# Bond-length dependence of phonon frequencies in tetrahedrally coordinated semiconductors

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**Abstract.** A scaling law of force constants versus equilibrium bond length is found, which gives a good account of phonon energies in tetrahedrally coordinated semiconductors. The law gives the bond-length dependence of bond-stretching and bond-bending parameters which enter the valence force field model used to describe the lattice dynamics of these materials. This is obtained after a theoretical fitting to the experimental optic phonons in II–IV–$V_2$ chalcopyrite semiconductors. To test the validity of the proposed law, we calculated phonon energies in several III–V zincblende compounds at different points in the Brillouin zone. A good agreement is found with experimental results for most of the phonon energies. The small discrepancies obtained at intermediate frequencies are mainly due to the limitation of the valence force field model used and cannot be imputed to the scaling law. The law permits us to predict phonon energies in other compounds within the family. As an example, we calculate optic phonons of $CdSiAs_2$, one of the chalcopyrite compounds with a larger cation–anion bond length difference, and discuss the results in terms of phonon energies in zincblende analogues.

## 1. Introduction

It is well known that the dispersion of phonon energies in simple compounds can be obtained from *ab initio* calculations. However, up to now, semiempirical calculations have been most widely used because they are simpler, they can be applied to complex structures, they permit us to assign a physical meaning to the parameters involved in calculations and, most importantly, by selecting the adequate model one gets a fairly good description of experimental results. A further step in the analysis of phonons is the attempt to correlate parameters within a family of compounds and estimate the evolution of modes in the series. With respect to this, Harrison [1] has shown that the most important parameter that describes phonons in zincblende compounds, the bond-stretching force constant of the bond, depends on the equilibrium bond length through a −4 power law as can be inferred from the $d^{-2}$ scaling of the bonding energy in tetrahedral $sp^3$ hybrid bonds. As regards experiments, in the past, several studies have been devoted to analysing the dependence of optic phonon energies with interatomic distances in group IV semiconductors [2] and other cubic compounds [3]. More recently, Pascual *et al* have extended the study correlating bond-stretching parameters and bond lengths in two II–IV–$V_2$ chalcopyrite compounds ($CdGeP_2$ and $CdGeAs_2$) and the corresponding zincblende analogues [4]. It was found that the

bond-stretching force constants calculated from a simple valence force field (VFF) model were in fairly good agreement with Harrison's predictions.

In the present work we focus our attention on the determination of a scaling law for the parameters which enter calculations in the case of III–V zincblende and II–IV–V$_2$ chalcopyrite compounds, two related families of tetrahedrally coordinated semiconductors. Indeed, II–V and IV–V bonds in the ternary compounds show bond lengths not far from cation–anion bond distances in the III–V analogues and, because optic phonons keep a strong local bond character, a one-to-one correspondence can be established between specific modes in both kinds of compound [4]. This justifies the global study of both types of compound, which will be developed in this work. In fact, if optic phonons are roughly governed by local bonding interactions, the scaling law must apply to all tetrahedrally coordinated covalent bonds and predictions should be inferred for the vibrational energies of new materials.

## 2. Phonon energies and model parameters

A fairly good fit to experimental phonon dispersion curves for diamond and zincblende compounds and optical phonons in chalcopyrite compounds can be obtained using a VFF model that takes into account stretching forces localized in the tetrahedral bonds and bending force constants between two adjacent tetrahedral bonds [5–7]. However, because of the simplicity of the model, the description of specific details in the lattice dynamics depends on the way in which the fitting procedure has been performed. For instance, fitting the experimental elastic constants [5], one overestimates the frequency of transverse acoustic (TA) phonons at the Brillouin zone edge. In the case of chalcopyrites, since there are two different bonds, two stretching force constants at least are needed in calculations. As regards the bending force constants that enter the model, reasonable results have been obtained [7–9] by taking a mean bending to describe all interactions between adjacent bonds. However, low-energy modes are highly sensitive to the bending parameter, and calculations with an average bond-bending parameter cannot account for the width of the lowest frequency band. One can improve the agreement by taking two different bond bending parameters to describe the two kinds of interaction between like adjacent bonds, and a mean bond bending parameter for the force constant between unlike adjacent bonds. This introduces a total of four parameters in the model, which is enough to get a satisfactory fit with optical results [8, 9]. The drawback is that one of the parameters is unreasonably small and negative; this is a consequence of the model. The physical reason is that we ignore additional force constants associated with second neighbours and, also, the influence of fifth neighbours. The latter are located behind the first-nearest neighbours and strongly influence calculations of low-energy branches [6].

