PHYSICAL REVIEW B VOLUME 30, NUMBER 4 15 AUGUST 1984

Solid-state shifts of core-electron binding energies in tetrahedral semiconductors from tight-binding theory

R. Enderlein*
Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

W. A. Harrison
Applied Physics Department, Stanford University, Stanford, California 94305

(Received 1 August 1983; revised manuscript received 23 April 1984)

Solid-state shifts of core-electron binding energies are calculated for tetrahedral semiconductors with the valence-band maximum as reference level. A Born-Haber cycle is used to relate binding-energy shifts to changes of bond energies due to the excitation of core electrons. These energies are obtained from tight-binding theory with universal parameters. Metallization was included as a correction to the bond-orbital approximation. Shifts calculated entirely in terms of tight-binding parameters are compared with experimental data for the least-bound core electrons. Overall agreement is within 1 to 2 eV in most cases.

I. INTRODUCTION

Binding energies of core electrons are sensitive to the chemical and structural properties of their solid-state environment. They have been widely used for experimental studies of surface chemistry and physics of solids. Theoretical predictions of core-electron binding energies were attempted by several authors during the last few years.[1–8] In the case of metals, a semiempirical approach using a Born-Haber cycle and empirical cohesive energies and heats of solution has been proposed by Johansson and Martensson. (Johansson and Martensson[1] draw attention to the incomplete screening of an excited core hole in the case of semiconductors, and to the difficulties which arise from this fact for the applicability of their calculation scheme to such materials. The variability of the Fermi level of semiconductors mentioned in the text is only another formulation for the same difficulty. Yin and Tosatti[2] implicitly used the assumption of a Fermi energy just below the core exciton level.) With a slight modification, Yin and Tosatti[2] used this approach to obtain estimates of binding energies of the group-IV semiconductors.[2] A more direct method for calculation of core-electron binding energies of semiconductors has been developed by Bechstedt *et al.*[3] on the basis of earlier work by other authors.[4–9] It has been shown that the solid-state shift of binding energies decomposes into an initial-state or core-level shift and a final-state or relaxation shift. The relaxation effect due to the core hole in the final state can be calculated with good accuracy for weakly bound core electrons.[9,3] The determination of the core-level shift in second-order perturbation theory reduces to the calculation of the Coulomb potential of the solid-state valence electrons within the core region. In principle, such a calculation could be done by using the valence electronic structure from pseudopotential, linear combination of atomic orbitals (LCAO), or any other band theory, but no attempt has been published so far following this line. There are indeed computational difficulties with such an approach; e.g., obtaining the self-consistent pseudopotential in the core region. In Refs. 6, 7, 10, and 3, instead of a calculated valence-charge distribution the Phillips bond-charge model[11] was used which, however, introduces new parameters which are only poorly known.

Core-level shifts and relaxation energies are simultaneously treated if one uses a Born-Haber cycle for the binding-energy calculation as was done in Refs. 1 and 2. The disadvantage of this approach is that one needs empirical values of cohesive energies and heats of solution. One can try to overcome this problem by calculating the needed values from tight-binding theory.[12] While one cannot expect to get precise theoretical predictions of core-electron binding energies in this way, one should be able to derive reasonable estimates without using adjustable parameters and to provide some insight into the importance of solid-state effects. In the present paper this approach will be developed in detail. We relate the core-electron binding energies to valence-band maximum energies and to bond energies, both calculated from tight-binding theory. Bond energies are treated within the bond-orbital approximation (Sec. II) and with the inclusion of metallization (Sec. III). In Sec. IV we apply the general results to obtain the binding-energy shifts for a series of tetrahedral semiconductors and binding energies for the least-bound core electrons of these materials.

We start with the definition of the binding energy which is measured by photoemission. In an elementary photoemission event, a photon of $\hbar\omega$ is absorbed and a photoelectron of kinetic energy E_{kin} is emitted. The solid changes from its initial state of energy E_{initial} to the final state of energy E_{final}. The energy balance of the event reads

$$-\hbar\omega+E_{\text{kin}}-E_{\text{initial}}+E_{\text{final}}=0\ . \tag{1}$$

Usually the initial state can be identified with the ground state of the solid. To obtain the correct final state one asserts that the sample is kept electrically neutral by allowing an electron from the ground to flow into the solid.

The energy of the compensating electron within the solid, after thermodynamic equilibrium has been established, is equal to the solid-state Fermi energy E_F. The effect on the solid of a photoemission experiment, therefore, is the creation of an electron-hole pair with the hole at the core level and the electron at the Fermi level. The excitation energy, $E_{\text{final}}-E_{\text{initial}}$, equals the binding energy E_B^F of the core electron with respect to the Fermi level,

$$E_B^F=E_{\text{final}}-E_{\text{initial}} \; . \tag{2}$$

Combining relations (1) and (2) one obtains

$$E_B^F=\hbar\omega-E_{\text{kin}} \; , \tag{3}$$

which is used to convert photoelectron kinetic energy data into binding energies of core electrons with respect to the Fermi level.

