Electronic structure of filled tetrahedral semiconductors

D. M. Wood, Alex Zunger, and R. de Groot*

Solar Energy Research Institute, Golden, Colorado 80401

We discuss the susceptibility of zinc-blende semiconductors to band-structure modification by insertion of small atoms at their tetrahedral interstitial states. GaP is found to become a direct-gap semiconductor with two He atoms present at its interstitial sites; Si does not. Analysis of the factors controlling these filling-induced electronic modifications allows us to predict that LiZnP [viewed as a zinc-blende-like $(ZnP)^-$ lattice partially filled with He-like Li^+ interstitials], as well as other members of the Nowotny-Juza compounds $A^I B^{II} C^V$, are likely to be a novel group of direct-gap semiconductors.

Zinc blende, wurtzite, and carborundum-type binary crystals are the most loosely packed structures consistent with the tetrahedral coordination for both types of atoms.[1] Their openness is highlighted by the fact that for the homopolar members the ratio of the volume of touching atomic spheres to that of the unit cell is 0.34, less than half that for the close-packed element structures (0.74). These "homeotect" structures may be characterized by the existence of four vacant (V) lattice sites (holes) at the tetrahedral interstitial sites nearest the anion A (sites V_A) and four nearest the cation C (sites V_C), both at the normal nearest-neighbor tetrahedral distance. Hence, as we traverse the $\langle 111 \rangle$ body diagonal in the zinc-blende CA crystal, with the origin, say, at the cation site $C(0,0,0)$, we encounter the anion A at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, the V_A site at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and the V_C site at $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$, both unoccupied in normal tetrahedral structures. We may structurally designate this arrangement as $V_C C A V_A$. While this minimal packing fraction reflects the effectiveness of pure sp^3 tetrahedral bonding in forming stable compounds with low coordination number, denser packing is by no means unusual in these structure types.[2-6] This can be effected by diffusion of interstitial impurities (e.g., the $3d$ impurities[2a] or H, He, and Li in silicon,[2b] occupying the $V_A = V_C$ sites), by stoichiometric substitution of one type of vacant site (e.g., the Nowotny-Juza $C^{II} A^V V_A^I$ compounds[3] with $V_A^I = Li$, Cu, Ag, $C^{II} = Be$, Mg, Zn, Cd, and $A^V = N$, P, As, Sb, and Bi, the antifluorite compounds[4] $MgA^V Mg$ with $A^V = Si$, Ge, Sn), or by substitution of both types of vacant sites (e.g., the $B32$ Zintl compounds[5] LiAl, NaTl, or the $L2_1$ Heusler alloys[6] $V_C MnA V_A$, with $V_A = V_C = Co$, Ni, Cu, Pd and $A = Al$, In, Sb, Sn). We refer to the structures with partially or completely occupied V_A and V_C sites as "filled tetrahedral compounds."

In this work we will examine filled tetrahedral compounds whose electronic structures represent recognizable distortions of the underlying (parent) binary CA materials and, through the techniques of self-consistent band theory,[7] study the filling-induced changes in total energy, charge density, and band structures. Particular emphasis will be placed on the degree to which filling the empty tetrahedral interstitial sites can alter the direct versus indirect nature of the lowest optical gaps. Defining the "degree of indirectness" $\delta = 2(E_D - E_I)/(E_D + E_I)$ in terms of the direct (E_D) and indirect $(E_I$, evaluated here at the X point in the Brillouin zone) band gaps, we will determine, following Rompa,

Schuurmans, and Williams[8] (RSW), whether indirect-gap materials $(\delta > 0)$ can be made direct $(\delta < 0)$ by filling the *interstitial* sites, rather than by the conventional *substitutional* insertion (e.g., alloying indirect-gap GaP with direct-gap InP). We will then demonstrate how insights deduced from simple and (so far) hypothetical filled tetrahedral structures (He in Si and GaP) can be applied to hitherto unknown properties of existing filled tetrahedral structures, i.e., the prediction of a new class of direct-gap tetrahedral semiconductors.

