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Theory of optical-phonon deformation potentials in tetrahedral semiconductors

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A nonlocal pseudopotential theory of the optical-phonon deformation potentials in 11 diamond and zinc-blende semiconductors is presented. The one-phonon deformation potentials associated with the major conduction- and valence-band states at the Γ, *L*, and *X* point are calculated. The effect of the spin-orbit interaction on the optical deformation potentials is examined in detail. The published experimental data are compared both to one another and to the present theory. In addition, an analytical linear combination of atomic orbitals (LCAO) model is developed which predicts the optical deformation potentials for any tetrahedral semiconductor in a simple yet accurate way. The optical deformation potentials are presented for 37 semiconductors. The LCAO model also yields an analytical expression for the optical deformation potentials in terms of the observed optical gaps of the semiconductors.

I. INTRODUCTION

The dominant scattering mechanism of charge carriers in semiconductors is provided by the electron-phonon interaction except at the lowest temperatures. This paper is specifically concerned with the interaction between charge carriers and optical phonons in semiconductors. The electron—optical-phonon interaction enters the Ohmic and non-Ohmic mobility and provides the dominant energy-loss mechanism for warm and hot carriers.[1,2] It is responsible for the phonon Raman scattering and plays a crucial role in the free-carrier absorption.[1,3,4] The phonons which usually dominate in the scattering probability are long-wavelength optical phonons. In first-order Raman scattering processes this follows from momentum conservation and in transport this is the case for intravalley scattering.

The long-wavelength optical phonons set up a short-range potential in the crystal which shifts the electronic band states.[5] In polar semiconductors, the longitudinal optical phonons are also accompanied by a long-range macroscopic electric field which produces additional scattering. This long-range polar-optical interaction potential is strictly additive to the short-range potential[6,7] and its coupling constants are well established.[8] It will not be considered in this paper.

The nonpolar optical-phonon—electron interaction dominates in diamond-type crystals, particularly in *n*-Ge, and in the total (nonpolar plus polar) optical-phonon scattering rate for holes in *p*-Ge, *p*-Si, *p*-type III-V's, and II-VI's. The shifts of the band states per unit ionic displacement associated with a long-wavelength optical phonon are called deformation potentials.[5] The deduction of optical deformation potentials (ODP's) from either transport or Raman data is quite involved. The corresponding analysis of low-field transport data in *p*-type materials was developed by Bir and Pikus,[9] Lawaetz,[10] and Costato *et al.*,[11] and the deduced ODP's have been reviewed by Wiley.[12] A sensitive probe for ODP's is provided by the shifts and the broadening of the Raman lines with increasing carrier concentration as observed in *p*-type semiconductors. Such data were analyzed by Cerdeira and Cardona[13] for Si and Ge and recently by Lawaetz[14] for most standard semiconductors. The ODP's determined from Raman experiments have been reviewed by Richter.[4] Theoretical model calculations of ODP's have been performed mostly for Si (Ref. 15) and Ge (Refs. 16 and 17) and for a few other cases (see Table III). As a consequence of the rather indirect measurements, the ODP's which appear in the literature for a particular band state and material vary substantially, up to 50% and more.

In this paper we present a systematic theoretical investigation of optical deformation potentials for a large class of tetrahedral semiconductors. The purpose of this analysis is to establish a set of consistently determined values for the various optical deformation potentials in semiconductors. We have performed a nonlocal pseudopotential calculation of ODP's at the main high-symmetry points of the conduction and valence bands for 11 semiconductors. In addition, a simple LCAO model is developed which allows one to predict the ODP's for any tetrahedral semiconductor in an exceedingly simple yet quantitatively meaningful way; we present the results for 37 materials. Both methods give results consistent with one another and with the majority of the experimental data. The linear combination of atomic orbitals (LCAO) model yields analytical expressions for the ODP's in terms of the band structure and reveals the origin of the weak chemical trends of ODP's.

The outline of this paper is as follows. The precise meaning, the notation, and the symmetry properties of ODP's are given in Sec. II. Section III contains the detailed definitions of the ODP's for the various band states and $\vec{k}$ points. The main results of this paper appear in Tables III–VI, which summarize the outcome of the pseudopotential calculations presented in Sec. IV. In Sec. V the LCAO model is presented; its results are shown in Table VIII.

II. THE ELECTRON–OPTICAL-PHONON INTERACTION

A. Electron-phonon matrix elements

The matrix element for scattering from an electron state $\vec{k}$ in band n to $\vec{k}+\vec{q},n'$ with absorption of a single optical phonon with wave vector $\vec{q}$ can be written as

$$M_{kq}(\text{opt}) = \langle N_q - 1, n'\vec{k}+\vec{q} \,|\, H_{\text{opt}}(\vec{q},\vec{r}) \,|\, n\vec{k}, N_q \rangle \;, \tag{2.1}$$

where $H_{\text{opt}}(\vec{q},\vec{r})$ is the electric potential induced by the displacement field associated with the optical phonon and N_q is the phonon occupation number. In this paper we consider specifically scattering by long-wavelength optical phonons, $\vec{q}\rightarrow 0$, and intraband scattering, which includes the scattering between energetically degenerate states.

In general, the potential $H_{\text{opt}}(\vec{q},\vec{r})$ consists of long-range and short-range contributions. In polar crystals, the long-range part of $H_{\text{opt}}(\vec{q},\vec{r})$ gives rise to the polar-optical Fröhlich interaction. Here we will be concerned solely with the short-range part of $H_{\text{opt}}(\vec{q},\vec{r})$. It dominates in diamond-type crystals and in most p-type (diamond or zinc-blende) semiconductors.