In contrast to metals, the Fermi energy of a semiconducting material can be changed, by varying preparation conditions, within a certain energy interval ranging from the upper part of the valence band to the lower part of the conduction band.[7] To eliminate the related change of core-electron binding energies E_B^F with sample preparation it is most convenient to refer to a p-type sample with the Fermi level at the valence-band maximum E_{VBM}:

$$E_F=E_{\text{VBM}} \; . \tag{4}$$

The principal reason for this choice is the identical symmetry and location of the valence-band maximum for all zinc-blende semiconductors.

The calibration, Eq. (4), of the Fermi level will be used throughout the paper, and the corresponding core-electron binding energy will be denoted by E_B^{VBM}. Any experimental measurement can be immediately shifted to this scale, assuming the doping of the specimen is known.

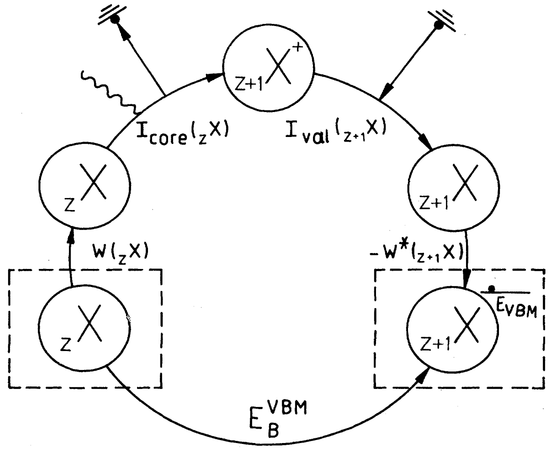

FIG. 1. Born-Haber cycle for the calculation of E_B^{VBM}.

II. CALCULATION SCHEME, BOND-ORBITAL APPROXIMATION

A convenient way of obtaining E_B^{VBM} from Eq. (2) is to use an indirect path between the initial and final states instead of the direct one described in Sec. I. The indirect path and the direct path combine to make the Born-Haber cycle shown in Fig. 1. We use this cycle to obtain the shifts of core-electron binding energies theoretically in terms of the tight-binding parameters describing the electronic structure of the solid.

Crystalline semiconductors of diamond or zinc-blende type are considered. The two atoms of the primitive cell are denoted by A and B, where A denotes the cation and B the anion in the case of III-V or II-VI compounds. We start with the AB solid in its ground state. In a first step we remove the atom (the core electron of which will later be excited) from the solid to infinity where it is a free atom. This atom may be either A or B and will be denoted by $_ZX$ which stands for A or B with atomic number Z. The work which must be done in this step is the energy of atomization $W(_ZX)$. In a second step we ionize the core level; i.e., we remove one core electron from the $_ZX$ atom and put it at the vacuum level. This takes the ionization (or binding) energy of the core electron of the free atom, $I_{\text{core}}(_ZX)$. The $_ZX$ atom with one hole in the core, to a good approximation, can be treated as an atom $_{Z+1}X^+$ with atomic number $Z+1$ (referred to as a "$Z+1$ one atom" in the following) and with one electron missing in the outermost valence shell. In the third step we take the electron at the vacuum level and put it in this shell of the $Z+1$ atom, forming in this way a neutral $Z+1$ atom ($_{Z+1}X^0$) in its ground state. The work to be done in this step is $-I_{\text{val}}(_{Z+1}X)$, the negative of the ionization energy of the outermost valence shell of the $Z+1$ atom. As the fourth step we bring the $Z+1$ atom to the solid and put it into the vacancy left behind by the removed $_ZX$ atom. One of the valence electrons of the $Z+1$ atom is put at the valence-band maximum of the solid. The total work for the fourth step is denoted by $-W^*(_{Z+1}X)$, the negative of the work for the removal of the $Z+1$ atom with one of the electrons at the valence-band maximum. The state we have reached after the last step is exactly the final state of the photoemission experiment, the difference between the $Z+1$ atom and the $_ZX$ atom with a core hole being neglected.

Now the cycle can be closed by taking the direct path from the initial to the final state, requiring the energy $-E_B^{\text{VBM}}(_ZX)$. The energy balance for the cycle yields the following expression for $E_B^{\text{VBM}}(_ZX)$:

$$\begin{aligned}E_B^{\text{VBM}}(_ZX)=&\,W(_ZX)-W^*(_{Z+1}X)\\&+I_{\text{core}}(_ZX)-I_{\text{val}}(_{Z+1}X) \; .\end{aligned} \tag{5}$$

The atomic ionization energies on the right-hand side of Eq. (5) are known from atomic calculations,[13] and, in some cases, from experiment.[14] The removal energies $W(_ZX)$ and $W^*(_{Z+1}X)$ are related to cohesive energies and heats of solution, and, in principle, could be derived from experimental data. Such a procedure is not useful for semiconductors where the heats of solution are unknown or poorly known. The idea underlying the present paper is to use tight-binding theory with universal parameters[11] developed by one of us, for the calculation of $W({}_{Z}X)$ and $W^*({}_{Z+1}X)$.