It would be desirable to retain the physical meaning of the force constants used in the calculations, despite the fact that this implies less agreement with experimental results. The bulk modulus and the shear elastic constant are, within the simple Keating model, described in this work, directly related to the bond-stretching $K_r$ and bond-bending $K_\theta$ force constants [10] and in zincblendes, both physical quantities scale with the bond length in the same way [11]. This suggests that a fairly good description of the lattice dynamics can be carried out in chalcopyrites by taking two bond-stretching and two bond-bending force constants but on the condition that the

scaling of the stretching to the bending force constants is the same for both cation–anion bonds. With this restriction: (i) one differentiates inequivalent cation–anion pairs of adjacent bonds; (ii) one gets a reasonable description of the width of the lowest optical band of phonon multiplets; (iii) the bond-bending force constants in chalcopyrites are in close correspondence with bond-bending parameters in the related zincblende binaries.

**Table 1.** Comparison of the Raman frequencies of $CdGeAs_2$ [4] with theoretical calculations. The different approaches correspond to least mean square fits to experimental results with: (*a*) four parameters and the constraint of the same bond-bending to bond-stretching ratio for each bond; (*b*) the four-parameters model; (*c*) the three parameters with a mean bond-bending force constant for all the bonds. In the three cases calculations have been performed using an ideal undistorted lattice. (All force constants are in units of $10^3$ dyn cm$^{-1}$ and the frequencies in units of cm$^{-1}$.)

| Mode symmetry | Raman frequency | This work (*a*) | VFF four parameters (*b*) | VFF three parameters (*c*) |
|---|---|---|---|---|
| $\Gamma_4$ | 273 | 282 | 281 | 281 |
| $\Gamma_5$ | 275 | 280 | 281 | 279 |
| $\Gamma_5$ | 259 | 257 | 256 | 257 |
| $\Gamma_3$ | 260 | 254 | 251 | 254 |
| | | | | |
| $\Gamma_2$ | — | 201 | 195 | 202 |
| $\Gamma_5$ | 203 | 205 | 206 | 207 |
| $\Gamma_4$ | 205 | 211 | 212 | 212 |
| $\Gamma_1$ | 196 | 182 | 182 | 182 |
| $\Gamma_5$ | 160 | 155 | 154 | 156 |
| $\Gamma_3$ | 165 | 162 | 168 | 162 |
| $\Gamma_2$ | — | 169 | 175 | 169 |
| | | | | |
| $\Gamma_5$ | 96 | 80 | 93 | 77 |
| $\Gamma_4$ | 73 | 76 | 76 | 76 |
| $\Gamma_3$ | 75 | 75 | 71 | 75 |
| $\Gamma_5$ | 46 | 65 | 47 | 67 |
| | | | | |
| $\alpha_{Cd-As}$ | — | 26.12 | 26.99 | 26.34 |
| $\alpha_{Ge-As}$ | — | 39.55 | 37.78 | 39.60 |
| $\beta_{Cd-As}$ | — | 2.30 | −0.30 | 2.85 |
| $\beta_{Ge-As}$ | — | 3.48 | 6.38 | 2.85 |

In order to test the model, let us apply it to a prototype of the family. Table 1 displays the results of calculations of optical phonons in $CdGeAs_2$. Notice that for the three models the bond-stretching parameters for Cd–As and Ge–As bonds are very similar. The different values of like parameters found in In–As and Ga–As bonds, the two III–V zincblende analogues [12], can be explained bearing in mind that the equilibrium bond lengths of In–As (2.61 Å) and Ga–As (2.45 Å) are, respectively, shorter and longer than the related bond lengths in $CdGeAs_2$ [$d$ (Cd–As) = 2.63 Å and $d$ (Ge–As) = 2.43 Å]. With respect to the bond-bending force constants, no correlation can be found between the two independent parameters which enter the four-parameter model and the corresponding bendings in the two zincblende binaries [12]. In contrast, the bending entering in the three-parameter model is close to the mean value of the two GaAs and InAs bendings. Finally, the two bendings proposed in this work are not far from the bendings that fit phonon energies in the like binaries.

