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Deformation potentials at the valence-band maximum in semiconductors

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The deformation potentials d_0 and d' are calculated for 22 elemental and compound semiconductors. The calculations are based on the self-consistent relativistic linear combination of muffin-tin orbitals band-structure method. It is demonstrated that perturbations caused by strain-induced changes in the nonspherical potential are significant. Chemical trends are discussed in terms of potential parameters relating to a first-principles tight-binding scheme.

I. INTRODUCTION

The deformation potentials of the electronic states at the Brillouin-zone center ($\mathbf{k}=\mathbf{0}$) for semiconductors play an important role in many physical phenomena of these compounds. A review of the importance of these quantities, their definition,[1] and methods of calculation[2] was given recently by Blacha *et al.*[3]

The valence-band maximum in the zinc-blende-type semiconductors is a Γ_8 state at $\mathbf{k}=(0,0,0)$. It is fourfold degenerate (counting spin), and splits under uniaxial strain into two doublets. In the presence of a phonon which changes the bond length along [111] by an amount u, this splitting, $\delta\omega_0$, is related to the optical-phonon deformation potential d_0 through

$$\delta\omega_0 = d_0 \frac{u}{a_0} , \tag{1}$$

where a_0 is the lattice constant.

A pure rhombohedral strain (δ) (i.e., a trigonal deformation with an [111] direction as strain axis) produces a splitting of Γ_8^v, $\delta\omega$, related to the deformation potential d through

$$\delta\omega = 2\sqrt{3} d \delta . \tag{2}$$

The relation between d and d_0 is complicated by the fact that the anion and cation sublattices do not "follow" each other in a rhombohedral strain—there is an *internal* strain characterized by the *internal-strain* parameter ζ. This parameter, which was introduced by Kleinmann,[4] specifies for the strained lattice the position, $\mathbf{R}_1'$, of the atom which in the unstrained crystal is at $\mathbf{R}_1=(1,1,1)a_0/4$ through

$$\mathbf{R}_1' = [\overleftrightarrow{\mathrm{E}} - \zeta(\overleftrightarrow{\mathrm{E}} - \overleftrightarrow{1})]\mathbf{R}_1 , \tag{3}$$

where $\overleftrightarrow{\mathrm{E}}$ is the transformation matrix for the Bravais lattice expressing a volume conserving rhombohedral strain.[5]

The deformation potentials d and d_0 are related linearly through the internal-strain parameter:[3]

$$d = d' - \tfrac{1}{4}\zeta d_0 . \tag{4}$$

Experimentally it is relatively straightforward to obtain d by means of optical techniques under strain. A direct measurement of ζ, on the other hand, is rather difficult since it requires the measurement of the intensity of an x-ray reflection forbidden in the unstrained crystal. Therefore only few experimental data for ζ, not all in agreement with each other, are available.[6-9] The extraction,[10,11] of d_0 from observed Raman intensities is possible, but usually associated with considerable uncertainty. Other techniques, such as transport measurements[12] and deductions from Lorentzian widths of optical structures,[13] are also indirect and not very reliable. We have earlier[5,14,15] calculated d' and d_0 for several compound semiconductors from first-principles self-consistent linear muffin-tin-orbital[16] (LMTO) band structures. It appeared that the calculated d_0 values, in general, came out considerably smaller than those determined experimentally. For GaAs, for example, we calculated[5,15] $d_0 \simeq 18$ eV, whereas experimental values as high as 41 eV are quoted. The values of ζ which we deduced, using the relation (4) together with measured values of d and calculated d' and d_0, also seemed to disagree with experiments. For Si and GaAs, however, our ζ values were in good agreement with the theoretical predictions[17,18] obtained from self-consistent pseudopotentials. These calculations simultaneously gave values of d_0 smaller than those derived from Raman data, but still somewhat larger than ours; Nielsen and Martin[18] calculated for GaAs $d_0 \simeq 23$ eV.

Since the quantitative values of the deformation potentials in semiconductors are important we felt that the controversies indicated above required a new investigation of the accuracy of our calculations. One may, of course, invoke inaccuracies in the experimental data to explain our low values of d_0 obtained with the LMTO method. Nevertheless, the observation that these values[5,14,15] are also systematically lower than those derived with the pseudopotential method remains particularly disturbing. The present work will show why the LMTO values are too low, typically by amounts of the order of 5–9 eV.