We have studied the electronic and structural properties of $V_C GaP$, $GaP V_A$, $V_C GaP V_A$, $V_1 Si$, and $V_1 SiSi V_2$ for $V = He$. We selected these host crystals since they are both indirect-gap semiconductors at zero pressure when unfilled (experimental values,[9] $\delta_{Si} = 1.15$ and $\delta_{GaP} = 0.15$), whereas GaAs, chosen by RSW is, even without V_A or V_C occupation, a direct-gap material[9] ($\delta_{GaAs} = -0.13$). Helium was selected as a filling atom because of the simplicity of its interaction with the host (see below). It is also a commonly introduced fast diffusing[10] interstitial species in semiconductor technology, used as the inert atmosphere in crystal growth, for etching, sputtering, and cleaning of surfaces, in epitaxial regrowth of amorphous silicon,[11] as probing particles in Rutherford backscattering experiments, stabilization of void morphology,[12] and is a participating center in many native defects.[13]

We use the self-consistent local-density approximation (LDA) pseudopotential total-energy method,[7] utilizing the semirelativistic nonlocal pseudopotentials for Si, Ga, and P tabulated in Ref. 14 and the Ceperley-Alder exchange correlation functional given in Ref. 15. A basis set consisting of 459 plane waves at the Γ point of the Brillouin zone (BZ) (i.e., a kinetic energy cutoff of about 21 Ry), retention of the corresponding 3527 momentum components of the charge density, a BZ sampling of two special k points and a self-consistency tolerance of ≤ 0.4 mRy are sufficient to assure a precision of 0.02 eV in the band energies and 2 mRy in the relative total energies. For each system we minimize the total energy with respect to the lattice parameter, keeping the He atoms in the tetrahedral interstitial sites.

We avoid the spherical approximation to the atomic potentials underlying the method used by RSW; a more significant difference is the way the localized He $1s$ states are treated. The LDA severely underestimates removal (ionization) energies from tightly bound orbitals, e.g., the He $1s$ orbital,[15] whose calculated ionization energy $E_{1s}^{LDA} = 15.5$ eV

is far smaller than the experimental value $E_{1s}^{expt} = 24.6$ eV. Most of this discrepancy can be removed by canceling the spurious self-interaction associated with the LDA, yielding a self-interaction corrected (SIC) value[15] E_{1s}^{SIC} of 25.8 eV. Were He to interact negligibly with the host crystals, it would give rise to a narrow He $1s$ band located approximately at $E_{1s} - \Phi$ below the valence-band maximum (E_{VBM}), where Φ is the intrinsic host work function (5.2, 5.9, and 5.5 eV, respectively, for Si, GaP, and GaAs). Using $E_{1s} = E_{1s}^{LDA}$ in these semiconductors puts such a band at about $E_{VBM} - 10$ eV, where it was found by RSW (Ref. 8) and in our earlier, conventional LDA calculations.[16] This spurious positioning of the He $1s$ band in resonance with the host valence band (the valence-band width is ~ 12.5 eV) induces substantial repulsion of host states of the same symmetry. Using, however, either E_{1s}^{SIC} or E_{1s}^{expt} one predicts instead a dispersionless He $1s$ band at 19–20 eV below E_{VBM}, i.e., well *below* the valence-band minimum. When constructing a pseudopotential for He, then, it is natural to adopt a configuration which places the $1s$ orbitals in the core (unlike that used by Bachelet, Hamann, and Schlüter in their He potential[14]), thereby generating (using the SIC procedure[17]) an essentially *repulsive* potential (since the $1s$ orbital is pseudized by the $2s$). Its radius reflects the core size of He, much as does an empty core pseudopotential, defining a volume excluding other electrons through Pauli repulsion. Hence, in our calculations the presence of helium atoms will be manifest not by where valence electrons are *found*, but rather by where they are *not found*. The problem of finding the changes induced in the electronic structure by insertion of He atoms in the empty interstitial sites is now mapped into the more transparent problem of calculating the response of the host electronic structure to electron-repelling potential wells at these sites.

