Intervalley Gamma -X deformation potentials for top valence bands in III-V zincblende semiconductors by ab initio pseudopotential calculations

Intervalley Γ–X deformation potentials for top valence bands in III–V zincblende semiconductors by *ab initio* pseudopotential calculations

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Abstract. We have calculated Γ–X hole–phonon scattering matrix elements for the top valence bands in nine III–V zincblende semiconductors AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs and InSb, by *ab initio* pseudopotential calculations. At the same time, we have calculated the eigenfrequencies and eigenvectors of transverse acoustic (TA) and optic (TO) phonons at X in these materials, which agree very well with the available experimental results. We have evaluated the Γ–X intervalley deformation potentials (IVDPs) for the longitudinal phonons and transverse phonons, respectively. The IVDPs for the TAX phonon are very small, as expected from symmetry. The IVDPs for the TOX phonon do not vary appreciably from one semiconductor to another, averaging about 5 eV Å^{-1}. IVDPs for the longitudinal phonon with X_1 symmetry are generally larger than those of X_3 symmetry. This is due to more screening to the long-range electron–phonon interaction for the X_3 phonon by electron redistribution, resulting in smaller IVDPs.

1. Introduction

Intervalley electron–phonon and hole–phonon interactions play an important role in many optical, transport and electrical phenomena in semiconductors. Effects of intervalley scattering are observed in optical absorption measurements in indirect gap semiconductors where the photon absorption is assisted by intervalley phonon scattering [1–4], in electrical measurements where negative differential resistance [5, 6] and microwave oscillations (Gunn effect) [7, 8] are observed, and in high-field carrier transport properties [9] and hot-electron phenomena [10, 11] in semiconductors. The virtual intervalley transitions by electron–phonon interaction are the major causes for the band energy shifting and the phonon-induced lifetime broadening of the electronic states and the critical points in semiconductors [12–14], e.g. in Si, Ge and GaAs. Recently, intensive interest has been focused on studying the initial relaxation of photo-excited carriers in III–V zincblende semiconductor GaAs, where intervalley scattering processes are believed to be the dominant energy loss mechanism [15–22]. The photo-excited carriers in the Γ valley are scattered to the other valleys, e.g. X or L, in sub-picosecond time scale, by transfering excess energy to the lattice by electron–phonon interactions. The study of the dynamic behaviours of the hot electrons in the semiconductor system and the dependence of carrier distribution on the intervalley

scattering rate is of critical importance in characterizing the performance for ultrafast semiconductors devices.

The deformation potential (DP), as first introduced by Bardeen and Shockley [23] and extended by Herring and Vogt [24], Dumke [25] and Harrison [26], was originally intended to describe the interaction between electron (hole) and the long-wavelength acoustic [23–25] and optic [26] phonons. This is the intravalley electron (hole) scattering by phonons of momentum $q \approx 0$. This idea was later extended [27–32] to the case of intervalley (IV) scattering where carriers are scattered from one valley of state vector k to a different valley of a different state vector k', by long-range forces (Fröhlich interaction [33]) presented in ionic semiconductors. The phonons involved in IV scattering are of short wavelengths $|q| \simeq \pi/a$, where a is the lattice constant of the crystal. The intervalley deformation potential (IVDP) is defined to be proportional to the electron(hole)–phonon scattering matrix element between the two carrier states concerned [27–32].

By definition, the deformation potential is an important electron–phonon interaction parameter for characterizing various physical or performance properties in semiconductor systems or devices, e.g. in determining the device intrinsic response times, etc. Thus various attempts have been made from direct experimental measurements to determine the desired DP constants in some typical semiconductors [15, 22, 34–36]. Unfortunately, the DPs extracted from various measurements are very scattered, differing by an order of magnitude. This is largely due to the fact that the simple model derivations used in these studies have neglected many complicating factors and involved too many approximations, and also due to the difficulty of excluding undesirable and uncontrollable factors in the measurements. Thus reliable experimentally determined values of DPs, and IVDPs in particular, are very scarce in the literature, even for the most common semiconductor materials. For example, for an important semiconductor such as GaAs, the experimentally derived values [15, 22, 34-36] for $D_{\Gamma L}$, the deformation potential for intervalley scattering of conduction electron between the Γ minimum to the L valley, range from 1.5 eV Å^{-1} from time-resolved Raman scattering experiments [34] to 10 eV Å^{-1} by fitting I–V curves [35]. The experimentally determined DPs for Γ–X intervalley scattering $D_{\Gamma X}$ are even rarer in the literature [34].

In their recent work determination of IV scattering rates in GaAs by sub-picosecond luminescence spectroscopy Shah *et al* [15] have fitted their experimental spectra with an model calculation in which they estimated IV time constants from effective mass band structure and by Monte Carlo simulation. The good agreement of their calculated luminescence spectra evolving with time with the experiments has depended critically on the choices of $D_{\Gamma L}$. In an even more recent study, Fasol *et al* [22] have obtained related DPs in GaAs from the derived Γ–L scattering times by the measured luminescence spectra from electrons recombining with holes on acceptors by continuous-wave spectroscopy [22].