In a long-wavelength optical phonon the two sublattices vibrate rigidly against each other. For a nondegenerate band state one can expand the Bloch function $|n\vec{k}+\vec{q}\rangle$ and $H_{\text{opt}}(\vec{q},\vec{r})$ in Eq. (2.1) in powers of $\vec{q}$. For $\vec{q}\rightarrow 0$ Eq. (2.1) can then be written in the form

$$\begin{aligned} M_{kq}(\text{opt}) &= \langle n\vec{k} \,|\, \vec{V}_{\text{opt}}(\vec{r}) \,|\, n\vec{k} \rangle \cdot \vec{u}_{\text{rel}} \\ &= \vec{D}_{\text{opt}}(\vec{k}) \cdot \vec{u}_{\text{rel}} \;. \end{aligned} \tag{2.2}$$

where $\vec{u}_{\text{rel}}$ is the relative sublattice displacement, which can be expanded in normal modes. $\vec{D}_{\text{opt}}(\vec{k})$ is the shift of the band-state energy per unit relative displacement of the sublattices by virtue of Feynman's theorem[18] and is called the optical deformation potential. For degenerate states, the long-wavelength limit is tricky because the Bloch functions are not analytic functions of the wave vector. The matrix element M_{kq} for this case has been given by Bir and Pikus[9] and Lawaetz.[10] In any case, however, the determination of the electron–one-optical-phonon scattering probability for a long-wavelength phonon can be reduced to the determination of band energy shifts induced by $\vec{u}_{\text{rel}}$. Terms of higher order in $\vec{q}$ in Eq. (2.2) are small and usually neglected.[19]

B. Notation

The space groups of the two crystal classes considered are O_h^7 (diamond) and T_d^2 (zinc blende). The three optical phonon branches at $\vec{q}=0$ transform as (xy,yz,zx), which corresponds to the point group representation Γ_{25}^+ for O_h^7 and to Γ_{15} for T_d^2. Henceforth, we treat the representations of O_h^7 and T_d^2 together and use the notation $\Gamma_{25}^+(\Gamma_{15})$. The splitting of transverse optical and longitudinal optical modes at $\vec{q}=0$ in zinc-blende crystals can be ignored for our purposes; this is consistent with the neglect of the long-range fields. From the point of view of symmetry, the $\vec{q}=0$ optical phonons can be treated in the same manner as the traceless part of a strain caused by a $\langle 111 \rangle$ stress with $\Gamma_{25}^+(\Gamma_{15})$ symmetry.[20] The physical parameters and the actual atomic displacements are different, however, for a macroscopic strain and a purely internal strain as represented by $\vec{u}_{\text{rel}}$.

Kane[21] and Richter[4] have introduced a unified notation for deformation potentials which we follow in this paper. The optical one-phonon deformation potential for a particular band and wave vector $\vec{k}$ is denoted by

$$d_{io}^{5} \equiv d_{io} \;, \tag{2.3}$$

where i denotes the irreducible representation of the group of $\vec{k}$ obtained from decomposing the $\Gamma_{25}^+(\Gamma_{15})$ deformation according to this group. The subscript o is used to distinguish optical phonons from stress-induced deformation potentials. The superscript comes from the phonon representation and will be omitted since we consider only $\vec{q}=0$ phonons. The various specific optical deformation potentials are defined in detail below.

C. Selection rules

A general group-theoretical analysis of deformation potentials has been given in Ref. 21. In the present paper the symmetry-allowed ODP's have been obtained by imposing two symmetry requirements on the electron-phonon matrix element. We consider an electronic band state at $\vec{k}$ which transforms according to the spin representation $D_{\text{el}}^{\text{spin}}$. Assume that this representation arises from the single-valued representation $D_{\text{el}}^{\text{single}}$. By D_{ph} we denote an irreducible representation of the phonon deformation with respect to the group of $\vec{k}$. Since we are concerned with intraband scattering, the symmetric Kronecker product of the representations which characterize the state $\vec{k}$ enters the matrix element. This gives the first condition,

$$\text{(I)}\quad (D_{\text{el}}^{\text{spin}}\times D_{\text{el}}^{\text{spin}})_{\text{sym}}\ \text{must contain}\ D_{\text{ph}}\ . \tag{2.4}$$

The second condition results from a slight approximation, namely the neglect of any strain dependence of the spin-orbit interaction. In other words, it is assumed that H_{opt} in Eq. (2.1) does not act on the spin variables. We have not used this approximation in our actual calculations which are presented in Sec. IV, but it greatly facilitates the symmetry analysis. This will be discussed further in Sec. IV. As a consequence of this assumption the matrix elements must also be invariant with respect to the spatial part alone, i.e.,

$$\text{(II)}\quad (D_{\text{el}}^{\text{single}}\times D_{\text{el}}^{\text{single}})_{\text{sym}}\ \text{must contain}\ D_{\text{ph}}\ . \tag{2.5}$$

III. DEFINITION OF THE OPTICAL DEFORMATION POTENTIALS

A. Γ point, $\vec{k}=(0,0,0)$

To first order in $\vec{u}_{\text{rel}}$, the relative sublattice displacement $\vec{u}_{\text{rel}}=\vec{u}_1-\vec{u}_2=2\vec{u}_1=-2\vec{u}_2$ splits the fourfold-degenerate states of $\Gamma_8^+(\Gamma_8)$ symmetry but leaves all other states unaffected.[22] The splitting ΔE_Γ of the $\Gamma_8^+(\Gamma_8)$ valence band, i.e., the splitting of the light- and heavy-hole band induced by $\vec{u}_{\text{rel}}$, is governed by the deformation potential d_{5o}. It is defined by

$$\Delta E_\Gamma=\frac{1}{\sqrt{2}}\frac{|\vec{u}_{\text{rel}}|}{a}d_{5o}\ . \tag{3.1}$$

Here a is the lattice constant. The splitting is independent of the direction of $\vec{u}_{\text{rel}}$ and preserves the center of gravity of the $\Gamma_8^+(\Gamma_8)$ band, since $\vec{u}_{\text{rel}}$ is a traceless deformation. It is more common, particularly in transport studies, to define a deformation potential d_o which is related to Eq. (3.1) by

$$d_o=\frac{1}{\sqrt{2}}d_{5o}\ . \tag{3.2}$$

Based on Ref. 9, Lawaetz[10] has derived the expression for the optical-phonon—induced transition rate for states in the vicinity of the $\Gamma_8^+(\Gamma_8)$ valence band extremum in terms of d_o [see Eq. (2.31) of Ref. 10]. The definition Eq. (3.2) for d_o also agrees with the one used in Refs. 20, 23, and 24, while Bir and Pikus[9] introduced the constant $d_o(\text{Bir-Pikus})=d_o/a$.

