Linearized force constants method for lattice dynamics in mixed semiconductors

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Abstract. A simple and accurate method of calculating phonon spectra in mixed semiconductors alloys, on the basis of preliminarily (from first principles) relaxed atomic structure, is proposed and tested for (Zn,Be)Se and (Ga,In)As solid solutions. The method uses an observation that the interatomic force constants, calculated ab initio for a number of microscopic configurations in the systems cited, show a clear linear variation of the main (diagonal) values of the interatomic force constants with the corresponding bond length. We formulate simple rules about how to recover the individual $3 \times 3$ subblocks of the force constants matrix in their local (bonds-related) coordinate systems and how to transform them into a global (crystal cell-related) coordinate system. Test calculations done for 64-atom supercells representing different concentrations of (Zn,Be)Se and (Ga,In)As show that the phonon frequencies and compositions of eigenvectors are faithfully reproduced in a linearized force constants calculation, as compared to true ab initio calculations.

Calculation of phonon spectra in the harmonic approximation (frequencies $\omega$, eigenvectors $A^\beta_k$) becomes straightforward from a simple diagonalization,

$$\sum_{\beta,k} \left[ \omega^2 \delta_{\alpha\beta} \delta_{ik} - \frac{D^\alpha\beta_{ik}}{\sqrt{M_\alpha M_\beta}} \right] A^\beta_k = 0 \quad (1)$$

($\beta$ runs over atoms in the unit cell, $k$ over Cartesian directions) once the matrix of force constants,

$$D^\alpha\beta_{ik} = \frac{\partial^2 E_{\text{tot}}}{\partial X_\alpha^i \partial X_\beta^k} = D^{\beta\alpha}_{ki}$$

is known. In the adiabatic Born–Oppenheimer approximation, the forces and their derivatives over small atomic displacements can be well yielded by a density functional theory (DFT).

The calculation approaches, in their turn, are either of linear-response type (see Ref. [1] for a review), or of frozen-phonon [2] or otherwise finite-displacement type – see, e.g., Ref. [3]. All ab initio methods work reasonably well for perfect crystals and not so large supercells. The situation becomes more difficult if dynamic properties of alloys must be analyzed. In the present contribution, we deal with substitutionally disordered II-VI and III-V semiconductor alloys $A_x B_{1-x} C$ in the absence of structural defects, so that the topological structure of cation/anion sublattices in the zincblende phase is preserved. However, chemical substitutions on either cation or anion sublattice yield considerable displacements of ions from perfect crystallographic...
It is known since early 1980s [4] that the average lattice constant in a semiconductor alloy follows Vegard’s law whereas individual A-C, B-C anion-cation bond lengths tend to maintain their values as in parent binary compounds. A complex relaxation pattern appears from an interplay of these two tendencies in each given microscopic configuration. The variations of bondlengths according to local environment are up to several per cent, and may give rise to well resolved Raman lines. In fact, the Raman spectroscopy can serve as a tool for probing these local environments, that would ideally require a reference to model first-principle calculations, imitating different environments. An example of such treatment for (Zn,Be)Se alloys in the context of elucidating the effects of structural “percolation” is given in Ref. [5], and in the context of partial ordering tendencies in the same alloy – in Ref. [6]. The lattice relaxation (which requires forces on atoms to be available in a calculation) is by far easier than the subsequent calculation of force constants by linear response or finite-displacement method. In order to overcome this bottleneck, we propose in the present contribution a fast and simple way to estimate the force constants in any given atomic configuration of a pseudobinary semiconductor alloy. Our approach is based on clear trends resulting from a number of first-principle calculations, and does not need empirical parameters to match the experimental data.

Our two basic assumptions are the following:

1) the interatomic interactions in the force constant matrix of a semiconductor alloy can be limited by the nearest neighbours (NN; cation–anion) and next-nearest neighbours (NNN; cation–cation and anion–anion) terms and discarded for more distant pairs, at least for the sake of obtaining the vibration spectra with accuracy typical for the Raman spectra of these crystals;

2) the NN and NNN blocks of the force constants matrix can be recovered from the corresponding interatomic distances and angles. The actual prescription for this follows from fully ab initio (finite-displacements) phonon calculations done by the SIESTA method[7].

The supercells used were a prototype “chain+impurities” Be6Zn26Se32 one described in Ref. [5], “Be-clustering” supercells of the same size containing 1...4 Be atoms grouping around the same Se atom in ZnSe; the same supercells constructed for (Ga,In)As system, and a number of smaller (32-atom) supercells for both alloys, which were subject to discussion in Ref. [6]. The phonon densities of states (PhDOS) of species α discussed in the following are zone-center-

Figure 1. Main elements of the force constants blocks relating NN and NNN in (Zn,Be)Se and (Ga,In)As alloys. The data are collected over a number of 64-atom supercells with different concentration. The NNN interactions in the (Zn,Be)Se system were shown in Fig. 6 of Ref. [5].
projected components of eigenvectors, sampled as

\[ n_{\{\alpha\}}(\omega, \mathbf{q}) = \sum_{\nu} \delta(\omega - \omega_{\nu}) \sum_{\alpha} \left| \sum_{i} A_{\alpha}^{\nu}(\omega_{\nu}) e^{i\mathbf{qR}_{\alpha}} \right|^2 \]

(\mathbf{q}=0 in our case), and technically obtained from zone-center discrete vibration spectra \( \omega_{\nu} \) in various supercells, artificially broadened with half-width parameter of 10 cm\(^{-1}\).

