,4} & H_{2,4} \\ 3 & H^\dagger_{1,3} & H^\dagger_{1,4} & E_c & 0 \\ 4 & H^\dagger_{1,4} & H^\dagger_{2,4} & 0 & E_c \end{array}\ ,$$

and the crystal eigenstates are a linear combination of the above Bloch-type basis states:

$$|\vec{k},\lambda\rangle=\sum_{n,b}|n,b,\vec{k})(n,b,\vec{k}\,|\,\vec{k},\lambda\rangle \ .$$

Each element of this matrix is a 4×4 matrix. The on-site matrix for the anion (atom 1 and atom 2) is

$$E_a=\begin{array}{c|cccc|} & |s,1) & |p_z,1) & |p_x,1) & |p_y,1) \\ (s,1| & E(s,a) & E(s,p_z,a) & 0 & 0 \\ (p_z,1| & E(s,p_z,a) & E(p_z,a) & 0 & 0 \\ (p_x,1| & 0 & 0 & E(p_x,a) & 0 \\ (p_y,1| & 0 & 0 & 0 & E(p_x,a) \end{array} \ ,$$

where $E(s,p_z,a)$ is taken to be zero and $E(p_z,a)=E(p_x,a)=E(p,a)$, in the approximation that the local environment is tetrahedral (T_d instead of C_{3v}; see Ref. 6). The on-site matrix E_c for the cation (atom 3 and atom 4) is identical in form to E_a, except that the index a is replaced by c everywhere.

The off-site matrices are $H_{1,4}=g_3(\vec{k})M_{1,4}$, $H_{2,4}=g_2(\vec{k})M_{2,4}$, and $H_{1,3}=g_1(\vec{k})M_{1,3}$, where we have

$$M_{1,4}=\begin{array}{c|cccc|} & |s,4) & |p_z,4) & |p_x,4) & |p_y,4) \\ (s,1| & U(s,s) & U(s,z) & 0 & 0 \\ (p_z,1| & U(z,s) & U(z,z) & 0 & 0 \\ (p_x,1| & 0 & 0 & U(x,x) & 0 \\ (p_y,1| & 0 & 0 & 0 & U(x,x) \end{array} \ ,$$

$$M_{2,4}=\begin{array}{c|cccc|} & |s,4) & |p_z,4) & |p_x,4) & |p_y,4) \\ (s,2| & f_0^*U'(s,s) & f_0^*U'(s,z) & -f_1^*U'(s,x) & -\frac{\sqrt{3}}{2}f_-^*U'(s,x) \\ (p_z,2| & f_0^*U'(z,s) & f_0^*U'(z,z) & -f_1^*U'(z,x) & -\frac{\sqrt{3}}{2}f_-^*U'(z,x) \\ (p_x,2 & -f_1^*U'(x,s) & -f_1^*U'(x,z) & \begin{matrix} f_1^*U'(x,x) \\ +\frac{3}{4}f_+^*(U'(x,x)+U'(y,y)) \end{matrix} & -\frac{\sqrt{3}}{4}f_-^*(U'(x,x)-U'(y,y)) \\ (p_y,2| & -\frac{\sqrt{3}}{2}f_-^*U'(x,s) & -\frac{\sqrt{3}}{2}f_-^*U'(x,z) & -\frac{\sqrt{3}}{4}f_-^*(U'(x,x)-U'(y,y)) & \begin{matrix} f_1^*U'(y,y) \\ +\frac{3}{4}f_+^*(U'(x,x)+U'(y,y)) \end{matrix} \end{array}$$

$$M_{1,3}=\begin{array}{c|cccc|} & |s,3) & |p_z,3) & |p_x,3) & |p_y,3) \\ (s,1| & f_0U'(s,s) & f_0U'(s,z) & f_1U'(s,x) & \frac{\sqrt{3}}{2}f_-U'(s,x) \\ (p_z,1| & f_0U'(z,s) & f_0U'(z,z) & f_1U'(z,x) & \frac{\sqrt{3}}{2}f_-U'(z,x) \\ (p_x,1| & f_1U'(x,s) & f_1U'(x,z) & \begin{matrix} f_1U'(x,x) \\ +\frac{3}{4}f_+(U'(x,x)+U'(y,y)) \end{matrix} & -\frac{\sqrt{3}}{4}f_-(U'(x,x)-U'(y,y)) \\ (p_y,1| & \frac{\sqrt{3}}{2}f_-U'(x,s) & \frac{\sqrt{3}}{2}f_-U'(x,z) & -\frac{\sqrt{3}}{4}f_-(U'(x,x)-U'(y,y)) & \begin{matrix} f_1U'(y,y) \\ +\frac{3}{4}f_+(U'(x,x)+U'(y,y)) \end{matrix} \end{array}$$

