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Force constants for substitutional alloys

Marcel H. F. Sluiter
Institute for Materials Research, Tohoku University, Aoba-ku, 980-77 Sendai, Japan

M. Weinert
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973-5000

Yoshiyuki Kawazoe
Institute for Materials Research, Tohoku University, Aoba-ku, 980-77 Sendai, Japan

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Recently, the importance of the vibrational aspects of alloy phase stability has attracted much interest. There is much controversy over the extent to which the vibrational free energy affects order-disorder temperatures and other phase equilibria. Here, we examine the feasibility of defining transferable force constants for an alloy in much the same spirit as tight-binding Slater-Koster parameters can be defined for substitutional alloys. In particular, the predictive ability of such alloy specific, but configuration independent, force constants for the elastic, relaxation, and vibrational properties is examined. [S0163-1829(99)09205-X]

I. INTRODUCTION

The theory of alloy phase stability has received much attention in recent years.[1] Until now, the theoretical description has accounted mainly for the configurational contributions.[2] This assumption appeared reasonable because other contributions, such as from electronic excitations, are generally much smaller.[3] However, recently it has been suggested that vibrational contributions are on par with configurational effects.[4–9] From the allotropic transformations occurring in a multitude of pure elements it can be concluded that in general vibrational entropy differences should play a large role when different crystal structures are involved. However, in the case of ordered alloys, where the main distinction between competing phases is the degree of long- or short-range order, the issue is far from clear. A case in point is the vibrational contribution to the order-disorder transformation of Ni_3Al. Widely varying vibrational entropy differences have been reported in theoretical work, and the experimental data appears very ambiguous because slight differences in the model with which the data is analyzed result in completely different interpretations.[10–12]

In the theoretical calculations so far, only completely ordered and completely disordered configurations have been considered. While such calculations provide important data such as the maximal attainable value of the vibrational entropy difference, it does not represent well the actual situation in the vicinity of an order-disorder transformation. At a first-order order-disorder transformation at finite temperature, the ordered phase is only partially ordered and the disordered phase it is in equilibrium with, has short range order. Examination of the correlation functions has shown that ordered and disordered states exhibit rather similar atomic configurations. Consequently, it must be expected that the vibrational entropy differences computed so far are much exaggerated. Although this is a well-known fact, it is not easy to produce more realistic values for the vibrational entropy difference because proper inclusion of partial order, or short-range-order effects within the relatively small supercells that can be treated is difficult. Another aspect of the work done so far is that many effects contribute at once, making it difficult to pin-point the precise cause of a large or small value for the vibrational entropy; e.g., differences in the lattice parameters of ordered and disordered states, relaxation of atomic positions as a result of atomic size differences, as well as the effect of atomic configurations on the actual vibrational density of states all play a role. Therefore, the construction of a simple model that allows one to separate the various contributions to the vibrational entropy difference is highly desirable.

In the case of ordering in transition metal alloys, much insight into trends and causality was gained by combining the tight-binding approximation, the coherent potential approximation, and the generalized perturbation method.[1] Typically, the electronic structure was described by a simple non-spin-polarized *d*-electron-only tight-binding Hamiltonian. Using this Hamiltonian, configurationally disordered substitutional alloys were represented by the coherent potential approximation, and the properties of alloys with nonrandom configurations were obtained by a perturbation expansion, usually to second order in the site occupation variables only.[13] This work, while based on a series of approximations, rather accurately reproduced the tendencies towards ordering and clustering in alloys.[1] It thus allowed the extraction of the relevant parameters which determine the tendencies towards ordering and clustering, and rules of thumb could be derived. Some of these rules allowed the construction of even simpler models.[14]

There exists a natural analogy between the two-center Slater-Koster (SK) tight-binding method[15] for the electronic structure and the Born-von Karman model[16] for the vibrational properties. In both cases the real-space Hamiltonian consists of short-ranged pairwise terms which are projections of the SK parameters in case of the former, and force constants (FCs) in case of the latter. Likewise, a coherent potential approximation and a generalized perturbation method can be defined for the vibrational Hamiltonian. As a consequence then, an analysis of the contribution of the vibrational degrees of freedom to the order-disorder transformations in alloys is possible. However, before such a study can be carried out, the validity of a ''tight-binding-like'' vibrational Hamiltonian for alloys needs to be examined.

In the usual two-center SK tight-binding method for alloys, it is tacitly assumed that the SK parameters are configuration independent, i.e., the SK parameters are the same for two different superstructures if the composition and interatomic distances are the same. For example, the SK parameters for a nearest neighbor Ni-Ti pair are the same for an intermetallic Ni_3Ti with an $L1_2$ or with a DO_{22} structure provided that both have the same interatomic distances, that is, when the DO_{22} has the ideal c/a ratio of 2. This configuration independence of the SK parameters can be derived in the special case of the linear-muffin-tin-orbital based tight-binding formalism.[17–19] In the case of FCs, however, there is no clear evidence that configuration independent, i.e., ''transferable,'' FCs can be defined.[20] On the contrary, below it will be shown that the existence of invariance requirements for the FCs (Ref. 21) suggests that such FCs can exist only as an approximation. Even approximate ''transferable'' FCs would be useful though, as they might provide a way to easily predict positionally relaxed structures, and the corresponding relaxation energies. Also, the phonon dispersion as well as the elastic tensor could be easily evaluated for arbitrary atomic configurations, and this in turn could clarify the interplay between state of long- or short range order and displacive transformations.

Transferability can mean many things; tight-binding SK parameters have been defined that can describe the electronic structure of molecules and solids with widely varying structures and coordination numbers.[22] Here, the weakest form of transferability will be examined. We will examine if one set of FCs can describe the properties of different configurations which are the same in all other aspects, such as underlying lattice, lattice parameter, and composition. Thus, the vibrational properties of various configurations will be computed ''exactly,'' and then we will examine to what extend one set of configuration independent (''transferable'') FCs can describe the ''exact'' results for the various configurations.

The ''exact'' results are configuration specific (CS). Thus, there are CS FCs, and all the properties that depend on those CS FCs such as the phonon dispersion and the elastic tensor. The configuration independent FCs should represent any arbitrary configuration. Therefore, it is reasonable to approximate these configuration independent FCs by configuration averaged (CA) FCs. The CA FCs will be considered ''transferable'' if they can reproduce the results from CS FCs, including results pertaining to configurations that were not included in the averaging to obtain the CA FCs.