B. L point, $k=(2\pi/a)(\pm\frac{1}{2},\pm\frac{1}{2},\pm\frac{1}{2})$

At L the phonon displacement decomposes into $\Gamma_{25}^+\rightarrow L_1^+ + L_3^-$ $(\Gamma_{15}\rightarrow L_1+L_3)$. The L_1 part of the deformation causes a shift δE_L of each band edge,

$$\delta E_L=d_{1o}\frac{\hat{e}_{\text{valley}}\cdot\vec{u}_{\text{rel}}}{2a}\ , \tag{3.3}$$

where $\hat{e}_{\text{valley}}$ is a unit vector parallel to the vector location of the valley minimum. Equation (3.3) holds for each band, giving $d_{1o}(\text{con})$, $d_{1o}(\text{val})$, and $d_{1o}(\text{split})$ for the conduction band, the upper valence band, and the split-off valence band, respectively. In addition, the difference $d_{1o}(\text{diff})=d_{1o}(\text{con})-d_{1o}(\text{val})$ is a useful quantity by itself since it enters the Raman tensor. In transport studies of n-Ge it is common to introduce a deformation potential D [see Eq. (3.6.7) of Ref. 1] which is related to Eq. (3.3) by

$$D=\frac{d_{1o}(\text{con})}{2a}\ . \tag{3.4}$$

In the approximation that the strain dependence of the spin-orbit interaction is neglected, $d_{1o}(\text{val})=d_{1o}(\text{split})$. If the spin-orbit interaction is neglected altogether, the L_3 part of $\vec{u}_{\text{rel}}$ splits the doubly degenerate valence band edge $L_3^-(L_3)$ by

$$\Delta E_L = \frac{|\hat{e}_{\text{valley}} \times \vec{u}_{\text{rel}}|}{a} d_{3_o} \ . \tag{3.5}$$

With spin-orbit interaction included, the deformation potential d_{3_o} causes an interband coupling of the valence band and split-off band. It is significant for the E_1 gap deformation potential Raman scattering.[4]

C. Δ axis, X point, $\vec{k} = (0,0,k)$

These ODP's are relevant mainly for Si, so we consider only the diamond structure. Along Δ there are no intraband ODP's. At X the conduction- as well as the valence-band edge is fourfold degenerate and will be split by $\vec{u}_{\text{rel}}$ by an amount ΔE_X. The point group notation and Kane's classification is not applicable at X. We therefore introduce deformation potentials $d_{Xo}(\text{cond})$ and $d_{Xo}(\text{val})$ by

$$\Delta E_X = \frac{|\hat{e}_{\text{valley}} \cdot \vec{u}_{\text{rel}}|}{a} d_{Xo} \ . \tag{3.6}$$

The ODP D_o introduced in Ref. 25 is related to Eq. (3.6) by

$$D_o = \frac{1}{2\sqrt{3}} d_{Xo}(\text{con}) \ . \tag{3.7}$$

D. The role of the spin-orbit interaction

The definition of d_{5_o} given in Sec. III A tacitly assumes that the splitting ΔE_Γ induced by $\vec{u}_{\text{rel}}$ is small compared to the spin-orbit splitting Δ_0. This can be seen as follows. In the opposite case of negligible Δ_0 one deals with a triply degenerate $\Gamma_{25}^{+}(\Gamma_{15})$ state which behaves differently under the phonon displacement than a $\Gamma_8^{+}(\Gamma_8)$ state. Specifically, for $\vec{u}_{\text{rel}} = (a/4)(\delta,\delta,\delta)$ the $\Gamma_{25}^{+}(\Gamma_{15})$ state splits into a doublet and a singlet state. The energy difference between these states is for spin-orbit << strain,

$$\Delta E(\Gamma_{25}^{+}) = (\tfrac{3}{2})^{3/2} \frac{\delta}{4} d_{5_o} \ . \tag{3.8}$$

In the limit of large Δ_0, on the other hand, the fourfold $\Gamma_8^{+}(\Gamma_8)$ band splits into two states while the split-off band remains unchanged; we have for spin orbit >> strain,

$$\Delta E(\Gamma_8^{+}) = (\tfrac{3}{2})^{1/2} \frac{\delta}{4} d_{5_o} \ . \tag{3.9}$$

Although the same ODP constant d_{5_o} enters in both cases (Δ_0 is considered to be independent of strain), the energy splittings differ by a factor $\frac{3}{2}$ in the two limits. We remark that this difference is strongly enhanced for the second-order deformation potentials at Γ, i.e., for the energy splittings which are of second order in $\vec{u}_{\text{rel}}$. In the limit of Eq. (3.9) they are $\sim d_{5o}^2/\Delta_0 \approx 60\,000$ eV for Si. For negligible Δ_0, however, they are only ≈ 50 eV.[16]

In transport as well as in optics the limit of large spin-orbit splitting is appropriate, even for the lightest semiconductors. In the case of hole scattering, for example, the mean atomic displacement associated with all optical phonons is roughly $[\hbar/(M\omega_0)]^{1/2} \approx 0.05$ Å. The phonons which contribute to the hole scattering rate have $|\vec{q}| \lesssim \frac{1}{10}$ BZ (Brillouin zone), i.e., only 10^{-3} of all phonons contribute. The displacements associated with them are therefore $\langle u_{\text{opt}}^2 \rangle^{1/2} \approx 5 \times 10^{-5}$ Å. Even for diamond $\Delta_0 = 0.002$ eV so that the condition $\Delta E_\Gamma << \Delta_0$ is well fulfilled. A similar result follows from an estimation of $\langle u_{\text{opt}}^2 \rangle^{1/2}$ in Raman experiments.[4]

IV. PSEUDOPOTENTIAL THEORY

The ODP's represent the first-order change in the band structure when the sublattices of the crystals are displaced against each other. They depend on the perfect-crystal potential and its change with the sublattice separation. First-order electron-phonon matrix elements can be generally expressed in terms of the pseudo-wave-functions and pseudopotentials, as was proved by Sham.[26] Thus pseudopotential theory provides a quantitative as well as a convenient scheme to calculate deformation potentials.

