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Proposed explanation of the p-type doping proclivity of ZnTe

John D. Dow
*Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287-1504**
and Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

Run-Di Hong, Stefan Klemm, Shang Yuan Ren, and M.-H. Tsai
Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

Otto F. Sankey
Department of Physics, Arizona State University, Tempe, Arizona 85287-1504

R. V. Kasowski
Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station,
Wilmington, Delaware 19898

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An explanation is proposed for the fact that ZnTe is unique among the II-VI compound semiconductors in that it can be doped p type rather easily: a p-like deep-level resonance lies within the valence band of ZnTe and emerges into the fundamental band gap with increasing Se content x in $\mathrm{ZnTe}_{1-x}\mathrm{Se}_x$ random alloys. This level generates free holes when it lies below the Fermi energy in the valence band, making its parent defect a shallow acceptor. When the level moves into the gap, the impurity becomes a deep hole trap. The native and foreign antisite defects $\mathrm{Zn}_{\mathrm{Te}}$ and $\mathrm{Li}_{\mathrm{Te}}$ are suggested as possible parent defects of the relevant deep level; they are predicted to be shallow acceptors in ZnTe, while the corresponding defects are deep traps in other II-VI compound semiconductors. Tests of this proposal are suggested and the substitutional s- and p-bonded deep levels of ZnSe and ZnTe are predicted, extending the theory of Hjalmarson *et al.* [Phys. Rev. Lett. **44**, 810 (1980)]. The possibility of doping ZnSe p type with (antisite) Be is also proposed and discussed.

I. INTRODUCTION

Most wide-band-gap II-VI compound semiconductors can be easily doped n type, but resist p-type doping. The most notable exception is ZnTe which is easily doped p type, but not n type. The different and singular doping behavior of ZnTe is not presently understood.

The purpose of this paper is to offer an explanation of this difference in terms of a defect that undergoes a shallow-deep transition as a function of alloy composition x in $\mathrm{ZnTe}_{1-x}\mathrm{Se}_x$, so that it is an acceptor in ZnTe but a hole trap in ZnSe. We present calculations that suggest that such a transition occurs for the native and foreign antisite defects $\mathrm{Zn}_{\mathrm{Te}}$ and $\mathrm{Li}_{\mathrm{Te}}$ in ZnTe. And we suggest specific tests of the explanation, which has a firm, but admittedly not unshakable, theoretical foundation. Indeed, the reader should accept this work for its intended purpose: to sketch a simple model which can be tested experimentally and which appears to offer an explanation of the p-type doping proclivity of ZnTe in terms of the natural occurrence of certain defects. The theoretical tools are presently not available to predict with 100% confidence if these defects form in sufficient concentration with precisely the electronic structures we find. Nevertheless, the picture we propose is simple enough to lend itself readily to experimental tests, while presenting an attractive alternative explanation of the doping properties of ZnTe to mechanisms which rely on self-compensation or the relative solubilities of impurities in different hosts.

We propose that p-type conductivity is most easily achieved in ZnTe of the II-VI semiconductors because defects that produce p-like deep traps lying slightly above the valence-band maximum in most II-VI semiconductors instead have these levels lying below the band edge in ZnTe. Each such level for a neutral defect is naturally occupied by both electrons and holes when it lies within the fundamental band gap, and so can trap holes. When the level descends below the valence-band maximum, its holes are autoionized and become carriers at room temperature. (At zero temperature they are trapped in shallow acceptor levels.) Hence the defects generate holes in ZnTe, but trap them in other semiconductors. More specifically, our proposal is that the native antisite defect Zn on a Te site, $\mathrm{Zn}_{\mathrm{Te}}$ (and even the antisite dopant $\mathrm{Li}_{\mathrm{Te}}$) is a shallow acceptor in ZnTe and dopes the material p type, compensating any n-type impurities that might otherwise themselves compensate acceptors: In other II-VI semiconductors, neither the cation-on-anion-site defect nor antisite Li yields a shallow acceptor, but instead produces a deep-trap level in the fundamental band gap. The antisite defects $\mathrm{Zn}_{\mathrm{Se}}$ (and $\mathrm{Li}_{\mathrm{Se}}$) neither dope the material p type nor produce thermally ionizable holes; instead they trap carriers, holes in particular.

We arrived at the conclusion that the defect responsible for the resistance of most II-VI semiconductors to p-type doping might be the cation-on-anion-site defect after having examined predictions for deep levels of all the *s*- and *p*-bonded substitutional impurities in all of the major II-VI semiconductors. During this examination we asked the questions (i) "Can impurities explain the different doping proclivities of ZnTe and the other II-VI semiconductors" and (ii) "Does any impurity that is likely to occur in significant concentrations have a deep-level structure that is different in ZnTe from in the other II-VI semiconductors?"

The classical mechanism that has been proposed to explain the resistance of II-VI semiconductors to *p*-type doping is self-compensation: The introduction of an acceptor such as Li or Na onto a cation site is thought to simultaneously produce an anion vacancy which is a double donor and compensates the acceptor, leaving the material semi-insulating or doping the material *n* type rather than *p* type.[1-6] If the self-compensation mechanism is indeed operative in most II-VI semiconductors and cannot be blocked for at least some *p*-type dopants, then II-VI semiconductors are unlikely to become important electronic materials, regardless of the purity of the materials. The self-compensation is thought to be an intrinsic property of the doping, regardless of the quality of the undoped semiconductor: *p*-type doping produces compensating anion vacancies. Therefore, the fact that ZnTe is naturally *p* type is an important clue to understanding and overcoming self-compensation (if it occurs)—and perhaps the key to developing electronic-grade II-VI semiconductors.

The explanation often given for the singular behavior of ZnTe is that its band gap is smaller than that of other II-VI semiconductors,[1-3] and so the energy generated by the self-compensation, which is approximately the energy of the gap, is too small to produce a vacancy in ZnTe, but is adequate for vacancy formation in other II-VI semiconductors. At first, this argument appears attractive, because it correlates with the fact that self-compensation is most commonly found in large-band-gap semiconductors. Upon closer examination, however, the argument is difficult to reconcile with the fact that the band gaps of ZnSe and ZnTe are not very different or with the fact that stoichiometric CdTe, which has a significantly smaller band gap than ZnTe, resists *p*-type doping (although less so than other II-VI compounds). Therefore we conclude that an alternative explanation of the singular *p*-type character of ZnTe is needed.

Self-compensation by vacancies is not universally accepted as the mechanism by which II-VI semiconductors resist *p*-type doping. Some other explanations point to the different solubilities of impurities on different sites and interstitial self-compensation: For example, Na can occupy a cation site as an acceptor in ZnSe, but becomes a donor at interstitial sites,[7] and so interstitial Na can compensate substitutional Na. Other mechanisms have also been suggested to account for the resistance of II-VI semiconductors to *p*-type doping: The acceptor binding energies of some II-VI semiconductors can be rather large, >0.1 eV, making the acceptors difficult to ionize thermally and frustrating *p*-type conductivity.[8] The incorporation of the standard *p*-type dopants into a II-VI host can be severely limited by the chemistry of the host.[9] Unanticipated deep-level formation may occur, in the sense that impurities such as those from column V of the Periodic Table, when occupying a column-VI site, may produce deep levels in the fundamental band gap of some wurtzite-structure II-VI compound semiconductors rather than the expected shallow acceptors.[10] Indeed, it is conceivable that the II-VI semiconductor doping problem is a consequence of rather complicated defect and impurity dynamics. Currently there are many efforts in progress to overcome the *p*-doping problem by improving the quality of II-VI materials, for example, by employing molecular-beam epitaxial techniques of crystal growth; these efforts implicitly assume that impurities and defects, not self-compensation, cause the *p*-type doping problem.[11-14]

Clearly there are a variety of detailed mechanisms for explaining the resistance of most wide-band-gap II-VI semiconductors to the *p*-type doping. However, a satisfactory explanation of why ZnTe is almost singularly compatible with *p*-type doping is lacking—and could provide a vital clue for doping the other II-VI semiconductors *p*-type.

The purpose of this paper is to offer a simple but general explanation of the ZnTe doping singularity. This explanation does not depend on any detailed model of dopant compensation or theory of the resistance of II-VI semiconductors to *p*-type doping. It merely asserts (on the basis of a theory of deep levels) that ZnTe is unique in having a native antisite defect, $\mathrm{Zn_{Te}}$, that is a strong *p*-type dopant, capable of generating holes and compensating donors of any origin. ZnTe is also unique in that its antisite dopant $\mathrm{Li_{Te}}$ is also a shallow acceptor, not a deep trap. The electronic structures of these antisite defects provide a simple, general, and experimentally verifiable explanation of why ZnTe is easily doped *p* type, and allow us to avoid the more difficult issue of specifying the detailed mechanisms by which most II-VI semiconductors occur *n* type. Hence, instead of asking "Why are ZnSe and most other II-VI semiconductors *n* type" we address the question "what unique feature of ZnSe and ZnTe causes them to *change* their doping proclivities from *n* type for ZnSe to *p* type for ZnTe"? We propose that the relevant feature is the shallow acceptor character of the $\mathrm{Zn_{Te}}$ antisite defect.