To study the feasibility of ''transferable'' FCs, a model system is examined in detail, using FCs computed from plane wave pseudopotential local-density-functional calculations[21,23] using the direct method.[24–29] FCs are computed for several ordered configurations, such as the $L1_2$, DO_{22}, and other structures to be described below. As just mentioned, all these structures are based on the same underlying fcc crystal structure and differ in the atomic occupancy only.

The alloy Al_3Li has been selected because (1) the FCs in this alloy decrease rather rapidly as a function of distance, (2) much experimental and theoretical thermodynamic data is available, and (3) the elastic constants of this compound are known. Also, in this alloy Al and Li have about the same partial molar volume so that relaxation effects are small.[30] Indeed, when the c/a ratio was computed for the DO_{22} structure, a value very close to the ideal ratio of 2 was found.[31]

It should be noted that the effects of lattice parameter changes as a result of changes in temperature or state of order, that occur in actual alloys, are neglected in this study. This is done because in this study we seek to examine ''transferability'' in its most restrictive form where truly the only difference between various states of order is the atomic decoration. It appears evident that FCs computed for structures that have the same lattice parameter would be more alike than FCs computed for structures with different lattice parameters. Therefore, it is to be expected that FCs are less ''transferable'' in real alloys, where changes in the state of order, or changes in the temperature, are accompanied by lattice parameter changes, than in the idealized model system studied here.

The paper is organized as follows: A general formalism for FCs and their applications is given. The FCs for a number of specific configurations are computed, as well as a configuration averaged set of FCs which are then examined for transferability. Various physical properties, such as the elastic tensor, relaxation displacements and energies, phonon dispersion and densities of states, and the vibrational thermodynamic properties are computed with CS and CA FCs. A comparison of those properties leads to conclusions regarding the validity of CA, or ''transferable,'' FCs.

II. THEORY

In the harmonic approximation, the potential energy Φ is expanded up to second order in the displacements u from the equilibrium positions,

$$\Phi=\Phi_0+\sum_{\mu,j}\frac{\partial\Phi}{\partial u_\mu(j)}u_\mu(j)+\frac{1}{2}\sum_{\mu\nu,jj'}\frac{\partial^2\Phi}{\partial u_\mu(j)\partial u_\nu(j')}u_\mu(j)u_\nu(j'), \tag{1}$$

where the subscripts μ and ν indicate the x, y, or z direction, the subscripts j and j' indicate a particular atom, and Φ_0 is the potential energy when all atoms are at their equilibrium positions. In a crystal it is possible to write the position of the atom as $r_j=r_l+r_k$, where r_l indicates the position of the unit cell, and r_k indicates the relative position of the atom in that unit cell. Thus, the index j is composed of an index l designating the unit cell, and an index k designating the particular atom within the unit cell. As all displacements u are defined with respect to the equilibrium positions, the first derivatives of Φ vanish. Thus, the second order term only matters for the vibrational properties.

The second order derivatives are the so-called FCs,

$$\phi_{\mu\nu}(j,j')=\frac{\partial^2\Phi}{\partial u_\mu(j)\partial u_\nu(j')}. \tag{2}$$

For each bond between atoms j and j' there is a 3×3 FC matrix. The nature of the bond is most readily interpreted through the eigenvectors and eigenvalues of this FC matrix. The eigenvectors indicate the principal axes with spring constants given by the corresponding eigenvalues. An isolated bond, i.e., a diatomic molecule, would have one longitudinal and two transverse axes. In crystals this is no longer necessarily so, but it is easy to prove that when at least two crystal symmetry elements leave the vector $r(j,j')=r_{j'}-r_j$ invariant exactly one longitudinal and two transverse modes exist. In highly symmetric crystals, such as bcc and fcc, many of the shorter bonds satisfy the above criterion.

Following Born and Huang,[16] the FCs must satisfy three fundamental invariances. They result from the invariance of the potential energy with respect to the translations, the rotations, and the crystal symmetry operations. When the crystal symmetry operations are applied, the translational I^T, and rotational I^R invariances take the following form:

$$I^T_{\alpha\beta}(k)=\sum_s\sum_p\sum_{\mu\nu}R^p_{\alpha\mu}R^p_{\beta\nu}\times\phi_{\mu\nu}(k,k+r^s)=0, \tag{3}$$

$$\begin{aligned}I^R_{\alpha\beta\gamma}(k)=&\sum_s\sum_p\sum_{\mu\nu\sigma}R^p_{\alpha\mu}R^p_{\beta\nu}R^p_{\gamma\sigma}\\&\times[\phi_{\mu\nu}(k,k+r^s)r^s_\sigma-\phi_{\mu\gamma}(k,k+r^s)r^s_\nu]\\=&0,\end{aligned} \tag{4}$$

where the Greek letters indicate the Cartesian coordinates $\{x,y,z\},k$ indicates an atom in the unit cell, s designates the coordination shell surrounding atom k, and p is the subset of point group elements R that generates the star of the vector r^s. These invariances must be explicitly imposed on the FCs derived from supercell calculations because errors due to incomplete basis sets, imperfect self-consistency, and numerical errors conspire to create violations.

In simple highly symmetric crystals, such as bcc and fcc, the crystal symmetry invariances encompass the rotational invariances,[32] and the translational invariances can be satisfied trivially by scaling the onsite FCs. Such is not the case in low-symmetry crystals. In fact, in general these three classes of invariances are insufficient to assure that the elastic tensor obeys the relationship $C_{ij}=C_{ji}$, where i and j designate the Voigt indices. To satisfy the above equality, the following 15 Huang invariances[16], $I^H=0$, must be satisfied in a crystal at equilibrium,

$$\begin{aligned}I^H_{\alpha\beta\gamma\lambda}=&\sum_k\sum_s\sum_p\sum_{\mu\nu\sigma\tau}R^p_{\alpha\mu}R^p_{\beta\nu}R^p_{\gamma\sigma}R^p_{\lambda\tau}\\&\times[\phi_{\mu\nu}(k,k+r^s)r^s_\sigma r^s_\tau-\phi_{\sigma\tau}(k,k+r^s)r^s_\mu r^s_\nu].\end{aligned} \tag{5}$$

Hence, aside from conditions imposed by the symmetry of the crystal, generally there are $9N_k$ translational (where N_k is the number of sites in the unit cell), $9N_k$ rotational, and 15 Huang invariances which must be imposed on the FCs.