In forming the AB solid in the bond-orbital approximation[12] (BOA) all valence electrons of the A and B atoms are put in sp^3-hybrid states of average hybrid energy $\overline{\epsilon}_h = \frac{1}{2}(\epsilon_h^A + \epsilon_h^B)$ with $\epsilon_b^{A,B} = \frac{1}{4}(\epsilon_s^{A,B} + 3\epsilon_p^{A,B})$, the hybrid energies of atom A and B, respectively. The energy per electron necessary for the promotion from the atomic to the hybrid configuration is denoted by $E_{\text{prom}}(AB)$. It amounts to

$$E_{\text{prom}}(AB) = \begin{cases} \frac{1}{8}(\epsilon_p^A - \epsilon_s^A + \epsilon_p^B - \epsilon_s^B) & \text{for } Z_A = Z_B \\ \frac{1}{8}(2\epsilon_p^A - \epsilon_s^A - \epsilon_s^B) & \text{for } Z_A = Z_B - 2 \\ \frac{1}{8}(3\epsilon_p^A - \epsilon_s^A - \epsilon_p^B - \epsilon_s^B) & \text{for } Z_A = Z_B - 4 \, . \end{cases} \tag{6}$$

Forming σ bonds between hybrids lowers the energy of each electron by $[V_2^2(AB) + V_3^2(AB)]^{1/2}$. Here V_2 is the covalent energy[11]

$$V_2 = \frac{1}{4}(V_{ss\sigma} - 2\sqrt{3}V_{sp\sigma} - 3V_{pp\sigma}) = -3.22\frac{\hbar^2}{md^2} \tag{7}$$

with m the free-electron mass and d the nearest-neighbor distance. V_3 is the polar energy,

$$V_3 = \frac{1}{2}(\epsilon_h^A - \epsilon_h^B) \, . \tag{8}$$

There is also a shift in all of the levels due to nonorthogonality of orbitals on adjacent atoms. The change in energy per electron pair is seen in Ref. 12 to be given approximately by $V_0 = \eta_0 V_a^2 / |\overline{\epsilon}_h|$ (η_0 being a dimensionless constant). This is an important contribution to the removal energy of an atom, but since we will replace the removed atom by a second atom (the ${}_{Z+1}X$ atom), the two shifts very nearly cancel and we ignore them. Note there *is* a shift which is generally less than a volt due to different $\overline{\epsilon}_h$. If we were going to include this we should also allow the neighboring atoms to relax, which would reduce the effect by a factor of order 2. We proceed without lattice relaxation and without this term. There is, however, a change of the valence-band maximum due to the nonorthogonality which is not cancelled and which will need to be included.

With the neglect of the nonorthogonality contribution the bond energy within the BOA becomes

$$E_{\text{bond}}^{\text{BOA}}(AB) = 2E_{\text{prom}}(AB) - 2[V_2^2(AB) + V_3^2(AB)]^{1/2} \, . \tag{9}$$

If an atom A is removed, four bonds with eight electrons are broken. Z_A of these eight electrons are taken out from the solid; $Z_B = 8 - Z_A$ remain. The state of the Z_A outside electrons is given by the atomic configuration of the free Z_A atom. The Z_B electrons within the solid will be distributed among the four states which are formed from the four dangling hybrids of an A vacancy. Let $E_s(Z_B)$ be the total energy of the Z_B electrons within the solid and $E_a(Z_B)$ their energy within a free B atom. If the energy of the Z_B electrons within the solid would be $E_a(Z_B)$ and not $E_s(Z_B)$, the removal work $W(A)$ would be equal to $-4E_{\text{bond}}(A,B)$. But it is $E_s(Z_B)$, and we obtain

$$W(A) = -4E_{\text{bond}}^{\text{BOA}}(AB) + E_s(Z_B) - E_a(Z_B) \, . \tag{10a}$$

The removal work for an atom B is accordingly

$$W(B) = -4E_{\text{bond}}^{\text{BOA}}(AB) + E_s(Z_A) - E_a(Z_A) \, . \tag{10b}$$

If a $Z_A + 1$ atom is taken from the solid, we have the following changes. Z_A of the eight electrons from the four ${}_{Z_A+1}A \; B$ bonds are removed and set in the atomic configuration of a $Z_A + 1$ atom with one electron of energy $\epsilon_{\text{val}}^{{}_{Z_A+1}A}$ missing in the outermost valence shell. The missing electron is taken from the valence band (VB) of the solid. The $Z_B = 8 - Z_A$ bond electrons which remain in the solid take the total energy $E_s(Z_B)$. The removal energy $W^*({}_{Z_A+1}A)$ becomes

$$W^*({}_{Z_A+1}A) = W({}_{Z_A+1}A) - [E_{\text{VBM}}(AB) - \epsilon_{\text{val}}^{{}_{Z_A+1}A}] \, . \tag{11a}$$

Accordingly we have

$$W^*({}_{Z_B+1}B) = W({}_{Z_B+1}B) - [E_{\text{VBM}}(AB) - \epsilon_{\text{val}}^{{}_{Z_B+1}B}] \, . \tag{11b}$$