and

$$g_1(\vec{k})=\exp[i(-k_1/3+k_2/3+k_3/8)]\ ,$$

$$g_2(\vec{k})=\exp[i(k_1/3-k_2/3+k_3/8)]\ ,$$

$$g_3(\vec{k})=\exp(-i3k_3/8)\ ,$$

$$f_0(\vec{k})=\exp(ik_1)+1+\exp(-ik_2)\ ,$$

$$f_1(\vec{k})=\exp(ik_1)-\tfrac{1}{2}-\tfrac{1}{2}\exp(-ik_2)\ ,$$

$$f_+(\vec{k})=1+\exp(-ik_2)\ ,$$

and

$$f_-(\vec{k})=1-\exp(-ik_2)\ .$$

Here we have $\vec{k}=k_1\vec{b}_1+k_2\vec{b}_2+k_3\vec{b}_3$; $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ are the reciprocal-lattice vectors divided by 2π, namely, $((2/\sqrt{3})/a,0,0)$, $((1/\sqrt{3})/a,1/a,0)$, and $(0,0,1/c)$, respectively.

The parameters used above are matrix elements of H_0 between localized orbitals $|n,b,\vec{R})$; for example, we have

$$E(s,a)=(s,1,\vec{R}\,|\,H_0\,|\,s,1,\vec{R})$$

$$=(s,2,\vec{R}\,|\,H_0\,|\,s,2,\vec{R})\ ,$$

$$E(s,p_z,c)=(s,3,\vec{R}\,|\,H_0\,|\,p_z,3,\vec{R})$$

$$=(s,4,\vec{R}\,|\,H_0\,|\,p_z,4,\vec{R})\ ,$$

$$U(x,x)=(p_x,1,\vec{R}\,|\,H_0\,|\,p_x,4,(\vec{R}-\vec{c}))\ ,$$

and

$$U'(z,z)=(p_z,1,\vec{R}\,|\,H_0\,|\,p_z,3,\vec{R})\ .$$

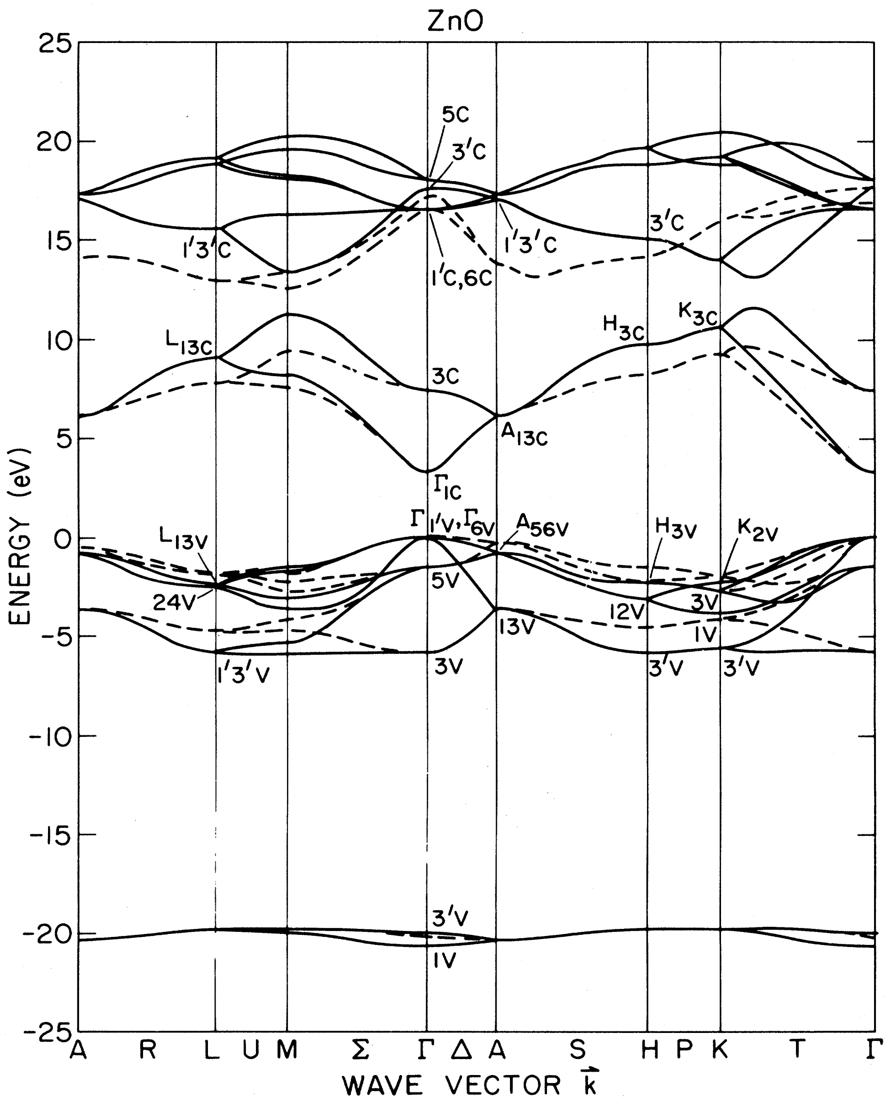

FIG. 2. Band structure of ZnO in the semiempirical tight-binding model (solid line) after Ref. 6 compared with the pseudopotential band structure (dashed line) by J. R. Chelikowsky, Solid State Commun. 22, 351 (1977).