The existence of invariances has as a consequence that one cannot arbitrarily discard elements from a set of FCs. After all, the invariances are satisfied by summations that include all FCs. Therefore, *a posteriori* truncation of a set of FCs will cause violations of the invariances and may result in unphysical features in the calculated phonon dispersion and elastic tensor.

The FCs are determined using a method which has recently become widely used.[21,26–29] In a large supercell where all atoms are at their equilibrium positions, a single atom j is given a displacement u from its equilibrium position. The resultant forces F on all the sites j' are calculated, and the FCs can then be determined from

$$F_\alpha(j')=\sum_\beta \phi_{\alpha\beta}(j,j')u_\beta(j), \tag{6}$$

where $F(j')$ is the force exerted on atom j' as a result of a displacement $u(j)$ of atom j. Again, as was done with the equations for the invariances, the crystal symmetry is explicitly imposed,

$$\sum_\gamma R_{\alpha\gamma}F_\gamma(j')=\sum_\beta \phi_{\alpha\beta}(j,j+r^s)\sum_\gamma R_{\beta\gamma}u_\gamma(j), \tag{7}$$

where R is the rotation which takes $r(j,j')$ into r^s

$$r^s_\alpha=\sum_\gamma R_{\alpha\gamma}r_\gamma(j,j'). \tag{8}$$

As is evident from Eqs. (3), (4), and (5), the invariances too, are linear in the FCs, so that this system of equations is easily solved. The equations are overdetermined and by using the singular value decomposition method an, in a least squares sense, optimal set of CS FCs is computed. In order to assure that the invariances are satisfied to a high precision, the invariance equations are weighted more heavily than Eq. (7). In the actual calculations the invariance equations were multiplied by a factor 100, but it was verified that the actual value of the factor was of no consequence. The crystal symmetry invariances are satisfied exactly because they were explicitly imposed in Eqs. (3), (4), (5), and (7).

To compute the CA FC matrices the following definitions are used. The CA FC matrices for a given neighbor-shell depend on the occupancy of the terminal sites only. Then, for a binary alloy of atomic species A and B, four FC matrices can be distinguished for each shell: ϕ^{AA} for an AA pair, ϕ^{AB} for an AB pair, and so forth. Let the occupancy $\sigma(j)$ of a site j be defined as a vector taking the value (1/0) when there is an A type atom, and taking the value (0/1) when there is a B type atom. The FC between sites j and j' can then be expressed in matrix form as follows:

$$\hat{\phi}(j,j')=\begin{pmatrix}\phi^{AA}(j,j') & \phi^{AB}(j,j')\\ \phi^{BA}(j,j') & \phi^{BB}(j,j')\end{pmatrix}. \tag{9}$$

where $\phi(j,j')$ is an appropriately rotated FC matrix $\phi(j,j+r^s)$. The potential energy, Eq. (1), with respect to equilibrium atomic positions can then be rewritten as

$$\Phi=\Phi_0+\frac{1}{2}\sum_{jj'}[\sigma(j)\cdot\hat{\phi}(j,j')\cdot\sigma(j')]u(j)u(j'), \tag{10}$$

TABLE I. Pair types occurring in some fcc-based ordered configurations at composition A_3B. Structures ''$O1$'' and ''$Z4$'' are explained in the text.

Pair type		$L1_2$	DO_{22}	$O1$	$Z4$
$\langle \frac{1}{2}\frac{1}{2}0\rangle$	AA	x	x	x	x
	AB	x	x	x	x
	BB			x	x
$\langle 100\rangle$	AA	x	x	x	x
	AB		x	x	x
	BB	x	x		x
$\langle 1\frac{1}{2}\frac{1}{2}\rangle$	AA	x	x	x	x
	AB	x	x	x	x
	BB			x	
$\langle 110\rangle$	AA	x	x	x	x
	AB	-	x	-	x
	BB	x	x	x	x
$\langle 111\rangle$	AA	x	x	x	x
	AB		x	x	x
	BB	x			

where the first order derivatives have been omitted. Previously given equations for invariances apply also to CA FCs provided that $\phi(j,j')$ is replaced with $[\sigma(j)\cdot\hat{\phi}(j,j')\cdot\sigma(j')]$. In order to simplify the notation, we will keep using $\phi(j,j')$. The CA FC matrices $\hat{\phi}$ can be obtained by solving Eq. (7) for several configurations at once while using the rotation matrices R associated with the underlying disordered (fcc) structure. Of course, solving Eq. (7) will only yield ϕ^{XY} if XY pairs actually occur in the structure. In the $\mathrm{Al_3Li}$ $L1_2$ structure e.g., no nearest neighbor Li-Li pairs occur so that solving Eq. (7) cannot give a result for the nearest neighbor $\phi^{\mathrm{Li\,Li}}$. In Table I the various types of pairs occurring in various simple ordered A_3B configurations are listed. The $L1_2$ and DO_{22} structures allow determination of most ϕ submatrices, except for those associated with the Li-Li pairs in the first and third nearest neighbor shells, see Table I. To compute those, a special configuration, called ''$O1$'' from now on, was constructed. The CA FCs are computed by solving Eq. (7) for the $L1_2$, DO_{22}, and ''$O1$'' structures simultaneously using singular value decomposition, so that a set of CA FCs is computed that optimally reproduces the forces in a least square sense.

The invariances are not imposed because they are configuration dependent, while the CA FCs are supposed to be configuration independent. This dependence is clear from the presence of the configuration dependent rotation matrices in Eqs. (3), (4), and (5). In general, invariances derived for different configurations will be in conflict. When CA FCs are derived while imposing the invariances of one configuration, the invariances for another configuration will not generally be satisfied. When the invariances of several configurations are imposed simultaneously, the system of equations becomes so overdetermined that the forces are no longer well reproduced by the FCs. Therefore, the CA FCs are computed without imposing the rotational and Huang invariances. When the CA FCs are used to compute the properties of a specific structure, the translational invariances are used to determine the onsite CA FCs, for reasons discussed below. The fact that the rotational and Huang invariances cannot generally be satisfied for an arbitrary configuration implies that strictly speaking, configuration independent FCs cannot exist. The best that can be done then, is to define approximate configuration independent FCs. Below, we will examine the consequences of the violations of the invariances on the computed physical properties.