Theoretical efforts have also been made by several research groups to calculate IVDPs in typical group IV diamond structure and III–V zincblende semiconductors either by empirical [31, 32, 37–40] or self-consistent [41, 42] calculation methods. The empirical pseudopotential method (EPM) was used by Glembocki and Pollak [37, 38] to have calculated Γ–Δ electron–phonon and hole–phonon scattering-matrix elements in Si and Ge, and by Herbert [39] to have calculated IV electron coupling constants (Γ–X or Γ–L) in III–V zincblende semiconductors GaAs and InP. The electron–phonon coupling constants evaluated by Herbert, although being proportional to

the electron–phonon matrix elements, were defined quite differently from the IVDPs defined and calculated for III–V zincblende semiconductors in recent work by Zollner *et al* [32]. In this latter work [32], the authors have systematically calculated, by using the empirical pseudopotential calculation method in the rigid-ion approximation, the IVDPs for both LA and LO phonons in a series of zincblende semiconductors, and have done a thorough analysis for the k-dependence of IVDPs and scattering rates in GaAs. In particular, IVDP constants between different valleys of the high-symmetry points (Γ–X, Γ–L, etc.) have been calculated. A most recent work involves the calculation of intervalley scattering rates in $Al_x Ga_{1-x} As$ to study the effects of alloy and phonon scattering [40].

Besides the empirical pseudopotential method, other empirical approaches have also been used for IVDP calculations. An empirical tight-binding method was employed [31] to calculate $D_{\Gamma L}$ for the conduction bands in GaAs. It is also worth mentioning the recent work of numerical simulation for Γ–L intervalley femtosecond carrier dynamics in GaAs by ensemble Monte Carlo calculation [43]. By comparing the calculated differential transmission with the experimental spectra and by adjusting the IVDP constant as a parameter to achieve the best match, they have derived a value of $D_{\Gamma L}$.

The self-consistent pseudopotential calculation method was first used to calculate Γ–X electron(hole)–phonon matrix elements in Si by Richardson *et al* [41], and recently has been used to evaluate Γ–Δ electron(hole)–phonon matrix elements in the same material [42] in the partial-density approximation. Recently, we have carried out and reported a systematic *ab initio* pseudopotential calculation of the Γ–X electron–phonon matrix elements and the corresponding IVDPs for LA and LO phonons in a series of nine III–V zincblende semiconductors AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs and InSb.

Due to the lack of corresponding experimental values for these constants, the best we could do was to compare our calculated *ab initio* IVDPs with the available theoretical results in previous calculations by other methods. The only available systematic evaluation of these IVDPs for the series of III–V zincblende semiconductors was the EPM calculation by Zollner *et al* [32]. It was to our surprise that our *ab initio* calculated Γ–X IVDPs of the lowest conduction bands for these semiconductors were in fairly good quantitative agreement with those of the EPM calculation only for the longitudinal phonons of X_1 symmetry. For the longitudinal phonons of X_3 symmetry the IVDPs calculated *ab initio* were consistently much lower than the corresponding constants of EPM calculations and than IVDPs of the X_1 phonon, by one order of magnitude for most materials. This has been attributed to the break down of the rigid ion approximation employed in EPM calculations [44]. The valence electron redistribution associated with the phonon distortion may be quite appreciable, thus is making important contribution to electron–phonon scattering process. It may be particularly the case for the longitudinal phonon of X_3 symmetry. The valence electron charge density calculated *ab initio* in the bond regions is distributed off-centre in III–V zincblende semiconductors, with the peaks of the distribution located closer to the anions than to the cations in the crystals [45]. The longitudinal phonon of X_3 symmetry is the oscillation mode where only the anions oscillate (the cations remaining stationary), whereas for that of X_1 symmetry the reverse is true. For the former distortion the valence electron redistribution is more appreciable, and there is more screening to the long-range Fröhlich interaction, resulting in smaller electron–phonon matrix elements. Thus, the contribution of electron redistribution should be included in the calculations.

There is one possible uncertainty associated with self-consistent first-principle calculations for the conduction band properties. The *ab initio* pseudopotential calculation and the other self-consistent first-principle calculations such as the linear muffin tin orbital (LMTO) method are based on the formalism of density functional theory (DFT) [46]. DFT is a ground-state theory, and thus, in principle should only be applied to study the ground-state properties of a many-electron system. As is well known, the band structure calculations in DFT within the local density approximation (LDA) have produced good valence band structures but systematically underestimated the band gaps in semiconductors [47–49].

The electron–phonon matrix elements in our previous work have been calculated by integrating the perturbed Hamiltonian by the phonon field between electron states in the conduction bands. The phonon perturbed Hamiltonian in the adiabatic approximation [50] evaluated in the frozen-phonon configuration is a ground-state property for the valence electron cloud, since in self-consistent calculations the valence electrons are allowed to redistribute with the phonon deformation. Thus it is accurately treated in the calculations. Sham has shown [51] that the use of a pseudopotential and pseudo-wavefunctions produces the same results when calculating electron–phonon matrix elements as using the real potential and real wavefunctions. The only source of uncertainty may come from the conduction electron wavefunctions. But the recent first-principle quasiparticle calculations in the GW approximation for the semiconductors and insulators have indicated that [52] the one-particle wavefunctions generated by the density functional band structure calculations coincide with the quasiparticle wavefunctions to better than 99.9%. Thus one would expect that little error is introduced by using the LDA wavefunctions in calculating electron–phonon matrix elements by the self-consistent pseudopotential calculation. This view is supported by the recent works of the LDA calculations for the pressure coefficients of the conduction bands in that the calculated pressure coefficients are more reliable than the absolute values of band energies [53]. However, due to the lack of direct confirmation of IVDP calculations, it is desirable to calculate the intervalley hole–phonon matrix elements and the corresponding IVDPs for the top valence bands in semiconductors by *ab initio* calculations, and compare the calculated results with experimental values or with the results of other calculations.