It may be conjectured that the source of the differences between the LMTO and pseudopotential results is the different treatment of the nonspherical parts of the potentials in the two schemes. The pseudopotential method applies a potential which is nonspherically symmetric around the atomic sites. The LMTO scheme, in the form which we used, averages the potentials spherically. Some compensation is, however, obtained

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by the introduction of "empty spheres," and the application of the "combined correction" term.[16] It was, in fact, found[19] that for (unstrained) Ge and GaAs, one obtains almost identical bands when the same prescriptions are used for construction of the exchange-correlation potential in the two schemes. Nevertheless, the present work shows that the *strain-induced* changes in the nonspherical parts of the potential are significant. This is demonstrated by applying to the LMTO calculations a simple perturbation scheme. These corrections turn out to have just the effect of bringing the d_0 values in close agreement with those found by Nielsen and Martin.[17,18] We also examine (as we did in the cases of Si and GaAs) the effects of the self-consistent charge transfer among the atomic spheres induced by the strain. These are negligible. It is only the redistribution on each site (in the ionic case mainly on the anion site) of the p_z versus the p_x and p_y components of the wave functions (z is the strain direction) that matters.

The nonspherical corrections are separated into a Hartree contribution from the electrons in the atomic cells plus a term arising from the motion with strain of the remaining part of the lattice, i.e., a nonspherical Madelung-type term. The perturbations take only the Coulomb parts into account.

The first-principles values are compared to empirical pseudopotential and tight-binding results.[3] Furthermore, they are also calculated from a simplified[15] version of the first-principles tight-binding schemes.[20] Chemical trends are illustrated by means of a first-principles ionicity scale[15] and the theoretical sp^3 bond orders.[15,21]

Section II describes briefly the calculation methods. The calculated values of the deformation potentials are given in Sec. III, which also describes the chemical trends. Conclusions and discussions not already given in this introduction follow in the summary (Sec. IV).

II. CALCULATION OF d' AND d_0

In this section we describe the perturbation calculation of the corrections to the deformation potentials produced by the changes in the nonspherical crystal potential when the strain is introduced. We only consider effects of the Coulomb potentials, i.e., we neglect the changes in the nonspherical part of the exchange-correlation potential. We need to calculate shifts in the strain-split levels of the type

$$\langle j\mathbf{k} \,|\, \Delta V(\mathbf{r}) \,|\, j\mathbf{k} \rangle \ , \tag{5}$$

where $\Delta V(\mathbf{r})$ contains two contributions

$$\Delta V(\mathbf{r}) = \Delta V^H(\mathbf{r}) + \Delta V^M(\mathbf{r}) \ . \tag{6}$$

The first term ΔV^H ("Hartree term") is due to the change in the nonspherical electron distribution upon strain, and $\Delta V^M(\mathbf{r})$ is due to the change in the nonspherical part of the potential from the part of the crystal outside the atom considered ("Madelung-type term"). This last term is calculated as the strain-induced change in the nonspherical Coulomb potential assuming that the main effect due to the surrounding lattice is due to the monopoles only. An extension to include higher-order multipoles is straightforward, but not necessarily within the present approximations.

Using (5) and (6) we get the deformation potentials as

$$d_0 \cong d_0^{\mathrm{LMTO}} + \Delta d_0^H + \Delta d_0^M \ , \tag{7a}$$

$$d' \cong d'_{\mathrm{LMTO}} + \Delta d'_H + \Delta d'_M \ , \tag{7b}$$

where d_0^{LMTO} is the result from the LMTO calculation using the self-consistent spherical potentials, and Δd_0^H and Δd_0^M are the corrections due to ΔV^H and ΔV^M.

A. Calculation of Δd_0^M and Δd_0^M

The electronic structures are calculated within the local-density scheme,[22] and the effective one-electron wave equation is solved self-consistently by means of the relativistic LMTO method. The combined correction is included, and as is usual for the zinc-blende structures, we include empty spheres, i.e., atomic spheres without nuclear charge. Thus the crystal is treated as an fcc Bravais lattice with four atoms in the basis. These are, taking ZnS as an example, Zn at (0,0,0), S at $(1,1,1)a_0/4$, E_1: $(-1,-1,-1)a_0/4$, and E_2: $(1,1,1)a_0/2$. Here E_1 and E_2 denote the two (in general inequivalent) empty spheres. In this way a crystal potential which is spherically symmetric [atomic sphere approximation (ASA)] inside each sphere is generated. We could now, from the LMTO eigenvectors generated in the last iteration of the self-consistency cycle, construct the full nonspherical charge distribution (see, e.g., Refs. 15, 21, and references therein), and then calculate a nonspherical potential by solving the Poisson equation. Instead of proceeding in that way, we repeat the ASA-type calculation for the strained crystal, and from the eigenvectors obtained from this new calculation and that of the undeformed crystal we find the strain-induced *change* in the nonspherical charge. This change is still calculated within each atomic sphere; it is obtained from the truncated one-center expansion of the wave functions. This means that we neglect the corners of the atomic polyhedra, but since we only need the *changes* in the nonspherical potential we assume that the errors caused by this approximation are less serious than would be the case if the full nonspherical terms were needed.