As regards vibrational frequencies, as shown in table 1, the three models fit well the energies of phonons associated with the folding of longitudinal acoustic (LA), longitudinal optic (LO) and transverse optic (TO) branches of the corresponding zincblende binaries. The discrepancies are confined to the different description they give of the four low-energy modes that are directly associated with the folding of TA branches in related III–V compounds. As expected, the four-parameter model (third column in table 1) gives the best agreement, whereas the use of a single mean bond-bending parameter (fourth column) reduces the phonon dispersion from 50 cm$^{-1}$, as measured in experiments (first column), to 10 cm$^{-1}$. A better compromise is obtained with the model proposed in this work. As shown in the second column of table 1, the energies of the lowest $2\Gamma_5 + \Gamma_3 + \Gamma_4$ modes span a wider band. The theoretical dispersion between the two low-$\Gamma_5$ modes is, as expected, smaller than the one found in experiments, but calculations show that atoms which vibrate are now in each case correctly predicted i.e., the lowest $\Gamma_5$ mode is associated with Cd–As vibrations and can safely be associated with the folding of the TA (X) phonon of InAs in the chalcopyrite Brillouin zone, whereas the upper $\Gamma_5$ mode derives from the folding of like phonons in GaAs.

## 3. Scaling of force constants versus bond length

We selected six II–IV–V$_2$ compounds for which optical phonons were unambiguously assigned by means of Raman and infrared experiments: ZnSiP$_2$ [7], ZnSiAs$_2$ [13], ZnGeP$_2$ [7], CdSiP$_2$ [7], CdGeP$_2$ [8] and CdGeAs$_2$ [4] and applying the model developed in the preceding paragraph we calculated the force constants which fit the experimental results. In the particular case of CdGeAs$_2$ discussed in detail in the preceding paragraph, the overall fitting gives force constants (see second column of table 1) which are close to the ones reported in the fourth column of the table giving rise to a similar estimate of optical phonon energies. The plot of the stretching force constants of different II–V and IV–V bonds with respect to bond length is shown in figure 1. The log–log plot gives a $-4.30$ dependence and a scaling law $K_r = 1.57 \times 10^6 / d^{4.30}$ ($K_r$ in dyn cm$^{-1}$ when $d$ is in Å). This is close to the $-4$ power law predicted by Harrison [1, 14]. With regard to the bond-bending parameter, the constraint that the bending to stretching ratio is the same for all kind of bond in the family gives a scaling factor of 0.11 with respect to the absolute value of the bond-stretching force constant. This is consistent with parameters used in previous studies [6].

In order to test the validity of the scaling law to describe phonons in tetrahedrally coordinated semiconductors we calculated phonon energies in III–V compounds taking as the sole input parameter the specific bond length for each particular compound. It is clear that the VFF model used in this work has limitations if one seeks details of phonon dispersion branches, as was noted in section 2. However, it gives a fairly good description of phonon dispersion curves along the main symmetry directions [6, 8]. Of particular interest are the phonon modes at $\Gamma$, X and W points in the Brillouin zone owing to their direct relationship with optical phonons in associated chalcopyrite compounds [12]. To test the model we have chosen six III–V zincblende compounds, for which phonons are experimentally well known, with bond lengths ranging in a regular way from GaP (both atoms have 'short' tetrahedral covalent radii) to InSb (both atoms have 'large' tetrahedral covalent radii). The results are
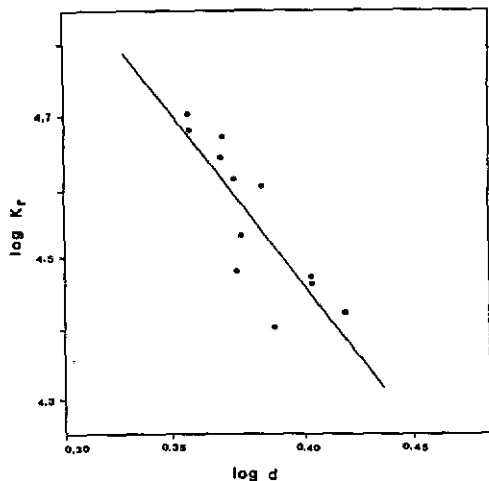
Figure 1. Log–log plot of the bond-stretching force constants $K_r$ (dyn cm$^{-1}$) versus the corresponding bond length $d$ (Å) for a series of II–IV–V$_2$ chalcopyrite compounds. The force constants have been obtained after application of the model discussed in this work.