At first glance, most of the mechanisms that might frustrate *p*-type doping appear to be smooth functions of the chemical compositions of the II-VI semiconductors, and so it is difficult to understand why ZnTe can be doped *p* type and most other II-VI semiconductors cannot. One might still expect that $\mathrm{ZnTe_{1-x}Se_x}$ (Ref. 15) or $\mathrm{(ZnTe)_{1-x}(CdSe)_x}$ alloys (Ref. 16) would smoothly change from *p*-type to semi-insulating to *n*-type conductivity as x increases. However the concept of abrupt deep-shallow transitions[17-23] of impurity character as a function of host chemical composition raises the possibility that a defect intimately involved in obstructing the *p*-type doping in most II-VI semiconductors might have quite a different character in ZnTe. We predict that the native antisite defect $\mathrm{Zn_{Te}}$ should be a shallow acceptor in ZnTe, but that its analog $\mathrm{Zn_{Se}}$ should be a deep trap in

ZnSe. At the extreme, even Li (a common dopant) has an antisite defect with the same character, changing from shallow in ZnTe to deep in ZnSe. The deep-shallow transition of the antisite defects' characters occur *abruptly* as functions of alloy composition x, and can naturally explain why ZnTe is p type while other II-VI semiconductors are not.

II. MODEL

Our model uses the well-established theory of deep levels,[18,19,24,25] which has successfully explained a broad range of data, including the physics of the N trap in $GaAs_{1-x}P_x$ (which produces an energetically "shallow" level within <0.1 eV of the conduction-band edge in GaP, a deep trap more than 0.1 eV below the edge for $x \simeq 0.5$, and a resonance in the conduction band of GaAs),[17,19,18] rapid III-V-compound laser degradation,[26] bulk and surface core excitons[27–31] in Si and III-V compound semiconductors, intrinsic surface states,[32,33] Schottky-barrier heights,[25–38] and the deep-shallow behavior of defects such as the DX center in $Al_xGa_{1-x}As$ semiconductors[39] and $GaAs/Al_xGa_{1-x}As$ superlattices.[20–23,40]

In this model, deep energy levels are obtained by solving the secular equation

$$\det[1-(E-H_0)^{-1}V]=0 ,$$

where H_0 is the host Hamiltonian operator, V is the defect potential operator, and the level's energy E is assumed to have an infinitesimal positive imaginary part. Hjalmarson *et al.*[19] have presented predictions of A_1 deep levels based on this theory. In a Löwdin basis[41] of sp^3s^* orbitals centered at each site[42] the defect potential is diagonal and related to atomic energies.[19] The host Hamiltonian is treated in an empirical tight-binding model, the parameters of which have been fit to observed band gaps in several semiconductors and follow chemical trends from one semiconductor to another.[42] Charge-transfer effects, such as those treated by Jansen and Sankey,[7] are not included explicitly in this model. Nevertheless the model produced excellent agreement with measured surface states of ZnSe and ZnTe,[33] and so is expected to describe well any localized perturbation associated with a defect. Details of the model have been published.[24,25,32] We consider only substitutional defects because common interstitials such as Li and Zn are normally donors[7] and because most interstitials are notoriously sensitive to charge transfer and the local environment,[7,43–45] a property that we regard as unlikely to be associated with the nearly universal doping properties of II-VI semiconductors—although we recommend the work of Chadi and Chang[46] for a somewhat different viewpoint.

III. RESULTS

As a test of the model's ability to describe defects in II-VI semiconductors, we first consider Li doping of zinc-blende-structure ZnSe and find Li_{Zn} to be a shallow acceptor, in agreement with the data.[47] Furthermore, experiments[47] reveal a deep acceptor related to Li 0.2 to 0.3 eV above the valence-band maximum. Since interstitial Li is a donor,[7] this acceptor can likely be associated with the theoretically predicted 0.4 eV antisite Li_{Se} deep level, and indicates that the theory lies only slightly above the data in energy.[48,49] Thus the Li doping data for ZnSe are well described by the present theory, lending support to the other theoretical predictions.

Since the spirit of the present work is to understand global chemical trends, we limit our discussion to a mean-field one-electron theory of neutral defects, and omit the Coulomb effects normally associated with small to moderate splittings of order 0.2 eV between different charge states of a defect.[7,43–35] This simplification makes all of the energy levels associated with different charge states of a defect degenerate and allows a simple discussion of global trends without concern for many-electron effects. Furthermore, the effects of these rather small effects can be included *a posteriori* with very little difficulty.[43–35]

Each of the s- and p-bonded impurities has eight "deep" spin orbitals with energies near the fundamental band gap, two A_1 or s-like and six T_2 or p-like spin-orbitals. Normally the energies of the T_2 spin orbitals lie above the A_1 spin orbitals. In fact, spin-orbit splitting, which is included in the theory, causes the T_2 levels to split slightly into $p_{3/2}$-like Γ_8 levels and $p_{1/2}$-like Γ_7 levels. However, for simplicity we shall refer to both levels as T_2 in the text, while plotting the spin-orbit split levels in the figures. (In the T_d double-group notation, A_1 becomes Γ_6).

The predictions of the theory for substitutional s- and p-bonded defects in ZnSe and ZnTe are summarized in Figs. 1–4. These figures indicate the doping character of each element of the Periodic Table.

A notable feature of the predictions is that the T_2 defect energy levels for Zn on either site in any host are virtually identical to those of the corresponding Li defect because these atoms have essentially the same atomic orbital energies. This means, in particular, that Zn_{Se} and Li_{Se} have about the same energy levels and the same doping character, except that Zn provides one more electron than Li.

Figures 1–4 should be examined as follows: In general the deep levels move up (down) as one moves to the left (right) across a row of the Periodic Table. The host atom has A_1 and T_2 levels occupied in the valence band and A_1 and T_2 levels empty in the conduction band. In the case of the Se-site Si in ZnSe, all the defect's levels lie above the corresponding Se levels, but the difference between Si and Se is not enough to cause any of the occupied deep levels to move up into the band gap. As a result, Si is a double acceptor (denoted $2A$) because it has two fewer electrons than Se, and these missing-electrons or holes "bubble up" from the deep Si levels in the valence band to the valence-band edge, where they are trapped in shallow acceptor levels by the Coulomb potential of the ionized Si atom. Similar reasoning applied to the empty levels indicates that Br on the Se site of ZnSe is a single donor. Because Br is more electronegative than Se, its energy levels lie lower than those of Se; but the

Impurities on Anion Site in ZnTe

	H 5 A								He 4 A
	Li 5 A	Be 4 A		B 3 A	C 2 A	N 1 A	O I	F 1 D	Ne 2 D
	Na 5h1e	Mg 4 A		Al 3 A	Si 2 A	P 1 A	S I	Cl 1 D	Ar 2 D
	K 5h1e	Ca 4h2e	Zn 4 A	Ga 3 A	Ge 2 A	As 1 A	Se I	Br 1 D	Kr 2 D
	Rb 5h1e	Sr 4h2e	Cd 4 h	In 3 A	Sn 2 A	Sb 1 A	Te I	I 1 D	Xe 2 D
Va 2DF	Cs 5h1e	Ba 4h2e	Hg 4h2e	Tl 3 A	Pb 2 A	Bi 1 A	Po I	At 1 D	Rn 2 D

FIG. 1. Predicted doping character of Zn-site substitutional *s*- and *p*-bonded atoms in ZnSe. The character is denoted *D* for donor, *A* for acceptor, and *I* for isoelectronic defect (with no deep level in the gap). If the impurity produces one or more deep trap levels in the gap, this is indicated for each atom by the number of holes and electrons trapped in those levels for a single neutral defect, e.g., $5h\,1e$ denotes 5 holes and 1 electron—in a *p*-like deep level. See the text for further explanation.