With this consideration in mind and realizing the importance of hole–phonon IVDPs in their own right, we have calculated, in this work, the intervalley Γ–X deformation potentials for the top valence bands in the same series of III–V zincblende semiconductors as in the previous work [44] by *ab initio* pseudopotential calculations. We have neglected the effects of spin–orbit interaction on the hole–phonon matrix elements and on the eigenfrequencies and displacement patterns of the related phonons. Such effects will be the subject of a future study. In calculating the Γ–X electron–phonon IVDPs for the lowest conduction bands in these semiconductors, due to the symmetry of the lowest conduction states at X, only longitudinal X phonons (acoustic LAX and optic LOX) contribute to the scattering process. And it is computationally less demanding to treat longitudinal phonons. In the present study where top valence bands are concerned, the top valence states at X are doubly degenerate and are of X_5 symmetry, neglecting the spin–orbit interaction. Thus, X transverse phonons (acoustic TAX and optic TOX), which are of X_5 symmetry, contribute to the hole–phonon scattering, as well as the longitudinal phonons, and should be included in the calculations. Along with calculating hole–phonon IVDPs, we have calculated from total energy calculations in the frozen-phonon approximation,

the TAX and TOX phonon frequencies and eigenvectors for these semiconductors.

The contents of the article are organized in the following order: in the following section, the theoretical formalism with which the IVDPs and phonon frequencies are calculated is outlined. In section 3, technical details of our calculations are given. We present and discuss the results of our calculated IVDPs of Γ–X valence states for the nine typical III–V zincblende semiconductors in section 4. TAX and TOX phonon frequencies calculated *ab initio* for these semiconductors are also given, and are compared with available experimental results. We have found very good agreement between our calculated phonon frequencies and the experimental values. Concluding remarks are in section 5.

2. IVDPs and phonon frequencies

The DP constant $D(q, j, k)$ is related to the scattering matrix element by [27–32]

$$|\langle nk|H_1|n'k \pm q\rangle| = \hbar(2NME_q^j)^{-1/2} D(q, j, k)\sqrt{N_q^j + \tfrac{1}{2} \pm \tfrac{1}{2}}. \quad (1)$$

In equation (1), H_1 is the perturbation Hamiltonian for a phonon to scatter an electron in state $|nk\rangle$ to state $|n'k \pm q\rangle$, where the plus and minus signs stand for phonon absorption or emission, respectively. The mass $M = M_a + M_c$ is the mass of the primitive cell, as the sum of the mass M_a of the anion and M_c of the cation, $E_q^j = \hbar\omega_q^j$ the phonon energy, and N_q^j the Bose–Einstein occupation factor of the phonon (q, j). The factor N is the total number of primitive cells in the crystal. And the factor $N_q^j + \tfrac{1}{2} \pm \tfrac{1}{2}$ in the square root is the number of phonons presented in the phonon field.

There have been some ambiguities in the definition of the DP in the literature [32]. This comes about because of the transition from the long-wavelength region ($|q| < 2\pi/a$) of continuous-medium limit to the short-wavelength region ($|q|$ comparable to $2\pi/a$). For a phonon in continuous medium limit, the overall averaged vibrational amplitude is one-half the maximum displacement of the classical phonon. When there are $N_q^j + \tfrac{1}{2} \pm \tfrac{1}{2}$ phonons presented in the phonon field, the average vibrational amplitude of the phonons is

$$u_{\text{eff}} = (\hbar^2/2NME_q^j)^{1/2}\sqrt{N_q^j + \tfrac{1}{2} \pm \tfrac{1}{2}} \quad (2)$$

treating the primitive unit cell as a point particle of mass M. So, this factor in equation (1) is an effective displacement of the classical phonon and $D(q, j, k)$ becomes the electron–phonon matrix element per effective phonon displacement. However, u_{eff} is not exactly equal to the true phonon displacement for most phonon modes.

In general, the overall averaged mean square amplitude u_κ^2 for the κth ion in the crystal after the spatial average can be expressed as

$$u_\kappa^2 = \langle|(u_\kappa)^2|\rangle = (\hbar/2\omega_q^j NM_\kappa)|\hat{e}(\kappa qj)|^2 2\beta_q^j(N_q^j + \tfrac{1}{2}) \quad (3)$$

where β_q^j is a factor due to spatial averaging, M_κ the mass of the ion concerned, and $\hat{e}(\kappa qj)$ the polarization vector for the κth ion. For a phonon in the long-wavelength

limit, the spatial average factor is $\beta = \frac{1}{2}$. For phonons of short-wavelengths with wavevectors comparable to the Brillouin zone (BZ) boundary ($|q| \simeq 2\pi/a$), the spatial average factor β_q^j can be different from $\frac{1}{2}$. For the zone boundary phonons at $q = (2\pi/a)(1,0,0)$ (X point) in III–V zincblende semiconductors, ions of the same type in adjacent primitive cells oscillate in opposite directions with a phase difference of 180°. The spatial average factor is $\beta = 1$. For phonons at other q points near the zone boundary or at other high-symmetry points in the BZ, appropriate averages are to be carried out according to the corresponding ionic and unit cell displacement patterns.