displayed in table 2 where one compares experimental phonon energies, phonon energies calculated according to the scaling law and phonon energies obtained from a fitting to experimental results. Unfortunately, the set of experimental phonon energies at point W has only been measured for GaAs [15]. It was noted that there is a fairly good agreement between the experimental frequencies and those calculated from the scaling law. The biggest discrepancy is found in the prediction of LA and LO phonon energies at X. However, it may be observed that these phonon energies are close to the ones obtained after a fitting to the experimental results. This suggests that the difference arises, mainly, from the limitations of the Keating model and not from the scaling law. As can be seen in table 2, this is particularly evident for GaP and InP compounds. Indeed, it is known that $X_3$ and $X_1$ symmetry modes are associated with independent movement of cations and anions in the lattice with an important contribution of bond-bending force constants [23]. In the model, one takes into account the kind of atoms associated with the bending but not if there is a cation or an anion in its apex, in spite of the fact that the different distribution of the electronic charge around cations and anions would give rise to inequivalent bending force constants.

A last comment is in order concerning the meaning and use of the dependence of force constants on interatomic bond lengths as obtained in this work. The law only predicts how the force constants can be deduced from the equilibrium bond length for different compounds in the family. However, this dependence does not mean that for a given compound the force constants scale in this way under distortion. For instance, the law cannot be applied to study the phonon frequency shift when an external pressure is applied to a compound. If a hydrostatic pressure is considered, it is known that the measurement Grüneisen parameter for optical phonons in zincblende compounds yields values from 1 to 2 [24]. A simple calculation [25] shows that this would imply power dependence ranging from $-6$ to $-12$, very far from the $-4$ power law predicted by Harrison [1, 14] for the case of atoms at equilibrium. Summing up, it is necessary to distinguish clearly two situations: the study when the atoms are forced out from their equilibrium positions in which case it is necessary to introduce hard-core effects [2] and the study of the bond-length dependence when the atoms are at equilibrium. This work and Harrison's predictions refer to the

Table 2. Comparison of the experimental phonon energies at Γ, X and W and theoretical calculations for several III–V compounds. sl refers to calculations by applying the scaling law; ft refers to calculations after performing a fitting to experimental results. (All frequencies are in units of $cm^{-1}$.)

| | GaAs | | | GaP | | | GaSb | | | InAs | | | InP | | | InSb | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | exp [15] | (sl) | (ft) | exp [16] | (sl) | (ft) | exp [18] | (sl) | (ft) | exp [19] | (sl) | (ft) | exp [21] | (sl) | (ft) | exp [22] | (sl) | (ft) |
| $\Gamma_{15}$ | 271 | 276 | 286 | 367 [17] | 387 | 388 | 229 | 211 | 233 | 220 | 212 | 231 | 305 | 309 | 307 | 180 | 160 | 188 |
| $X_5$ | 256 | 253 | 259 | 353 | 359 | 360 | 212 | 195 | 218 | 218 | 195 | 214 | 282 | 289 | 289 | 178 | 147 | 176 |
| $X_1$ | 225 | 195 | 203 | 366 | 329 | 329 | 166 | 130 | 143 | 203 | 168 | 183 | 315 | 280 | 278 | 143 | 114 | 133 |
| $X_3$ | 240 | 203 | 211 | 249 | 219 | 219 | 212 | 172 | 189 | 160 | 136 | 148 | 125 | 146 | 144 | 158 | 117 | 137 |
| $X_5$ | 82 | 85 | 93 | 107 | 109 | 107 | 57 | 62 | 61 | 54 | 64 | 67 | 67 | 76 | 73 | 41 | 49 | 49 |
| $W_4$ | 269 | 257 | 264 | 377 [17] | 360 | 362 | — | 199 | 222 | — | 197 | 215 | — | 290 | 290 | — | 149 | 178 |
| $W_2$ | 256 | 256 | 263 | — | 369 | 370 | — | 196 | 219 | — | 199 | 218 | — | 300 | 298 | — | 149 | 178 |
| $W_3$ | 208 | 193 | 199 | — | 209 | 210 | — | 164 | 181 | — | 130 | 141 | — | 139 | 138 | — | 112 | 132 |
| $W_1$ | 197 | 186 | 192 | — | 314 | 314 | — | 124 | 137 | — | 160 | 175 | — | 267 | 266 | — | 109 | 128 |
| $W_2$ | 114 | 95 | 104 | — | 120 | 117 | — | 70 | 69 | 83 [20] | 70 | 74 | — | 83 | 79 | 62 [20] | 55 | 55 |
| $W_4$ | 101 | 94 | 104 | — | 123 | 120 | — | 69 | 68 | 78 [20] | 71 | 75 | — | 86 | 82 | 55 [20] | 55 | 55 |

latter. This must be taken into consideration when one calculates phonon energies in unrelaxed materials like strained heterostructures or superlattices.