Impurities on Anion Site in ZnSe

	H 5h1e								He 4h2e
	Li 5h1e	Be 4 A		B 3 A	C 2 A	N 1 A	O I	F 1 D	Ne 2 D
	Na 5h1e	Mg 4h2e		Al 3 A	Si 2 A	P 1 A	S I	Cl 1 D	Ar 2 D
	K 5h1e	Ca 4h2e	Zn 4h2e	Ga 3 A	Ge 2 A	As 1 A	Se I	Br 1 D	Kr 2 D
	Rb 5h1e	Sr 4h2e	Cd 4h2e	In 3 A	Sn 2 A	Sb 1 A	Te I	I 1 D	Xe 2 D
Va 2DF	Cs 5h1e	Ba 4h2e	Hg 4h2e	Tl 3 A	Pb 2 A	Bi 1 A	Po I	At 1 D	Rn 2 D

FIG. 3. Predicted doping character for Zn-site substitutional atoms in ZnTe, as in Fig. 1.

Br-Se difference is not enough to pull one of the empty Se deep levels in the conduction band down into the gap. As a result, the extra electron of the neutral Br defect (relative to the Se atom the Br replaced) falls out of the deep level in the conduction band, the Br is autoionized, and the extra Br electron falls to the conduction-band edge, where it becomes a shallow donor electron orbiting the ionized Br impurity (denoted $1D$). As one moves to the left in the Periodic Table, the deep levels that were within the valence band for the host atom move up, sometimes into the band gap, becoming deep traps—as for $\mathrm{Cs_{Se}}$, which (when neutral) has a *p*-like T_2 level in the gap occupied by five holes and one electron, and an A_1 state *below* the valence-band maximum filled by two electrons, and therefore is denoted $5h\,1e$. In some cases the defect is so electropositive that the relevant occupied deep levels pass through the gap into the conduction band, as for the anion vacancy (which is infinitely electropositive[50] and is denoted as the element "Va" in the figures). The A_1 and T_2 levels of the vacancy lie in the conduction band, with the six electrons of the T_2 level removed along with the Se atom during vacancy creation. Thus the Se vacancy is a double donor ($2D$) and has a false valence (F) with respect to Se, allowing it to donate $+2$ electrons rather than -6, because eight spin orbitals ($2A_1+6T_2$) have crossed the gap into the conduction band as the Se host atom has been "transmuted" into a vacancy. Similarly a Zn-site Cl atom has deep levels derived from the empty conduction-band levels of Zn; the A_1 level is pulled down

Impurities on Cation Site in ZnTe

	H 1A								He 2 h
	Li 1A	Be I		B 1 D	C 2 e	N 2e1D	O 2e2D	F 2e3D	Ne 2h6e
	Na 1A	Mg I		Al 1 D	Si 2 D	P 2e1D	S 2e2D	Cl 2e3D	Ar 2e4D
	K 1A	Ca I	Zn I	Ga 1 D	Ge 2 D	As 2e1D	Se 2e2D	Br 2e3D	Kr 2e4D
	Rb 1A	Sr I	Cd I	In 1 D	Sn 2 D	Sb 3 D	Te 2e2D	I 2e3D	Xe 2e4D
Va 2h6e	Cs 1A	Ba I	Hg I	Tl 1 D	Pb 2 D	Bi 3 D	Po 2e2D	At 2e3D	Rn 2e4D

FIG. 2. Predicted doping character for Se-site substitutional atoms in ZnSe, as in Fig. 1.

Impurities on Cation Site in ZnSe

	H 2h1A								He 2 h
	Li 1A	Be I		B 1h1e	C 2 e	N 2e1D	O 4h4e	F 3h5e	Ne 2h6e
	Na 1A	Mg I		Al 1 D	Si 2 e	P 2e1D	S 2e2D	Cl 2e3D	Ar 2h6e
	K 1A	Ca I	Zn I	Ga 1 D	Ge 2 e	As 2e1D	Se 2e2D	Br 2e3D	Kr 2e4D
	Rb 1A	Sr I	Cd I	In 1 D	Sn 2 e	Sb 2e1D	Te 2e2D	I 2e3D	Xe 2e4D
Va 4h2e	Cs 1A	Ba I	Hg I	Tl 1 D	Pb 2 D	Bi 2e1D	Po 2e2D	At 2e3D	Rn 2e4D

FIG. 4. Predicted doping character for Te-site substitutional atoms in ZnTe, as in Fig. 1. Note that the Zn antisite defect produces a shallow [quadruple (Ref. 51)] acceptor.

into the gap because Cl is more electronegative than Zn, while the T_2 levels remain in the conduction band. The five extra electrons of neutral Cl distribute themselves with two in the A_1 deep level and three in the conduction band; hence Cl produces a deep doubly occupied A_1 level (2 *e*) and a triple donor (3 *D*). Some defects, such as oxygen on a Se-site in ZnSe neither change the number of electrons nor introduce new deep levels into the gap, and so are termed isoelectronic (*I*).

By generating Periodic Tables such as Figs. 1–4 for a wide range of II-VI semiconductors, we have been able to determine how the predicted characters of defects are different in various semiconductors. Here we discuss only ZnSe, which has similar defect deep-level behavior to other II-VI semiconductors, and ZnTe, which exhibits unusual *p*-type doping behavior.

The theory predicts that neutral Zn_{Te} in ZnTe is a quadruple[51] acceptor (4 *A*), whereas native cation-on-anion-site defects in other II-VI semiconductors produce T_2-symmetric deep traps in the band gap: e.g., ($4h2e$) for Zn_{Se} in ZnSe. (See Figs. 1 and 3). Charge-transfer and Coulomb splitting effects omitted from the model may actually prevent the formation of the quadrupole acceptor state, but some level of acceptor character is nevertheless to be expected. (Sec. IV treats this issue in more detail.) This native antisite defect yields four holes to the valence band and is a powerful *p* dopant *in ZnTe only.* Moreover, as a function of alloy composition *x* in $\text{ZnTe}_{1-x}\text{Se}_x$ or $(\text{ZnTe})_{1-x}(\text{CdSe})_x$, the relevant deep level should move from below the valence-band maximum into the gap—and the character of the Zn-on-anion-site defect should change rather *abruptly* from a *p*-type acceptor to a deep trap which no longer dopes the material *p*-type. (See Figs. 5 and 6). Hence the material should change, rather abruptly, from being *p* type to *n* type. The abrupt character of this transition should be an experimental signature of the antisite-defect doping mechanism, which perhaps can be detected by a sudden change of doping character with alloy composition *x* in $\text{ZnTe}_{1-x}\text{Se}_x$ or $(\text{ZnTe})_{1-x}(\text{CdSe})_x$, by optical spectroscopy (allowing for the fact that both the valence-band edge and the deep level have T_2 symmetry), or by pressure or strain measurements which cause the deep level to move into or out of the fundamental band gap.

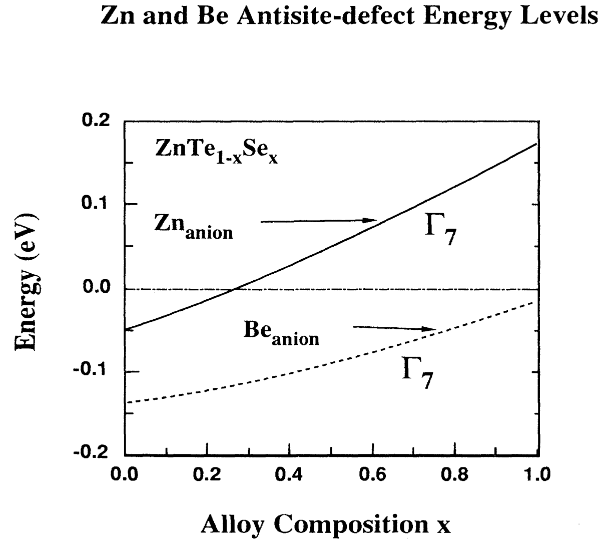

FIG. 5. Predicted dependence on alloy composition x of the energy levels (in eV) for the anion-site defects Zn_{anion} (solid line), Li_{anion} (the same solid line), and Be_{anion} (dashed) in $\text{ZnTe}_{1-x}\text{Se}_x$. The $p_{1/2}$-like level derived from the T_2 deep level is labeled Γ_7.