In the following discussions we will only be concerned with $q = X$ phonons in III–V zincblende semiconductors. In the frozen-phonon approximation employed in our calculations we consider a phonon with an actual displacement pattern (u_1, u_2) relative to the perfect lattice. By solving the dynamic matrix equation for the eigen-frequencies and the displacement patterns of the corresponding X phonons as will be discussed below, one can obtain the displacement ratio of anions versus cations $r = u_2/u_1$, or its inverse $r' = r^{-1} = u_1/u_2$, where u_1 is the displacement of the cation and u_2 that of the anion in a primitive cell. For longitudinal X phonons, there are two modes available, LA and LO modes, involving [54, 55] either sublattice A or B oscillating longitudinally while the other sublattice remains at rest, i.e. we have either $r = 0$, or $r' \equiv r^{-1} = 0$. For the transverse modes both sublattice A and B oscillate transversely and in general $r \neq 0$, $r' \neq 0$ and $r \neq r'$. According to equation (3) and the fact that $\beta(q = X) = 1$, we can solve for the displacement of the cation u_1 and that of the anion u_2 as

$$|u_1| = (\hbar/2\omega_q^j N M)^{1/2} (2(M_1 + M_2)/(M_1 + M_2 r^2))^{1/2} (N_q^j)^{1/2} \tag{4a}$$

$$|u_2| = (\hbar/2\omega_q^j N M)^{1/2} (2(M_1 + M_2)/(M_1 r'^2 + M_2))^{1/2} (N_q^j)^{1/2}. \tag{4b}$$

Here, we have neglected zero-point motion and $M = M_1 + M_2$. The IVDP is evaluated from the following formula

$$D(q, j, k) = (|\langle nk|H_1|n'k + q\rangle|)/u_1 (2(M_1 + M_2)/(M_1 + M_2 r^2))^{1/2} \tag{5a}$$

that is

$$D(q, j, k) = (|\langle nk|H_1|n'k + q\rangle|/u_2)(2(M_1 + M_2)/(M_1 r'^2 + M_2))^{1/2} \tag{5b}$$

where $k = 0$ and $q = X$ for Γ–X IV scattering. The above formulation can be generalized to IVDPS between other intervalley states, e.g. Γ–L or X–L, by multiplying by the factor $\sqrt{\beta_q^j}$ of appropriate phonon (q, j) involved. But, in calculating matrix elements in equation (5), one has to use the symmetry of the distorted crystal to obtain all the quantities self-consistently to avoid the problem of numerical offsets in the calculations due to difference in symmetry when subtracting the contribution from the zero-displacement limit [56, 57].

To solve for the transverse phonon modes at X we calculate the increase of the total energy ΔE_{tot} in an arbitrary displacement pattern (u_1, u_2) which can be expressed as

$$\Delta E_{tot} = E_{tot}(u \neq 0) - E_{tot}(u = 0) = [u_1 \; u_2] \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} \tag{6}$$

within the harmonic approximation. The transverse displacements for TOX and TAX phonons in III–V zincblende semiconductors are coupled by the generalized coordinates S_1 and S_2 of the corresponding modes of the diamond structure [58, 59]. For the S_1 mode $u_1 = u_2 = u$, and for S_2 mode $u_1 = -u_2 = u$. To determine the coefficients in equation (6), we used four different displacement patterns S_1, S_2, $S_1 + S_2$ and $S_1 - S_2$. In fact, by symmetry $a_{12} = a_{21}$, there are only three undetermined coefficients. One needs three of these modes to obtain the a_{ij}. The fourth one can be used to check for the accuracy and to reduce the error of the calculations. Once the coefficients of the dynamic matrix are obtained from the calculations one can solve for the phonon frequencies and the displacement patterns of the phonons by solving the following equation of motion

$$\left[\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} - \omega^2 \begin{pmatrix} M_1 & 0 \\ 0 & M_2 \end{pmatrix} \right] \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = 0. \tag{7}$$

3. Calculation technical details

The relativistic norm-conserving pseudopotentials [60–64] were used for our self-consistent calculations in the LDA approximation. The kinetic energy cutoff for expanding the Bloch wavefunctions in the planewave basis was chosen to be $E_{cut} = 14$ Ryd for all the nine semiconductors. The second cutoff g_{max}^2 for the overall cutoff of the G-vectors in the reciprocal G space, e.g. the expansion of charge density, was chosen to be $G_{max}^2 = 49$ Ryd. For the full symmetry of the perfect crystal (T_d), we used ten special Chadi k-points [65] in the irreducible Brillouin zone (IBZ) for mapping out the k-space. Special k-points of this density are dense enough to obtain accurate and reliable calculation results as was shown previously [56, 57] from the convergence tests of the calculated DP constants with respect to the number of k-points, provided that the contribution of the zero-phonon displacement limit is subtracted off correctly. For the distorted crystal by X phonons, due to the increased size for the primitive super cell in real space which is twice the size of the primitive cell of the undistorted crystal, the Brillouin zone of the X phonon-distorted crystal is reduced by one half compared to the undistorted case. Thus to achieve the same accuracy in the calculated results, one needs to generate a k-point mesh of the same order [66] as the ten special points in the undistorted crystal. For longitudinal X phonons, there are three corresponding special k-points for the IBZ of the distorted lattice, whereas for the transverse X phonons, due to the increased IBZ size by the reduced symmetry of the transverse phonons, there are eight special k-points in the IBZ.