Here $W({}_{Z_A+1}A)$ and $W({}_{Z_B+1}B)$ are given by Eqs. (10a) and (10b) with the replacement of A by ${}_{Z_A+1}A$ and B by ${}_{Z_B+1}B$, respectively, and with Z_A by $Z_A + 1$ and Z_B by $Z_B + 1$, respectively. To avoid ambiguities we assume the $Z_A + 1$ atom always to be a cation. For $A = B$, therefore, the combination for the $Z_A + 1$ atom is forbidden; the promotion energies necessary for the calculation $W^*({}_{Z_A+1}A)$, $W^*({}_{Z_B+1}B)$ from Eqs. (11), (10), and (9) must be taken from Eq. (6) with the replacement of $\epsilon_{s,p}^A$ by $\epsilon_{s,p}^{{}_{Z_A+1}A}$ for $E_{\text{prom}}({}_{Z_A+1}AB)$ and $\epsilon_{s,p}^B$ by $\epsilon_{s,p}^{{}_{Z_B+1}B}$ for $E_{\text{prom}}(A \, {}_{Z_B+1}B)$.

The valence-band maximum E_{VBM} is given by the expression[12]

$$E_{\text{VBM}} = \frac{1}{2}(\epsilon_p^A + \epsilon_p^B) + \frac{1}{2}V_0(AB) - \left[\left[\frac{\epsilon_p^A - \epsilon_p^B}{2} \right]^2 + \left[1.28\frac{\hbar^2}{md^2} \right]^2 \right]^{1/2} \, . \tag{12}$$

Here $\frac{1}{2}V_0(AB)$ is the shift in each hybrid energy due to nonorthogonality. It may be evaluated by adding $V_0(AB)$ to Eq. (9) and requiring the result to be a minimum with respect to variation of d. It is

$$V_0(AB) = \frac{V_2^2(AB)}{[V_2^2(AB) + V_3^2(AB)]^{1/2}} \, . \tag{13}$$

Now using expressions (10) and (11) the binding energy $E_B^{\text{VBM}}(X)$ from Eq. (5) may be decomposed into the atomic ionization energy I_{core} and a solid-state contribution, ΔE_B^{VBM}, according to

$$E_B^{\text{VBM}}(X) = \Delta E_B^{\text{VBM}}(X) + I_{\text{core}}(X) \tag{14}$$

with

$$\Delta E_B^{\mathrm{VBM}}(X)=\Delta E_{\mathrm{bond}}^{\mathrm{BOA}}(X)+E_{\mathrm{VBM}}(AB)\ , \tag{15}$$

$$\Delta E_{\mathrm{bond}}^{\mathrm{BOA}}(A)=-4[E_{\mathrm{bond}}^{\mathrm{BOA}}(AB)-E_{\mathrm{bond}}^{\mathrm{BOA}}({}_{Z_A+1}AB)]\ , \tag{16}$$

$$\Delta E_{\mathrm{bond}}^{\mathrm{BOA}}(B)=-4[E_{\mathrm{bond}}^{\mathrm{BOA}}(AB)-E_{\mathrm{bond}}^{\mathrm{BOA}}(A_{Z_B+1}B)]\ . \tag{17}$$

Note that the unknown energies $E_s(Z_B)-E_a(Z_B)$ and $E_s(Z_A)-E_a(Z_A)$ do not enter these equations. The reason is that they are related to an intermediate state of the solid which is irrelevant for the energy balance between initial and final states. Similarly, surface dipoles (which contribute to the work function) do not enter.

The energy $\Delta E_B^{\mathrm{VBM}}$ from Eqs. (14) and (15) represents the difference of the binding energy E_B^{VBM} of a semiconductor core electron related to the valence-band maximum and the binding energy of the corresponding core electron of a free atom related to the vacuum level. It will be referred to as the solid-state binding-energy shift. In an integral way $\Delta E_B^{\mathrm{VBM}}$ accounts both for changes of the initial-state energy, the core-level shift, and of the final-state energy, the relaxation-energy shift. The two effects, however, cannot be separated in Eqs. (14)—(17). In Eq. (15) the difference between the Hartree-Fock term value, ϵ_{val}, and the ionization energy I_{val} of the outermost valence shell has been neglected since it is small compared to the other two terms.

As will be shown below, the bond-orbital approximation considered so far gives the main contribution to the solid-state binding-energy shift $\Delta E_B^{\mathrm{VBM}}$. The interaction between neighboring bonds and antibonds, i.e., the effect of metallization (in the terminology of Ref. 11) has a small, but far from negligible, effect on $\Delta E_B^{\mathrm{VBM}}$. In the next section it will be calculated.

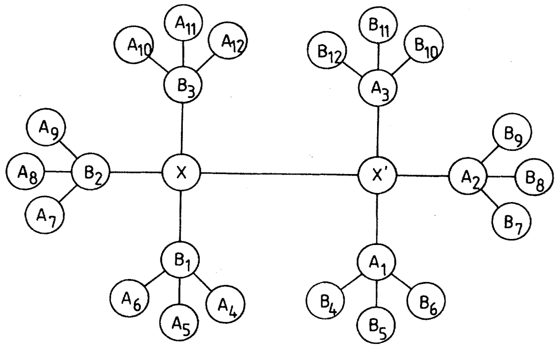

FIG. 2. Nearest and second-nearest neighbors of an atomic pair XX'. $X=A$ or ${}_{Z_A+1}A$. $X'=B$ or ${}_{Z_B+1}B$.