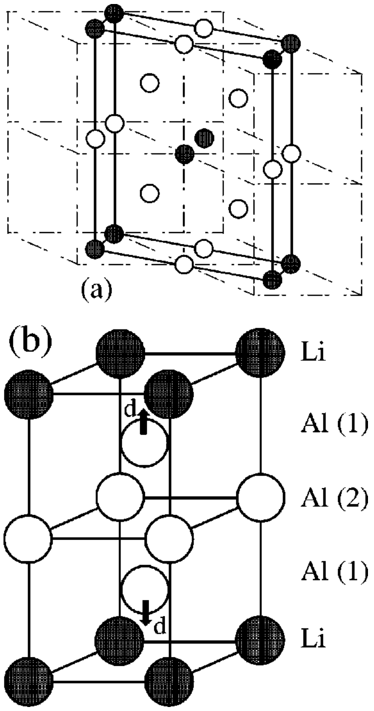

FIG. 1. Crystal structures: (a) ''$O1$'' and (b) ''$Z4$.'' For clarity, fcc cubes have been outlined with dashed lines for the ''$O1$'' structure. The internal degree of freedom in the ''$Z4$'' structure associated with the relaxation of the Al (1) sites is indicated with arrows.

The ''$O1$'' structure is, to the best of the authors knowledge, not observed in Nature. It has as primitive translations $\langle 200\rangle$,$\langle 110\rangle$, and $\langle \frac{1}{2}0\frac{1}{2}\rangle$; see Fig. 1. There are 8 atoms in the base centered orthorhombic unit cell (spacegroup 65, standard Hermann-Mauguin notation: $Cmmm$, Wyckoff positions: $2a$, $2b$, and $4f$) and there are no internal degrees of freedom. This means that just as for the $L1_2$ and DO_{22} structures, all atomic positions are fixed by symmetry, and that the forces on every site vanish for an arbitrary choice of the a, b, and c lattice parameters. Most other unit cells have internal degrees of freedom which need to be optimized in order for all forces to vanish. To illustrate this, we consider the so-called ''$Z4$'' structure which consists of a periodic stacking of four (001) planes, one of the planes is occupied exclusively by Li atoms, the other three planes are occupied by Al atoms only, see Fig. 1. The primitive translations are $\langle \frac{1}{2}\frac{1}{2}0\rangle$, $\langle \frac{1}{2}\bar{\frac{1}{2}}0\rangle$, and $\langle 002\rangle$ (space group 123, standard Hermann-Mauguin notation: $P4/mmm$, Wyckoff positions: $1a$,$1b$, and $2h$). In this structure there are 2 types of Al planes, type (1) which is located between a Li and an Al plane, and type (2) which is sandwiched between two Al (1) planes. The Al (1) planes are not fixed by symmetry and have one internal degree of freedom δ associated with the difference in the interplanar spacing with the Li and with the Al (2) plane. Hence, generally when in such a structure all sites are kept at their underlying fcc lattice positions, there will be nonvanishing forces on the Al (1) sites.

The energy associated with the optimization with respect to internal degrees of freedom is called the relaxation energy Φ_{relax}. When the $L1_2$, DO_{22}, and ‘‘$O1$’’ structures are used to determine the CA FCs on the underlying fcc crystal structure, there are no internal degrees of freedom. However, these CA FCs can be used to calculate the relaxation energy of other structures. In the case of the ‘‘$Z4$’’ structure there are generally nonvanishing forces on the Al (1) planes when all atoms are kept at their underlying fcc positions. How much the Al type (1) planes would relax, can be calculated from the FCs, obtained from the previously mentioned three structures, and from the forces on sites in the unit cell using an expression analogous to Eq. (7),

$$F_\alpha(j')=\sum_j \phi(j,j')\,\delta(j). \tag{11}$$

Then, the relaxation energy is given simply by a variant of Eq. (10),

$$\Phi_{\mathrm{relax}}=\frac{1}{2}\sum_{jj'} \phi(j,j')\,\delta(j)\,\delta(j'). \tag{12}$$

Of course, the relaxation energy can also be computed directly from *ab initio* calculations by performing an actual minimization over the internal degree of freedom.

The elastic tensor is computed[33,43,44] analytically from the FCs (CS and CA) by the method due to Born[16] according to

$$C_{\alpha\gamma,\beta\lambda}=[\alpha\beta,\gamma\lambda]+[\beta\gamma,\alpha\lambda]-[\beta\lambda,\alpha\gamma]+(\alpha\gamma,\beta\lambda), \tag{13}$$

where the square brackets (Eq. 26.32 in Ref. 16) are associated with homogeneous elastic strains, and the round bracket (Eq. 26.33 in Ref. 16) is associated with the relaxation of the internal coordinates. Mechanical stability requires that $C_{\alpha\gamma,\beta\lambda}$ and $[\alpha\beta,\gamma\lambda]+[\beta\gamma,\alpha\lambda]-[\beta\lambda,\alpha\gamma]$ form positive-definite matrices because any deformation must increase the internal energy (free energy at nonzero temperature). However, the round brackets form a negative-definite matrix because relaxation of the internal coordinates always lowers the energy. Although not every element of the $(\alpha\gamma,\beta\lambda)$ matrix needs to be negative, generally speaking, relaxation lowers the elastic constants. In simple structures without internal degrees of freedom, such as $L1_2$, DO_{22}, and ‘‘$O1$,’’ the round brackets vanish.

The nonvanishing of the Huang invariances for the CA FCs may cause an unphysical asymmetry in the calculated elastic tensor and this may serve as an indication for the errors incurred by using CA FCs.

The phonon dispersion $\omega(q)$ is computed from

$$\det[\sqrt{m_k m_{k'}}\,\omega^2(q)\,\delta_{\alpha\beta}\delta_{kk'}-D_{k\alpha,k'\beta}(q)]=0, \tag{14}$$

where m_k is the mass of atom k, and D is the dynamical matrix given by the Fourier transform of the FCs,

$$D_{k\alpha,k'\beta}(q)=\sum_{ll'} \phi_{\alpha\beta}(lk,l'k')\,e^{-2i\pi\mathbf{q}\cdot\mathbf{r}(\mathbf{lk},\mathbf{l'k'})}, \tag{15}$$

where the site j is represented by a pair of indices lk, with l as the index for the particular unit cell, and k as the index for the site within a unit cell, as described earlier.