In calculating the phonon frequencies and in evaluating the IVDPs by equation (5), several values of the phonon displacement u for the generalized coordinate S_1 and S_2 were used to ensure the harmonicity in the calculated phonon energies and the linearity in the hole–phonon matrix elements. To eliminate contributions made by higher-order terms (u^4 terms in phonon energies and u^3 in hole–phonon matrix elements), we used three values of u for these materials, including 0, $2 \times 10^{-3} a / \sqrt{2}$ and $4 \times 10^{-3} a / \sqrt{2}$. For AlP, AlAs, AlSb, GaP, GaAs and GaAs we also included $u = -2 \times 10^{-3} a / \sqrt{2}$ to check for the symmetry of the phonon distortion energies, and of the hole–phonon matrix elements. We have found that the phonon deformation

energies for u and $-u$ are equal, indicating that the odd power terms in the power expansion of the phonon deformation energies ΔE_{tot} in the phonon amplitude u are zero. Thus, ΔE_{tot} can be fitted to u in the form of $\Delta E_{tot} = A + Bu^2 + Cu^4 + O(u^6)$, where A, B and C are the expansion coefficients. The dynamic matrix coefficients a_{ij} in equation (6) are related to the quadratic coefficients B in a straightforward way.

The hole–phonon matrix elements $P = \langle |H_1| \rangle$ were zero in the calculations at $u = 0$ and they only changed sign upon changing from $+u$ to $-u$. Thus they can be expanded with respect to u as $P = Du + Eu^3 + O(u^5)$ and $P/u = D + Eu^2 + O(u^4)$, where D and E are appropriate expansion coefficients. From the fitted coefficients D the deformation potential constants DP can be obtained as $DP = (P/u)\,|_{u \to 0} = D$. By choosing two non-zero values of u and by the fitting to the powers u^3 in the calculated hole–phonon matrix elements one can extrapolate the linear coefficient D from the calculations of finite displacement values u.

4. Results and discussion

In order to evaluate IVDPs for transverse phonon modes, one has to determine the displacement patterns (u_1, u_2) for corresponding phonons, in particular the displacement ratio $r' = u_1/u_2$, as shown by equation (5). By using an *ab initio* pseudopotential calculation we have calculated the dynamical matrix elements a_{ij} and the corresponding phonon frequencies (TAX and TOX) for the nine III–V zincblende semiconductors, AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs and InSb. The atomic displacement ratios $r' = u_1/u_2$ of the cation and the anion in the TAX and TOX phonons are listed in table 1, in the fourth and the fifth columns, respectively. In the sixth column, we list the mass ratio M_2/M_1 between the anion and the cation for the corresponding III–V zincblende semiconductor. Observing the atomic displacement ratios of the TAX phonon we notice that the values of u_1/u_2 (TAX) are consistently very close to -1 for all the nine zincblende semiconductors. This means that the cation and the anion in the same primitive unit cell move in phase with respect to each other with approximately the same vibration amplitude, i.e. the cation and the anion in the primitive cell oscillate almost together as a whole in the TAX phonon. Only the adjacent unit cells oscillate in opposite direction with a phase difference of 180°. Thus, there is not much bond stretching and the restoring force is mainly due to the bond bending and hence is relatively weak, resulting in a lower vibrational frequency. In the TOX phonon mode, on the other hand, the cation and the anion in the same primitive cell oscillate in the opposite direction with respect to each other, so $u_1/u_2 > 0$. The displacement ratios u_1/u_2 in the fifth column for the TOX phonon are approximately equal to the mass ratios M_2/M_1 in the sixth column for these nine semiconductors consistently, even though the displacement ratios u_1/u_2 themselves vary by one order of magnitude across the column from one semiconductor to the other. Thus for the TOX mode, the cation and the anion in the primitive cell are displaced in the oscillation in inverse proportion to their respective masses, so that the centre of the mass of the cell is displaced by a relatively small amplitude. The restoring force in the oscillation is mainly due to strong bond stretching, resulting in a much higher frequency. Since there is no experimental information available for the phonon eigenvectors in these semiconductors, the displacement ratios listed in table 1 can be used as references when they are needed in other work.

Table 1. Phonon displacement pattern.

Materials	a(Å) Theory	a(Å)[a] Expt.	u_1/u_2 (TAX)	u_1/u_2 (TOX)	(M_2/M_1)
AlP	5.429	5.467	−1.211	0.948	1.148
AlAs	5.648	5.639	−1.042	2.665	2.776
AlSb	6.116	6.136	−0.970	4.652	4.513
GaP	5.429	5.447	−1.435	0.310	0.444
GaAs	5.617	5.654	−1.213	0.886	1.074
GaSb	6.058	6.095	−1.110	1.573	1.746
InP	5.851	5.869	−1.521	0.177	0.270
InAs	6.036	6.058	−1.164	0.560	0.652
InSb	6.423	6.479	−1.167	0.909	1.060

[a] [67].