The first of the above statements is verified by comparing the PhDOS calculated with the elements of \( D^{\alpha\beta} \) set to zero beyond the second neighbours. The result was found, for any practical purpose, indistinguishable from that calculated with the full force constants matrix. On the contrary, an omission of NNN interactions leads to unacceptable damage of the PhDOS.

In order to understand the behaviour of NN and NNN force constants, we diagonalized them blockwise, for each given pair of atoms involved. More specifically, \( D^{\alpha\beta} \) and \( D^{\beta\alpha} \) blocks of the global force constant matrix, both having dimension 3\( \times \)3, can be cut out of the global matrix to form a (symmetric) 6\( \times \)6 block. Its diagonalization yields antisymmetric (three positive and three negative) values. Let us discuss first the diagonal elements of the force constants matrix for the NN. The major element comes from the central force, acting along the corresponding bond, and two minor elements from tangential forces of markedly similar size, revealing an essentially axial anisotropy of NN interaction with respect to the bond direction. Fig. 1 shows diagonalized force constants for (Zn,Be)Se alloys (those previously shown in Ref. [5]) along with new results for (Ga,In)As. We address the reader to Ref. [5] for a discussion on a more ionic character of Zn–Se bonds in contrast to more covalent character of the Be–Se bonds which follows from these results; obviously there is no such strong distinction in the degree of covalence between Ga–As and In–As bonds. What is striking for both mixed systems is a markedly linear variation of the force constant values with the bond length. We emphasize that the data shown in Fig. 1 are collected over a number of supercells with different concentrations, hence this trend must be quite independent on the details of microscopic structure. We approximated this dependence by a linear function, with different coefficients for each given cation-anion pair. With the diagonal elements coming from the fit, one has yet to specify the local system in which the force constant matrix is reduced to its main axes. Analyzing the transformation matrices (those which yield diagonalization) over a number of systems, we conclude that the main axis should indeed be directed along the bond, and the orientation of two others is in fact irrelevant because of the abovementioned axial symmetry; we arbitrarily set the second axis in the plane passing through the cation–anion pair and whatever the closest third atom to any of them.

For NNN interactions, the orientation of the local system which diagonalizes the force constants matrix is not that straightforward. Our analysis shows that the main axis of cation–cation or anion–anion interaction lies in the plane which passes through these two atoms and the third one (anion or cation, respectively) which is bonded to the two in question; see Fig. 2. The direction of this main axis in not along the line connecting the NNN in question, but forms with it an angle \( \Theta \), practically unaffected by the NNN distance, but different for different types of NNN. The angles \( \Theta \) for (Zn,Be)Se systems are \(-47^\circ \) (Be-Be and Be-Zn), \(-39^\circ \) (Zn-Zn), \(+16^\circ \)

\[ \text{Figure 2. The orientation of local axes (in which the two-atom block of the force constant matrix is diagonalized) for cation–cation and anion–anion NNN. Note that } \Theta < 0 \text{ in the first case and } > 0 \text{ in the second. See text for details.} \]
Figure 3. Zone-center projection of the local PhDOS in several supercells of (Zn,Be)Se and (Ga,In)As composition. Shaded areas: fully \textit{ab initio}, thick lines: with linearized force constants. (Se-Se); for (Ga,In)As system, $-52^\circ$ (Ga-Ga), $-41^\circ$ (In-In), $-46^\circ$ (In-Ga), $+28^\circ$ (As-As). The second (in the size of the corresponding element) main axis is also in the plane connecting three atoms and normal to the first, and the third one (not shown in Fig. 2) is normal to the plane.

It rests to specify the on-site $D^{\alpha\alpha}$ blocks of the force constant matrix, which are clearly dominant and strongly dependent on each atom’s environment in crystal. We recovered these blocks from the acoustic sum rule, $\sum_\beta D^{\alpha\beta}_{ij} = 0 = \sum_\alpha D^{\alpha\beta}_{ij}$, assuming $D^{\alpha\beta}=0$ beyond NNN.

In conclusion, we test the results of the phonon spectrum calculations with the parametrized force constants, against those obtained with the “true” force constants from \textit{ab initio} calculations for the corresponding supercells. The PhDOS shown in Fig. 3 show, to our opinion, a quite satisfactory level of agreement, which is about the same for all supercells we have considered. Based on this, we suggest that the present approach of “linearized force constants” may be useful for fast calculations of vibration spectra in large supercells.

The present contribution serves the justification and description of our approach. New results obtained with this method for larger supercells, along with the parametrizations for other mixed semiconductor systems we have studied, will be reported elsewhere.

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