At the zone center, the dynamical matrix,

$$D_{k\alpha,k'\beta}(q=0)=\sum_{ll'} \phi_{\alpha\beta}(lk,l'k'), \tag{16}$$

is closely related to the translational invariances [Eq. (3)],

$$\sum_{k'} D_{kk'}(q=0)=I^T(k), \tag{17}$$

where for brevity, the coordinate subscripts have been omitted. If the translational invariances are satisfied $[I^T(k)=0]$, then the determinant of $D_{kk'}$ can be rewritten such that for $k=1$ the row and the column are equal to zero. This means that there are three vanishing eigenvalues of $D_{kk'}$ at the zone center, one for each coordinate x, y, and z. When the translational invariances are not satisfied, there are generally not three vanishing eigenvalues, and in fact, the eigenvalues at the zone center could take any, including negative, values. Therefore, in order to avoid unphysical phonon dispersions the translational invariances must always be imposed. In the case of CA FCs then, we have imposed the translational invariances by adjusting the onsite CA FCs [of the form $\phi(j,j)$] for each configuration individually, i.e., we treat the onsite CA FCs as purely adjustable parameters.

The vibrational density of states (VDOS) $n(\omega)$ is obtained by an integration over the first Brillouin zone Ω of the crystal structure,

$$n(\omega)=\frac{1}{\Omega}\int_\Omega dq\,\delta(\omega-\omega(q)). \tag{18}$$

The vibrational internal energy E_v and the vibrational entropy S_v are calculated from

$$E_v=\int d\omega\hbar\omega n(\omega)\left[\frac{1}{2}+\frac{\vartheta}{1-\vartheta}\right] \tag{19}$$

and

$$S_v=-k_B\int d\omega\frac{n(\omega)}{(1-\vartheta)}[\vartheta\log(\vartheta)+(1-\vartheta)\log(1-\vartheta)], \tag{20}$$

where $\vartheta=e^{-\hbar\omega/k_BT}$, k_B is Boltzmann's constant, $\hbar$ is Planck's constant, and T is the temperature. The vibrational internal energy E_v includes the zero-point motion (first term in square brackets). The vibrational free energy F_v is obtained simply from $F_v=E_v-TS_v$.

III. RESULTS AND DISCUSSION

FCs were calculated using the ‘‘direct method’’ discussed above. A cubic supercell consisting of 8 fcc cubes was selected which allowed determination of FCs up to the fifth nearest neighbor shell. The electronic structure was calculated using a plane-wave pseudopotential method.[23,34] Forces were calculated using the Hellmann-Feynman equation after displacing a site by $0.005\times a_{\mathrm{fcc}}$, where a_{fcc} is the lattice parameter of the underlying fcc crystal structure. Anhar-

TABLE II. Configuration specific (CS) FCs for Al-Al nearest neighbors in various configurations in THz^2 amu (atomic mass unit). For comparison, the configuration averaged (CA) FCs are given at the bottom-left corner.

$L1_2$			DO_{22}			"$O1$"			"$Z4$"		
	r_j			r_j			r_j			r_j	
	$r_{j'}$			$r_{j'}$			$r_{j'}$			$r_{j'}$	
	$\phi(j,j')$			$\phi(j,j')$			$\phi(j,j')$			$\phi(j,j')$	
0.5	0.5	0	0.5	0.5	0	0.5	0.5	0	0	0	1
0	0.5	0.5	0	0.5	0.5	1	0.5	0.5	0.5	0.5	1
6783	0	−7592	6866	0	−7263	6244	−49	6512	7414	7313	0
0	792	0	0	687	0	−49	740	49	7314	7414	0
−5681	0	6783	−5908	0	6817	6512	49	6244	0	0	−845
			0	0.5	0.5	0.5	0.5	0	0	0.5	0.5
			0.5	0	0.5	1	0	0	0	0	1
			6328	−6618	507	6341	−6946	−507	−613	0	0
			−6618	6328	507	−7756	6376	582	0	7182	−7663
			507	507	735	527	−544	200	0	−8161	7106
						0.5	0.5	0	0	0.5	0.5
						0	0.5	0.5	0.5	0	0.5
						6260	−1295	−6394	6774	−6732	−18
						1295	1562	−1295	−6732	6774	18
	CA					−6394	1295	6260	20	−20	1254
0.5	0.5	0				1	0	0			
0	0.5	0.5				1.5	0	0.5			
6593	0	−6961				6589	0	7473			
0	539	0				0	−1000	0			
−6961	0	6593				7473	0	6589			

monic effects were verified to be negligible by applying both smaller and larger displacements. All subsequent calculations have been performed at the lattice parameter computed for the Al_3Li $L1_2$ structure. It was computed to be 0.3921 nm, in good accord with other LDA results[30,31,35–37] and with the actually measured value of 0.3972 nm.[38] In the supercell there are 32 atoms, 24 Al atoms and 8 Li atoms. Various configurations were considered, in particular those corresponding to the $L1_2$, DO_{22}, "$O1$," and "$Z4$" structures. The number of Eqs. (7) ranged from 96 ($L1_2$) to 224 ("$Z4$"), and the number of invariances ranged from 3 ($L1_2$) to 61 ("$O1$"). The number of independent nonzero elements in the FC matrices ranged from 44 ($L1_2$) to 171 ("$O1$"). A few elements of the FC matrices for the third, fourth, and fifth nearest neighbor pairs cannot be determined with the 2×2×2 supercell used here, and the corresponding values have been set to zero. In Table II the Al-Al nearest neighbor FCs as computed with Eqs. (3), (4), (5), and (7) for each structure are listed. The CA FCs, computed from the forces in the $L1_2$, DO_{22}, and "$O1$" configurations using Eq. (7) only, are given for comparison. Taking into account the different orientations of some of the pairs, it is clear that even though there is a considerable spread in the values, generally the larger FCs in all of the configurations are rather similar. For example, the ϕ_{xx} element for a vector $\langle \frac{1}{2}\frac{1}{2}0\rangle$ takes values ranging from 6244 (in "$O1$") to 7414 (in "$Z4$"), while the smaller ϕ_{zz} element can take both positive and negative values. For more distant pairs, where the FCs take much smaller values, the influence of the configuration becomes overwhelming and no similarities between FCs from different configurations can be discerned.