## 4. Optical phonons of CdSiAs$_2$

The scaling of force constants versus bond length in II–IV–V$_2$ compounds can be used to determine optical phonons and phonon-dispersion branches in new compounds within the family. As a specific example, we discuss in this paragraph the prediction of optical phonon energies of CdSiAs$_2$. This is a chalcopyrite compound for which important research has been performed concerning its electronic properties, paying particular attention to the electronic states associated with the fundamental gap [26]. By contrast, no study has been carried out concerning its vibrational properties. One of the most interesting aspects of this compound is the different size of the two cations. This makes CdSiAs$_2$ one of the II–IV–V$_2$ compounds with the largest tetrahedral distortion [27] so that it is an appropriate compound to test the efficiency of the scaling law when experimental results become available.

The binary analogues to this compound are InAs and AlAs, with equilibrium bond lengths [28] slightly shorter [$d$(In–As) = 2.623 Å against $d$(Cd–As) = 2.629 Å] and appreciably longer [$d$(Al–As) = 2.451 Å against $d$(Si–As) = 2.356 Å] than the related bonds in the ternary compound. Moreover, because GaAs can be considered to a certain extent as an average of InAs and AlAs we shall follow the evolution of phonon-like energies in GaAs, InAs and AlAs and, finally, CdSiAs$_2$. The results are summarized in figure 2. For CdSiAs$_2$, the sequence of optical phonons is accommodated in three main bands: the high energy manifold contains four frequencies, the intermediate manifold divides into two groups, one of slightly higher energy made up of two frequencies and a lower one of three frequencies, and lastly, there is a low-energy band with four frequencies. In order to understand this disposition of phonon energies, let us try to explain the evolution of equivalent phonons in the series GaAs, (Al+In)As, CdSiAs$_2$ exclusively from the corresponding changes in the respective bond lengths and cation masses.

Phonon energy calculations for GaAs at Γ, X and W give three clearly differentiated bands (see figure 2): a high energy band made up of phonons of the TO branch, an intermediate band with phonons coming from the LO and LA branches, and the low manifold issued from the TA branch. Because the Ga and As masses are much the same, the splitting of LA and LO branches at the Brillouin-zone edge is small (see figure 2). This explains why corresponding X and W phonons group in a single band.

Let us now consider the two binaries AlAs and InAs. As regards AlAs it is interesting to notice that the bond length is practically the same as that in GaAs and the difference in the grouping of phonons arises from the influence the light mass of Al exerts on the corresponding frequency. As in GaAs, the phonons span three bands but the difference between Al and As masses opens a gap between LO and LA modes at the Brillouin-zone edge: the LO modes associated mostly with Al vibrations ($X_3 + W_3$) rise up and reach the phonon energy band associated with the TO branch, while the LA modes, directly related to As vibrations ($X_1 + W_1$) keep the same energy as corresponding modes in GaAs. Finally, the TA modes renormalize to energies that are slightly higher than like modes in GaAs because the Al+As mass is smaller than that of Ga+As. In the case of InAs a similar discussion is in order, differing in that the roles of Al and As are now changed to As and In respectively. In
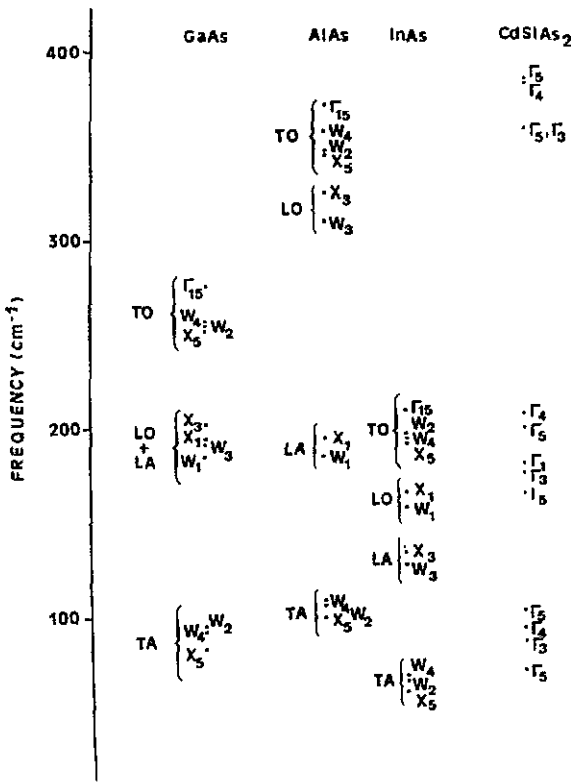
**Figure 2.** Evolution of theoretical energies in the series: GaAs, AlAs+InAs and CdSiAs$_2$. The first column displays GaAs phonons in a fictitious chalcopyrite Brillouin zone. The second and third columns display folded modes for AlAs and InAs, the two III–V compounds analogous to CdSiAs$_2$. The last column shows predicted optical modes of CdSiAs$_2$ as computed in this work.