The interactions between atoms 1 and 4 or atoms 2 and 3 are denoted by U's, which are different from U''s (interactions between atoms 1 and 3 or atoms 2 and 4), because of the symmetry of wurtzite structure (see Fig. 1). But in the approximation that the local environment is tetrahedral, U's and U''s are not independent and are related to each other as tabulated in Ref. 6.

The matrix elements of this nearest-neighbor tight-binding Hamiltonian have been determined[6] by fitting the band structure at selected wave vectors [in Ref. 6 only the Γ point ($\vec{k}=0$) is selected, which corresponds in a rough sense to fitting the Γ and L points of the band structure for zinc-blende compounds].[13] The resulting parameters reproduce all the sp^3-bonding valence bands and the lowest conduction band quite well. Typical results[6] for ZnO are given in Fig. 2.

Details of the fitting procedure have been given elsewhere,[6] but an important point is that the matrix elements E, U, and U' exhibit chemical trends. The differences of anion-site and cation-site matrix elements E, by construction, obey the rule of Vogl *et al.*[7] that they are proportional to corresponding differences in neutral free-atom Hartree-Fock orbital energies $w(l,a)$ and $w(l,c)$:

$$E(l,a)-E(l,c)=\beta_l[w(l,a)-w(l,c)] \ . \tag{1}$$

Here the proportionality constants, $\beta_0=0.8$ for $l=0$, s states, and $\beta_1=0.6$ for $l=1$, p states, are the same as used by Vogl *et al.*[7] for zinc blendes. The diagonal matrix elements E depend on the atomic-orbital energies[7] of neutral free atoms, but are independent of the bond length $d=(\sqrt{6}/4)a$, where a is the length of a hexagonal side (3.23 Å for ZnO). The off-diagonal matrix elements U and U' do not vary with the chemistry of the semicondutor's constituents, but do scale in proportion to the inverse square of the bond length (Harrison's d^{-2} rule[8]). Because of these chemical trends in the parameters of the host Hamiltonian H_0, a Hamiltonian can be constructed for a host with a substitutional defect, $H=H_0+V$, using the scaling rules.

The calculation of defect levels involves solving the Schrödinger equation

$$(H_0+V)\,|\,\psi\rangle=E\,|\,\psi\rangle \ , \tag{2}$$

for energy levels E, where V is the defect potential. In the localized sp^3 basis employed here, the defect potential reduces to a 4×4 matrix, because matrix elements of V between orbitals centered on different sites vanish in the present theory (which neglects lattice relaxation). This is the case because the off-diagonal matrix elements of H_0 for all the wurtzites were required to exhibit chemical trends (they scale roughly as d^{-2},[8] where d is the bond length). Thus H_0+V should have the same off-diagonal matrix elements as H_0 if there is no lattice relaxation. Hence V has nonzero matrix elements only at the defect site in the empirical tight-binding basis. The diagonal matrix elements of V are fixed by the chemical trends in the difference of diagonal matrix elements of H_0 which, to an adequate approximation, are proportional to corresponding differences of atomic-orbital energies as in Eq. (1).

The defect potential in the localized-orbital basis centered at the defect is

$$V=\begin{array}{c|cccc|} & |s\rangle & |p_z\rangle & |p_x\rangle & |p_y\rangle \\ \hline (s\,| & V^{ss} & V^{sz} & 0 & 0 \\ (p_z\,| & V^{zs} & V^{zz} & 0 & 0 \\ (p_x\,| & 0 & 0 & V^{xx} & 0 \\ (p_y\,| & 0 & 0 & 0 & V^{xx} \end{array} \ ,$$

where V^{sz} and V^{zs} are taken to be zero, and $V^{zz}\simeq V^{xx}=V^p$, $V^{ss}=V^s$ in the approximation that the local environment is tetrahedral (T_d rather than C_{3v}; see the Appendix and also Ref. 6). Here we have

$$V^l=\beta_l[w(l,\ \text{impurity})-w(l,\ \text{host})] \ ,$$

and the atomic-orbital energies $w(l)$'s have been tabulated.[7]

The deep impurity levels in the gap are obtained by solving Eq. (2), which is expeditiously accomplished using the Green's-function technique. From the perfect crystal host Hamiltonian H_0, we construct the Green's function

$$G_0(E)=(E-H_0)^{-1} \ .$$

The eigenvalues E are determined from the secular equation

$$\det[1-G_0(E)V]=0$$

for a given potential V. An advantage of the Green's-function technique is that the size of the determinant is determined only by the range of the defect potential V; in the present case V is spanned by s,p_x,p_y,p_z orbitals centered at the site (0,0,0). Thus the determinant is 4×4.