III. CORRECTIONS TO THE BOND-ORBITAL APPROXIMATION: METALLIZATION

A bond orbital between two atoms X and X' is coupled to six neighboring bond and six neighboring antibond orbitals (see Fig. 2). The bond-bond interaction can be omitted for our purpose since it results only in a symmetric splitting of the bond energy which does not change the total energy of bond electrons. The bond-antibond interaction, however, shifts the bond energy by a certain energy E_{met} which must be taken into account. For the calculation of E_{met} various kinds of bonds must be distinguished (see Fig. 2). First, bonds between an $X=A$ and $X=B$ atom in a pure AB solid; their energy change will be denoted by $E_{\mathrm{met}}(AB\,|\,O)$. Second, bonds between an $X={}_{Z_A+1}A$ and an $X'=B$ or an $X=A$ and an $X'={}_{Z_B+1}B$ atom in a pure AB solid; the bond-energy change is denoted by $E_{\mathrm{met}}({}_{Z_A+1}AB\,|\,O)$ and $E_{\mathrm{met}}(A\,{}_{Z_B+1}B\,|\,O)$, respectively. Third, bonds between an A and a B atom with one of the six nearest neighbors of the pair being an $X={}_{Z_A+1}A$ or $X'={}_{Z_B+1}B$ atom; the notations $E_{\mathrm{met}}(AB\,|\,{}_{Z_A+1}A)$ and $E_{\mathrm{met}}(AB\,|\,{}_{Z_B+1}B)$ are used for the bond-energy change.

The calculation of $E_{\mathrm{met}}(AB\,|\,O)$ proceeds as follows. The interaction-matrix element of the AB bond with the AB_1, AB_2, and AB_3 antibonds in Fig. 2 is $\frac{1}{2}(1-\alpha_{AB}^2)^{1/2}V_1(A)$ and with any A_1B, A_2B, or A_3B antibond is $\frac{1}{2}(1-\alpha_{AB}^2)^{1/2}V_1(B)$, where

$$V_1(X)=-\tfrac{1}{4}(\epsilon_p^X-\epsilon_s^X)\ , \tag{18}$$

$$\alpha_{AB}=\frac{V_3(AB)}{[V_2^2(AB)+V_3^2(AB)]^{1/2}}\ . \tag{19}$$

With the energy separation between an AB bond and an AB antibond equal to $-2V_2(AB)/(1-\alpha_{AB}^2)^{1/2}$, one obtains in second-order perturbation theory

$$E_{\mathrm{met}}(AB\,|\,O)=\frac{3}{4V_2(AB)}(1-\alpha_{AB}^2)^{3/2}[V_1^2(A)+V_1^2(B)]\ . \tag{20}$$

In the same way one obtains

$$E_{\mathrm{met}}({}_{Z_A+1}AB\,|\,O)=\frac{3}{2V_2(AB)}\left[\tfrac{1}{2}(1-\alpha_{{}_{Z_A+1}AB}^2)^{3/2}V_1^2({}_{Z_A+1}A)+\frac{(1+\alpha_{{}_{Z_A+1}AB})(1-\alpha_{AB})}{(1-\alpha_{AB}^2)^{-1/2}+(1-\alpha_{{}_{Z_A+1}AB}^2)^{-1/2}+\beta_{{}_{Z_A+1}AB}}V_1^2(B)\right]\ , \tag{21}$$

$$E_{\mathrm{met}}(A\,{}_{Z_B+1}B\,|\,O)=\frac{3}{2V_2(AB)}\left[\frac{(1-\alpha_{A\,{}_{Z_B+1}B})(1+\alpha_{AB})}{(1-\alpha_{A\,{}_{Z_B+1}B}^2)^{-1/2}+(1-\alpha_{AB}^2)^{-1/2}+\beta_{A\,{}_{Z_B+1}B}}V_1^2(A)+\tfrac{1}{2}(1-\alpha_{A\,{}_{Z_B+1}B}^2)^{3/2}V_1^2({}_{Z_B+1}B)\right]\ , \tag{22}$$

$$E_{\mathrm{met}}(AB\,|\,{}_{Z_A+1}A)=E_{\mathrm{met}}(AB\,|\,O)+\frac{V_1^2(B)}{2V_2(AB)}\left[-\frac{(1-\alpha_{AB}^2)^{3/2}}{2}+\frac{(1-\alpha_{{}_{Z_A+1}AB})(1+\alpha_{AB})}{(1-\alpha^2_{{}_{Z_A+1}AB})^{-1/2}+(1-\alpha_{AB}^2)^{-1/2}-\beta_{{}_{Z_A+1}AB}}\right], \quad (23)$$

$$E_{\mathrm{met}}(AB\,|\,{}_{Z_B+1}B)=E_{\mathrm{met}}(AB\,|\,O)+\frac{V_1^2(A)}{2V_2(AB)}\left[-\frac{(1-\alpha_{AB}^2)^{3/2}}{2}+\frac{(1+\alpha_{A\,{}_{Z_B+1}B})(1-\alpha_{AB})}{(1-\alpha^2_{A\,{}_{Z_B+1}B})^{-1/2}+(1-\alpha_{AB}^2)^{-1/2}-\beta_{A\,{}_{Z_B+1}B}}\right], \quad (24)$$

where $\beta_{XX'}$ is given by the relation

$$\beta_{{}_{Z_A+1}AB}=\frac{1}{2V_2(AB)}(\epsilon_h^{{}_{Z_A+1}A}-\epsilon_h^{A})\,,\quad \beta_{A\,{}_{Z_B+1}B}=\frac{1}{2V_2(AB)}(\epsilon_h^{{}_{Z_B+1}B}-\epsilon_h^{B})\,. \quad (25)$$

