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# THEORY OF ONE- AND TWO-PHONON DEFORMATION POTENTIALS IN SEMICONDUCTORS

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Abstract.- A theory of deformation potentials for charge carriers in tetrahedral semiconductors is presented. The model is based on an LCAO-formulation and is able to predict optical one-phonon deformation potentials for 36 materials and intravalley two-phonon deformation potentials in Ge,Si and III-V compounds. The comparison with the known experimental deformation potentials shows very good agreement between theory and experiment.

## I. INTRODUCTION

Optical deformation potential ("ODP") scattering provides the leading energy loss mechanism for carriers in nonpolar semiconductors and contributes also strongly to the energy relaxation of holes in polar materials. Both one- and two-phonon processes have been found and studied in high field transport, magnetic resonance phenomena and in Raman spectra, but due to the difficult analysis of the experiments only a few ODP's have so far been safely determined, viz. 1-phonon ODP's in Si and Ge from transport and Raman data (1,2).Including some theoretical estimates (listed in table I) these 1-ph ODP's provide a rather inconsistent set of parameters, because there are large discrepancies between values obtained from different methods or by different authors. Some experimental evidence for large 2-ph ODP's (of the order of 1000 eV) has been found in GaP (2,4) and InSb (5), but conclusive theoretical estimates have been made for Ge only (3) (see also ref.6 for a discussion of earlier theoretical work).

In view of this situation we present a systematic theoretical investigation of ODP's for a large class of tetrahedral semiconductors.

A simple LCAO-model is developed which enables us to predict ODP's in a physically transparent way. The 1-phonon ODP's and their chemical trends are directly related to a few optical gaps.

We have calculated 1-ph ODP's for 36 materials and find very good agreement with the existing experimental data (see table I).

The model also allows a nonperturbative and simple calculation of 2-ph deformation potentials associated with intravalley scattering in Ge, Si and III-V compounds. It is able to explain the origin of the anomalously large couplings found by experiment without the frequently encountered convergence difficulties of perturbative approaches.

## II. THEORY

Deformation potentials are changes of the band energies due to ionic displacements. The recently developed empirical LCAO-theory (8) is especially well suited for a calculation of such quantities, because of the universal dependence of the Hamiltonian on the local arrangement of the ions.

Four or five basis states per atom (the outermost s and p valence

states, and the first excited s state, when electronic states at zone-boundaries are involved) as well as nearest neighbour interactions suffice to give semiquantitative valence- and conduction-band energies for all tetrahedral semiconductors (8). The diagonal elements of the Hamiltonian matrix are free atomic energies $\varepsilon_s, \varepsilon_p, \varepsilon_s^*$, the intra-atomic nondiagonal elements contain the spin-orbit ("SO") interaction between p-orbitals (9), and the interatomic off-diagonal terms are geometrically determined linear combinations of overlap integrals, each of which scales with the interatomic distance d as $d^{-2}$.

Any perturbation due to a frozen-in lattice wave for zone-boundary phonons can therefore be easily incorporated through the corresponding changes of $d^{-2}$ and of some angular coefficients.

The resulting Hamiltonian is exactly diagonalised, and the 1-ph or 2-ph deformation potentials can then be determined from suitable combinations of the band shifts of first or second order in the displacements. This allows a systematic analysis of the influence of certain band features, such as SO-splittings, on the nature and magnitude of the band shifts and deformation potentials.

The empirical tight-binding parameters used for our 1-ph ODP's are those of Harrison's 8-band model (8,9). Since a higher accuracy is needed for the parametrization of conduction bands for certain second order couplings, we use the 10-band LCAO-model of Vogl et al. (10) for the calculation of 2-ph deformation potentials.

## III. CALCULATIONS AND RESULTS

1 - Phonon ODP's:

By symmetry the only nonzero 1-ph ODP coupling for phonons of wavevector q=o and carriers of wavevector k=o are those for holes. Using a basis of one atomic s- and three p-functions ($p_x, p_y, p_z$) per atom we express the nearest neighbour overlap integrals through Harrison's σ- and π-bonding parameters (8,11). For the central ion a (= anion in III-V's) and its four nearest neighbours $c_j$ (=cations in III-V's) at their equilibrium positions $\vec{\tau}_j$, the unperturbed values of the p-state matrix-elements are (11)

$$V_{xx}=\langle\phi_{xa}|H|\phi_{xc}^j\rangle=\cos^2\Theta_{jx}V_{pp\sigma}+(1-\cos^2\Theta_{jx})V_{pp\pi} \quad , \tag{1}$$

$$V_{xy}=\langle\phi_{xa}|H|\phi_{yc}^j\rangle=\cos\Theta_{jx}\cos\Theta_{jy}(V_{pp\sigma}-V_{pp\pi}) \quad , \tag{2}$$

where $\Theta_{jx}$ is the angle between $\vec{\tau}_j$ and the x-axis. The matrix-elements involving s-states do not contribute to the 1-ph couplings.