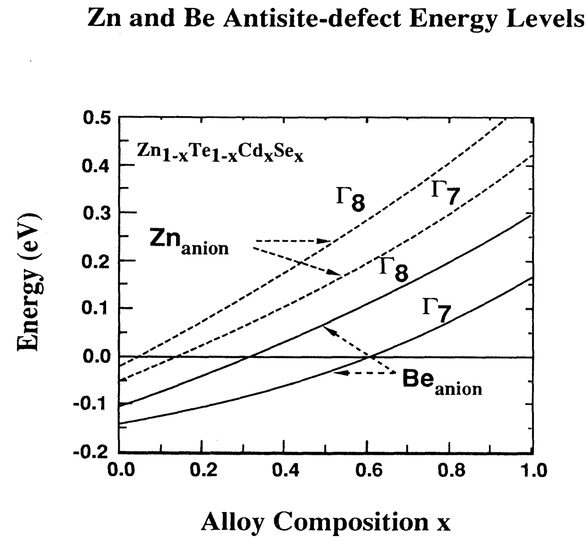

FIG. 6. Predicted dependence on alloy composition x of the energy levels (in eV) for the anion-site defects Zn_{anion} (solid line) and Be_{anion} (dashed) in $(\text{ZnTe})_{1-x}(\text{CdSe})_x$. The $p_{3/2}$-like ($p_{1/2}$-like) levels derived from the T_2 deep levels are labeled Γ_8 (Γ_7). For $x=0$, and for a neutral Zn_{Te} defect, the Γ_7 level is occupied by two electrons and the Γ_8 level by four holes.

Zn is not the only antisite defect that is predicted to produce a strong *p* dopant. Li_{Te} (although unlikely to occur in large concentrations) is likewise a shallow acceptor yielding nominally five holes[51] to the valence band. The energy of the foreign antisite Li deep level is essentially the same as that of native antisite Zn—and so substitutional antisite Li should also undergo a similar deep-shallow transition as a function of alloy composition. (Note that this paper does not consider the questions of whether the Li would be mechanically stable on such a site or whether it would naturally occupy such a site with reasonable probability.) Thus, for example, if we assume an oversimplified situation for the Li doping of ZnTe in which there are no vacancies or other defects, and if we denote the concentrations of interstitial-, Zn-site, Te-site, and Se-site Li by $[\text{Li}_I]$, $[\text{Li}_{\text{Zn}}]$, $[\text{Li}_{\text{Te}}]$, and $[\text{Li}_{\text{Se}}]$, then the conditions for *p*-type character in ZnTe and ZnSe are

$$5[\text{Li}_{\text{Te}}]+[\text{Li}_{\text{Zn}}]-[\text{Li}_I]>0 \ ,$$

and

$$-[\text{Li}_{\text{Se}}]+[\text{Li}_{\text{Zn}}]-[\text{Li}_I]>0 \ .$$

Clearly the antisite Li could make a difference in the doping character of the host, *provided its concentration is large enough.* Now, in an equilibrium situation, the Li_{Te}

concentration is likely to be exponentially smaller than [$\mathrm{Li}_{\mathrm{Zn}}$], and so Li by itself should not change the doping character of a II-VI semiconductor; but this example illustrates in a simple case how the concentrations of the different point defects determine the doping character.

Another interesting prediction of the theory is that Be on an anion site is a (quadruple[51]) acceptor in both ZnSe and ZnTe, while remaining isoelectronic when occupying a Zn site. (See Fig. 5). This means that heavy Be doping may also make ZnSe p type.[52]

On the anion site, only Zn, Mg, Cd, Li, and H and He are predicted to have different doping characters in ZnSe and ZnTe. On the cation site Ar, F, O, Bi, Sb, Sn, Ge, Si, B, H and the vacancy have different doping characters. See Figs. 1–4. Predicted energy levels are given in Figs. 7–22. (Impurities with no deep levels near the fundamental band gap behave according to the conventional rules and are not displayed.)

It is noteworthy that the anion vacancy is a double donor for both ZnSe and ZnTe—as anticipated by the extensive self-compensation literature. This is a case of false valence,[53] because the removal of a column-VI atom should add six holes to the valence band, not two electrons to the conduction band. The removal of, say, Te in ZnTe is achieved theoretically by driving its atomic energies to infinity as well as adding six holes. In the case of ZnTe and other II-VI semiconductors, this causes an A_1 and a T_2 level to move from the valence band into the conduction band.

Within the context of the conventional self-compensation picture, each acceptor in p-type doped ZnSe is compensated by a double-donor anion vacancy generated as a result of acceptor doping. If the same energy that produced an anion vacancy instead produced an anion-site antisite Zn, then in ZnSe every antisite defect would compensate roughly two acceptors (or one vacancy), but in ZnTe this would not happen. Moreover, in ZnTe roughly every two vacancies would be compensated by one antisite defect, blocking the conventional self-compensation process. Antisite defects are common in a variety of semiconductors, as argued by Van Vechten and others.[54] The formation energy should be less for the an-

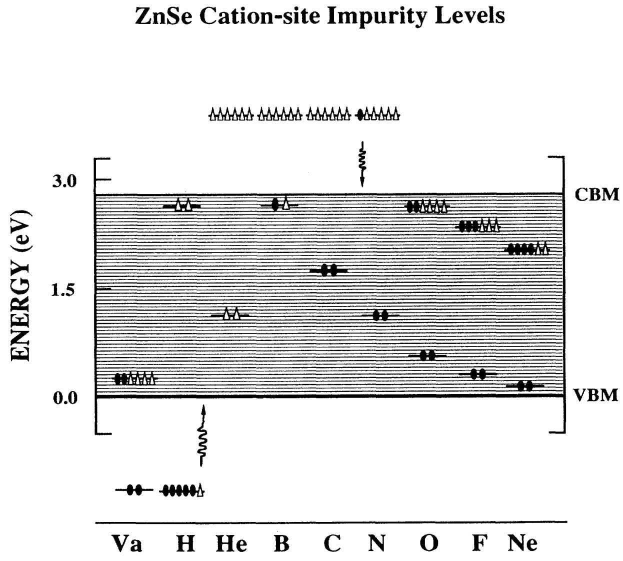

FIG. 7. Predicted deep energy levels in the gap (striped) of ZnSe due to s- and p-bonded substitutional impurities on the Zn site. The impurities are indicated on the abscissa. Their occupancies, when neutral, are indicated by open triangles for holes and by closed circles for electrons.

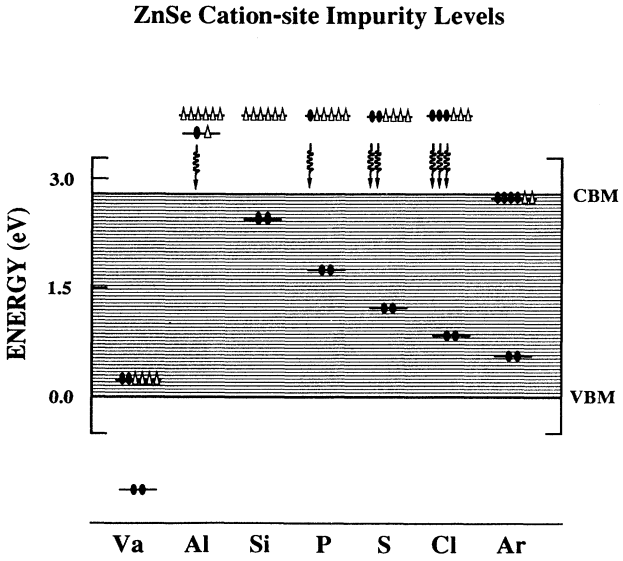

FIG. 8. Predicted deep energy levels in the gap of ZnSe due to s- and p-bonded substitutional impurities on the Zn site. The impurities are indicated on the abscissa.

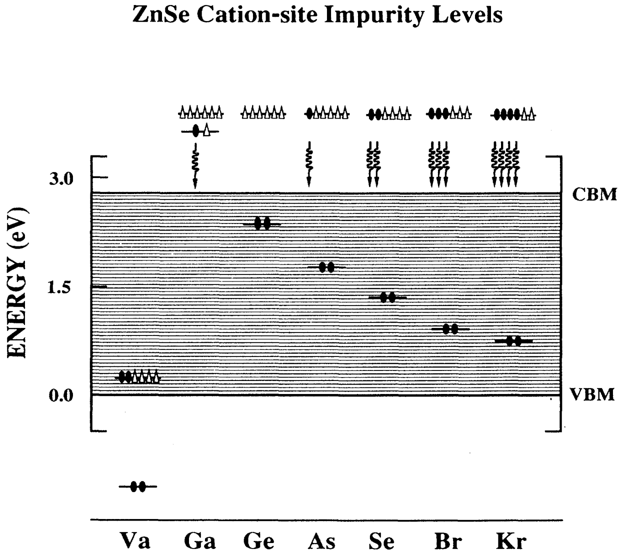

FIG. 9. Predicted deep energy levels in the gap of ZnSe due to s- and p-bonded substitutional impurities on the Zn site. The impurities are indicated on the abscissa.