With this formulation of the problem, it is straightforward to understand the potential susceptibility of zinc-blende materials to band modification by insertion of closed-shell atoms at the interstitial sites. The high tetrahedral symmetry, but different chemical content, of the *occupied* C and A sites in the (highly directional) sp^3-bonded zinc-blende materials implies very different, quite spatially inhomogeneous charge distributions for Bloch states $\psi_{nk}(\mathbf{r})$ (of band index n, wave vector $\mathbf{k}$) for different high-symmetry points in the BZ (band-by-band or *state* selectivity of the charge density), unlike the roughly uniform valence charge density for, e.g., s electron metals. Moreover, the *vacant* interstitial V_A and V_C sites possess this same high symmetry, and perturbing potentials centered on these sites will *selectively* affect bands associated primarily with these sites. One expects the principal effect of insertion of a closed-shell atom on a given state to be simply expulsion from the Pauli exclusion volume of its contribution to the valence charge density (thereby raising the kinetic energy of the corresponding orbitals, and hence the single-particle band eigenvalue for this state). These circumstances raise the possibility that filling the tetrahedral sites will have a chemically specific, *selective* effect on certain bands.

The emphasis above on sites and excluded volume makes it natural to seek an explanation in the charge densities for the relevant states. Whereas the charge densities of the occupied (bonding) bands at V_A and V_C are small, even a minor rearrangement can have a major effect on their anti-bonding (i.e., conduction band) counterparts. In Fig. 1 we display for GaP and Si the partial (pseudo) charge density

$\rho_{nk}(\mathbf{r}) = |\psi_{nk}(\mathbf{r})|^2$ in the zinc-blende (110) plane for the lowest conduction bands at X (X_{3c} and X_{1c} for GaP, X_c for Si). In all cases regions of *high* charge density are indicated by dot shading; diagonal shading indicates *low* charge density. This figure suggests the lowest conduction bands will show extreme selectivity with respect to insertion of closed-shell atoms: the X_{3c} (X_{1c}) band density has maxima (minima) at or near V_C and minima (maxima) at or near V_A, whereas the Γ_{1c} band (not shown) has a much smaller V_A-V_C charge-density disparity.

Figure 2 shows the self-consistent band structures of GaP [2(a)], HeGaPHe [2(b)], Si [2(c)], and HeSiSiHe [2(d)], each evaluated at the lattice constant which minimizes the total energy. Expectations based on the arguments above are borne out by these results: because of the extremely high pseudo charge density at the V_C for the X_{3c} band, but not for the X_{1c} or Γ_{1c} states, we observe insertion of a He atom at V_c (yielding what we will call HeGaP) to *selectively perturb* upward the energy of the X_{3c} conduction band. Conversely, insertion of He at V_A ("GaPHe") selectively raises the X_{1c} state. For Si the V_A-V_C distinction cannot exist [we have labeled the corresponding sites V_1 and V_2 in
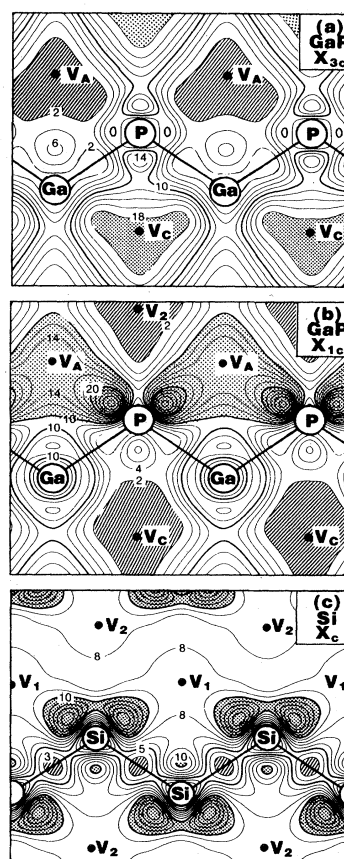