One now forms the LCAO-Bloch-states and the 8x8 Bloch-Hamiltonian, e.g.

$$H_{xa,yc}(\vec{k}) = \sum_{j=1}^{4} \exp(i\vec{k}\vec{\tau})\langle\phi_{xa}|H|\phi_{xc}^j\rangle \ . \tag{3}$$

For an optical mode of infinite wavelength (Γ-phonon) and a resulting relative shift of the two sublattices of the form $\vec{u}_{rel}$ = = (2a) (δ,δ,δ), where a is the lattice constant, one can easily calculate the corresponding change in the V's (through their $d^{-2}$ dependence) and of the cosines.

The optical deformation potential $d_o$ at k=o is defined in terms of the phonon-induced splitting of the light and heavy $\Gamma_8^+$ ($\Gamma_8$) - valence bands as

$$\delta E_\Gamma = \left|\frac{\vec{u}_{rel}}{a}\right| d_o \quad . \tag{4}$$

To first order in δ, only $V_{xy}$ is changed (to $V_{xy}$ + 32 $V_{xy}$ δ/3). After diagonalizing the Hamiltonian one gets

Table I: The optical deformation potentials $d_o$ (in eV) for the upper valence band edge at the Γ-point.

| Compound | This Work | Previous Theories | Experiment |
|---|---|---|---|
| Si | 45.9 | 39.5[12], 38.1[12] 40.0[15], 32.5[16] | 26.6[13], 27.0[14] (24.4 - 33.6)[17] |
| Ge | 42.6 | 40.0[15], 31.4[18], 28.3[21] 33.0[22], 38.0[3] | 36.0[23], 39.0[14], 41.6[19] (29.0 - 33.2)[17], 40.3[20] |
| α-Sn | 32.3 | 24.0[24] | |
| GaP | 39.4 | 44.0[15], 26.3[25] | 47.0[14] |
| GaAs | 37.0 | 41.0[15], 31.5[26] | 41.0[14], 48.0[27] |
| GaSb | 32.3 | 39.0[15] | 32.0[14] |
| InP | 32.0 | 42.0[15] | 35.0[14] |
| InAs | 31.0 | 42.0[15] | |
| InSb | 27.4 | 39.0[15], 24.0[24] | |
| ZnSe | 28.1 | 27.0[28] | 27.0[14] |
| CdTe | 20.1 | | 22.0[14] |

Table II: The optical deformation potentials $d_o$ (in eV) for the upper valence band edge at the Γ-point (present theory).

| Compound | $d_o$ | Compound | $d_o$ | Compound | $d_o$ | Compound | $d_o$ |
|---|---|---|---|---|---|---|---|
| C | 106.9 | AlN | 57.7 | GaN | 53.8 | ZnO | 39.8 |
| SiC | 69.3 | AlP | 39.2 | InN | 39.7 | ZnS | 30.4 |
| BN | 96.7 | AlAs | 37.7 | BeO | 71.8 | CuF | 40.4 |
| BP | 64.0 | AlSb | 31.9 | BeS | 44.4 | CuCl | 23.0 |
| BAs | 58.4 | MgTe | 20.3 | BeSe | 41.0 | CuBr | 20.2 |
| CdS | 23.7 | ZnTe | 24.4 | BeTe | 34.7 | CuI | 18.7 |
| CdSe | 20.1 | | | | | | |

$$d_o = \frac{1}{\sqrt{3}} \frac{32}{3} V_{xx} V_{xy} \left[\frac{1}{4}(\varepsilon_{pa}-\varepsilon_{pc})^2 + V_{xx}^2\right]^{-1/2} . \qquad (5)$$

We now use the simple dependence of certain undisturbed energy gaps on the V's. In Si and Ge, for example, $d_o$ can be expressed as

$$d_o = \frac{1}{\sqrt{2}} \left[\frac{32}{6} E(\Gamma_{15}{}^c) - \frac{32}{3} E(X_5^v)\right] , \qquad (6)$$

where the zero of energy is taken at the top of the valence band.

Using Harrison's universal scaling law

$$V_{xx} = 2.16\ \hbar^2 m^{-1} \tau^{-2} \quad \text{and} \quad V_{xy} = 5.40\ \hbar^2 m^{-1} \tau^{-2}$$

(m = free electron mass), one can evaluate $d_o$ for any tetrahedral semiconductor.

Moreover, since $E(X_5{}^v)$ varies little among these materials, an increase of $d_o$ with increasing $E_o$-gap is predicted for elemental semiconductors, in agreement with experimental findings.

For the polar materials this tendency is compensated by the polarity $\varepsilon_{pa} - \varepsilon_{pc}$ in eq. (5), which explains the experimentally observed small chemical trends of $d_o$ in III-V compounds.