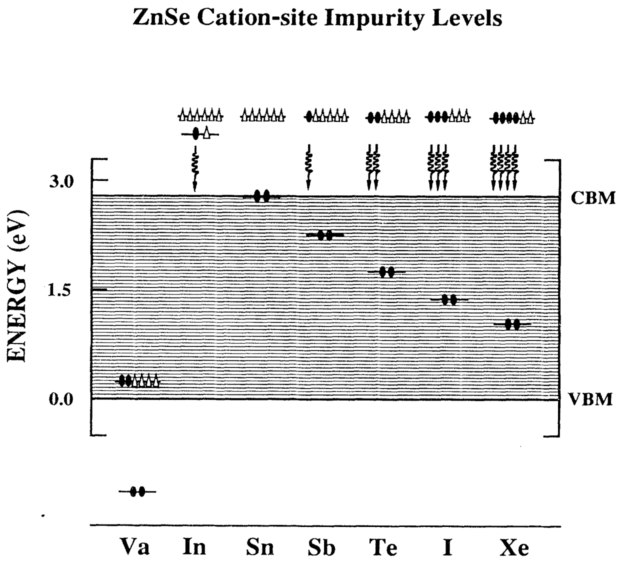

FIG. 10. Predicted deep energy levels in the gap of ZnSe due to *s*- and *p*-bonded substitutional impurities on the Zn site. The impurities are indicated on the abscissa.

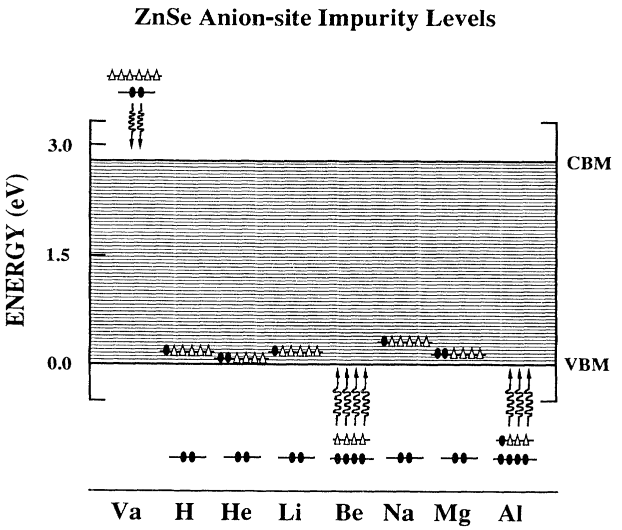

FIG. 12. Predicted deep energy levels in the gap of ZnSe due to *s*- and *p*-bonded substitutional impurities on the Se site. The impurities are indicated on the abscissa.

tisite defect than for the vacancy, and the number of antisite defects to be expected at equilibrium should exceed the number of vacancies. Stated more simply, it normally costs less energy to rearrange a bond than to break it. Hence in most crystal-growth processes, an adequate number of $\mathrm{Zn_{Te}}$ defects should be created, and the self-compensation would be expected to be impotent in ZnTe but not inZnSe. For example (Fig. 23), in ZnSe with one Na acceptor, one Se vacancy, and one $\mathrm{Zn_{Se}}$ antisite defect, the shallow Na acceptor level is filled by one of the vacancy's two electrons, with the other electron occupying the T_2 Zn deep level in the gap (leaving it with three electrons and three holes). There is no *p*-type conductivity. In contrast, the same situation in ZnTe leaves the two electrons from the vacancy occupying two of the five empty shallow orbitals of both Na and $\mathrm{Zn_{Te}}$, leaving three thermally ionizable holes and *p*-type conductivity. Therefore, we propose that *p*-type conductivity is rather easily achieved only in ZnTe of the common II-VI semiconductors because only in ZnTe is the antisite defect $\mathrm{Zn_{Te}}$ a shallow acceptor rather than a deep trap.

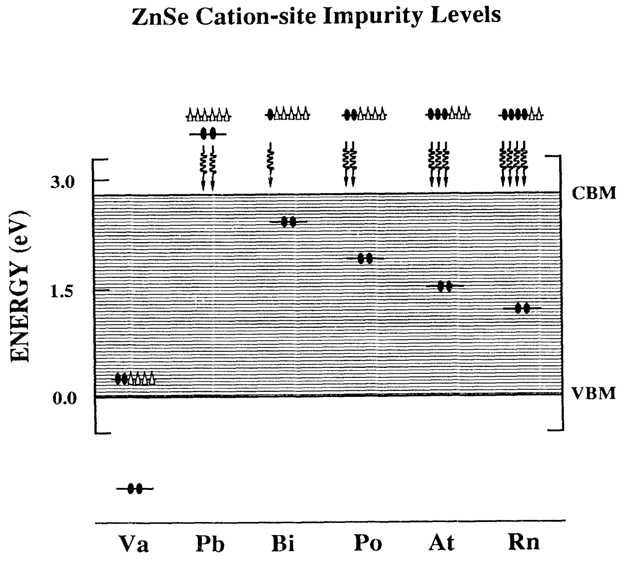

FIG. 11. Predicted deep energy levels in the gap of ZnSe due to *s*- and *p*-doped substitutional impurities on the Zn site. The impurities are indicated on the abscissa.

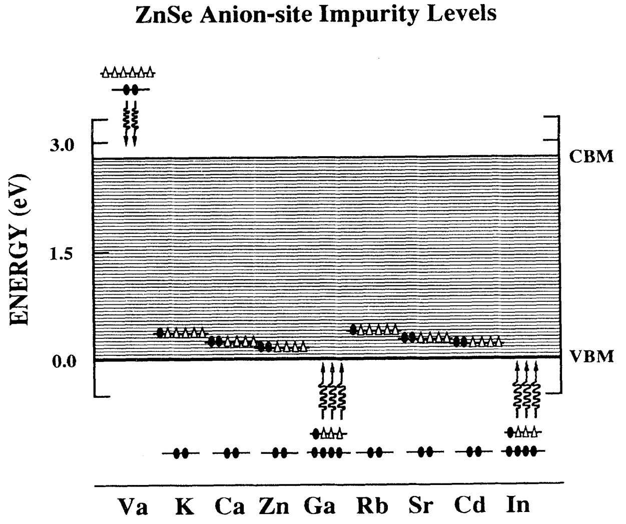

FIG. 13. Predicted deep energy levels in the gap of ZnSe due to *s*- and *p*-bonded substitutional impurities on the Se site. The impurities are indicated on the abscissa. Al (not shown) has a similar electronic structure to Ga.

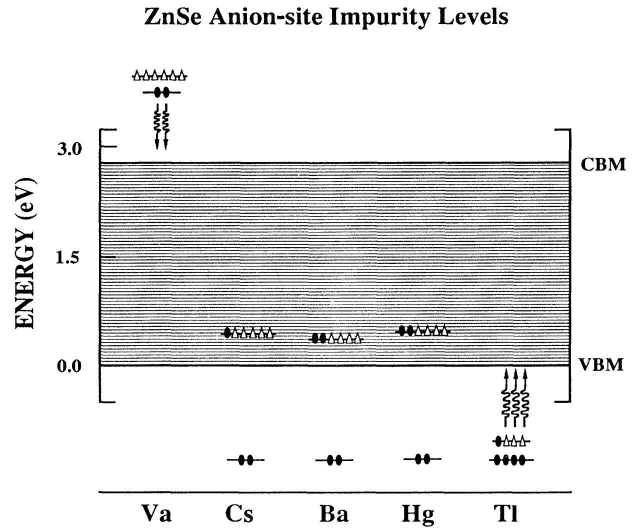

FIG. 14. Predicted deep energy levels in the gap of ZnSe due to s- and p-bonded substitutional impurities on the Se site. The impurities are indicated on the abscissa.

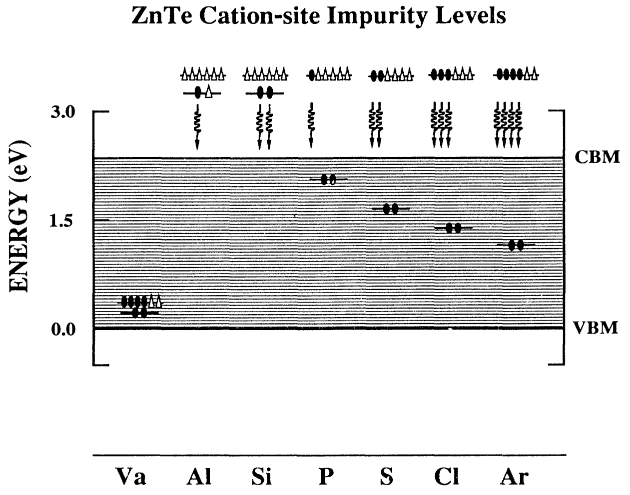

FIG. 16. Predicted deep energy levels in the gap of ZnTe due to s- and p-bonded substitutional impurities on the Zn site. The impurities are indicated on the abscissa.