The wave functions which we use are of the form

$$\psi_j^{\mathbf{k}}(\mathbf{r}) = \sum_{L,q} C_{Lq}^{j\mathbf{k}} \Phi_{Lq}^{\mathbf{k}j}(\mathbf{r}) \ , \tag{8}$$

where $L \equiv (l,m)$ is a combined angular momentum quantum number q atomic-sphere index (for the sphere centered at $\mathbf{R}_q$), and j is the band index. The functions Φ are

$$\Phi_{Lq}^{\mathbf{k}j}(\mathbf{r}) = \Phi_{lq}^{j\mathbf{k}}(r_q) Y_l^m(\hat{\mathbf{r}}_q) \ . \tag{9}$$

Here the radial function $\Phi_{lk}^{j\mathbf{k}}$ evaluated at the eigenenergy $E_j^{\mathbf{k}}$ is obtained from the Taylor expansion in terms of ϕ and $\dot{\phi}$ (see, e.g., Ref. 16), and $\mathbf{r}_q \equiv \mathbf{r} - \mathbf{R}_q$.

Now we choose a coordinate system with the z axis pointing along the direction of the trigonal strain, i.e., $\hat{\mathbf{z}} \| [111]$. The strain does not change the charge in the spheres, but it produces a redistribution of the occupancies of the p_z versus the (p_x, p_y) orbitals as compared to the unstrained case. Thus denoting by $\bar{Y}_1^{x_i}$ $(i=1,2,3)$ the real spherical harmonics $(l=1,\ x_1=x,\ x_2=y,\ x_3=z)$, the strain-induced change in the nonspherical electron density in sphere q is

$$\Delta n_q(\mathbf{r}_q)=\sum_{j,\mathbf{k}}^{\text{occ}}\sum_{i=1}^{3} A_{1,jq}^{\mathbf{k}i}\,|\Phi_{1q}^{j\mathbf{k}}(r_q)|^2[\bar{Y}_1^{x_i}(\hat{\mathbf{r}}_q)]^2\ , \tag{10}$$

and $(l=1)$,

$$A_{l,jq}^{\mathbf{k}i}=2\left[|C_{L_iq}^{j\mathbf{k}}|^2-\tfrac{1}{3}\sum_{\nu=1}^{3}|C_{L_\nu q}^{j\mathbf{k}}|^2\right]. \tag{11}$$

The L_ν index in (11) is now the combination of l and i indices. [The factor 2 in Eq. (11) is due to the spin].

The k space summation in Eq. (10) is performed here in the simplest possible way. We just sum over the star (k_B^*) of single Baldereschi points (24 points). With the relation

$$A_{1,jq}^{x_i}\equiv\tfrac{1}{24}\sum_{k_B^*}A_{1,jq}^{\mathbf{k}_Bi}\ , \tag{12}$$

and noting that

$$A^y=A^x=-\tfrac{1}{2}A^z\ , \tag{13}$$

we have

$$\Delta n_q(\mathbf{r}_q)=\sum_{j}^{\text{occ}}A_{1,jq}^{z}\,|\Phi_{1q}^{jk_B}|^2[(\bar{Y}_1^z)^2-\tfrac{1}{2}(\bar{Y}_1^x)^2-\tfrac{1}{2}(\bar{Y}_1^y)^2]\ . \tag{14}$$

We have used the same radial wave function $\Phi_{lq}^{j\mathbf{k}_B}$ $(l=1)$ at all $\mathbf{k}_B$, a fact which is only strictly correct for the unstrained crystal. Rewriting the term in square brackets in (14) we get

$$\Delta n_q(\mathbf{r})=F_2^q(r_q)Y_2^0(\hat{\mathbf{r}}_q)\ , \tag{15}$$

where

$$F_2^q(r)=\sum_{j}^{\text{occ}}\frac{3}{8\pi}\left[\frac{16\pi}{5}\right]^{1/2}|\Phi_{1q}^{jk_B}(r)|^2A_{1,jq}^{z}\ . \tag{16}$$

The perturbing Hartree potential $\Delta V_q^H(\mathbf{r})$ in sphere q is obtained from Poisson's equation (Ry units, $e^2=2$):

$$\nabla^2[\Delta V_q(\mathbf{r})]=-8\pi\Delta n_q(\mathbf{r})\ , \tag{17}$$

giving [only the $(l,m)=(2,0)$ part]

$$\Delta V_q^H(\mathbf{r})=U_{l=2}^q(r)Y_2^0(\hat{\mathbf{r}})\ . \tag{18}$$

The radial part $U_l^q(r)$ satisfies

$$\frac{1}{r^2}\frac{\partial}{lr}\left[r^2\frac{\partial U_l^q}{\partial r}\right]-\frac{l(l+1)}{r^2}U_l^q=F_l^q\ , \tag{19}$$

with F_l^q given in our case $(l=2)$ in Eq. (16).