A. Formalism

Here we shall adopt the nonlocal empirical pseudopotential method with inclusion of the spin-orbit interaction.[27] For the perfect crystal, the Hamiltonian consists of a spatial part H plus the spin-orbit Hamiltonian H^{SO}. The former is given[27]

$$\begin{aligned} H_{\vec{K}\vec{K}'} = {} & \frac{\hbar^2}{2m} K^2 \delta_{\vec{K}\vec{K}'} + [V^S(|\vec{K}-\vec{K}'|) + V^S_{NL}(\vec{K},\vec{K}')] \cos[(\vec{K}-\vec{K}')\cdot\vec{\tau}] \\ & + i[V^A(|\vec{K}-\vec{K}'|) + V^A_{NL}(\vec{K},\vec{K}')] \sin[(\vec{K}-\vec{K}')\cdot\vec{\tau}] \ , \end{aligned} \tag{4.1}$$

$$V_{NL}^{S,A} = (V_{NL}^1 \pm V_{NL}^2)/2,\quad \vec{\tau} = \frac{a}{8}(1,1,1)\,, \tag{4.2}$$

$$V_{NL}^i(\vec{K},\vec{K}') = \frac{4\pi}{\Omega_a}\sum_{l=0,2} A_l^i(2l+1)P_l(\cos\theta_{\vec{K}\vec{K}'})F_l^i(K,K')\,, \tag{4.3}$$

$$A_0^i = \alpha_0^i + \beta_0^i\frac{\hbar^2}{2m}(KK' - k_F^2),\quad A_2^i = \alpha_2^i\,, \tag{4.4}$$

$$F_l^i(K,K') = \int_0^\infty dr\, r^2 j_l(Kr) f_l^i(r) j_l(K'r)\,, \tag{4.5}$$

$$f_l^i(r) = \theta(R_l^i - r)\ \text{or}\ \exp(-r^2/R_l^{i2})\,. \tag{4.6}$$

In these equations, $\vec{K} = \vec{k} + \vec{G}$ and $\vec{K}' = \vec{k} + \vec{G}'$, where $\vec{k}$ is the wave vector in the first BZ and $\vec{G}$ and $\vec{G}'$ are reciprocal-lattice vectors. V^S and V^A are the local symmetric and antisymmetric form factors, a is the lattice constant, Ω_a the atomic volume, and $k_F = (96\pi^2)^{1/3}/a$ the Fermi momentum. $P_l(x)$ denote the Legendre polynomials, $\theta_{\vec{K}\vec{K}'}$ is the angle between $\vec{K}$ and $\vec{K}'$, and the $j_l(x)$ are the spherical Bessel functions. Following Ref. 27, for the lth angular momentum component of the nonlocal potential form factors $f_l^i(r)$ we generally use a square well; for Ge, GaAs, and ZnSe a Gaussian with radius R_l^i is used. The superscript i denotes the atomic species $i = 1,2$. Only $l = 0$ and $l = 2$ are included in the sum on the right-hand side of Eq. (4.3). The integral in Eq. (4.5) can be evaluated explicitly.[28] The material parameters entering this Hamiltonian are summarized in Table I.

The spin-orbit Hamiltonian is

TABLE I. Pseudopotential parameters for the tetrahedral semiconductors.

				Form factors (Ry)					Lattice
Compound	$V^S(3)$	$V^S(4)$	$V^S(8)$	$V^S(11)$	$V^A(3)$	$V^A(4)$	$V^A(8)$	$V^A(11)$	constant (Å)
Si	−0.257	−0.203	−0.040	0.033	0	0	0	0	5.43
Ge	−0.221	−0.160	0.019	0.056	0	0	0	0	5.65
α-Sn	−0.190	−0.144	−0.008	0.040	0	0	0	0	6.49
GaP	−0.230	−0.166	0.020	0.057	0.100	0.070	0.035	0.025	5.45
GaAs	−0.214	−0.157	0.014	0.067	0.055	0.038	0.008	0.001	5.65
GaSb	−0.220	−0.163	0.005	0.045	0.040	0.030	0.007	0.000	6.10
InP	−0.235	−0.176	0.000	0.053	0.080	0.060	0.033	0.030	5.86
InAs	−0.230	−0.172	0.000	0.045	0.055	0.045	0.020	0.010	6.05
InSb	−0.200	−0.153	−0.010	0.044	0.044	0.030	0.017	0.015	6.47
ZnSe	−0.218	−0.155	0.029	0.064	0.139	0.062	0.023	0.016	5.65
CdTe	−0.220	−0.165	0.00	0.062	0.060	0.050	0.029	0.025	6.48

			Nonlocal parameters					Radii (Å)		
		Cation			Anion		Cation		Anion	
Compound	α_0 (Ry)	β_0	A_2 (Ry)	α_0 (Ry)	β_0	A_2 (Ry)	R_0	R_2	R_0	R_2
Si	0.55	0.32	0	0.55	0.32	0	1.06	0	1.06	0
Ge[a]	0	0	0.275	0	0	0.275	0	1.22	0	1.22
α-Sn	0	0.40	0.70	0	0.40	0.70	1.06	1.41	1.06	1.41
GaP	0	0.30	0.40	0.32	0.05	0.045	1.27	1.180	1.06	1.180
GaAs[a]	0	0	0.125	0	0	0.625	1.27	1.223	1.06	1.223
GaSb	0	0.20	0.20	0	0.30	0.60	1.27	1.321	1.06	1.321
InP	0	0.25	0.55	0.30	0.05	0.35	1.27	1.269	1.06	1.269
InAs	0	0.35	0.50	0	0.25	1.00	1.27	1.310	1.06	1.310
InSb	0	0.45	0.55	0	0.48	0.70	1.27	1.40	1.06	1.40
ZnSe[a]	0	0	−0.125	0	0	0.925	0	1.223	0	1.223
CdTe	0	0.4	0.00	1.37	0.4	2.00	1.37	1.40	1.06	1.40