FIG. 1. Partial-band pseudo charge densities (in e/primitive cell, normalized to 8) for the lowest [X_{3c} in (a)], and next [X_{1c} in (b)] GaP conduction states at X, and the lowest [X_c in (c)] band in Si, each for the experimental lattice constant. V_A and V_C (V_1 and V_2 for Si) denote the empty tetrahedral sites. High- (low-) density regions are highlighted by dotted (dashed) shading.
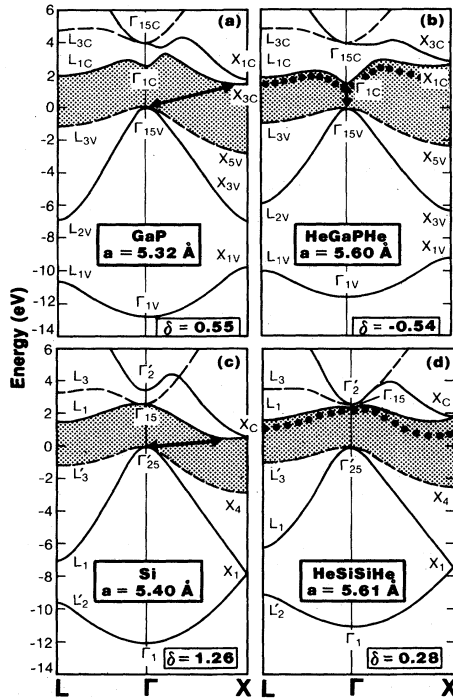
FIG. 2. Band structures of GaP (a), HeGaPHe (b), Si (c), and HeSiSiHe (d), at their respective theoretical equilibrium lattice constants. Origin for (a), (b) is at Ga, for (c),(d) is at bond center. Dotted lines in (b),(d) indicate lowest conduction bands for GaP, Si at equilibrium lattice constant of HeGaPHe and HeSiSiHe, respectively.

Fig. 1(c)], and it is largely the *differential* susceptibility to He insertion between the X and Γ BZ points which accounts for the dependence of δ on the presence/absence of He. Insertion of He dramatically reduces the indirectness parameter δ by comparable amounts for GaP and for Si (changes in δ of -0.99 and -0.98, respectively), *converting* GaP *into a direct-gap material* (since its theoretical initial $\delta_{GaP} = 0.55$ was small), but leaving Si, in contrast with the results of RSW, slightly indirect (since its theoretical initial $\delta_{Si} = 1.26$ was larger), with the direct gap little changed from pure Si. We note that, whereas the X_{3c}-X_{1c} splitting in HeGaPHe is little changed from GaP, *the order of the X_{3c} and X_{1c} bands has interchanged,* due to the large energy shift of the phosphorus-like X_{3c} state in response to the occupation of the V_C site next to Ga. In contrast to the RSW results,[8] we find none of the substantial (~ 2.4 eV) He-induced broadening of the valence bands (indeed, we find some narrowing), and the upward shift in the lowest conduction band at X (1.2 eV) is only about half their shift for HeGaAsHe (2.4 eV). Both differences are directly attributable to the unphysically high energy of the He $1s$ band (inside the host valence band) within the LDA, with its attendant strong band-repulsion effects.

We find that insertion of He into the two interstitial sites in GaP and Si dilates the lattices by 5.3% and 3.9%, respectively. It is interesting to inquire how much of the change in band indirectness $\Delta\delta^{tot} = \delta_{HeCAHe}(a_{eq}^{HeHe}) - \delta_{CA}(a_{eq}^{CA})$ (where a_{eq}^{HeHe} is the equilibrium lattice constant of HeCAHe and a_{eq}^{CA} is that of CA) is due merely to