A further point of interest is the role of the spin-orbit coupling for ODP's. It is most easily demonstrated in the two extreme limits, where the shift of the band energies due to the lattice waves is either much larger or much smaller than the SO-splitting: The limit of vanishing $\Delta$ would result in a triply degenerate $\Gamma_{25}^{+}$ ($\Gamma_{15}$) valence state. For our choice of $\vec{u}_{rel}$ this state would split into a doublet and a singlet by an amount of

$$\delta E_{\Gamma} = 3\sqrt{3}\ d_o \cdot \delta \ . \qquad (7)$$

This has to be compared with eq.(5), obtained in the limit of large $\Delta$:

$$\delta E_{\Gamma} = 2\sqrt{3}\ d_o \cdot \delta \ . \qquad (5')$$

Since $\Delta$ depends only negligibly on the lattice displacement (12) eqs.(7) and (5') differ by a factor of 3/2.

This influence of SO-couplings on ODP's of holes is even much more pronounced in 2-ph-couplings, as will be shown below.

It is easily seen, that the limit of large $\Delta$ is appropriate for our calculations. Taking the lightest materials, the mean vibrational amplitude $(\hbar/(M\omega_o))^{1/2}$ is less than 0.05Å, where M is an atomic mass and $\omega_o$ an optical phonon frequency. Only phonons of wave vector

$$q < 0.1\ q_{zb} = 0.1\ (\pi/a)$$

contribute to hole scattering in charge transport, so that only $10^{-3}$ of all modes are efficient; their corresponding mean amplitude is therefore $0.05 \cdot 10^{-3}$ Å . Even for the very small SO-splitting of 0.044 eV in Si the condition of $\delta E_{\Gamma} \ll \Delta$ is well satisfied, because in eq.(4) $d_o < 100$ eV for all materials.

In table I we list our results, together with previous theoretical results and existing experimental data for eleven semiconductors. The 1-ph ODP's $d_o$ obtained from our exceedingly simple formulae eqs. (5) or (6) show excellent agreement with previous theories and experiments.

Table II shows our predictions for additional 25 materials, for which no previous information has been obtained to our knowledge.

## 2 - Phonon ODP's :

Because of the much weaker symmetry requirements for two-phonon scattering processes almost all pairs of phonons couple to all types of carriers in semiconductors.

Let us first consider the coupling of pairs of $\Gamma$-phonons to holes of $\Gamma_8$ -symmetry in Si and Ge for a relative sublattice displacement $\vec{u}_{rel} = 2a(\delta,\delta,\delta)$. Keeping now terms up to second order in $\delta$, the three eigenvalues at k = 0 for light, heavy and split-off holes are obtained as

$$E_{lh} = \varepsilon_p - V_{xx} + \frac{1}{3}\Delta + \frac{32}{3} V_{xy} \cdot \delta + \left(-\frac{64}{3} V_{xx} + 64 V_{xy}\right) \cdot \delta^2 \ , \qquad (9)$$

$$E_{hh} = \varepsilon_p - V_{xx} + \frac{1}{3}\Delta - \frac{32}{3} V_{xy} \cdot \delta + \left(-\frac{64}{3} V_{xx} - 64 V_{xy} + \frac{2048}{9\Delta} V_{xy}^2\right) \cdot \delta^2 \ , \qquad (10)$$

$$E_{so} = \varepsilon_p - V_{xx} - \frac{2}{3}\Delta \qquad + \left(-\frac{64}{3} V_{xx} \qquad - \frac{2048}{9\Delta} V_{xy}^2\right) \delta^2 \ . \qquad (11)$$

We define the three second order ODP's $D_{ao}^{2\Gamma}$, $D_{bo}^{2\Gamma}$ and $D_{o}^{2\Gamma}$ through the shift of the "center of mass" of the valence bands

$$D_{ao}^{2\Gamma} \cdot (u_{rel}/a)^2 = -(64/3) \cdot V_{xx} \cdot \delta^2 \ , \qquad (12)$$

through the symmetric part of the relative l.h.- and h.h.-shift

$$D_{bo}^{2\Gamma}\cdot(u_{rel}/a)^2 = 128.V_{xy}.\delta^2 \quad (13)$$

and through the symmetric part of the relative h.h.-s.o.-shift

$$D_{o}^{2\Gamma}.(u_{rel}/a)^2 = (4096/(9\Delta))V_{xy}^2.\delta^2. \quad (14)$$

Since $\Delta$ and the V's are small on the eV-scale of our energies, the by far dominating term for the second order change of the energies is due to the small energy denominator in $D_o^{2\Gamma}$ . To a high accuracy one can therefore define this leading ODP in terms of the second order change in $E_{hh}-E_{so}$ as

$$D_{o}^{2\Gamma} = \delta^{(2)} (E_{hh}- E_{so}) \cdot (a/u_{rel})^2 \quad . \quad (15)$$

Using eq.(14) and $\Delta$(Si)=0.044 eV, $V_{xy}$(Si)=4.575 eV, $\Delta$(Ge)=0.290 eV and $V_{xy}$(Ge)=4.900eV we obtain $D_o^{2\Gamma}$(Si)=18040 eV and $D_o^{2\Gamma}$(Ge)=3140 eV.