[a] Gaussian nonlocal well.

$$H_{ss'}^{\mathrm{SO}}(\vec{\mathrm{K}},\vec{\mathrm{K}}') = (\vec{\mathrm{K}} \times \vec{\mathrm{K}}') \cdot \vec{\sigma}_{ss'} \left[\frac{a}{(2\pi)} \right]^2 \{ -i\lambda^S(K,K') \cos[(\vec{\mathrm{K}} - \vec{\mathrm{K}}') \cdot \vec{\tau}] + \lambda^A(K,K') \sin[(\vec{\mathrm{K}} - \vec{\mathrm{K}}') \cdot \vec{\tau}] \} , \tag{4.7}$$

$$\lambda^{S,A} = (\lambda_1 \pm \lambda_2)/2 , \tag{4.8}$$

$$\lambda_1(K,K') = \mu B_{n_1}(K) B_{n_1}(K') , \tag{4.9}$$

$$\lambda_2(K,K') = \alpha\mu B_{n_2}(K) B_{n_2}(K') , \tag{4.10}$$

$$B_2(K) = (1+\kappa_2^2)^{-3}, \;\; B_3(K) = (5-\kappa_3^2)/[5(1+\kappa_3^2)^4] , \tag{4.11}$$

$$B_4(K) = (5-3\kappa_4^2)/[5(1+\kappa_4^2)^5] . \tag{4.12}$$

This model for the spin-orbit pseudo-Hamiltonian is due to Bloom and Bergstresser.[29] In Eq. (4.7), s and s' are the spin states, $\vec{\sigma}$ are the Pauli matrices, and μ and α are given in Table II. The B_{n_i} arise from integrals involving the outermost p-core states of the atom of species i, where n_i is their principal quantum number. Hence $n_i = 2,3,4$ for the Si-, Ge-, and Sn-row atoms. The parameters $\kappa_n = K(a_B/\zeta_n)$ contain the dimensionless radial extent parameter ζ_n of these core states, given in Table II, and a_B is the Bohr radius.

The material parameters of the Hamiltonian equations (4.1) and (4.7) are fitted to reproduce the known energy gaps of the various semiconductors. They generally agree with the values given in Ref. 27; since the parameters ζ_n and α were not given there, however, we have obtained somewhat different spin-orbit parameters.

For the calculation of the band structure, the Hamiltonian equation (4.1) is diagonalized in a basis of 89 plane waves. Then H^{SO} is diagonalized in the basis of the resulting Bloch eigenstates; for our purposes it is sufficient to include the 15 lowest states.

Next we calculate the crystal potential of the deformed crystal, with the two sublattices rigidly shifted against each other. For this purpose we use the rigid-ion approximation and assume that the ionic pseudopotentials move rigidly with the ions. With this approximation a relative sublattice shift $\vec{\mathrm{u}}_{\mathrm{rel}} = (a/4)(\delta,\delta,\delta)$ affects the Hamiltonian equations (4.1) and (4.7) in two ways. (i) The vectors $\vec{\tau}$ in Eqs. (4.1) and (4.7) are replaced by

$$\vec{\tau}_{\mathrm{displaced}} = \vec{\tau} + (a/8)(\delta,\delta,\delta) . \tag{4.13}$$

(ii) The local form factors $V^S(4)$ and $V^A(8)$ contribute to the Hamiltonian equation (4.1). For the perfect lattice, these two form factors drop out due to the symmetry. We have obtained these additional form factors by a smooth (cubic spline) interpolation through the given Fourier coefficients of V^S and V^A.

The ODP's can now be obtained by diagonalizing numerically the total Hamiltonian at $\vec{\mathrm{k}} = \Gamma,X,L$ for several displacements. We have chosen

TABLE II. Spin-orbit parameters for the tetrahedral semiconductors.

Compound	Spin-orbit parameters ζ_{cation}	ζ_{anion}	α	μ (Ry)
Si	4.60	4.60	1.00	0.0
Ge	5.34	5.34	1.00	0.000 69
α-Sn	4.95	4.95	1.00	0.002 25
GaP	5.34	4.60	0.52	0.0
GaAs	5.34	5.34	2.58	0.000 80
GaSb	5.34	4.95	5.58	0.000 462
InP	4.95	4.60	0.20	0.000 76
InAs	4.95	5.34	1.00	0.001 13
InSb	4.95	4.95	2.16	0.001 12
ZnSe	5.34	5.34	7.78	0.000 105
CdTe	4.95	4.95	5.73	0.000 46

$0 < \delta < 0.001$. The resulting band-energy changes are fitted to a polynomial in δ and the first-order coefficients give the ODP's.

B. Results

The resulting deformation potentials are presented in Tables III–VI for 11 semiconductors. These tables contain the central results of this work. It should be noted that no parameters have been adjusted to fit the properties of the deformed crystal; only the perfect-crystal band structure has been considered as input to this calculation.

1. Comparison with experiment

Our results show that all deformation potentials exhibit rather weak chemical trends. This imposes limits on the various ODP's and can provide a useful criterion for the reliability of experimental values. For example, the published values for d_{3o} vary from 19 to 41 eV in GaAs, while other data give $d_{3o} = 37$ eV for Si. Our calculation strongly supports $d_{3o} \approx 40$ eV for Si as well as for GaAs and generally predicts a result close to 40 eV for all semiconductors.