The change of bond energy by metallization has also an effect on the nonorthogonality shift of all energy levels mentioned in Sec. II. For the same arguments as used there, this effect can be neglected for the removal work but must be included for the valence-band maximum. In Eq. (12) for E_{VBM} one has now $V_0+\delta V_0$ instead of V_0 with

$$\delta V_0(AB)=\tfrac{1}{2}E_{\mathrm{met}}(AB\,|\,O)\,. \quad (26)$$

Equation (26) follows by again minimizing the new bond energy $E_{\mathrm{bond}}+E_{\mathrm{met}}$ with respect to the interatomic distance d.

The change of bond energies and of E_{VBM} due to metallization results in shifts $\Delta E_B^{\mathrm{MET}}$ of core-electron binding energies which are to be included in addition to $\Delta E_{\mathrm{bond}}^{\mathrm{BOA}}$ and E_{VBM} to obtain the total solid-state shift

$$\Delta E_B^{\mathrm{VBM}}=\Delta E_{\mathrm{bond}}^{\mathrm{BOA}}+\Delta E_B^{\mathrm{MET}}+E_{\mathrm{VBM}}\,. \quad (27)$$

By using the Born-Haber cycle from Fig. 1 one obtains

$$\begin{aligned}\Delta E_B^{\mathrm{MET}}(A)=&-4[E_{\mathrm{met}}(AB\,|\,O)-E_{\mathrm{met}}({}_{Z_A+1}AB\,|\,O)]\\&-12[E_{\mathrm{met}}(AB\,|\,O)-E_{\mathrm{met}}(AB\,|\,{}_{Z_A+1}A)]\\&+\tfrac{1}{4}E_{\mathrm{met}}(AB\,|\,O)\,,\end{aligned} \quad (28)$$

$$\begin{aligned}\Delta E_B^{\mathrm{MET}}(B)=&-4[E_{\mathrm{met}}(AB\,|\,O)-E_{\mathrm{met}}(A\,{}_{Z_B+1}B\,|\,O)]\\&-12[E_{\mathrm{met}}(AB\,|\,O)-E_{\mathrm{met}}(AB\,|\,{}_{Z_B+1}B)]\\&+\tfrac{1}{4}E_{\mathrm{met}}(AB\,|\,O)\,.\end{aligned} \quad (29)$$

IV. RESULTS AND DISCUSSION

In this section we apply the theory to obtain core shifts $\Delta E_B^{\mathrm{VBM}}$ for a series of IV-IV, III-V, and II-VI semiconductors. The required tight-binding parameters are listed in Table I. In Table II calculated shifts are shown both for the cations and anions together with the various contributing energies. The largest contribution to $\Delta E_B^{\mathrm{VBM}}$ turns out to be E_{VBM}, i.e., the change of the reference level between the free and the solid-state atom. This means that the accuracy of E_{VBM} is critical to our calculations. Nevertheless we have used the rough approximation (12) for E_{VBM}. Better values of E_{VBM} are necessary if one aims to get more precise predictions of $\Delta E_B^{\mathrm{VBM}}$. The second largest contribution to $\Delta E_B^{\mathrm{VBM}}$ is the change of the bond energy of an ${}_ZX$ and $Z+1$ atom within the BOA. This shift is positive, i.e., the binding is smaller for the $Z+1$ than for the ${}_ZX$ atom, in the case of cations. The opposite trend is observed in the case of anions. The main reason is that the polarity of an ${}_{Z_A+1}AB$ bond is smaller, and that of $A\,{}_{Z_B+1}B$ bond larger, than that of the reference AB bond. The smallest contribution to $\Delta E_B^{\mathrm{VBM}}$ is the change $\Delta E_B^{\mathrm{MET}}$ of the bond energy due to metallization. For cations $\Delta E_B^{\mathrm{MET}}$ is always negative and its absolute value relatively large. For anions the sign of $\Delta E_B^{\mathrm{MET}}$ is either positive or negative and the absolute value is relatively small. This behavior of $\Delta E_B^{\mathrm{MET}}$ reflects two different trends. First, the metallic energy V_1 is always larger for the $Z+1$ than for the ${}_ZX$ atom. Second, the overlap between neighboring bonds and antibonds decreases with increasing polarity.

TABLE I. Input parameters for the calculation of solid-state shifts of core-electron binding energies. $\epsilon_{s,p}$ from Ref. 13; V_2 calculated from Eq. (7).