this case both the mass of In and the larger In–As distance contribute to an absolute lowering of phonon energies with respect to GaAs. The effect of the force constant can be observed by comparing the $X_1$ modes in both compounds given that it is a pure mode of anions. As can be seen in figure 2, the frequency of the $X_1$ mode falls about 15% in relation to the frequency of this symmetry mode in GaAs. Accordingly, the TO and LO phonons are mostly governed by As vibrations and their energies are close to the energies of longitudinal phonons in GaAs. At lower energies one gets the modes associated with the LA branch and finally, the TA modes are found at energies slightly lower than the corresponding modes in GaAs because the In+As mass is heavier than the Ga+As mass.

With respect to CdSiAs$_2$, the distribution of phonons is clear: at high energies there are six eigenstates dominated by Si–As vibrations whereas twelve eigenstates of AlAs are found in this energy range. This is due to the fact that there are half the number of Si–As bonds in the ternary compound as there are Al–As bonds in the binary. The slightly higher frequency of Si–As modes is explained in view of the shorter Si–As bond length with respect to Al–As bonds. At intermediate energies one finds a small splitting into two multiplets; the one at higher energy, in which the phonons with $\Gamma_4$, $\Gamma_5$ symmetry participate, is associated with the $\Gamma_{15}$ triplet of

InAs. In this case, since In–As and Cd–As bond lengths are much the same, they show similar phonon energies. The low-energy multiplet is made up of the breathing mode of anions $\Gamma_1$ and the symmetry modes $\Gamma_3 + \Gamma_5$. It is worth mentioning that the analysis of the $\Gamma_3$ eigenmode gives a similar contribution of anions and cations. This can be explained if one bears in mind that it comes from the folding of the longitudinal acoustic branch at point X. In the case of AlAs, where the anion is heavier than the cation, this is a mode of anions whereas the contrary occurs with InAs for which the longitudinal acoustic mode at X is a mode of cations. If we use $X_3$ to designate cation modes, the intermediate $\Gamma_3$ can be considered to be a mixture of $X_1$ in AlAs plus $X_3$ in InAs, and, as found in calculations, the frequency of $\Gamma_3$ is predicted to be close to the average frequencies of these two modes. This is also what happens with the breathing mode $\Gamma_1$, intermediate between the two pure anionic modes $W_1$ of AlAs and InAs. Finally, the modes at the lower energy band have a clear assignment: the two $\Gamma_5$ modes are very close to the TA branches of AlAs (upper) and InAs (lower) while the two intermediate $\Gamma_3 + \Gamma_4$ modes are a mixture of AlAs and InAs modes and are found not far from TA modes in GaAs.

## 5. Conclusions

The use of a VFF model to describe optic phonons in II–IV–V$_2$ chalcopyrite compounds has permitted us to obtain a scaling law for the force constants versus bond length suitable for the determination of phonon energies in tetrahedrally coordinated semiconductors. The model only takes into account bond-stretching force constants localized in cation–anion bonds and bond-bending force constants between adjacent bonds with two constraints: first, a mean parameter is taken for the bending between unlike bonds, and second, the same bond-length dependence is used to describe all force constants. One predicts a $d^{-4.30}$ power law and a bending to stretching ratio of 0.11. The application of the scaling law to III–V compounds gives phonon energies in fairly good agreement with experimental results. The discrepancies may be attributed mainly to the simplicity of the model used to compute phonon energies rather than to the scaling law. This is particularly striking in the case of phosphorus compounds. We apply this law to forecast phonon energies in CdSiAs$_2$, a chalcopyrite compound with strong lattice distortion, and these are compared with phonons in AlAs and InAs, the two zincblende analogues of CdSiAs$_2$.

## Acknowledgment

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