We have already remarked that the determination of ODP's from experimental data is rather involved. As a consequence it is often difficult to distinguish strictly between "experimental" and "theoretical" values. It is probably best to compare theory and experiment for d_{5o} or d_o where most of the data are available. This is done in Table III. Comparing the present pseudopotential results for d_o with the values deduced from the observed shifts and broadening of Raman lines with carrier concentration (Refs. 13 and 14), we find the latter to be systematically higher than the calculated values by 20–30%. In part, this discrepancy can originate in the approximations involved in our pseudopotential model. They are likely to affect the results by roughly 10% as will be discussed below. In addition, two effects were neglected in the determination of d_o in Refs. 13 and 14 which could account for this discrepancy: d_o is proportional to the electron-phonon matrix element of zeroth order in the phonon wave vector [see Eq. (2.2)]. The first-order term is usually neglected but has been shown[19] for n-Si to increase the total scattering rate by 10–20%. This effect is generally present and will—when not taken into account explicitly—renormalize and increase the apparent d_o values. Two-phonon scattering is expected to show the same trend.[41,42]

Next we consider the ODP's at L. Our calculated deformation potentials, given in Tables IV and V, generally agree well with experiment. We note that the Raman experiments are sensitive to the ratio d_{3o}/d_{1o}(diff) given in Table V but less so to the separate deformation potential constants given in Table IV. Generally we conclude that the ODP's presented here agree with the majority of the experimental values within the experimental uncertainties. The ODP's at the X point are given in Table VI for Si, Ge, and α-Sn.

2. Strain dependence of the spin-orbit interaction

The strain dependence of H^{SO} in Eq. (4.7) results from the strain dependence of the sublattice separation $\vec{\tau}$. This strain dependence implies additional symmertry-allowed ODP's which we did not consider in Sec. III, e.g., there is a nonzero d_{3o}(con). For acoustic phonons, the effect of this strain dependence of H^{SO} is quite noticeable.[48,49] We find, however, that it plays a negligible role for the optical deformation potentials.

The difference of d_{1o}(val) and d_{1o}(split) comes solely from the strain dependence of H^{SO} and is seen to be small from Table IV. In addition, we have calculated d_{5o} and d_{1o}(con) by artificially ignoring the sublattice displacement $\vec{u}_{\mathrm{rel}}$ in H^{SO}, thereby keeping H^{SO} strain independent. For α-Sn, where the effect should be largest, the resulting deformation potentials d_{5o} and d_{1o}(con) differ by less than 2% from those given in Tables III and IV. Furthermore, we find for the above-mentioned ODP $d_{3o}(\mathrm{con}) \lesssim 1$ eV which is about the limit of our numerical resolution.

3. Numerical tests of approximations

Several tests have been performed to estimate the accuracy of the presented results. As customary in the empirical pseudopotential theory, the local pseudopotential form factors V^S and V^A are truncated at $|\vec{G}|^2 = 11$. If $V^S(12)$ is included, the ODP d_{5o} slightly increases for all semiconductors by 2–5%. A variation of the interpolated form factors $V_S(4)$ and $V_A(8)$ by 10% alters the ODP's by typically 4%. It is also gratifying that the nonlocal pseudopotential calculation gives results which are close to those obtained with local pseudopotential models.[15,16] Using the local form factors of Ref. 50 or the self-consistent local pseudopotential of Ref. 51 for Si, we find $d_{5o} = 53.8$ and 56.6 eV, respec-

TABLE III. The optical deformation potentials d_o and $d_{5o} = d_o\sqrt{2}$ for the upper valence-band edge at the Γ point. For the definitions, see Sec. III A.

	Theory			Experiment
	This work		Previous results	
Compound	d_{5o} (eV)	d_o (eV)	d_o (eV)	d_o (eV)
Si	53.6	37.9	39.5,[a]38.1,[a] 40.0,[d]32.5[e]	26.6,[b]27.0,[c] (24.4–33.6)[f]
Ge	52.3	37.0	40.0,[d]31.4,[g] 28.3,[j]33.0,[k] 38.0[m]	41.6,[h]40.3,[i] 36.0,[l]39.0,[c] (29.0–33.2)[f]
α-Sn	42.9	30.3	24.0[n]	
GaP	37.5	26.5	44.0,[d]26.3[p]	47.0[c]
GaAs	41.1	29.1	41.0,[d]31.5[q]	41.0,[c]48.0[r]
GaSb	41.4	29.3	39.0[d]	32.0[c]
InP	44.9	31.7	42.0[d]	35.0[c]
InAs	40.3	28.5	42.0[d]	
InSb	40.2	28.4	39.0,[d]24.0[n]	
ZnSe	30.6	21.6	27.0[s]	27.0[c]
CdTe	43.1	30.5		22.0[c]

[a] Reference 15.
[b] Reference 30.
[c] Reference 14.
[d] Reference 12.
[e] Reference 31.
[f] Reference 13.
[g] Reference 17.
[h] Reference 32.
[i] Reference 33.
[j] Reference 34.
[k] Reference 20.
[l] Reference 35.
[m] Reference 16.
[n] Reference 36.
[p] Reference 37.
[q] Reference 38.
[r] Reference 39.
[s] Reference 40.

tively. This compares favorably with the present result of $d_{5o} = 53.6$ eV.

The main approximation used in this paper is the rigid-ion approximation. A large number of lattice-dynamical quantities has been successfully predicted or reproduced by using this approximation, e.g., acoustic deformation potentials,[6,52,53] the pressure dependence of gaps,[54] and the long-wavelength phonon spectrum.[55] For long-wavelength distortions it is therefore very unlikely that this approximation causes serious errors.

V. LCAO THEORY

We finally present a semiquantitative LCAO method which predicts optical deformation potentials (ODP's) in an exceedingly simple and general way for all semiconductors. It relates the ODP's to optical band gaps of the semiconductor and explains the weak chemical trend which is observed for the ODP's.