The CA FCs have been listed in Table III. The 44 nonzero CA FC matrix elements were obtained from 480 Eqs. (7). The FCs rapidly decay for more distant shells: those for the fourth and fifth shells are orders of magnitude smaller than those of the nearest neighbor shell. Moreover, the Al-Al near neighbor bonds are much stiffer than those of Li-Li type. This is particularly evident when the eigenvalues of the FCs are examined; see Fig. 2. Apparently, Li-Li nearest neighbors make a structure "soft." This behavior is maybe

TABLE III. Configuration averaged (CA) FCs in THz^2 amu (atomic mass unit).

Shell	Type	ϕ_{xx}	ϕ_{xy}	ϕ_{xz}	ϕ_{yy}	ϕ_{yz}	ϕ_{zz}
$\langle \frac{1}{2}\frac{1}{2}0\rangle$	Al-Al	6593	−6961	0	6593	0	539
	Li-Al	3298	3107	0	3298	0	353
	Li-Li	2138	1797	0	2138	0	633
$\langle 100\rangle$	Al-Al	678	0	0	−76	0	−76
	Li-Al	565	0	0	−81	0	−81
	Li-Li	−89	0	0	−20	0	−20
$\langle 1\frac{1}{2}\frac{1}{2}\rangle$	Al-Al	260	0	0	−198	−11	−198
	Li-Al	217	0	0	−131	24	−131
	Li-Li	122	0	0	−137	−17	−137
$\langle 110\rangle$	Al-Al	137	0	0	137	0	−148
	Li-Al	−3	0	0	−3	0	−158
	Li-Li	−133	0	0	−133	0	−90
$\langle 111\rangle$	Al-Al	25	0	0	25	0	25
	Li-Al	−11	0	0	−11	0	−11
	Li-Li	0	0	0	0	0	0

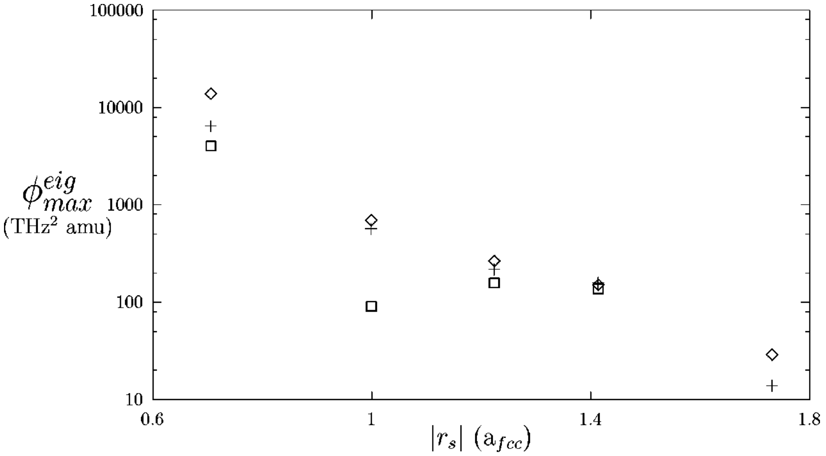

FIG. 2. Maximum eigenvalues of the CA FC matrices, as a function of the interatomic distance $|r_s|$, in units of the fcc lattice parameter a_{fcc}. The square, plus sign, and diamond symbols refer to Li-Li, Al-Li, and Al-Al bonds respectively.

not so surprising considering that the elastic constants of Li are much smaller than those of pure Al, but it should be kept in mind that Li atoms in the alloy are highly compressed compared to the pure elemental Li case.

The elastic tensor for the Al_3Li $L1_2$ structure as computed with the CS and CA FCs and Eq. (13) is compared with data in the literature in Table IV. It is noteworthy that the elastic tensor computed in this work compares very well with the experimental data,[39,40] especially that of Sakai *et al.*[40] The comparison with other electronic structure calculations,[36,37] both with the full-potential augmented plane wave method, is not quite as good. Considering how much these results differ from each other and from the experimental data that might not be so bad. It should be mentioned though that the theoretical values pertain to zero temperature, whereas the experimental data pertains to room temperature, so that the theoretical values should be about 10–20 % higher than the experimental values.[40] In light of the large differences between the experimental and theoretical results, it appears that the CS and CA FCs give results that are very similar and in good agreement with experiment.

The CS and the CA FCs can be used into Eq. (13) to give the elastic tensor and the bulk modulus; see Table V. The CS results should be considered exact and the CA results are approximate because taking configurational averages of the FCs is at best an approximation as was discussed above. Concerning the bulk moduli, the CS results show that while

TABLE IV. Elastic constants C_{ij} and bulk modulus B in GPa for the Al_3Li $L1_2$ structure, as determined from experimental measurements (expt), as computed with local-density-functional electronic structure methods (theory), and as computed in this work with CS and CA FCs using Eq. (13).

C_{11}	C_{12}	C_{44}	B	Method	Reference
123.6	37.2	42.8	66.0	expt	39
114.7	39.1	37.8	64.3	expt	40
158.0	29.4	57.7	72.3	theory	36
139.8	33.7	40.7	69.1	theory	37
116	45	40	68.3	CS FCs	This work
109	53	34	71.3	CA FCs	This work

TABLE V. Elastic tensor C_{ij} and bulk modulus B for various structures in GPa computed with configuration specific (CS) FCs and configuration averaged (CA) FCs.