Atom	$-\epsilon_s$	$-\epsilon_p$	Solid	$-V_2$
Al	10.73	5.71	SiSi	4.44
Si	14.84	7.58	GeGe	4.08
P	19.31	9.53	SnSn	3.10
S	24.14	11.57		
Cl	29.39	13.87	AlP	4.40
			AlAs	4.15
Zn	8.12	3.89	AlSb	3.47
Ga	11.82	5.56		
Ge	15.52	7.33	GaP	4.40
As	19.40	9.00	GaAs	4.08
Se	23.48	10.65	GaSb	3.49
Br	27.78	12.51		
			InP	3.80
Cd	7.66	3.92	InAs	3.60
In	10.79	5.34	InSb	3.10
Sn	13.88	6.79		
Sb	17.07	8.21	ZnS	4.48
Te	20.39	9.66	ZnSe	4.08
I	23.86	11.10	ZnTe	3.52
			CdS	3.83
			CdSe	3.54
			CdTe	3.11

TABLE II. Core-electron binding-energy shifts of cations $\Delta E_B^{\rm VBM}(A)$ and anions $\Delta E_B^{\rm VBM}(B)$, related to the valence-band maximum, and the various contributions. All are in eV.

A	B	$\Delta E_{\rm bond}^{\rm BOA}(A)$	$\Delta E_{\rm bond}^{\rm BOA}(B)$	$E_{\rm VBM}(AB)$	$\Delta E_B^{\rm MET}(A)$	$\Delta E_B^{\rm MET}(B)$	$\Delta E_B^{\rm VBM}(A)$	$\Delta E_B^{\rm VBM}(B)$	$I_{\rm val}(z_A+1A)$	$I_{\rm val}(z_B+1B)$
Si	Si		1.09	−7.13		−1.83		−7.87		8.70
Ge	Ge		0.97	−6.92		−1.99		−7.94		8.29
Sn	Sn		0.60	−6.48		−1.78		−7.66		7.65
Al	P	4.12	−1.59	−8.30	−2.82	−0.16	−6.93	−9.98	6.78	10.45
Al	As	3.97	−1.05	−7.88	−3.37	−0.26	−7.28	−9.19	6.78	9.76
Al	Sb	3.28	−0.78	−7.27	−4.01	−0.09	−8.00	−8.14	6.78	8.98
Ga	P	3.67	−1.37	−8.27	−2.87	−0.13	−7.47	−9.77	6.59	10.45
Ga	As	3.58	−0.97	−7.86	−3.53	−0.20	−7.82	−9.03	6.59	9.76
Ga	Sb	3.15	−0.57	−7.23	−3.90	−0.07	−8.28	−7.89	6.59	8.98
In	P	3.84	−2.32	−8.46	−2.51	+0.07	−7.13	−10.71	6.19	10.45
In	As	3.73	−1.64	−8.01	−2.98	+0.08	−7.26	−9.57	6.19	9.76
In	Sb	3.23	−2.48	−7.34	−3.57	+0.17	−7.68	−9.66	6.19	8.98
Zn	S	4.77	−1.80	−10.45	−2.05	−0.27	−7.73	−12.52	5.39	12.57
Zn	Se	4.73	−1.55	−9.64	−2.15	−0.06	−7.06	−11.26	5.39	11.48
Zn	Te	4.46	−1.03	−8.77	−2.18	+0.13	−6.49	−9.67	5.39	10.34
Cd	S	4.46	−2.41	−10.69	−1.30	+0.14	−7.53	−12.97	5.23	12.57
Cd	Se	4.46	−1.92	−9.84	−1.63	+0.13	−7.01	−11.63	5.23	11.48
Cd	Te	4.20	−1.28	−8.92	−1.79	+0.04	−6.51	−10.16	5.23	10.34

The shifts $\Delta E_B^{\rm VBM}$ from Table II do not differentiate between different core levels and can be used to calculate binding energies of any of them. In Table III we take the shallowest core levels to compare our calculated results with experimental ones. The experimental data depend to some extent on sample preparation and measuring condi-

TABLE III. Calculated and experimental core-electron binding energies related to the valence-band maximum for the shallowest core levels of cations $E_B^{\rm VBM}(A)$ and anions $E_B^{\rm VBM}(B)$. Experimental values for Si, Ge, and Sn are from Ref. 14, for AlAs from Ref. 15, for AlSb from Ref. 16, for the Ga and In compounds from Ref. 5, and for the Zn and Cd compounds from Ref. 15. The gap energy has been subtracted from the data in Refs. 5 and 16. Theoretical free-atom ionization energies are from Ref. 12. All are in eV.