He-induced volume dilation (VD) [i.e., $\Delta\delta_{VD} = \delta_{CA}(a_{eq}^{HeHe}) - \delta_{CA}(a_{eq}^{CA})$] of the host crystal and how much to a specific chemical effect (CE), i.e., $\Delta\delta_{CE} = \Delta\delta^{tot} - \Delta\delta_{VD}$. The dotted lines in Figs. 2(b) and 2(d) indicate the positions of the lowest conduction bands of pure GaP and Si, respectively, calculated self-consistently at the equilibrium lattice constants of their He-containing analogs, i.e., at a_{eq}^{HeHe}; Figs. 2(a) and 2(c) indicate results for the pure compounds, i.e., CA at a_{eq}^{CA}. We find for GaP and Si that only 55% and 32%, respectively, of the change in indirectness is a volume dilation effect $\Delta\delta_{VD}$. To better appreciate the nature of the chemically specific He effects, we show in Fig. 3 the He-induced changes in ground-state charge densities $\Delta\rho(\mathbf{r}) = \rho(\text{He}CA\text{He}) - \rho(CA)$ for GaP [Fig. 3(a)] and Si [Fig. 3(b)], at the experimental bulk lattice constants (the qualitative features change little with a). It is seen that He expels charge from the interstitial channels (dashed contours, representing negative $\Delta\rho$), and places some extra charge on the covalent bonds (solid contours, representing positive $\Delta\rho$), suggestive of the formation of He-host "antibonds" by He [Ref. 13(b)] without formation of He–He bonds. This destabilizes the structure. Indeed, all of the calculated He-induced changes in total energy ΔE_{tot} are positive. They are 0.803, 0.913, 1.59, 0.882, and 1.65 eV per primitive cell for HeGaP, GaPHe, HeGaPHe, HeSiSi, and HeSiSiHe, respectively, indicating an overall destablization of ~ 0.9 eV per He atom in both host crystals, similar to the observed[10] heat of solution ΔE_s of He in Si of ~ 0.5 eV. We note also a small preference for the V_{Ga} site over the V_P site, and a near additivity of the effects of single versus double substitution, indicating the near independence of the two distinct He atoms. In analogy with what was done above for δ, one may decompose the He-induced changes in total energy into volume dilation and chemically specific contributions, i.e., $\Delta E_{tot} = \Delta E_{VD} + \Delta E_{CE}$.
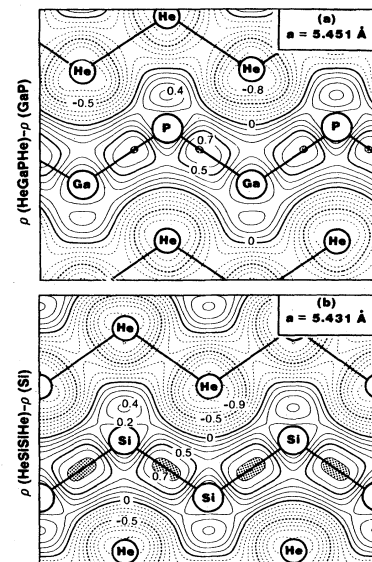

FIG. 3. He-induced ground-state charge redistributions for (a) HeGaPHe with respect to GaP at $a = 5.45$ Å; (b) HeSiSiHe with respect to Si at $a = 5.431$ Å.

Interestingly, ΔE_{VD} for HeGaPHe and HeSiSiHe constitutes only a small part (18% and 11% in GaP and Si, respectively) of ΔE_{tot}, the rest being a chemically specific electronic effect resulting from the He-induced charge redistribution (Fig. 3). While such effects have been considered for He in metals,[18] their neglect in the pioneering calculations for He in semiconductors[19(a)] has resulted in an underestimation of ΔE_s (by a factor of about 8) and an associated overestimation (by 10^5) of its solubility; a more recent calculation[19(b)] overestimates ΔE_s by about the same factor.

The foregoing analysis indicates that directness of the band gap can be enhanced by placing electron-repelling objects in the tetrahedral interstitial sites where the lowest conduction band has a higher electron density than other bands and hence is selectively shifted upwards. Can we use this rule to predict direct gap filled tetrahedral structures, where the stuffing atom is *stably* bound to the lattice (i.e., $\Delta E_{tot} < 0$, unlike the He case)? We suggest that this is the case for the Nowotny-Juza compounds[3] of the LiZnP type. In this structure, the Zn and P atoms take up the regular cation and anion positions, respectively, of the zinc-blende lattice, whereas the Li atoms fill half of the tetrahedral interstitial sites. We suggest that in analogy with GaPHe, this structure be viewed conceptually as a zinc-blende $(ZnP)^-$ crystal (where the extra electron is compensated by a uniformly distributed positive background of one charge) plus an interstitial Li^+ cation (isoelectronic with He). Figure 4(a) depicts the band structure of $(ZnP)^-$ calculated with the augmented spherical wave method[20] showing, in fact, the same qualitative features as the bands of GaP (except
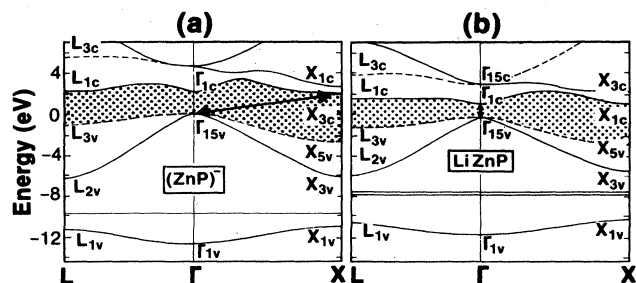