Symmetry considerations further reduce the size of the secular determinant. The point group is C_{3v}; thus, in an sp^3 basis, the secular determinant factors into smaller subdeterminants: a 2×2 of A_1 (s-like and p_z-like) symmetry and a doubly degenerate 1×1 of E (p_x- and p_y-like) symmetry. The A_1 levels have wave functions which have components on the defect site that are linear combinations of the s and p_z orbitals of the defect. However, the coupling of

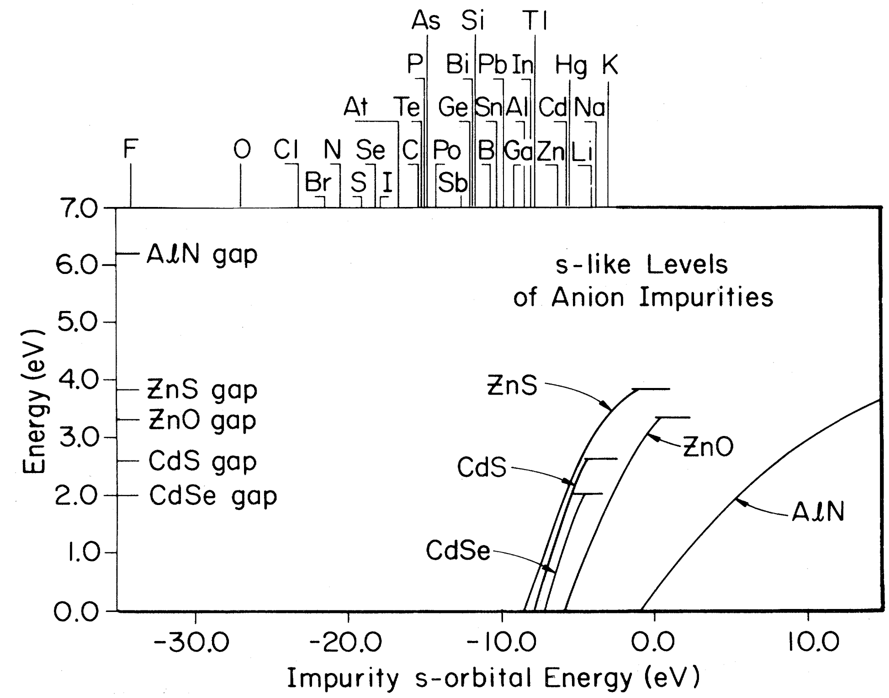

FIG. 3. Predicted s-like deep energy levels (in eV) of anion-substitutional impurities in wurtzite hosts vs impurity s-orbital energy "in the solid" of Ref. 7. The horizontal bar at the top of each curve indicates the energy of the band gap or conduction-band edge. The zero of energy is the valence-band edge. The deep impurity levels are obtained by dropping a vertical line from the impurity (at the top of the figure) until it intersects with the curve of a particular host. If no intersection occurs, the impurity is predicted to have at most shallow levels (bound by the long-ranged part of the Coulomb potential omitted from the present model). Shallow-deep "borderlines" occur where the curves enter the valence and conduction bands.

these two orbitals by the lattice is extremely small (it vanishes in the cubic zinc-blende structure for which the C_{3v} symmetry reduces to T_d), so that the defect energy levels are overwhelmingly controlled by one or the other defect orbital. This yields A_1 levels which are virtually entirely s-like and A_1 levels which are almost entirely p_z-like. The p_z-like level is also virtually identical to the doubly degenerate E (p_x- and p_y-like) level. In the presentation of our results, we neglect this difference and treat the three p-like levels as triply degenerate and the s-like level as singly degenerate. The details of solving the secular equation are described in the Appendix.

III. RESULTS

The materials which we have considered are ZnO, ZnS, CdS, CdSe, and AlN. AlN is a group III-V material and has been studied only very little experimentally. The other materials are II-VI compounds and all have the property that they can be doped only n-type. In the results we are about to discuss, we assume that the impurity is substitutional and that there is no relaxation around the impurity.

A. Anion-site impurities

The predicted levels in the gap for a number of impurities occupying the anion site are shown in Figs. 3 and 4. Also shown for comparison in Fig. 4 are the corresponding results of Hjalmarson *et al.*[5] for the less-ionic zinc-blende semiconductor ZnTe.