CS						CA					
$L1_2$											
		68.3						71.3			
116	45	45	0	0	0	109	53	53	0	0	0
	116	45	0	0	0		109	53	0	0	0
		116	0	0	0			109	0	0	0
			40	0	0				34	0	0
				40	0					34	0
					40						34
DO_{22}											
		71.6						72.1			
108	45	59	0	0	0	105	56	59	0	0	0
	108	59	0	0	0		105	59	0	0	0
		103	0	0	0			109	0	0	0
			23	0	0				30	0	0
				23	0					30	0
					43						32
“$O1$”											
		63.2						73.2			
102	45	45	0	3	0	112	54	56	0	3	0
	98	45	0	2	0	53	110	52	0	0	0
		102	0	3	0	57	55	111	0	3	0
			41	0	−3	0	0	0	33	0	0
				35	0	2	−1	3	0	35	0
					41	0	0	0	0	0	33
“$Z4$”											
		59.7						62.8			
113	23	52	0	0	0	109	58	50	0	0	0
	113	52	0	0	0	58	109	50	0	0	0
		83	0	0	0	48	48	103	0	0	0
			24	0	0	0	0	0	27	0	0
				24	0	0	0	0	0	27	0
					72	0	0	0	0	0	37

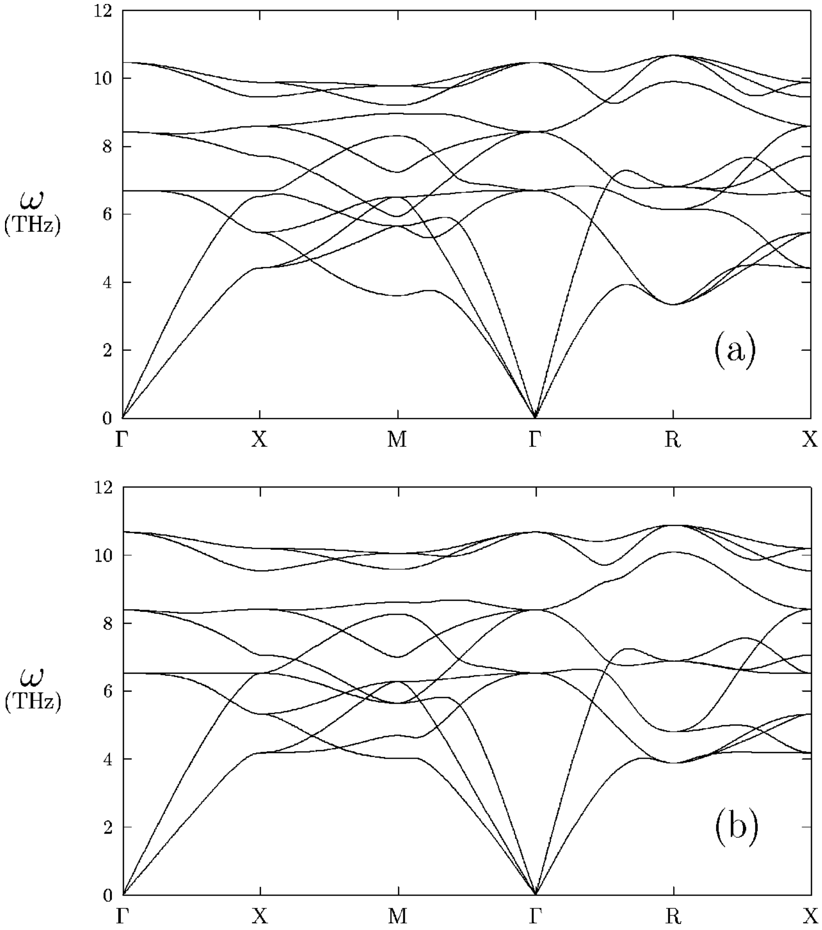

FIG. 3. Phonon dispersion of the $L1_2$ structure (a) as computed with CS FCs and (b) as computed with CA FCs.

the $L1_2$ and DO_{22} structures have about the same value, the ‘‘$O1$’’ and ‘‘$Z4$’’ structures are notably softer. The CA approximation fails to reproduce this trend, giving similar bulk moduli for all structures. However, it gives bulk moduli that reproduce the $L1_2$ and DO_{22} data rather well.

The elastic tensors are given with respect to the *x*, *y*, and *z* axis aligned with the axis of the underlying fcc structure. This choice of axis facilitates comparisons, but causes extra nonzero elements in the tensor of the base centered orthorhombic structure ‘‘$O1$.’’ It should be remarked that as the CA FCs do not generally satisfy the invariances, the elastic tensor is not necessarily properly symmetric. Fortunately, the violations of the invariances do not appear to cause very significant changes as can be seen for the ‘‘$O1$’’ and ‘‘$Z4$’’ results. The CA elastic constants are accurate to within about 10 GPa, or even a little less, for the $L1_2$, DO_{22}, and ‘‘$O1$’’ structures, but for the ‘‘$Z4$’’ structure the C_{12}, C_{33}, and C_{66} elastic constants have very large errors of 20 to 35 GPa. That these elastic constants should take extreme values is related to the alternating pure Li and pure Al (001) planes. It should be noted that the ‘‘$Z4$’’ structure has been structurally relaxed, that is, the Al type (1) atoms have been allowed to take their equilibrium values, in the calculation of the elastic tensor and phonon related properties.

As was noted before, all FCs have been derived from Al-Li alloys with composition Al_3Li. To examine if the CA FC can be applied at other compositions, the elastic tensor of pure Al was computed both from the CA FCs and from an *ab initio* electronic structure calculation. In the pure Al *ab initio* calculation is performed at the same lattice parameter of 0.3921 nm as all the other calculations. The *ab initio* results give for C_{11}, C_{12}, C_{44} values of 163, 66, and 52 GPa respectively, making for a bulk modulus of 97.8 GPa. The CA FCs give 145, 71, 48, and 95.5 GPa, respectively. This agreement is about as good as that for the ordered configurations at composition Al_3Li, and it appears then that CA FCs can be used over a range of compositions.