IV. POTENTIAL PROBLEMS WITH THE MODEL

Two concerns that we have about the theory are (i) an explanation is required of why II-VI semiconductors other than ZnTe have an *n-type-doping* proclivity and (ii) the omission of Coulomb effects from the theory could cause our level predictions to be in error more than we currently believe.

A. n-type doping

If the antisite defects alone occur in the same concentrations in ZnSe and ZnTe, then one must explain why ZnSe apparently is more easily doped n type. In our model, the n-type dopants must first compensate all the antisite defects, after which they produce donors—and the physics is the same for ZnSe and ZnTe. However, we suspect that there are fewer Zn_{Se} defects in ZnSe than comparable antisite defects in ZnTe, basically because Zn is more similar to Te than to Se, both in its atomic size and its electronic energy levels. Doping the semiconductor n type with, say, Ga could exacerbate such differences. Therefore we believe that the n-type doping differences of ZnSe and ZnTe can be plausibly explained.

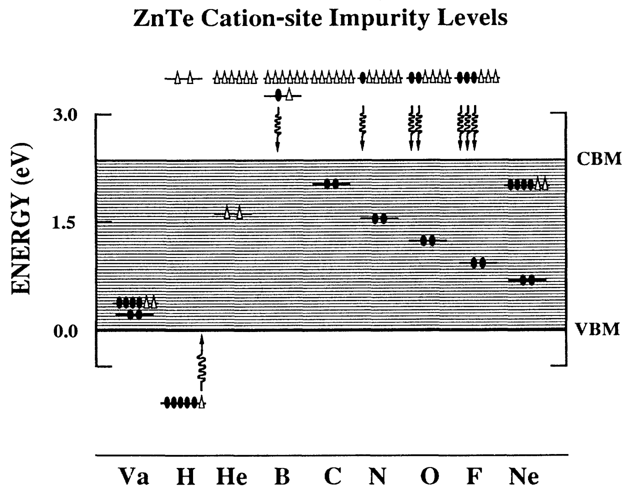

FIG. 15. Predicted deep energy levels in the gap of ZnTe due to s- and p-bonded substitutional impurities on the Zn site. The impurities are indicated on the abscissa.

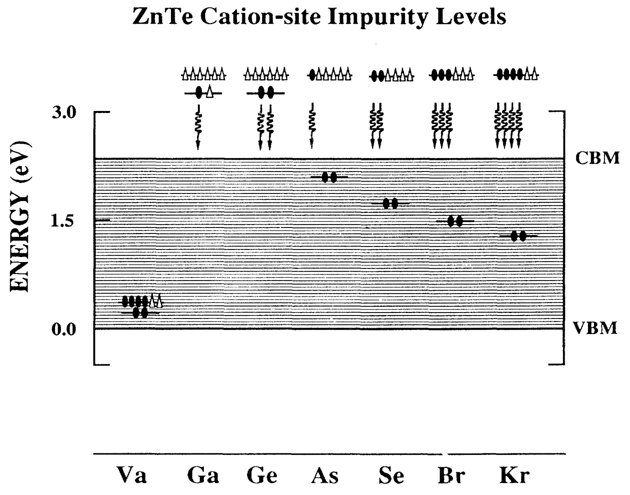

FIG. 17. Predicted deep energy levels in the gap of ZnTe due to s- and p-bonded substitutional impurities on the Zn site. The impurities are indicated on the abscissa.

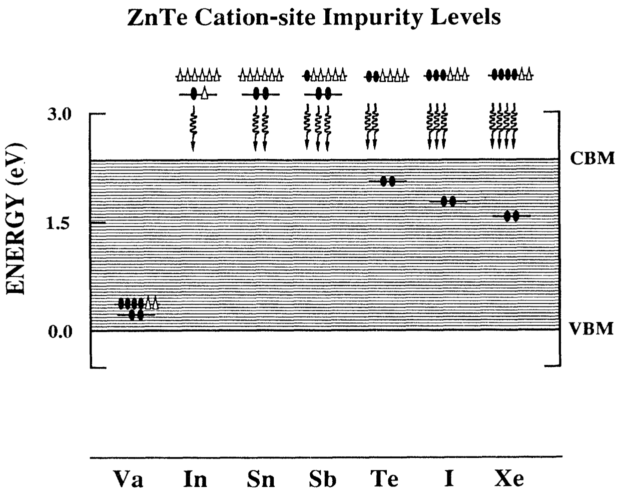
ZnTe Cation-site Impurity Levels

FIG. 18. Predicted deep energy levels in the gap of ZnTe due to *s*- and *p*-bonded substitutional impurities on the Zn site. The impurities are indicated on the abscissa.

B. Coulomb effects

It is very difficult to precisely determine the Coulomb effects on deep levels in II-VI semiconductors. Therefore we have actually executed three rather different theoretical calculations which generally agree that the position of the Zn_{Te} deep level with respect to the ZnTe valence-band edge is about 0.2–0.5 eV lower than the energy of the Zn_{Se} level with respect to the ZnSe band edge (in any charge state). These theories do not agree, however, on the precise location of the neutral Zn_{Te} deep level, which the present theory places in the ZnTe valence band, while the other two theories place the level near midgap (but with a theoretical uncertainty due to finite supercell size of order 1 eV).

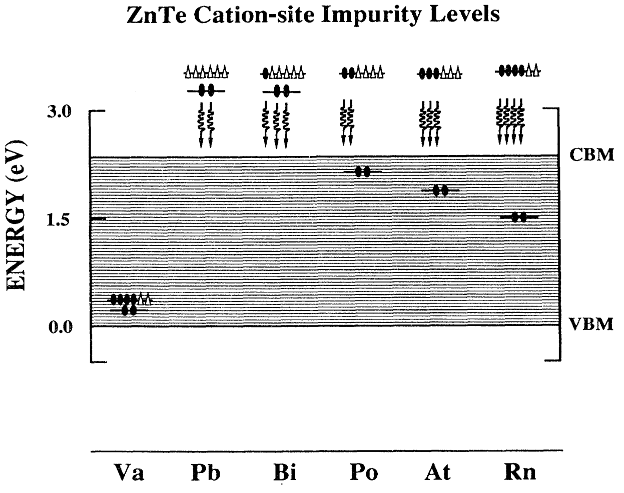
ZnTe Cation-site Impurity Levels

FIG. 19. Predicted deep energy levels in the gap of ZnTe due to *s*- and *p*-bonded substitutional impurities on the Zn site. The impurities are indicated on the abscissa.

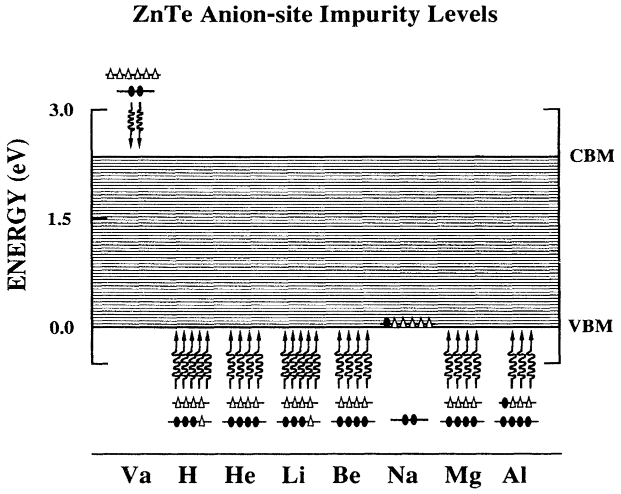
ZnTe Anion-site Impurity Levels

FIG. 20. Predicted deep energy levels in the gap of ZnTe due to *s*- and *p*-bonded substitutional impurities on the Te site. The impurities are indicated on the abscissa.