In solving Poisson's equation (17)–(19), we impose the boundary condition that the potential should be continuous at the sphere surface $(r=S_q)$, i.e., that it matches the multipole field outside the sphere. This implies that

$$U_2^q(S_q)=\frac{8\pi}{5}\frac{1}{S_q^3}q_2^q\ , \tag{20}$$

with

$$q_2^q=\int_0^{S_q}r^4\Delta n_q\,dr\ . \tag{21}$$

Now we obtain the Hartree perturbation to the p-like state at Γ ($\mathbf{k}=0$, but we retain the band index and $\mathbf{k}$ as labels for clarity) as

$$\langle j\mathbf{k}|\Delta V^H(\mathbf{r})|j\mathbf{k}\rangle=\sum_q\left[\int_0^{S_q}r^2dr\,|\Phi_{1q}^{j\mathbf{k}}(r)|^2U_2^q(r)\right]\frac{1}{\sqrt{5\pi}}(|C_{1zq}^{j\mathbf{k}}|^2-\tfrac{1}{2}|C_{1xq}^{j\mathbf{k}}|^2-\tfrac{1}{2}|C_{1yq}^{j\mathbf{k}}|^2)\ . \tag{22}$$

The eigenvectors $\bar{C}$ in Eq. (22) are those of the strain-split state considered as obtained from the LMTO calculation for the strained lattice. It is immaterial whether the radial functions Φ in Eq. (22) are taken from the self-consistent calculation from the strained crystal or from that of the undistorted case.

B. Calculation of Δd_0^M and $\Delta d_M'$

Assuming that the solid is divided into atomic polyhedra ("cells") with volumes Ω_j, we can write the Coulomb potential in cell i as

$$V(\mathbf{r}_i)=V_0^i(\mathbf{r}_i)+\sum_L U_L^{i*}r_i^lY_l^m(\hat{\mathbf{r}}_i)\ , \tag{23}$$

where V_0^i is the contribution from the cell no. i itself, and the sum represents the rest. The coefficients U_L^i are[23]

$$\begin{aligned}U_L^i&=\frac{4\pi}{2l+1}\sum_{j(\neq i)}\int_{\Omega_j}\frac{\rho(\mathbf{r})}{r_i^{l+1}}Y_l^m(\hat{\mathbf{r}}_i)d\mathbf{r}\ ,\\&=\sum_{j(\neq i)}\sum_{L'}(-1)^{l'+m'}Q_{L'}^jA_{L'L}\frac{Y_{l+l'}^{m-m'}(\hat{\mathbf{R}}_{ij})}{|\mathbf{R}_{ij}|^{l+l'+1}}\ ,\end{aligned} \tag{24}$$

where $\mathbf{R}_{ij}$ is the vector connecting the atoms i and j.

The Q's represent the multipole moments of the charge distribution ρ and

$$A_{LL'}=\left[4\pi\frac{(2l+1)(l+l'+m-m')!(l+l'-m+m')!}{(2l+2l'+1)(2l'+1)(l'+m')!(l'-m')!(l+m)!(l-m)!}\right]^{1/2}. \tag{25}$$

Here we approximate the cells by atomic spheres, and we wish only to include the monopole contributions $L'=(0,0)$. Thus

$$U_L^i=\sum_{j(\neq i)}(4\pi)^{3/2}q^j\frac{1}{(2l+1)}\frac{1}{R_{ij}^{l+1}}Y_l^m(\hat{\mathbf{R}}_{ij})\ , \tag{26}$$

where q^j is the charge on sphere j.