FIG. 4. Band structures of (a), the hypothetical zinc-blende $(ZnP)^-$ compound and its filled analog LiZnP, (b).

for the narrow Zn $3d$ band in the lower part of the valence band). In particular, the system has an indirect gap. When we insert Li^+ at the interstitial V_P site [Fig. 4(b)], the X_{3c} conduction band is shifted to higher energies more than do the other bands, exposing the Γ_{1c} point as the conduction-band minimum. The system has become a direct-gap material. However, in contrast with HeGaPHe, we find LiZnP to be *stable* towards disproportionation. In fact, we find a preference for Li to reside at V_P rather than at V_{Zn}, suggesting an ordered interstitial compound. While to our knowledge it is not yet experimentally known if the Nowotny-Juza compounds are semiconductors, let alone direct, this study predicts such systems to be direct gap (in the range of 1.3–2 eV) stable semiconductors, hence of potential technological interest.

*Permanent address: The Research Institute for Materials, Faculty of Sciences, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

[1] E. Parthé, Z. Kristallogr. 115, 52 (1961); *Crystal Chemistry of Tetrahedral Structures* (Gordon and Breach, New York, 1964), p. 19.

[2] (a) E. R. Weber, Appl. Phys. A 30, 1 (1983); A. Zunger and U. Lindefelt, Phys. Rev. B 26, 5989 (1982); (b) See, e.g., S. T. Picraux and F. L. Vook, *ibid.* 18, 2066 (1978).

[3] H. Nowotny and K. Bachmayer, Monatsh. Chem. 81, 488 (1950); R. Juza and F. Hund, Z. Anorg. Chem. 257, 1 (1948).

[4] O. Madelung, in *Semiconductors: Physics of Non-tetrahedrally Bonded Elements and Binary Compounds I*, edited by O. Madelung, Landolt-Börnstein New Series, Group 3, Vol. 17, Pt. e (Springer-Verlag, Berlin, 1983), pp. 163 and 432.

[5] E. Zintl and G. Brauer, Z. Phys. Chem. B 20, 245 (1933); A. Zunger, Phys. Rev. B 17, 2582 (1978).

[6] F. Heusler, Verh. Dtsch. Phys. Ges. 5, 219 (1903); J. Kübler, A. R. Williams and C. B. Sommers, Phys. Rev. B 28, 1745 (1983); R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, Phys. Rev. Lett. 15, 2024 (1983).

[7] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C 12, 4409 (1979).

[8] H. W. A. M. Rompa, M. F. H. Schuurmans, and F. Williams, Phys.

Rev. Lett. 52, 675 (1984).

[9] W. H. Strehlow and E. L. Cook, J. Phys. Chem. Ref. Data 2, 172 (1973).

[10] A. Van Wieringen and N. Warmoltz, Physica 22, 849 (1956); L. C. Luther and W. J. Moore, J. Chem. Phys. 41, 1018 (1964).

[11] M. Wittmer, J. Roth, P. Revesz, and J. W. Mayer, J. Appl. Phys. 49, 5207 (1978).

[12] S. I. Romanov and L. S. Smirnov, Radiat. Eff. 37, 121 (1975).

[13] (a) N. Bürger, K. Thonke, R. Sauer, and G. Pensl. Phys. Rev. Lett. 52, 1645 (1984); (b) V. D. Tkachev, A. V. Mudryi, and N. S. Minaev, Phys. Status Solidi A 81, 313 (1984).

[14] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B 26, 4199 (1982).

[15] J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).

[16] D. M. Wood and A. Zunger, Bull. Am. Phys. Soc. 29, 392 (1984).

[17] A. Zunger, Phys. Rev. B 22, 649 (1980).

[18] D. E. Rimmer and A. H. Cottrell, Philos. Mag. 2, 1345 (1957).

[19] (a) K. Weiser, J. Phys. Chem. Solids 17, 149 (1960); (b) J. A. Van Vechten, in *Handbook on Semiconductors, Vol. 3: Materials, Properties and Preparation*, edited by S. P. Keller (North-Holland, Amsterdam, 1980), pp. 93–94.

[20] A. R. Williams, J. Kübler, and C. D. Gelatt, Phys. Rev. B 19, 6049 (1979).