The theoretical lattice constants a_{theo} for these zincblende semiconductors derived from our calculations are listed along with the experimental lattice constants [67] a_{expt} in table 1, in the second and the third columns, respectively. The agreement between the theoretically calculated lattice constants and the experimental ones are excellent, with an overall agreement better than 1.0%.

The norm-conserving pseudopotentials used in this study were optimized with respect to the electronic occupancies in s, p and d orbitals for each element. In general the errors in the calculated lattice constants are caused by the approximations in constructing pseudopotentials. In particular, the calculated equation of state (EOS) and lattice constant depend sensitively on the electronic configuration used in generating pseudopotentials. The essential error is caused by changes in the electronic occupancies of orbitals from the atomic to the crystalline environment. When proper electronic configurations are used, the calculated EOS and lattice constant are closest to experimental values. In the calculation, we started by adjusting the occupancies and the core radii r_c in the three orbitals to obtain the optimized match for the electron wavefunctions and eigenenergies between those calculated by all electron and by pseudopotential calculations. Then the EOS is calculated and examined about the equilibrium over $\simeq 20\%$ volume change. Generally, the pseudopotentials thus generated will produce well behaved EOS. But if the EOS curve deviates severely from a smooth and simple form, one has to readjust the electronic configurations iteratively. This type of approach has enabled us to achieve much closer agreement in the calculated lattice constants in these semiconductors than previous calculations. Indeed it can be used to develop a formal formalism for generating good pseudopotentials in *ab initio* calculations. A recent study by M Teter [68] has provided such a formal method of performing the optimization adjustment for generating pseudopotentials.

We list the calculated results for the TAX and TOX phonon frequencies in table 2 for the nine semiconductors. The corresponding experimental values are also listed for comparison [69–76]. By comparing the phonon frequencies calculated *ab initio* with the experimental values we observe that the agreement between them is very good, particularly for TOX phonons for which there is only a few per cent difference. *Ab initio* phonon calculations for the X phonons of III–V zincblende semiconductors have been previously carried out for AlP [77], AlAs [59] GaP [55] and GaAs [78]. We list results of these calculations in table 2.

Table 2. Transverse phonon frequencies.

Materials	TAX (THz)			TOX (THz)		
	This Work	Others	Expt.	This Work	Others	Expt.
AlP	4.32	4.95[a]		12.49	11.80[a]	
AlAs	3.05	3.02[b]	3.26[c]	10.03	9.76[b]	10.0[c]
AlSb	1.91		2.05[d]	8.60		8.84[d]
GaP	3.32	3.30[e]	3.13[f]	10.80	10.71[e]	10.65[f]
GaAs	2.43	1.87[g]	2.41[b]	7.79	7.94[g]	7.56[b]
GaSb	1.41		1.70[i]	6.21		6.36[i]
InP	2.45		2.05[j]	9.52		9.70[j]
InAs	1.27		1.62[k]	6.31		6.55[k]
InSb	1.23		1.12[l]	5.15		5.38[l]

[a] [77], [b] [59], [c] [69], [d] [70], [e] [55], [f] [71], [g] [78], [h] [72], [i] [73], [j] [74], [k] [75], [l] [76].

The accuracy in the frozen-phonon calculations was generally to within a few per cent. The worst cases were for TAX phonons since they are of much lower values of frequency than the TOX phonons. The higher-order contributions ($O(u^4)$ and higher) beyond the harmonic terms to the calculated dynamic matrix elements a_{ij} were AlP 0.9%, AlAs 0.5%, AlSb 1.3%, GaP 0.8%, GaAs 0.4%, GaSb 0.9%, InP 1.9%, InAs 0.8% and InSb 0.05%, for a displacement of $u = 2 \times 10^{-3} a/\sqrt{2}$ in the S_1 mode. There was another more serious source of error in the calculated dynamic matrix elements a_{ij} from which the phonon frequencies and the eigenvectors were determined. These coefficients in equation (6) can be determined from total energy calculations from different displacement patterns (u_1, u_2). The natural choice [59] is to use the four displacement modes S_1, S_2, $S_1 + S_2$ and $S_1 - S_2$. However, only three of the four modes are independent. One can choose only three modes, say, S_1, $S_1 + S_2$ and $S_1 - S_2$, to calculate the dynamic matrix elements a_{ij}. Accordingly, the off-diagonal elements $a_{12} = a_{21}$ can be determined either by $a_{12} = (\Delta E_1 - \Delta E_2)/4u^2$ from the four-mode calculations or by $a_{12} = [2\Delta E_1 - 0.5(\Delta E_3 + \Delta E_4)]/4u^2$ from the three-mode calculations. The off-diagonal element a_{12} evaluated from the former calculations is presumably more accurate than that from the latter, due to the fact that only two calculations ΔE_1 and ΔE_2 are used to derive a_{12} in the former case, whereas in the latter case three calculations ΔE_1, ΔE_3 and ΔE_4 are used. Thus the accumulative error in the latter case is larger than that in the former one. For AlAs and GaAs, we used four displacement modes S_1, S_2, $S_1 + S_2$ and $S_1 - S_2$ to evaluate the dynamic matrix. The off-diagonal element a_{12} evaluated by the two different methods differed by 2.9% for AlAs and 1.3% for GaAs.