The perturbation $\Delta V_M^0(\mathbf{r})$ for the phonon mode relating to d_0 is first derived. Using the coordinate system with origin on the atom which we wish to consider, and $\hat{\mathbf{z}}=(1,1,1)/\sqrt{3}$, $\hat{\mathbf{x}}=(1,-1,0)/\sqrt{2}$, and $\hat{\mathbf{y}}=(1,1,-2)/\sqrt{6}$, the nearest-neighbor atomic positions (labeled below by $a1$) in the rhombohedrally strained zinc-blende crystal are

$$\begin{aligned}
\mathbf{R}_1&=(1+\delta)\frac{a_0\sqrt{3}}{4}\hat{\mathbf{z}}\ ,\\
\mathbf{R}_2&=\left[(3\delta-1)\frac{\sqrt{3}}{3}\hat{\mathbf{z}}-\frac{2\sqrt{6}}{3}\hat{\mathbf{y}}\right]\frac{a_0}{4}\ ,\\
\mathbf{R}_3&=\left[(3\delta-1)\frac{\sqrt{3}}{3}\hat{\mathbf{z}}-\frac{\sqrt{2}}{2}\hat{\mathbf{x}}+\frac{\sqrt{6}}{3}\hat{\mathbf{y}}\right]\frac{a_0}{4}\ ,\\
\mathbf{R}_4&=\left[(3\delta-1)\frac{\sqrt{3}}{3}\hat{\mathbf{z}}+\frac{\sqrt{2}}{2}\hat{\mathbf{x}}+\frac{\sqrt{6}}{3}\hat{\mathbf{y}}\right]\frac{a_0}{4}\ .
\end{aligned} \tag{27}$$

The total number of electrons[24] minus the atomic number in these atomic spheres is called q^{a1}. The difference between the potential (in Ry units) created by point charges at these positions for $\delta\neq 0$ and for $\delta=0$ is [only $(l,m)=(2,0)$ important]

$$\Delta V_{\mathrm{NN}}^M(\mathbf{r})=-\frac{8\pi}{5}\left[\frac{5}{16\pi}\right]^{1/2}r^2\frac{1}{(a_0\sqrt{3}/4)^3}\tfrac{40}{3}q^{a1}Y_2^0(\hat{\mathbf{r}})\delta\ . \tag{28}$$

We have here only considered the four nearest real atoms $(a1)$. The same shell of the undistorted crystal also contains four empty spheres. We let these empty spheres follow the atom which is considered in the displacement. Therefore they will not contribute to ΔV_{NN}^M. The next set of spheres that contribute to $\Delta V_M^0(\mathbf{r})$ consist of the four empty spheres, labeled $e2$, at $(2+\delta)\sqrt{3}a_0/4\hat{\mathbf{z}}$, etc. [The empty spheres $e2$ will be either of type E_1 or E_2 (Sec. II A) depending on whether the potential at the anion or cation site is to be calculated.] Letting q^{e2} denote the number of electrons[24] in these empty spheres, the strain-induced change in the Madelung potential becomes, with inclusion of the contribution in Eq. (28),

$$\Delta V_M^0(\mathbf{r})=-\tfrac{256}{27}(240\pi)^{1/2}\frac{r^2}{a_0^3}\delta(q^{a1}+\tfrac{1}{16}q^{e2})Y_2^0(\hat{\mathbf{r}})\ . \tag{29a}$$

TABLE I. Optical-phonon deformation potentials d_0, and corrections Δd_0^H and Δd_0^M as described in text. The fourth column (d_0) gives our theoretical values. The next three columns are tight-binding results $d_0^{\text{FP-TB}}$, our first-principles TB values (Ref. 15); d_0^{TB}, $d_0^{\text{TB}*}$, sp^3, and sp^3s^* TB results from Ref. 3; d_0^{EPM}: empirical pseudopotential calculation (Ref. 3). The first-principles pseudopotential calculations from Refs. 18 and 26 (NM) are given in the next column, and the last column contains experimental data. All values are in eV.

Compound	d_0^{LMTO}	Δd_0^H	Δd_0^M	d_0	$d_0^{\text{FP-TB}}$	d_0^{TB}	$d_0^{\text{TB}^a}$	d_0^{EPM}	d_0^{NM}	Expt. d_0[a]
C	52.5	1.90	6.85	61.3	68.7	106.2	74.7	90.4	63.1	90, 69[b]
Si	20.9	0.97	5.20	27.1	36.0	45.8	32.9	35.0	29.8	40, 27[c,d]
Ge	22.4	2.43	4.45	29.3	33.9	42.3	29.8	34.7		34, 39[c]
AlAs	14.9	3.43	3.63	22.0	30.5	36.2	20.9			
AlP	14.4	3.68	4.01	22.1	29.5	37.9	21.4			
AlSb	16.1	2.55	2.68	21.3	29.0	31.8	19.0	34.0		37
BN	32.0	3.50	4.50	40.0	55.9	95.9	60.2	28.2		
BP	28.1	0.63	7.07	35.8	46.4	65.1	45.1	60.3		
BeO	13.1	5.94	2.39	21.4	31.8					
CdTe	5.7	7.11	6.01	18.8	14.8	19.4	9.2	22.8		22
GaAs	16.8	4.80	3.40	25.0	31.4	36.3	20.9	36.4	23.5	48,[e] 41[c]
GaP	16.2	4.37	3.73	24.3	31.1	38.1	21.5			44, 47[c]
GaSb	18.7	2.35	2.43	23.4	30.5	32.2	19.2	32.3		32
InAs	13.8	4.95	2.04	20.8	21.3	29.5	16.1	33.3		42
InP	10.1	5.48	4.51	20.1	24.8	30.5	16.3	35.6		35
InSb	14.3	2.85	2.60	19.7	25.3	26.9	15.2	26.8		39
MgS	6.7	6.79	1.76	15.2	16.0					
SiC	18.7	2.80	9.30	30.8	41.5	66.5	42.2			
SiGe	21.4	1.65	5.12	28.2	32.7					
ZnS	5.2	10.97	7.40	23.5	17.9	28.7	13.8	24.4		4
ZnSe	7.1	7.25	4.91	19.2	23.7	27.0	13.1	25.2		12, 27[c]
ZnTe	10.3	2.08	1.43	13.8	22.2	23.6	11.5	26.3		23