The first calculations, the ones we have described here, are based on an empirical tight-binding model of electronic structure, and incorporate Coulomb effects only implicitly in the parameters of the model. These calculations are, strictly speaking, for *neutral defects* in the ZnSe or ZnTe host, and do not directly consider the negative charging of Zn_{Te} as the holes in the Zn deep level bubble up to the valence-band maximum. This charging will cause the deep level to move up in energy about 0.2–0.3 eV for each additional electron trapped in the deep level[7] (an effect omitted from the model)—hence the Zn_{Te} level may move into the gap after the first or second electron is trapped on the Zn (i.e., after one or two holes "bubble up" to the valence-band maximum)—making Zn_{Te} a single or double acceptor rather than a full fourfold accep-

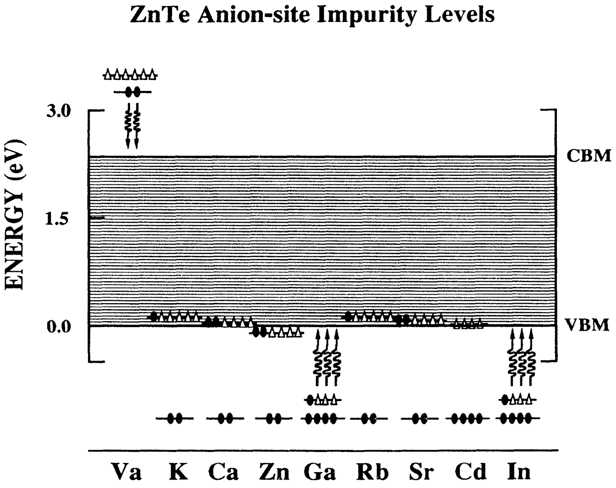
ZnTe Anion-site Impurity Levels

FIG. 21. Predicted deep energy levels in the gap of ZnTe due to *s*- and *p*-bonded substitutional impurities on the Te site. The impurities are indicated on the abscissa. Al (not shown) has a similar electronic structure to Ga.

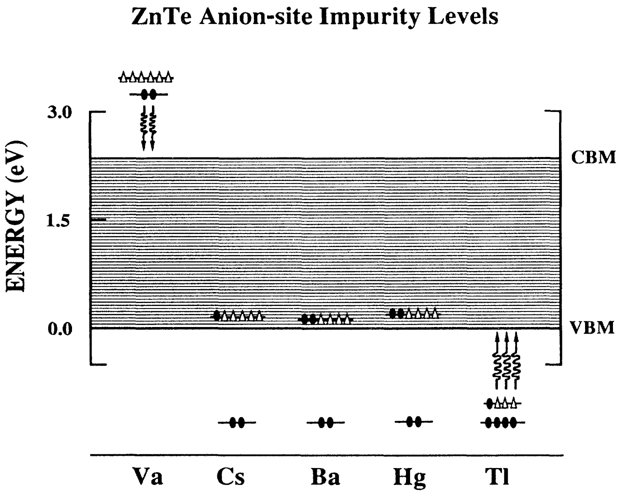

FIG. 22. Predicted deep energy levels in the gap of ZnTe due to *s*- and *p*-bonded substitutional impurities on the Te site. The impurities are indicated on the abscissa.

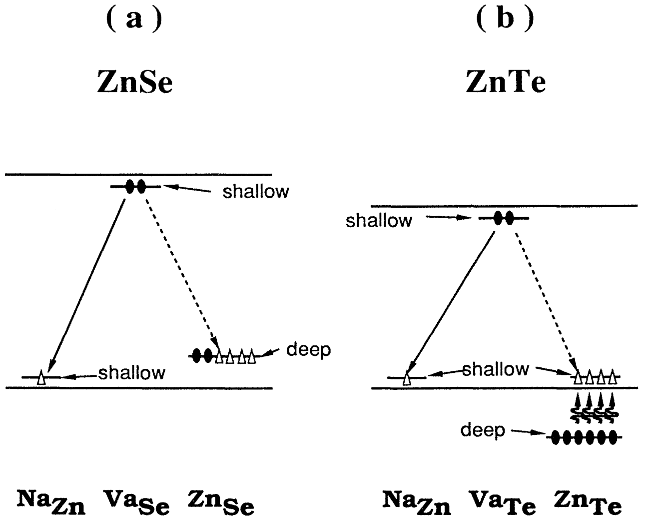

FIG. 23. Illustrating (a) self-compensation in the presence of a Zn_{Se} defect in ZnSe and (b) "anti-self-compensation" by Zn_{Te} in ZnTe. The self-compensation mechanism assumes that doping with an acceptor such as Na_{Zn} leads to production of a compensating double-donor anion vacancy. For simplicity we assume that there are only three defects: Na_{Zn}, the anion vacancy Va_{anion}, and the Zn-antisites Zn_{Se} and Zn_{Te}. In both cases, an electron (solid circle) from the anion vacancy's shallow donor level compensates (solid lines) the hole (open triangles) of the Na_{Zn} defect's shallow acceptor level. The remaining vacancy electron is trapped (dashed lines) (a) by the Zn_{Se} deep level in ZnSe or (b) by the shallow acceptor level in ZnTe, because the holes of the Zn_{Te} deep T_2 level have bubbled up (wiggly lines) to the shallow acceptor level. The remaining three holes in the Zn_{Te} shallow level are thermally ionizable in ZnTe, render the self-compensation by the vacancy impotent, and dope the material *p* type, whereas the holes in the deep level of ZnSe are not thermally ionizable, so that the Zn_{Se} level traps both electrons and holes, reducing conductivity.

tor. Thus the qualitative physics governing doping proclivity will be the same, although the number of free holes per defect will be smaller, so long as the deep level of the neutral Zn_{Te} defect is correctly predicted to lie below the valence-band maximum.

The second[7] and third[55] theories are local-density theories for a defect in a supercell of finite size, and produces levels for the neutral defect Zn_{Te} somewhat higher than the levels of the present theory. However, due to the finite size of the supercells, the predicted levels are actually bands of order 1 eV wide. Furthermore local-density theory is known to produce incorrect band gaps—and this can lead to errors in deep-level energies.[56]

The second theory is the tight-binding-like version of local-density theory discussed by Jansen and Sankey,[7] while the third is a pseudofunction[55] implementation of local-density theory. We executed the pseudofunction calculations for supercells of $N_s = 16$ and $N_s = 32$ atoms, and found that (relative to the valence-band maximum) the deep level moved down in energy with increasing supercell size, as the level's width decreased. Perhaps the local-density-theory levels of Zn_{Te} would also lie in the valence band if the supercell size were increased until convergence were achieved.

We conclude on the basis of these theories that we cannot definitively place the neutral Zn_{Te} deep level below the Zn_{Te} valence-band maximum—nor can we place it in the gap definitively. Therefore the issue of the location of this level will have to be determined experimentally.

In this regard we note that Li doping produces a mysterious deep level in ZnSe just above the valence-band maximum,[47] and no corresponding level in the gap of ZnTe—as the present (first) theory predicts. While this fact lends credence to the present theory, it does not confirm the theory unambiguously (because the nature of the Li-related defect is unknown).

We conclude that there is good circumstantial evidence for the Zn_{Te} defect yielding a deep level in the valence band of ZnTe, the kind of deep level needed to explain the *p*-type doping proclivity of ZnTe. The case is not airtight, appears to be unresolvable by theory, and calls for careful experimental investigation. In particular, careful studies of the dependence of doping proclivity on stoichiometry and on alloy composition in $ZnTe_{1-x}Se_x$ might confirm or exclude the present model. (Note that a rather sudden change in doping proclivity as a function of alloy content x is implied by the present model.)

V. SUMMARY

The viewpoint presented here is admittedly somewhat oversimplified in the interest of illustrating the essential physics of the problem. Nevertheless we hope that efforts to test this simple picture will be attempted because, if the picture is correct as we believe, then schemes for overwhelming the *p*-type doping problem in some other II-VI semiconductors than ZnTe will be feasible.[8] Two obvious schemes are (i) to grow ZnSe under conditions unfavorable to Zn_{Se} formation, and (ii) to engineer the electronic structure of a perturbed version of ZnSe so that the antisite defect's deep level is resonant with the valence band.

Finally our conclusions are based only on the occurrence of defects with deep-level electronic structures similar to those predicted for the Zn (and Li) antisite defects. The model for the *p*-type doping will still be valid if another defect has similar electronic structures in ZnSe and ZnTe. Furthermore the model does not rely in any way on a detailed picture of the "self-compensation" process or a knowledge of the detailed forces on defects.

ACKNOWLEDGMENTS

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*Present and permanent address.

[1] F. A. Kroger and H. A. Vink, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1956), Vol. III, p. 310.

[2] R. F. Brebick, J. Phys. Chem. Solids **4**, 190 (1958); **18**, 116 (1961).

[3] G. Mandel, Phys. Rev. **134**, A1073 (1964).

[4] P. J. Dean, Czech J. Phys. B **30**, 272 (1980).

[5] R. N. Bhargava, J. Cryst. Growth **59**, 15 (1982), and references therein.

[6] See, for example, C. H. Henry, K. Nassau, and J. W. Shiever, Phys. Rev. B **4**, 2453 (1971), and references therein.