The intervalley scattering between the lowest conduction state at Γ, Γ_{1c} and those at X, X_{1c} or X_{3c}, is allowed only for the longitudinal X phonons (LAX and LOX) but is forbidden for the transverse X phonons (TAX and TOX). This is due to the fact that the TAX and TOX phonons are of X_5 symmetry and LAX and LOX phonons are of X_1 or X_3 symmetry [79], while the symmetry of the lowest conduction state at X is either X_1 or X_3 [80]. For the Γ–X intervalley scattering of the top valence band, both the longitudinal and the transverse X phonons contribute the scattering probability. When the spin is neglected, the top valence states at Γ are of Γ_{15} symmetry, triply degenerate, while the top valence states at X are doubly degenerate

with X_5 symmetry. Thus we need to calculate the IVDPs for both the longitudinal phonons and the transverse phonons.

We first examine the hole–transverse-phonon scattering. The X_5 transverse phonons scatter holes in the Γ_4 singlet state to the X_5 states, but are forbidden from assisting in the transition from the other two states at Γ to the X_5 states. We present the calculated hole intervalley deformation potentials for the transverse phonons in table 3. The correction factor

$$\eta = [2(M_1 + M_2)/(M_1 + M_2 r^2)]^{1/2}$$

for each phonon mode is also presented in the column next to that of DPs for each phonon mode. When comparing DPs due to the TAX phonon and those due for TOX phonons, we observe the following: IVDPs for TAX phonons are much less than those of the TOX phonon, in most cases by one order of magnitude, for the nine semiconductors. This huge difference for different phonon modes is not due to the correction factor η, since the η-values of TAX and TOX for each semiconductor do not differ greatly and η-values of different semiconductors for the same phonon mode, e.g. TAX, do not vary dramatically going down the column. The large difference in DPs of different phonon modes is due to very small hole–phonon matrix elements for the TAX phonon. In crystal diamond structure the transition from the top valence states Γ'_{25} to the top valence states X_4 by TAX phonon is forbidden by symmetry. In zincblende crystals, due to the loss of inversion symmetry, the polarized charge distribution makes the transition allowed. The transition probability is, nonetheless, much smaller than the 'allowed' transition by TOX mode, resulting in much smaller IVDPs.

Table 3. Γ–X intervalley deformation potentials for transverse phonons.

Materials	TAX			TOX		
	D (eV Å^{-1})	η	NL (%)	D (eV Å^{-1})	η	NL (%)
AlP	0.191	1.552	0.02	4.784	1.374	0.10
AlAs	0.075	1.457	3.40	5.306	2.330	0.05
AlSb	0.083	1.379	1.70	5.893	3.021	0.05
GaP	1.424	1.541	0.06	6.040	0.716	0.14
GaAs	0.991	1.549	0.17	5.739	1.323	0.05
GaSb	0.612	1.507	0.29	5.641	1.795	0.04
InP	1.397	1.508	0.09	4.852	0.515	0.12
InAs	0.891	1.494	0.01	4.381	1.036	0.08
InSb	0.791	1.522	0.16	4.310	1.343	0.06

D relates to the IVDP for the top valence bands; $\eta = [2(M_1 + M_2)/(M_1 + M_2 r^2)]^{1/2}$, correction factor, and NL relates to the non-linear contributions to DP at $u = 2 \times 10^{-3} a/\sqrt{2}$ (in per cent).

In our calculations, as we chose the generalized mode $S_1 + S_2$ where only the cations were displaced from the equilibrium, the calculated hole–phonon matrix elements were generally approximately equal to and had the same signs as the matrix elements of the $S_1 - S_2$ mode. In the latter mode, the anions were displaced from equilibrium while the cations remain at rest. In an eigen-phonon mode both the

cations and the anions are displaced from equilibrium, with the appropriate ratio u_1/u_2 for the two types of ions. For the TAX mode, the displacement ratios u_1/u_2 as listed in the table 1 show that the cation and the anion in the same primitive cell oscillate in phase with almost the same amplitude, i.e. $u_1/u_2 \approx -1$. This is the case for all the nine zincblende semiconductors, no matter how disproportionate the masses of the two types of ions are. The hole–phonon matrix element P in an arbitrary displacement pattern of the cations and the anions (u_1, u_2) can be expressed as a linear combination of (in the linear region) $P = P_1 u_1 + P_2 u_2$, where P_1 is the matrix element per unit amplitude of the $S_1 + S_2$ mode when the cations are displaced alone and P_2 is that of the $S_1 - S_2$ mode. Thus, for the TAX mode, since $P_1 \approx P_2$ and $u_2/u_1 \approx -1$, we have $P = (P_1 + r'P_2)u_1 \approx 0$, resulting in a very small IVDP.

The DP values for TOX mode are, on the other hand, quite large, and do not vary appreciably across the nine zincblende semiconductors, with values of about 5 eV Å^{-1}, although the correction factor η of the TOX mode can vary widely from one semiconductor to another. Let us compare the two extreme cases of AlSb and InP. The correction factors of the two semiconductors are AlSb 3.021 and InP 0.515, differing by a factor of $\simeq 6$. But the DPs of the two materials, AlSb 5.893 and InP 4.852, do not differ much.