1. Group-V acceptors

The most interesting predictions for the anion-site defects are for the impurities N, P, As, Sb, and Bi, which one might naively expect to be shallow acceptors in the II-VI compounds. One should focus mainly on Fig. 4, the p-like levels, because the s-like levels are valence-band resonances and lie below the p-like levels. In AlN, ZnO, ZnS, CdS, and CdSe, the expected shallow acceptors (P, As, Sb, and Bi) produce levels near the shallow-deep borderline (i.e., where the theoretical curve merges with the valence band). Only in ZnTe (the only II-VI material shown in the figure which can currently be doped p-type) are these impurities all expected to be shallow (because the "deep" level is resonant with the valence band). Interestingly enough, the N impurity, due to

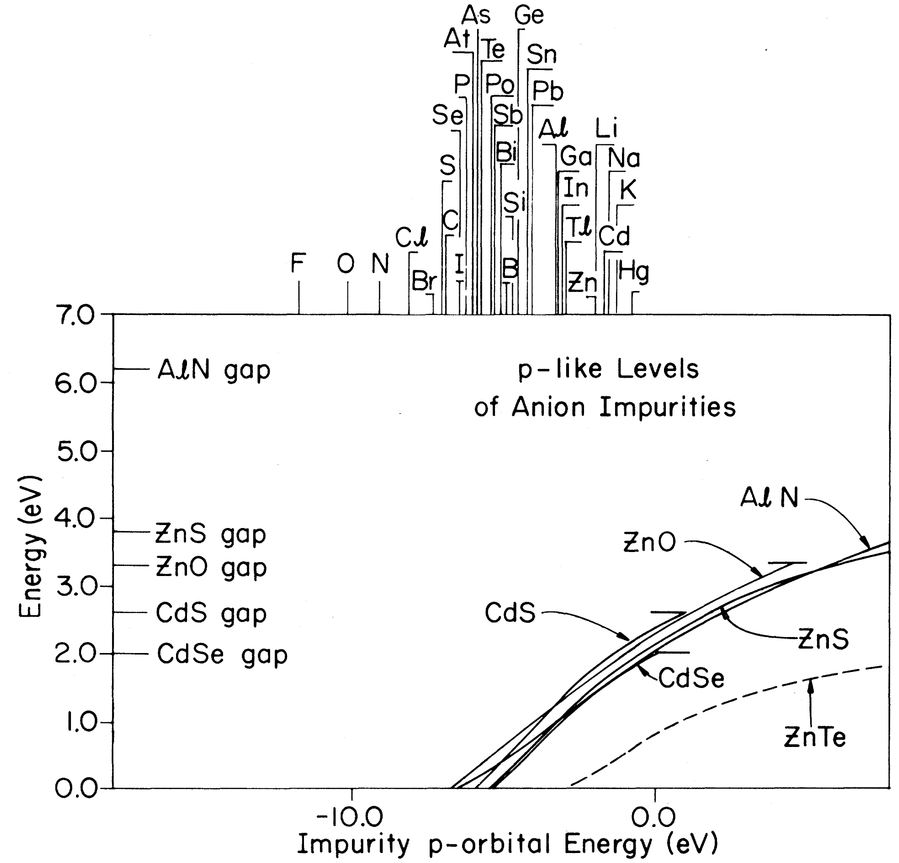

FIG. 4. Predicted p-like deep energy levels (in eV) of anion substitutional impurities in wurtzite host vs impurity p-orbital energy "in the solid" of Ref. 7.

its large electronegativity, lies well below the shallow-deep borderline in all of these materials and is predicted to yield only a shallow level (N, of course, is not an impurity in AlN).

N is not very soluble in these materials, and so doping with N may be achievable only by ion implantation. It is noteworthy, however, that our prediction that N would produce a shallow acceptor level[14] has recently been verified by luminescence measurements on N^+-implanted ZnSe.[15]

Further evidence supporting the theoretical predictions comes from studies of P and As in CdS (Ref. 2) and P, As, and Sb in ZnS (Ref. 16), which are reported to be deep. Indeed, the theory proposes a solution of the long-standing puzzle that P in CdS, which can be doped n-type only, is deep but that P in ZnTe, which can be doped p-type, is shallow. Moreover, one expects that the deep state, being localized, might exhibit a much larger Jahn-Teller coupling than the shallow P in ZnTe. (This is observed for the case of P- and As-doped ZnSe.[17])

2. *Isoelectric group-VI impurities*

The isoelectronic Te trap in CdS has been observed at ~0.25 eV (Refs. 18–20) (with respect to the valence-band maximum), in excellent agreement with the predicted ~0.1-eV level. Similarly, Fukushima and Shionoya[21] have reported a 3.4-eV luminescene in ZnS:Te, indicating a Te level at 0.44 eV in good agreement with the prediction that this level must lie very near the valence-band maximum.

3. *Group-VII donors*

The theory predicts that in all of the materials studied, halogens on anion sites produce shallow donors. Several experiments[22–24] have shown that F, Cl, and Br are shallow donors in CdS.