In this method,[56,57] the perfect-crystal Hamiltonian H_0 is represented in an orthonormal set of localized basis functions. Four basis states per atom, namely one s and three p functions, will be used and only nearest-neighbor interactions are included. The diagonal elements of H_0 are the orbital energies $\epsilon_s^{\text{anion}}$, $\epsilon_p^{\text{anion}}$, $\epsilon_s^{\text{cation}}$, and $\epsilon_p^{\text{cation}}$. From symmetry, there are four[58] nearest-neighbor Hamiltonian matrix elements $V_{ss\sigma}$, $V_{pp\sigma}$, $V_{pp\pi}$, and $V_{sp\sigma}$. Instead of constructing the basis functions and the Hamiltonian explicitly, these matrix elements are considered as parameters and are fitted to the band structure at high symmetry points.

Only during the last five years or so this old method, which has its roots in the 1950's, has been systematically applied to a broad spectrum of properties of solids and could be given a firm theoretical basis. We refer to the recent books by Harrison[57] and Heine and co-workers[59] for a review.

The keypoint of this empirical LCAO method lies in the remarkably simple and pronounced chemical trends of the Hamiltonian matrix elements. Harrison[57] found that for all semiconductors (i) the diagonal elements of H_0 are, in a good approximation, equal to the outermost s- and p-orbital energies

TABLE IV. The optical deformation potentials d_{1o}(split), d_{1o}(val), and d_{1o}(cond) for the split-off valence band, the upper valence-band edge, and the lower conduction-band edge at the L point, respectively. Previously calculated values are cited in parentheses below the theoretical results.

Compound	d_{1o}(split) (eV)	d_{1o}(val) (eV)	d_{1o}(cond) (eV)
Si	-16.4	-16.4	-10.4
	(-11^{a})	(-11^{a})	(-5.2^{a})
Ge	-10.7	-10.2	-27.7
	$(-17,^{b}-5^{c})$	$(-17,^{b}-5^{c})$	$(-5,^{b}-8^{c})$
α-Sn	-8.8	-7.3	-29.2
GaP	-11.4	-11.4	-17.7
GaAs	-11.8	-11.1	-21.7
GaSb	-12.9	-11.9	-30.6
InP	-14.5	-14.1	-24.8
InAs	-11.9	-11.1	-33.0
InSb	-11.5	-10.2	-28.0
	(-12^{d})	(-12^{d})	(-26^{d})
ZnSe	-14.6	-14.2	-8.9
CdTe	-18.8	-17.4	-27.5

[a] Reference 31.

[b] Reference 17.

[c] Reference 43.

[d] Reference 36.

TABLE V. The interband optical deformation potential d_{3o} and the ratio of d_{3o} and $d_{1o}(\text{diff}) = d_{1o}(\text{cond}) - d_{1o}(\text{val})$ at the L point. Only in GaAs is d_{3o} known experimentally (Ref. 39), $d_{3o}(\text{GaAs}) = 37.0$ eV.

	d_{3o} (eV) Theory		$\lvert d_{3o}/3_{1o}(\text{diff})\rvert$ Theory		
Compound	(This work)	(Previous results)	(This work)	(Previous results)	Experiment
Si	44.8	37.0,^{a} 15.4^{a}	7.5	6.4^{a}	
Ge	48.3	40.0,^{b} 33.0^{d}	2.8	3.3,^{b} 4.5,^{d} 7.14^{d}	1.5^{c}
α-Sn	37.6	18.0^{e}	1.7		3.5^{e}
GaP	38.5		6.1		
GaAs	40.3	41.0,^{f} 37.0,^{e} 19.0^{e}	3.8	0.6^{f}	3.0^{g}
GaSb	38.7		2.1		
InP	43.3	41.0^{h}	4.0		
InAs	40.3		1.8		2.0^{i}
InSb	38.2	31.0^{e}	2.1	2.0^{e}	7.0^{c}
ZnSe	28.9		5.5		
CdTe	42.5		4.2		

[a] Reference 31.

[b] Reference 17.

[c] Reference 44.

[d] Reference 4.

[e] Reference 36.

[f] Reference 38.

[g] Reference 45.

[h] Reference 46.

[i] Reference 4.

TABLE VI. The optical deformation potentials d_{X_0}(val) and d_{X_0}(cond) for the upper valence-band edge and the lower conduction-band edge at the X point, respectively. Previously determined values are cited in parentheses below the present theoretical results.

Compound	d_{X_0}(val) (eV)	d_{X_0}(cond) (eV)
Si	29.0 (17.5[a])	23.2 (28.0[b])
Ge	24.8	35.3
α-Sn	21.2	28.4

[a] Reference 31. [b] Reference 25.

of the free atoms and (ii) that the matrix elements $V_{ll'm}$ are universal functions of the nearest-neighbor distance $\tau = |\vec{\tau}|$,

$$V_{ll'm} = \eta_{ll'm}\tau^{-2} , \tag{5.1}$$

with coefficients η independent of the atomic constituents of the tetrahedral semiconductor. The physical origin of this behavior is discussed at length in Ref. 57.

We wish to apply this method to ODP's and particularly consider the deformation potential at Γ, namely d_o. Following Ref. 56, we first transform the $V_{ll'm}$ to a x,y,z basis. If $\vec{\tau}_j$ are the vectors pointing from the central site to the four nearest neighbors.

$$\begin{aligned} V_{xx} &\equiv \langle \phi_{xa} \,|H|\, \phi_{xc}^{j} \rangle \\ &= \cos^2(\theta_{jx}) V_{pp\sigma} + [1 - \cos^2(\theta_{jx})] V_{pp\pi} , \end{aligned} \tag{5.2}$$

$$\begin{aligned} V_{xy} &\equiv \langle \phi_{xa} \,|H|\, \phi_{yc}^{j} \rangle \\ &= \cos(\theta_{jx})\cos(\theta_{jy})(V_{pp\sigma} - V_{pp\pi}) . \end{aligned} \tag{5.3}$$

Here θ_{jx} is the angle between $\vec{\tau}_j$ and the x axis and we have put the anion (labeled by a) in the center, while the cations (label c) are at $\vec{\tau}_j$. Similar matrix elements can be defined for the s states but they do not enter d_o. Forming Bloch states, one gets the 8×8 Hamiltonian matrix $H(\vec{k})$, e.g.,

$$H_{xa,xc}(\vec{k}) = \sum_{j=1}^{4} \exp(i\vec{k}\cdot\vec{\tau}_j)\langle \phi_{xa} \,|H|\, \phi_{xc}^{j} \rangle . \tag{5.4}$$

At the high symmetry $\vec{k}$ points, the resulting band structure can be calculated analytically.[60] At the Γ point the top of the valence band is purely p like.