This finding is not specific to carriers of $\Gamma$-symmetry; quite generally we find large 2-ph ODP's whenever a phonon connects nearly degenerate unperturbed electronic band states. This conclusion has also recently been reached by Allen and Cardona (3). The resulting strong couplings have the form of squared interband 1-ph ODP's divided by a small energy denominator. For our case of Si or Ge $D_o^{2\Gamma} \approx d_o^2/\Delta$ as follows from eqs.(14) and (5) for $\varepsilon_{pa} = \varepsilon_{pc}$.

A similar analysis for zinc-blende symmetry leads to quite analogous results; e.g. for GaAs we find

$$E_{hh-so}^{2\Gamma} = 1.4\cdot 10^3 \, (u_{rel}/a)^2 \text{ eV} \quad , \quad (16)$$

so that $D_o^{2\Gamma}$ = 1400 eV $d_o^2/\Delta$.

For conduction band states, where no SO-splitting occurs, some 2-ph ODP's are still dominated by small energy denominators. Typical examples are 2-ph ODP's for zone-boundary conduction electrons of $X_6$ symmetry in III-V compounds, where the indirect interband coupling to the nearby $X_7$ -level dominates the energy shift:

$$\delta[E(X_6{}^c) - E(X_7{}^c)] \approx D^{2\Gamma}\cdot(\vec{u}_{rel}\cdot\vec{e}_v/a)^2 \quad , \quad (17)$$

where $\vec{e}_v$ is a unit vector along the X-valley. Representative values are $D_X^{2\Gamma}$(GaAs) = 1200 eV and $D_X^{2\Gamma}$(InSb) = 2800 eV.

Similarly, for electrons in the conduction band minima of Si ($\Delta_1$-symmetry, $D_\Delta^{2\Gamma}$ can be defined as

$$\delta[E(\Delta_3{}^c) - E(\Delta_1{}^c)] \approx D_\Delta^{2\Gamma} \cdot (\vec{u}_{rel}\cdot\vec{e}_v/a)^2 \, , \quad (18)$$

because the energy difference to the next higher $\Delta_3{}^c$-states is sufficiently small to make the indirect coupling the leading contribution. We find $D_\Delta^{2\Gamma}$(Si)= 425 eV.

Let us finally discuss the possibility of strong indirect intraband contributions to 2-ph deformation potentials.

We have calculated various couplings to two X-phonons of total wavevector zero, each phonon connecting energetically close band regions at $\Gamma$ and X. This case, as well as similar couplings to pairs of zone-boundary phonons of high symmetry with opposite wavevectors, can be directly incorporated into our model. Any such standing lattice wave has only one sublattice deformed. For X-phonons, each ion is then surrounded by two geometrically inequivalent pairs of nearest neighbours, so that two different types of atomic anion- or cation-states have to be considered in our LCAO-Hamiltonian. The corresponding formal doubling of the elementary cell along the x-direction leads to a folding of the outer half of the Brillouin zone along the $\Delta$-direction into the inner half. In this way both $\Gamma$ and X valence- and conduction-

band states are contained in the k=O 12x12 Hamiltonian for the two geometrically inequivalent s, $p_x$ and $s^*$ states for anions and cations respectively. Pairs of LO or LA phonons can be distinguished by displacing either the lighter or the heavier sublattice.

We define the dominant indirect couplings through the energy shifts of second order in the sublattice displacement $\vec{u}$ :

$$\delta E(\Gamma_6{}^c) = D_\Gamma^{2X(j)} \cdot (u/a)^2 \quad , \quad j = LA, LO. \tag{19}$$

For Ge as the best candidate for a small Γ-X energy difference we calculate $D_\Gamma^{2X}$(Ge) = -864 eV. But we find rather small values for III-V compounds (e.g. $D_X^{2X(LA)}$(GaP) = - 49 eV and $D_\Gamma^{2X}$(GaAs) = -31 eV), because no sufficiently small energy difference are involved. Somewhat larger values are found for indirect second order Γ- L couplings via two L-phonons, which, due to smaller Γ- L energy differences, should dominate the 2-ph deformation potentials for Γ-conduction-band electrons in most III-V compounds.

Our numerical results are in qualitative agreement with the existing theoretical (3) and experimental data (2,4), except for the extremely high value for InSb, proposed in ref.5.

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