In the columns under 'NL' we list the non-linear contribution (in per cent) with terms of the order $O(u^3)$ to DPs, at a displacement of $u = 2 \times 10^{-3}a/\sqrt{2}$ for both TAX and TOX phonon modes. In most cases, the non-linear contributions to the calculated DPs are less than a fraction of one per cent. The worst cases are for AlAs and AlSb in TAX mode, with 3.4% and 1.7% non-linear contributions, respectively. The IVDP values of TAX mode of the two materials are the lowest.

Table 4. Γ–X valence band IVDP for longitudinal phonons (eV Å^{-1}).

Materials		TAX		TOX	
		$D^1_{\Gamma X_5} = D^2_{\Gamma X_5}$	$D^3_{\Gamma X_3}$	$D^1_{\Gamma X_5} = D^2_{\Gamma X_5}$	$D^3_{\Gamma X_3}$
AlP	X_3	4.006	0	X_1 11.324	4.230
AlAs	X_3	3.360	0	X_1 14.095	5.516
AlSb	X_3	3.104	0	X_1 13.373	6.371
GaP	X_1	8.966	4.232	X_3 6.047	0
GaAs	X_3	4.661	0	X_1 10.009	5.130
GaSb	X_3	4.253	0	X_1 9.153	6.109
InP	X_1	7.098	2.916	X_3 4.784	0
InAs	X_1	7.604	3.370	X_3 3.666	0
InSb	X_3	3.404	0	X_1 7.146	3.978

$D^i_{\Gamma X_5}(i = 1, 2)$ is the DP for hole intervalley scattering between the ith degenerate valence state at Γ and the doubly degenerate X_5 states at X.
$D^3_{\Gamma X_3}$ is the DP for hole intervalley scattering between the third degenerate valence state at Γ and the X_3 valence state at X.

In table 4, we present Γ–X valence band IVDPs due to longitudinal phonons for the nine III–V zincblende semiconductors. Under the longitudinal X phonon distortion, the triplet of the top valence Γ_{15} states is split into a singlet of Γ_4 state and a doublet of Γ_5 state pair of the point group [81] D_{2d}, i.e. $\Gamma_{15} = \Gamma_4 + \Gamma_5$. Longitudinal phonons couple the Γ_5 doublet to the X_5 top valence states at X, and Γ_4 singlet to the X_3

valence state at X (by X_1 phonon only). The X_3 state is below the X_5 valence states. In table 4, $D^i_{\Gamma X_5}$, where $i = 1$ and 2, are the DPs for the hole scattering between the ith valence state of the doublet at Γ and the doubly degenerate X_5 states at X, and $D^3_{\Gamma X_3}$ is the DP between the Γ_4 singlet at Γ and the X_3 valence state at X. The symbols X_1 and X_3 in the second column and the fifth column indicate the phonon symmetry as have been determined previously [44]. Comparing the results for the LAX phonon with those of the LOX phonon, we observe that, consistently for all the semiconductors, the DP due to the phonon of X_1 symmetry is larger by a factor of 2–3 than that due to the X_3 phonon for each material. This situation is very similar to the case of Γ–X intervalley scattering of the lowest conduction states where $D_{\Gamma X}$ of the conduction electrons due to the X_3 phonon is much smaller than that due to the X_1 phonon. The significant difference in hole–phonon matrix elements between the X_1 phonon and the X_3 phonon can be explained by a similar argument as in [44]. More screening for the X_3 phonon to the long-range electron–phonon interaction due to valence electron redistribution results in smaller intervalley scattering probabilities.

5. Conclusions

We have calculated Γ–X hole–phonon scattering matrix elements for the top valence bands in the III–V zincblende semiconductors AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs and InSb, by *ab initio* pseudopotential calculations. At the same time, by phonon calculations in the frozen-phonon approximation under the local-density approximation, we have calculated the eigenfrequencies and eigenvectors of the transverse acoustic (TA) and optic (TO) X phonons in these semiconductors. The TAX and TOX phonon frequencies calculated *ab initio* from our calculations agree very well with the available experimental results. From the calculated Γ–X hole–phonon matrix elements and various phonon eigenmodes at X we have evaluated the Γ–X intervalley deformation potentials of the top valence bands for both the longitudinal and the transverse phonons in these semiconductors.

The calculated hole–phonon matrix elements for the TAX phonon are very small, as expected from symmetry considerations. This results in very small IVDP values for TAX for all the nine semiconductors. The IVDPs for the TOX phonon are, on the other hand, quite large, and do not vary appreciably from one semiconductor to the other, averaging about 5 eV Å^{-1}, even though the correction factors can differ greatly (by as much as a factor of $\simeq 6$) for different semiconductors. We have also calculated the IVDPs of the top valence bands for the longitudinal phonons (LAX and LOX), and have found that the IVDPs of longitudinal phonon with X_1 symmetry are generally larger than those of X_3 symmetry. This is due to the more complete screening of the electron–phonon interaction for the X_3 phonon due to larger electron redistribution, resulting in smaller IVDPs. The IVDPs due to the X_1 longitudinal phonon are also larger than those due to the TOX phonon, for most of the nine semiconductors. The calculated IVDPs, the phonon frequencies and eigenvectors are useful for other studies when information of these quantities is needed in the analysis. Our results can also be used to compare with other calculations to assess the validity of the approximations used in these calculations.

Acknowledgments

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