[a] All other experimental data are taken from Landolt-Börnstein, Ref. 11.

[b] C. Canali *et al.*, Ref. 12.

[c] P. Lawaetz, Ref. 13.

[d] C. Jacoboni *et al.*, Ref. 27.

[e] M. H. Grimsditch, D. Olego, and M. Cardona, Phys. Rev. B **20**, 1758 (1979).

The more distant neighbors give vanishingly small contributions to the perturbing potential $\Delta V_M^0(\mathbf{r})$.

The Madelung perturbation used in the calculation of $\Delta d'_M$ has a similar form:

$$\Delta V'_M(\mathbf{r}) = -\tfrac{512}{135}(240\pi)^{1/2}\frac{r^2}{a_0^3}\delta(q^{a1}+\tfrac{9}{80}q^{e2})Y_2^0(\hat{\mathbf{r}}) \ . \qquad (29b)$$

III. NUMERICAL RESULTS

Table I contains the d_0 values of selected elemental and compound semiconductors as well as the corrections caused by the perturbing potentials described in Secs. I and II. The values d_0^{LMTO} are those obtained from the self-consistent spherically symmetric potentials. Empirical pseudopotential results, d_0^{EPM}, were obtained by Blacha *et al.*,[3] and the same authors[3] also calculated d_0 ($d_0^{\mathrm{TB}}, d_0^{\mathrm{TB}*}$) from sp^3 and sp^3s^* tight-binding (TB) models.[2,25] Within the TB model, d_0 is given[2] by

$$d_0^{\mathrm{TB}} = \frac{32}{3\sqrt{3}}\frac{H_{xx}V_{xy}}{\{[(E_{pa}-E_{pc})/2]^2+H_{xx}\}^{1/2}} \ , \qquad (30)$$

where the matrix elements are as defined in Ref. 2, and E_{pa} and E_{pc} are the anion and cation p-level energies. Equation (30) further assumes that the interatomic p matrix elements scale[25] with the inverse bond length to the second power. The column labeled $d_0^{\mathrm{FP\text{-}TB}}$ lists d_0 values obtained from the same equation (30), but with H_{xx}, V_{xy}, E_{pa}, and E_{pc} as derived from our first-principles TB potential parameters.[15]

The calculated values of d' are given in Table II. In some cases we have also listed experimental values of d and the values of the internal-strain parameter ζ which we obtain from Eq. (4) using the calculated d', d_0, and the experimental d.

The nonspherical corrections (Tables I and II) to d_0 and d' are appreciable. For CdTe, for example, we find Δd_0^M as well as Δd_0^H almost as large as the "uncorrected" deformation potential d_0^{LMTO}. The valence-band maximum is the anion p state Γ_8^v. The corrections Δd_0^H to the splitting of this level are particularly large for the most ionic compounds. This is also to be expected since the number of valence electrons on the anion site is largest for the most ionic compounds, i.e., $\Delta V^H(\mathbf{r})$ is large. The chemical trends in Δd_0^H are illustrated in Fig. 1 showing Δd_0^H versus the first-principles ionicity values f_i^*.[15] It may appear surprising that Δd_0^M does not follow similar trends, but this is simply due to our particular way of dividing space into real-atomic spheres and empty-sphere regions. Thus, in diamond, for example, the two equivalent C sites have the same positive charge and the

TABLE II. Theoretical values (in eV) of d' and the nonspherical corrections $\Delta d'_H$ and $\Delta d'_M$ as explained in text. Experimental values, d(expt), of the deformation potential for the splitting of Γ_8^V are given in the fifth column (also in eV). The internal-strain parameter ζ is derived from d(expt) and our calculated d' and d_0 according to Eq. (4), whereas ζ(NM) gives the theoretical values calculated by Nielsen and Martin. Experimental internal-strain parameters are given in the last column, ζ (expt).