4. *Antisite defects*

The antisite defect levels of host cations on anion sites are all predicted to be deep, except the s-like level of Al at a N site in AlN and the s-like level of Zn at an O site in ZnO. These defects, having a natural charge-state difference of 4 from the host, are likely to be accompanied by significant charge transfer and to have levels with significant charge-state splittings. Their levels are thus not predicted with confidence in the present model. Nevertheless,

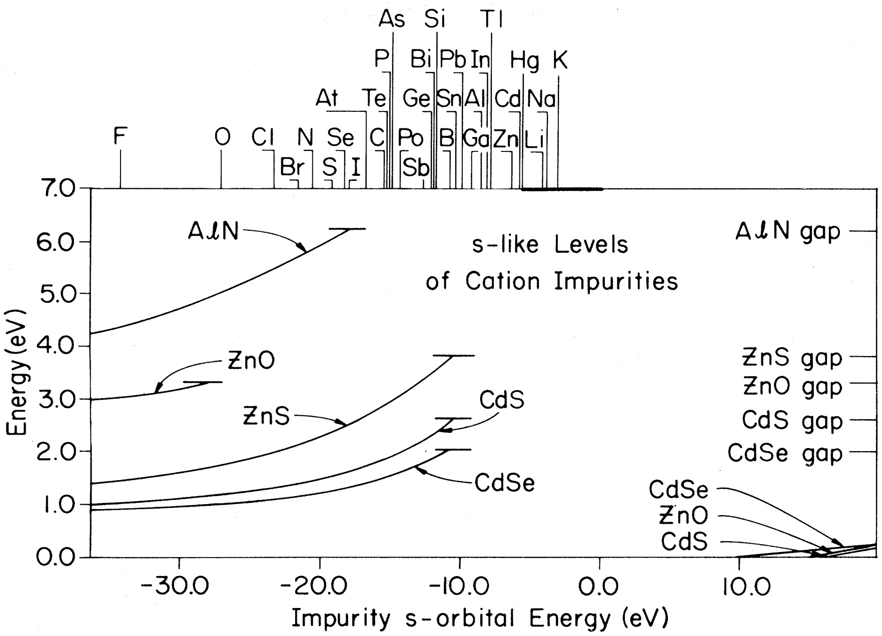

FIG. 5. Predicted cation-site *s*-like levels.

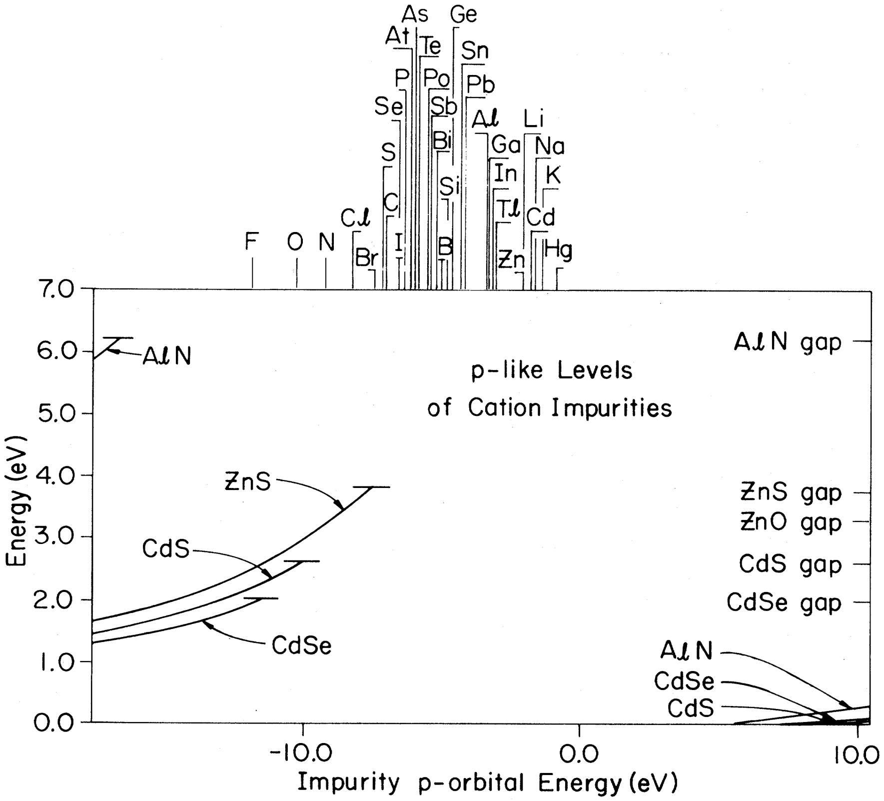

FIG. 6. Predicted cation-site *p*-like levels.

the importance of antisite defects in III-V materials[25] suggests that further study of II-VI antisites is needed.

B. Cation-site impurities

The predictions for cation-site defects are displayed in Figs. 5 and 6. The p-like levels normally lie above the s-like levels.