[7] R. W. Jansen and O. F. Sankey, Phys. Rev. B **39**, 3192 (1989); Solid State Commun. **64**, 197 (1987); J. Vac. Sci. Technol. B **6**, 1240 (1988). For Zn_{Te} and Zn_{Se} these authors find bands whose centers are at 1.2 and 1.5 eV above the respective valence-band maxima. R. W. Jansen, D. S. Wolde-Kidane, and O. F. Sankey, J. Appl. Phys. **64**, 2415 (1988).

[8] S. Y. Ren, J. D. Dow, and S. Klemm, J. Appl. Phys. **66**, 2065 (1989); J. Shen, J. D. Dow, and S. Y. Ren, J. Appl. Phys. **67**, 3761 (1990).

[9] See, for example, M. Aven and J. Z. Devine, J. Lumin. **7**, 195 (1973); Y. S. Park and B. K. Shin, *Topics in Applied Physics* (Springer, Berlin, 1977), p. 33, and references therein.

[10] A. Kobayashi, O. F. Sankey, and J. D. Dow, Phys. Rev. B **28**, 946 (1983).

[11] T. Yasuda, I. Mitsuishi, and H. Kukimoto, Appl. Phys. Lett. **52**, 57 (1988), and references therein.

[12] J. Nishijawa, K. Itoh, Y. Okuno, and F. Sakurai, J. Appl. Phys. **57**, 2210 (1985).

[13] T. C. McGill (private communication).

[14] F. Rong and G. D. Watkins, Phys. Rev. Lett. **56**, 2310 (1986); G. D. Watkins, *ibid.* **33**, 223 (1974).

[15] A. Koukitu, J. Cryst. Growth **84**, 425 (1987).

[16] S. A. Azimov, T. M. Razykov, V. I. Vyaly, and B. Kh. Kadyrov, Phys. Status Solidi A **96**, 281 (1986).

[17] D. J. Wolford, B. G. Streetman, W. Y. Hsu, J. D. Dow, R. J. Nelson, and N. Holonyak, Jr., Phys. Rev. Lett. **36**, 1400 (1976).

[18] W. Y. Hsu, J. D. Dow, D. J. Wolford, and B. G. Streetman, Phys. Rev. B **16**, 1597 (1977).

[19] H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, Phys. Rev. Lett. **44**, 810 (1980). For a discussion of the ideas on which Ref. 19 was based, see Ref. 18.

[20] S. Y. Ren, J. D. Dow, and J. Shen, Phys. Rev. B **38**, 10677 (1988).

[21] J. D. Dow, S. Y. Ren, and J. Shen, in *Deep Impurity Levels in Semiconductors, Semiconductor Alloys, and Superlattices,* Vol. 183 of *NATO Advanced Research Workshop on Properties of Impurity States in Superlattice Semiconductors,* edited by C. Y. Fong, I. P. Batra, and S. Ciraci (Plenum, New York, 1988), p. 175.

[22] R.-D. Hong, D. W. Jenkins, S. Y. Ren, and J. D. Dow, in *Interfaces, Superlattices, and Thin Films,* Vol. 77 of *The Materials Research Society Symposium Proceedings,* edited by J. D. Dow and I. K. Schuller (MRS, Pittsburgh, PA, 1987), p. 545.

[23] S. Y. Ren and J. D. Dow, J. Appl. Phys. **65**, 1987 (1989).

[24] J. D. Dow, *Localized Perturbations in Semiconductors,* In *Highlights of Condensed-Matter Theory,* Proceedings of the International School of Physics "Enrico Fermi," Course 89, Varenna, 1983, edited by F. Bassani, F. Fumi, and M. P. Tosi (Societa Italiana di Fisica, Bologna, Italy, 1985), pp. 465–494.

[25] J. D. Dow, in *Microscopic Identification of Electronic Defects in Semiconductors,* Vol. 46 of the *Materials Research Society Symposiums Proceedings,* edited by N. M. Johnson, S. G. Bishop, and G. D. Watkins (MRS, Pittsburgh, 1985), p. 71.

[26] J. D. Dow and R. E. Allen, Appl. Phys. Lett. **41**, 672 (1982).

[27] H. P. Hjalmarson, H. Büttner, and J. D. Dow, Phys. Rev. B **24**, 6010 (1981).

[28] R. E. Allen and J. D. Dow, Phys. Rev. B **24**, 911 (1981).

[29] H. P. Hjalmarson, H. Büttner, and J. D. Dow, Phys. Lett. **85A**, 293 (1981).

[30] K. E. Newman and J. D. Dow, Solid State Commun. **50**, 587 (1984). See B. A. Bunker, S. L. Hulbert, J. P. Stott, and F. C. Brown, Phys. Rev. Lett. **53**, 2157 (1984), for experimental confirmation of this theory.

[31] M. A. Bowen, R. E. Allen, and J. D. Dow, Phys. Rev. B **30**, 4617 (1984).

[32] J. D. Dow, R. E. Allen, and O. F. Sankey, in *Intrinsic and Extrinsic Surface Electronic States of Semiconductors. Chemistry and Physics of Solid Surfaces, V,* Vol. 35 of *Springer Series in Chemical Physics* edited by R. Vanselow and R. Howe (Springer-Verlag, Berlin, 1984), p. 483, and references therein.

[33] R. P. Beres, R. E. Allen, and J. D. Dow, Phys. Rev. B **26**, 769 (1982).

[34] J. D. Dow and R. E. Allen, J. Vac. Sci. Technol. **20**, 659 (1982).

[35] O. F. Sankey, R. E. Allen, and J. D. Dow, J. Vac. Sci. Technol. B **2**, 491 (1984).

[36] O. F. Sankey, R. E. Allen, and J. D. Dow, Solid State Commun. **49**, 1 (1984).

[37] O. F. Sankey, R. E. Allen, and J. D. Dow, J. Ultramicroscopy **14**, 127 (1984).

[38] J. D. Dow, O. F. Sankey, and R. E. Allen, Materials Science Forum **4**, 39 (1985).

[39] H. P. Hjalmarson and T. J. Drummond, Appl. Phys. Lett. **48**,

657 (1986).

[40] R. E. Allen and J. D. Dow, Phys. Rev. B **25**, 1423 (1982).

[41] P.-O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

[42] P. Vogl, H. P. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids **44**, 365 (1983).

[43] S. Lee, J. D. Dow, and O. F. Sankey, Phys. Rev. B **31**, 3910 (1985).

[44] G. Kim, J. D. Dow, and S. Lee, Phys. Rev. B **40**, 7888 (1989).

[45] G. Kim, J. D. Dow, and S. Lee, Arabian J. Sci. Engineer. **14**, 513 (1989).

[46] D. J. Chadi and K. J. Chang, Phys. Rev. B **39**, 10 063 (1989).

[47] M. E. Agel'menev, A. N. Georgobiana, Z. P. Ilyukhina, A. D. Levit, L. S. Lepnev, and M. I. Sluch, Sb. Kratk. Seobshch. Fiz. AN SSSR Fiz. Inst. P. N. Lebedeva (USSR), **6**, 18 (1987) [Sov. Phys.—Lebedev Inst. Rep. **6**, 25 (1987)].

[48] It has been shown in Ref. 49 that, to an adequate approximation, the deep-level spectrum of a cluster of substitutional defects is the sum of the constituents' spectra, a fact that allows us to consider only isolated substitutional impurities and interstitials.

[49] O. F. Sankey, H. P. Hjalmarson, J. D. Dow, D. J. Wolford, and B. G. Streetman, Phys. Rev. Lett. **45**, 1560 (1980).

[50] M. Lannoo and P. Lenglart, J. Phys. Chem. Solids **30**, 2409 (1969).

[51] The charge-state splitting effect omitted in the present theory could become significant when the defect becomes highly charged, and could alter the defect's mean-field energy levels so that the acceptor $\mathrm{Zn}_{\mathrm{Te}}$ would bind fewer than four holes in shallow levels.

[52] Be, being light, will tend to diffuse rapidly, and should occupy some anion sites, much as Li appears to.

[53] C. S. Lent, M. A. Bowen, R. S. Allgaier, J. D. Dow, O. F. Sankey, and E. S. Ho, Solid State Commun. **61**, 83 (1987).

[54] J. A. Van Vechten, J. Electrochem. Soc. **122**, 419 (1975); **122**, 423 (1975). See also J. P. Buisson, R. E. Allen, and J. D. Dow, Solid State Commun. **43**, 833 (1982), and references therein.

[55] R. V. Kasowski, M.-H. Tsai, T. N. Rhodin, and D. D. Chambliss, Phys. Rev. B **34**, 2656 (1986).

[56] R. E. Allen and J. D. Dow, J. Vac. Sci. Technol. **19**, 383 (1981).