A	B	$I_{\rm core}(A)$	$I_{\rm core}(B)$	$E_B^{\rm VBM}(A)$	$E_B^{\rm VBM,expt}(A)$	$E_B^{\rm VBM}(B)$	$E_B^{\rm VBM,expt}(B)$
Si	Si		108.44			100.17	99.0
Ge	Ge		36.10			28.16	28.7
Sn	Sn		31.35			23.69	24.1
Al	P	80.60	138.53	73.67		128.55	
Al	As	80.60	48.64	73.32	73.2	39.45	40.6
Al	Sb	80.60	39.50	72.60		31.36	30.6
Ga	P	24.59	138.53	17.12	16.9	128.76	127.0
Ga	As	24.59	48.64	16.77	17.9	39.61	39.4
Ga	Sb	24.59	39.50	16.31	19.3	31.61	31.6
In	P	23.36	138.53	16.23	16.3	127.82	
In	As	23.36	48.64	16.10	16.8	39.07	40.3
In	Sb	23.36	39.50	15.68	16.6	29.84	30.9
Zn	S	14.38	172.13	6.65	9.03	159.61	
Zn	Se	14.38	62.10	7.31	9.20	50.84	53.5
Zn	Te	14.38	48.27	7.88	9.84	38.60	40.9
Cd	S	16.19	172.13	8.67	9.64	159.16	
Cd	Se	16.19	62.10	9.18	10.04	50.47	
Cd	Te	16.19	48.27	9.68	10.49	38.11	40.2

tions and differ between different authors. The overall agreement with our calculated data is within 1 or 2 eV. For such agreement the inclusion of metallization was essential as it was for cohesive energy calculations.[11] The agreement is better for the IV-IV and III-V than for the II-VI materials. Whereas for the first two groups of materials there is no systematic trend in the deviations, the calculated binding energies are always lower than the experimental ones in the case of II-VI compounds. This is true both for cations and anions. The reason might be too deep a predicted value of E_{VBM} from Eq. (12) for these materials.

In Table II we show also ionization energies $I_{\mathrm{val}}({}_{Z_A+1}A)$, $I_{\mathrm{val}}({}_{Z_B+1}B)$ of the outermost valence shell of the Z_A+1 and Z_B+1 atoms, respectively. Note that the solid-state shifts $\Delta E_B^{\mathrm{VBM}}(A)$ and $\Delta E_B^{\mathrm{VBM}}(B)$ are close to $-I_{\mathrm{val}}({}_{Z_A+1}A)$ and $-I_{\mathrm{val}}({}_{Z_B+1}B)$. This means that the excitation energy from the core level to the outermost valence shell in the case of a free atom, which amounts to $I_{\mathrm{core}}({}_{Z}X)-I_{\mathrm{val}}({}_{Z+1}X)$, is not too far from $\Delta E_B^{\mathrm{VBM}}(X)$, i.e., the corresponding excitation energy from the core level to the valence-band maximum in the case of a solid-state atom. The various solid-state effects, i.e., the different core-level positions, the different core-hole relaxation energies, the shift and the splitting of the valence-state energies of an atom embedded in a solid compared to a free atom, obviously, cancel out each other to a certain extent. We have demonstrated this partial cancellation, not by calculating the energy changes directly, but by using a Born-Haber cycle and tight-binding theory with universal parameters. In conclusion we state that our approach is able to provide insight into qualitative features of core-electron binding energies and to reproduce experimental values within 1 to 2 eV without using any empirical parameters. We feel that still better quantitative results can be obtained with more complete calculations. Surface shifts of binding energies should be accessible by this approach.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation under Grant. No. DMR-80-22365.

---

[*] Permanent address: Sektion Physik, Alexander von Humboldt—Universität zu Berlin, DDR-1086 Berlin, Democratic Republic of Germany.

[1] B. Johansson and N. Martensson, Phys. Rev. B **21**, 4427 (1980).

[2] S. Yin and E. Tosatti, Proceedings of the International Conference on the Physics of Semiconductors, Kyoto, 1980 [J. Phys. Soc. Jpn. **49**, 105 (1980)].

[3] F. Bechstedt, R. Enderlein, and R. Wischnewski, Phys. Status Solidi B **107**, 637 (1981).

[4] R. Nordberg, R. G. Albridge, T. Bergmark, J. Heidman, C. Nordling, K. Siegbahn, and B. J. Lindberg, Ark. Kemi **28**, 257 (1967).

[5] W. Gudat, E. E. Koch, P. Y. Yu, M. Cardona, and C. M. Penchina, Phys. Status Solidi B **52**, 505 (1972).

[6] N. J. Shevchik, J. Tejeda, and M. Cardona, Phys. Rev. B **9**, 2627 (1974).

[7] K. Hübner and M. Schafer, Phys. Status Solidi B **76**, K63 (1976).

[8] K. Hübner and F. Bechstedt, Phys. Status Solidi B **96**, 351 (1979); **96**, 595 (1979).

[9] F. Bechstedt and R. Enderlein, Phys. Status Solidi B **94**, 239 (1979); **95** 185 (1979).

[10] L. Ley, R. Pollack, F. R. McFeely, S. P. Kowalczyk, and D. A. Shirley, Phys. Rev. B **9**, 600 (1974).

[11] J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).

[12] W. A. Harrison, Phys. Rev. B **27**, 3592 (1983); *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[13] K.-N. Huang, At. Data Nucl. Data Tables **18**, 249 (1976).

[14] J. P. Deslaux, At. Data Nucl. Data Tables **12**, 311 (1973).

[15] J. A. Bearden and A. F. Burr, Rev. Mod. Phys. **39**, 125 (1967).

[16] N. J. Shevchik, J. Tejeda, C. M. Penchina, and M. Cardona, Solid State Commun. **11**, 1619 (1972).