1. Group-III donors

The group-III donors B, Al, Ga, In, and Tl are all predicted to produce shallow levels (except the s-like level of B in ZnO, CdS, and CdSe, which lies near the shallow-deep borderline). These elements are the standard II-VI shallow donors.[22,24]

2. Group-I acceptors

The theory predicts that the alkali metals all produce shallow acceptors on the cation site. Thus alkali doping should produce p-type wurtzites. However, this is not the case experimentally.

There is evidence that alkali dopants leave the substitutional sites to become interstitial shallow donors, and compensate for any remaining substitutional acceptors.[26,27] The physics of this type of "self-compensation" is not fully understood.[28] Moreover, in at least one case, namely ZnO:Li, the substitutional alkali is reported to lead to a deep hole trap rather than a shallow acceptor[29]; but in this case much of the binding energy may be attributed to the distortion of the center. Apparently the physics of group-I doping is more complicated than previously imagined, as indicated by the self-compensation difficulties of the II-VI semiconductors and the importance of interstitials in these materials. Furthermore, cation-site deep hole traps, such as observed in ZnO:Li, are unusual for sp^3 bonded defects, in our experience.

Our present simple model treats only substitutional defects, and uses only a central-cell potential. The only confirmation of the theory for the *substitutional* impurities *at cation-sites* is that the group-III impurities produce shallow donors. This is not compelling evidence supporting the theory. Therefore, we propose that the cation-site defects in II-VI wurtzite structure are worthy of further theoretical investigation, including a better treatment of charge transfer and a thorough study of the dependence of the impurity levels on lattice relaxation and on the site of the defect: substitutional or interstitial.

C. Vacancies

The vacancy levels predicted by the model are given in Fig. 7. These are obtained by letting the atomic energies of the substitutional impurity go to infinity, thereby decoupling the "impurity" from the host.[30]

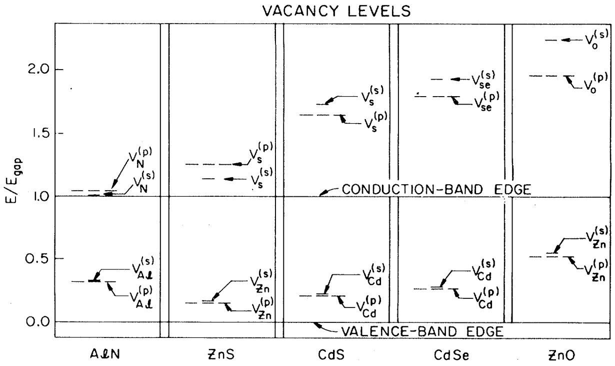

FIG. 7. Predicted vacancy levels in wurtzite hosts. The three p orbitals (p_x, p_y, p_z) are degenerate in our approximation, discussed in the Appendix.

For all five materials, the cation vacancy levels, both s- and p-like levels, are predicted to lie in the lower half of the fundamental band gap, or (in the case of ZnO) near midgap. Both s- and p-like levels are predicted to be nearly degenerate in this model, with the s-like level lying above the p-like level, but this prediction may be an artifact of this model, which neglects the effects both of excited-state orbitals at each site and of second and more-distant neighbors. Including either of these effects would undoubtedly increase the s-p splitting.[31] The expected electronic occupancy of these levels for II-VI semiconductors, if the vacancy is neutral, is six, therefore there are two holes at the highest level (at the s-like level lying in the lower half of the gap or near midgap for these materials), making it a deep double acceptor. For AlN, the occupancy is five.

The anion vacancy levels are all predicted to be resonant with the conduction band. But in the case of AlN, and perhaps ZnS, these theoretical resonances lie close enough to the band edge that, in reality, they could occur in the gap just below the conduction-band edge. The electronic occupancy of a II-VI anion neutral vacancy level is two, if the level is deep within the gap; however, the resonance states are unable to localize and bind the two electrons, and so the electrons spill out of the resonance and fall to the conduction-band edge where they can be captured into the effective-mass-type shallow levels by the long-ranged Coulomb potential omitted in the present model. Thus the anion vacancies in ZnS, ZnO, CdS, and CdSe are predicted to produce shallow double donors, while the N vacancy in AlN would produce a shallow triple donor.

IV. DISCUSSION

The present global theory accounts successfully for the energy levels of substitutional defects of wurtzite structure semiconductors. Its prediction that the expected shallow acceptor impurities P, As, Sb, and Bi lie near the borderline between shallow and deep, while N lies well into the shallow regime, is especially noteworthy.

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APPENDIX: SECULAR EQUATION

In order to demonstrate how the secular equation for the defect energy level is simplified, we consider the case of a substitutional impurity at anion site 2 in the cell at $\vec{R}=\vec{0}$. The impurity potential matrix $V=H-H_0$, in the basis of localized orbitals, is

$$(n,b,\vec{R}=\vec{0}\,|\,H-H_0\,|\,m,b',\vec{R}=\vec{0})=\begin{array}{c|cccc} b\backslash b' & |1) & |2) & |3) & |4) \\ \hline (1| & 0 & 0 & 0 & 0 \\ (2| & 0 & (2|H-H_0|2) & (2|H-H_0|3) & (2|H-H_0|4) \\ (3| & 0 & (3|H-H_0|2) & 0 & 0 \\ (4| & 0 & (4|H-H_0|2) & 0 & 0 \end{array}\;, \tag{A1}$$

where each element $(b\,|H-H_0|\,b')$ of this matrix is a 4×4 matrix in the sp^3 basis ($b,b'=1$, 2, 3, or 4, and $n,m=s, p_z, p_x$, or p_y).