In order to calculate the optical deformation potentials, the two sublattices are shifted relative to each other by $\vec{u}_{\text{rel}} = (a/4)(\delta,\delta,\delta)$ so that one should replace $\vec{\tau}_j$ by $\vec{\tau}_j + \vec{u}_{\text{rel}}$. This affects the Hamiltonian matrix elements via the angular factors in Eqs. (5.2) and (5.3) and via the τ^{-2} dependence of the $V_{ll'm}$ shown in Eq. (5.1). To first order in the displacement δ, only the matrix elements

$$\begin{aligned} H_{xa,yc}(\vec{k}=0) &= H_{ya,zc}(\vec{k}=0) \\ &= H_{za,xc}(\vec{k}=0) = \tfrac{32}{3} V_{xy}\delta , \end{aligned} \tag{5.5}$$

are affected by δ at $\vec{k} = (0,0,0)$. By diagonalizing the Hamiltonian one finally gets [see Eq. (3.2)]

$$d_o = \frac{1}{\sqrt{3}}\frac{32}{3}\frac{V_{xy}V_{xx}}{[\frac{1}{4}(\epsilon_p^a - \epsilon_p^c)^2 + V_{xx}^2]^{1/2}} . \tag{5.6}$$

TABLE VII. The LCAO parameters ϵ_p taken from Ref. 57. They have been chosen equal to the free atomic term values as calculated by Herman and Skillman (Ref. 61).

Element	$-\epsilon_p$ (eV)	Element	$-\epsilon_p$ (eV)	Element	$-\epsilon_p$ (eV)	Element	$-\epsilon_p$ (eV)
Cu	1.83	Be	4.14	B	6.64	C	8.97
Ag	2.05	Mg	2.99	Al	4.86	Si	6.52
		Zn	3.38	Ga	4.90	Ge	6.36
		Cd	3.38	In	4.69	Sn	5.94
N	11.47	O	14.13	F	16.99		
P	8.33	S	10.27	Cl	12.31		
As	7.91	Se	9.53	Br	11.20		
Sb	7.24	Te	8.59	I	9.97		

TABLE VIII. The optical deformation potential d_o at the Γ point as predicted by the present LCAO model.

Compound	d_o (eV)	Compound	d_o (eV)	Compound	d_o (eV)
C	106.9	GaN	53.8	MgTe	20.3
SiC	69.3	GaP	39.4		
Si	45.9	GaAs	37.0	ZnO	39.8
Ge	42.6	GaSb	32.3	ZnS	30.4
α-Sn	32.3	InN	39.7	ZnSe	28.1
		InP	32.0	ZnTe	24.4
		InAs	31.0	CdS	23.7
BN	96.7	InSb	27.4	CdSe	22.4
BP	64.0			CdTe	20.1
BAs	58.4				
AlN	57.7	BeO	71.8	CuF	40.4
AlP	39.2	BeS	44.4	CuCl	23.0
AlAs	37.7	BeSe	41.0	CuBr	20.2
AlSb	31.9	BeTe	34.7	CuI	18.7

The parameters V_{xx} and V_{xy} are expressible in terms of the energy gaps of the undistorted crystal. *For diamond-type crystals,* the relations are particularly simple:

$$V_{xx} = \tfrac{1}{2}E(\Gamma_{15}^{c}) \ , \tag{5.7}$$

$$V_{xy} = \tfrac{1}{2}E(\Gamma_{15}^{c}) - E(X_5^{v}) \ , \tag{5.8}$$

$$d_0 = \frac{1}{\sqrt{2}}[\tfrac{32}{6}E(\Gamma_{15}^{c}) - \tfrac{32}{3}E(X_5^{v})] \ . \tag{5.9}$$

In Eqs. (5.7)—(5.9) the energies of the conduction (c) and valence (v) bands are measured with respect to the top of the valence band. Harrison[57] determined the universal parameters η in Eq. (5.1) from the empirical band gaps of the perfect semiconductors and found

$$V_{xx} = 2.16\frac{\hbar^2}{m\tau^2}, \quad V_{xy} = 5.40\frac{\hbar^2}{m\tau^2} \ . \tag{5.10}$$

With these universal parameters and the atomic p energies which we list for convenience in Table VII, one can calculate d_o from Eq. (5.6) for any tetrahedral semiconductor. The results are shown in Table VIII. Experimentally $E(X_5^{v})$ varies very little from one material to the other. Therefore Eq. (5.9) exhibits that d_o is proportional to the E_0 gap in diamond-type crystals. Diamond has the largest E_0 gap and indeed one finds d_o (diamond) = 90.1 eV from Raman experiments[62] and 61.2 eV from transport measurements[63] as compared to 32.5 eV for Si. Ionic semiconductors also have a large E_0 gap but in these materials the polarity factor $\epsilon_p^a - \epsilon_p^c$ in the denominator of Eq. (5.6) becomes large as well. These two effects largely compensate. This explains the weak chemical trend of d_o for the standard semiconductors. For compounds containing C-row atoms or for very ionic materials like CuI this cancellation is not very effective. Therefore, the present LCAO model predicts significant variations of d_o over the Periodic Table.

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