Compound	d'_{LMTO}	$\Delta d'_H$	$\Delta d'_M$	d'	d(expt)[a]	ζ	ζ(NM)	ζ(expt)
C	−2.72	0.27	0.65	−1.80			0.108[b]	
Si	−2.90	0.13	0.49	−2.28	−5.3	0.45	0.53[c]	0.73,[d] 0.54[f]
Ge	−1.90	0.18	0.42	−1.30	−5.0	0.51	0.44[c]	0.72,[d] 0.54[f]
AlAs	−3.90	0.70	0.34	−2.86				
AlP	−3.62	1.09	0.38	−2.16				
AlSb	−3.17	0.67	0.25	−2.25	−4.3	0.38		
BN	−4.19	2.61	0.42	−1.15				
BP	−3.65	1.18	0.67	1.80				
BeO	−3.55	4.67	0.22	1.34				
CdTe	−2.79	1.78	0.50	−0.51	−4.8	0.91		
GaAs	−2.67	1.36	0.32	−0.99	−4.5	0.56	0.48[c]	0.76[e]
GaP	−3.21	2.04	0.35	−0.82	−4.5	0.88		
GaSb	−2.72	1.33	0.22	−1.17	−4.6	0.99		
InAs	−2.25	1.46	0.22	−0.57	−3.6	0.58		
InP	−3.14	2.06	0.43	−0.65	−5.0	0.87		
InSb	−2.83	2.04	0.24	−0.55	−5.0	0.90		
MgS	−2.90	0.47	0.17	−2.26				
SiC	−5.54	2.25	0.90	−2.39				
SiGe	−2.84	0.12	0.47	−2.25				
ZnS	−3.05	4.00	0.84	1.79	−3.7	0.93		
ZnSe	−3.02	2.76	0.56	0.30	−3.8	0.73		
ZnTe	−2.83	1.51	0.20	−1.12	−4.6	1.01		

[a] Landolt-Börnstein, Ref. 11.

[b] O. H. Nielsen, Ref. 26.

[c] O. H. Nielsen and R. M. Martin, Ref. 18.

[d] References 7 and 8.

[e] Koumelis *et al.*, Ref. 9.

[f] Cousins *et al.*, Ref. 29.

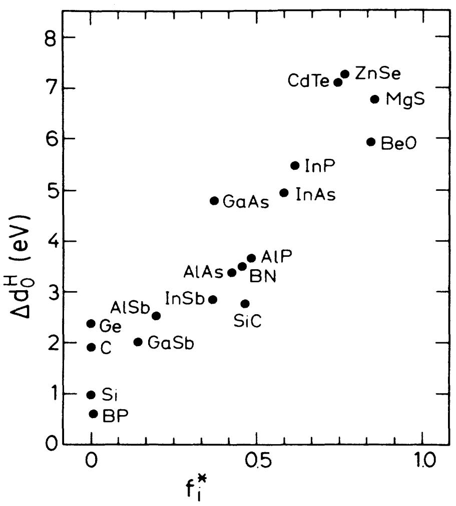

FIG. 1. On-site correction Δd_0^H to the deformation potential plotted vs the (first-principles) ionicity f_i^* (see Ref. 15). [The figure does not include ZnS for which Δd_0^H (Table I) is anomalously large.]

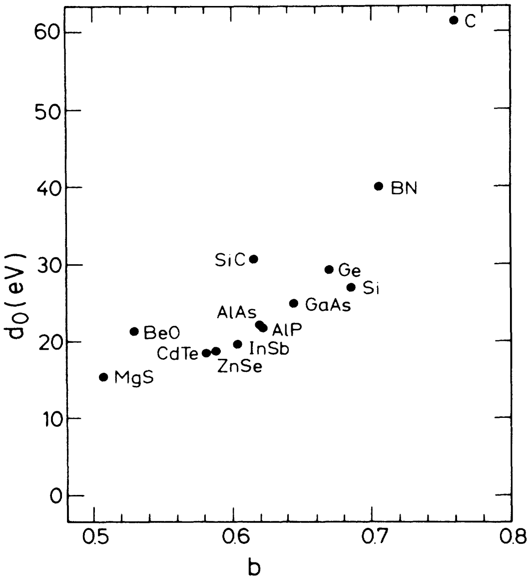

FIG. 2. "Chemical trend" of d_0 illustrated by plotting it against the sp^3 bond order b (see Ref. 15); $b \equiv \mathcal{B}-\mathcal{A}$, where $\mathcal{B}$ and $\mathcal{A}$ are the bonding and antibonding sp^3 projections integrated over the Brillouin zone.

empty spheres contain negative charge.