The scaling law with inverse bond length squared[8] tells us that the interatomic matrix elements depend only on the bond length. Therefore if we assume no lattice relaxation around the defect, the off-site matrix elements in Eq. (A1) vanish. Thus only $(2\,|H-H_0|\,2)$ is nonzero among all the submatrices in Eq. (A1). This determines the size of the determinant, which is now 4×4—spanned by s, p_z, p_x, and p_y basis orbitals at anion site 2 in the cell at $\vec{R}=\vec{0}$. Therefore the secular equation reduces to

$$\det\{(n,2,\vec{0}\,|\,1-G_0(E)V\,|\,m,2,\vec{0})\}=0\;. \tag{A2}$$

With the use of the C_{3v} point-group symmetry, this can be expressed as

$$\begin{vmatrix} 1-G_0^{ss}V^{ss}-G_0^{sz}V^{zs} & -G_0^{ss}V^{sz}-G_0^{sz}V^{zz} & 0 & 0 \\ -G_0^{zs}V^{ss}-G_0^{zz}V^{zs} & 1-G_0^{zs}V^{sz}-G_0^{zz}V^{zz} & 0 & 0 \\ 0 & 0 & 1-G_0^{xx}V^{xx} & 0 \\ 0 & 0 & 0 & 1-G_0^{xx}V^{xx} \end{vmatrix}=0\;. \tag{A3}$$

Since we ignore the small coupling of the s and p_z orbitals (which vanishes in the limit of C_{3v} becoming T_d symmetry, that is, in the limit of wurtzite becoming zinc blende), the above secular equation can be factored as

$$[1-G_0^s(E)V^s](1-G_0^pV^p)^3=0\;, \tag{A4}$$

where we set $G^{ss}=G^s$, $G_0^{xx}\simeq G_0^{zz}=G_0^p$, $V^{ss}=V^s$, $V^{xx}\simeq V^{zz}=V^p$, and $V^{sz}=V^{zs}\simeq 0$.

Similarly, the secular equation of the substitutional impurity at anion site 1 in the cell at $\vec{R}=\vec{0}$ is also expressed as Eq. (A4). Thus we are to solve the secular equation of the form Eq. (A4) with Green's functions obtained from only the perfect crystal eigenstates and eigenenergies,

$$G_0^s(E)=(2N)^{-1}\sum_{\lambda,\vec{k}}\frac{(s,1,\vec{k}\,|\,\vec{k},\lambda\rangle\langle\vec{k},\lambda\,|\,s,1,\vec{k})+(s,2,\vec{k}\,|\,\vec{k},\lambda\rangle\langle\vec{k},\lambda\,|\,s,2,\vec{k})}{E-\epsilon(\vec{k},\lambda)} \tag{A5}$$

and

$$G_0^p(E)=(2N)^{-1}\sum_{\lambda,\vec{k}}\frac{(p,1,\vec{k}\,|\,\vec{k},\lambda\rangle\langle\vec{k},\lambda\,|\,p,1,\vec{k})+(p,2,\vec{k}\,|\,\vec{k},\lambda\rangle\langle\vec{k},\lambda\,|\,p,2,\vec{k})}{E-\epsilon(\vec{k},\lambda)}\;. \tag{A6}$$

The factor of $\frac{1}{2}$ comes from there being two anion sites in the unit cell.[32]

A similar argument holds for the cation-site impurity and we obtain a similar equation for that case, with Green's functions

$$G_0^s(E)=(2N)^{-1}\sum_{\lambda,\vec{k}}\frac{(s,3,\vec{k}\,|\,\vec{k},\lambda\rangle\langle\vec{k},\lambda\,|\,s,3,\vec{k})+(s,4,\vec{k}\,|\,\vec{k},\lambda\rangle\langle\vec{k},\lambda\,|\,s,4,\vec{k})}{E-\epsilon(\vec{k},\lambda)} \tag{A7}$$

and

$$G_0^p(E)=(2N)^{-1}\sum_{\lambda,\vec{k}}\frac{(p,3,\vec{k}\,|\,\vec{k},\lambda\rangle\langle\vec{k},\lambda\,|\,p,3,\vec{k})+(p,4,\vec{k}\,|\,\vec{k},\lambda\rangle\langle\vec{k},\lambda\,|\,p,4,\vec{k})}{E-\epsilon(\vec{k},\lambda)}\ . \tag{A8}$$

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