A plot similar to that of Fig. 2 was presented earlier,[15] where, however, only the uncorrected $d_0^{\rm LMTO}$ values were discussed. Figure 2 shows the theoretical d_0 potentials plotted against the sp^3 *bond order*. This is calculated[15] by projecting out the sp^3 bonding ($\mathcal{B}$) and antibonding ($\mathcal{A}$) components and subsequently integrating over k space. The bond order b is $b = \mathcal{B}-\mathcal{A}$. The increase of d_0 with b is what one would intuitively expect. A certain relative displacement of the sublattices produces a larger splitting of the bonding state in a compound with a strong sp^3 bond (large value of b) than in a compound with a weaker bond.

IV. SUMMARY AND CONCLUSION

By means of simple perturbation calculations it has been shown that the strain-induced changes in the nonspherical potential are essential in determining the splitting at the valence-band maximum. In general, the "on-site term" (Δd_0^H) is of the same order of magnitude as the correction to the surrounding lattice (Δd_0^M). The magnitude of the on-site term increases with ionicity because the Γ_8^v state is predominantly of anion character. In the cases where a comparison is possible, the theoretical d_0 values presented here are now closer to those obtained by Nielsen and Martin.[15,18,26] For C, Si, and GaAs their first-principles norm-conserving pseudopotential calculations gave $d_0 = 63.1$, 29.8, and 23.5 eV, respectively. Our results (Table I) 62.5, 28.8, and 25.1 eV are in excellent agreement with these. We therefore assume that our theoretical values for the other semiconductors are also quite accurate. Thus when comparing to experimental data as derived from Raman intensities and other experiments, we suggest that the large discrepancies between theory and experiment found in some cases essentially are due to an overestimate of the values as deduced from experimental data. In the case of Si this assumption is further supported by the large spread in the experimental data. The lowest values of d_0 are $\simeq 27$ eV,[13,27] i.e., much lower than the Raman value 40 eV. Only the low values agree with our theoretical data for Si.

Our theoretical results for d_0 are in most cases also lower than the tight-binding calculations, $d_0^{\rm TB}$ of Ref. 3. The sp^3s^* (TB*) calculations gave somewhat lower values for ZnSe, InSb, CdTe, AlAs, InAs, and InP even lower than ours. The general trends in d_0 are essentially reproduced by our crude[15] first-principles tight-binding calculations ($d_0^{\rm FB\text{-}TB}$). We use here the relation Eq. (30), although we know[15] that the hopping matrix elements do not scale with bond length as assumed by Harrison.[25] However, our scalings[15] were calculated from the volume dependence of the first-principles matrix elements, and our TB scheme has *volume dependent* diagonal matrix elements[15] (the band-center parameters). In Harrison's TB model the E_p's [Eq. (30)] are fixed (atomic) levels with no volume dependence. Thus, a direct comparison of the *volume* dependence of our V_{xy} and those of Refs. 3 and 25 is not very relevant. In the calculation of d_0 we do *not* need the *volume* dependence for $V_{xy'}$ $H_{xx'}$ but rather their bond length dependence for distortions with fixed volume. This kind of scaling may be quite different from that of Ref. 15, and in view of the work by Brey *et al.*,[28] we assume that it is in fact close to the d^{-2} (d is here the bond length) scaling used by Harrison.[25] This is the reason why the estimates $d_0^{\rm FP\text{-}TB}$ were evaluated with Eq. (30).

The d' values are also increased by the nonspherical perturbations (Table II). Although d' as well as d_0 both are affected by the corrections, we still find [from the experimental values of d with Eq. (4)] (Table II) internal-strain parameters ζ close to the values obtained earlier.[5,14,15] In the few cases where experimental data exist (apart from very recent data,[29] see note added) (e.g., Si, Ge, and GaAs) they are substantially larger than ours. The calculations by Nielsen and Martin[16,18,26] yield elastic constants, higher-order elastic constants, and phonon frequencies in excellent agreement with experiments. They also give, simultaneously, the theoretical values of the internal-strain parameter, and it would be difficult to explain why this particular quantity should be in error in their calculations when the other data are that close to experiments. The ζ values of Refs. 17 and 18 are close to ours. We suggest that the experiments have overestimated ζ for Si and GaAs.

Note added. At the time of submission of the present paper, Cousins *et al.*[29] have published results of careful analyses of surface effects in uniaxially stressed Si and Ge crystals. They find that such effects strongly influence the internal-strain parameters, and their revised values of ζ agree extremely well with theory (see "f" in Table II).

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