The FCs can also be used to estimate the relaxation energy in the ‘‘$Z4$’’ structure, see Eqs. (11) and (12). Electronic structure calculations revealed that the Al (1) planes relax about $0.011\times a_{\mathrm{fcc}}$ toward the Li (001) planes with an energy lowering of 6.7 meV per formula unit Al_3Li. Using the CS FCs and the *ab initio* forces on the atoms at the fcc atomic positions, a relaxation of $0.0095\times a_{\mathrm{fcc}}$ toward the Al type (2) planes with a corresponding energy of 5.3 meV per formula unit (Al_3Li) was calculated. The CA FCs give similar results of $0.0080\times a_{\mathrm{fcc}}$ and 4.5 meV per formula unit (Al_3Li). As might be expected, the CS results agree a little better with the direct electronic structure calculations. Similar calculations have been performed for the $L1_2$ structure. A simple test consists of taking a supercell with a single intentionally displaced site, computed for the purpose of determining the FCs, and verifying if the FC properly reproduce the displacement and associated energy. The CS FCs gave

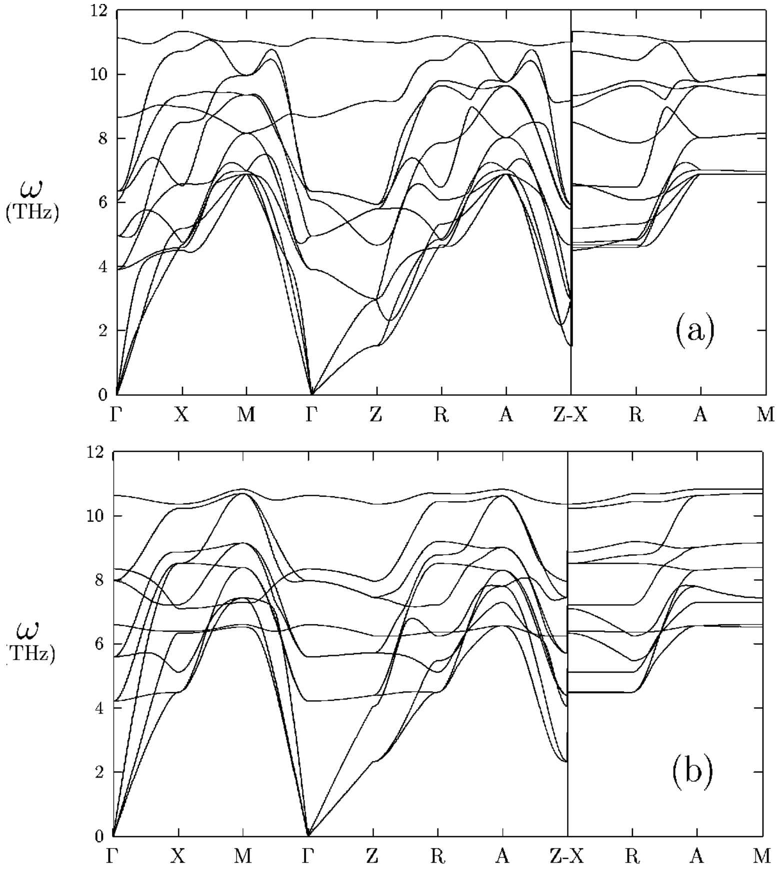

FIG. 4. Phonon dispersion of the ‘‘Z4’’ structure (a) as computed with CS FCs and (b) as computed with CA FCs.

essentially exact results, and the CA FCs was accurate up to a few percent in the displacement and relaxation energy.

The phonon dispersion has been computed with Eq. (14) and some results for the simple cubic $L1_2$ and the simple tetragonal ‘‘Z4’’ structure are shown in Figs. 3 and 4. In general, there appears to be an overall agreement between the CS and CA results, especially for the $L1_2$ case. For the ‘‘Z4’’ case, it should be noted that between the Γ to Z points the CA dispersion displays rather ‘‘flat’’ branches that are not apparent in the CS dispersion. In fact, the CA dispersion shows an almost flat branch across the figure at about 6.5 THz. Likewise, for the DO_{22} and ‘‘$O1$’’ structures the CA and CS agree rather well, except that in the DO_{22} case too, some erroneously flat branches occur in the CA result.

The flat branches have consequences for the VDOS, computed with Eq. (18), as is illustrated in Fig. 5. The CA-VDOS for the ‘‘Z4’’ structure has a sharp peak at about 6.5 THz that is absent in the CS result. The DO_{22} case is similar with an erroneous peak at the same frequency. Such incorrect features in turn affect the CA thermodynamic properties given by Eqs. (19) and (20).

In Fig. 6 the differences of the VDOS and the vibrational free energy between the $L1_2$ and DO_{22} structures ($\Delta n_v^{DO_{22}-L1_2}$ and $\Delta F_v^{DO_{22}-L1_2}$), as computed with the CS and CA FCs, are shown.

The differences in the zero-point energies of the $L1_2$ and DO_{22} structures can be recognized as the offset at zero temperature in Fig. 6(b). The CA FCs give the wrong sign for the zero-point energy difference of the $L1_2$ and DO_{22} structures. This is not so surprising considering that the zero-point energy is proportional to the first moment of the VDOS with respect to energy. The zero-point energy difference thus is proportional to the first moment of the VDOS difference (Δn). The VDOS differences as computed with the CA and the CS FCs are rather unalike, as is readily apparent from Fig. 6(a). The $\Delta F_v^{DO_{22}-L1_2}$, computed with CS or CA FCs, have about equal magnitude, but opposite sign, just like the zero-point energy differences. This too, is explained by the insufficiently accurate VDOS as computed with the CA FCs. Therefore, it appears that the CA FCs are too inaccurate to allow determination of the VDOS and vibrational thermodynamic properties.

The results derived from the CS FCs will be discussed in a little more detail. At the approximate order-disorder temperature of the Al$_3$Li $L1_2$ phase, about 600 K (Refs. 30 and 31) $\Delta F_v^{DO_{22}-L1_2}$ is about -0.86 kJ/mol f.u., where f.u. stands for formula unit Al$_3$Li. The vibrational free energy differences $\Delta F_v^{``O1''-L1_2}$ and $\Delta F_v^{``Z4''-L1_2}$ (computed with the CS FCs) at 600 K are of a similar magnitude, -0.83 and -0.08 kJ/mol f.u., respectively. To put the magnitude of the vibrational free energy difference in perspective, it is useful to compare it to the electronic total energy difference $\Delta E_{\rm tot}^{DO_{22}-L1_2}$. In Al$_3$Li,$\Delta E_{tot}^{DO_{22}-L1_2} \approx 1.3$ kJ/mol f.u.[31] In fact, the absolute value of $\Delta E_{\rm tot}^{DO_{22}-L1_2}$ is rather low in the Al-Li system, in other alloy systems[41] it can take values that are quite a bit larger. Hence, even when the lattice parameter is held at a fixed value, the vibrational free energy difference

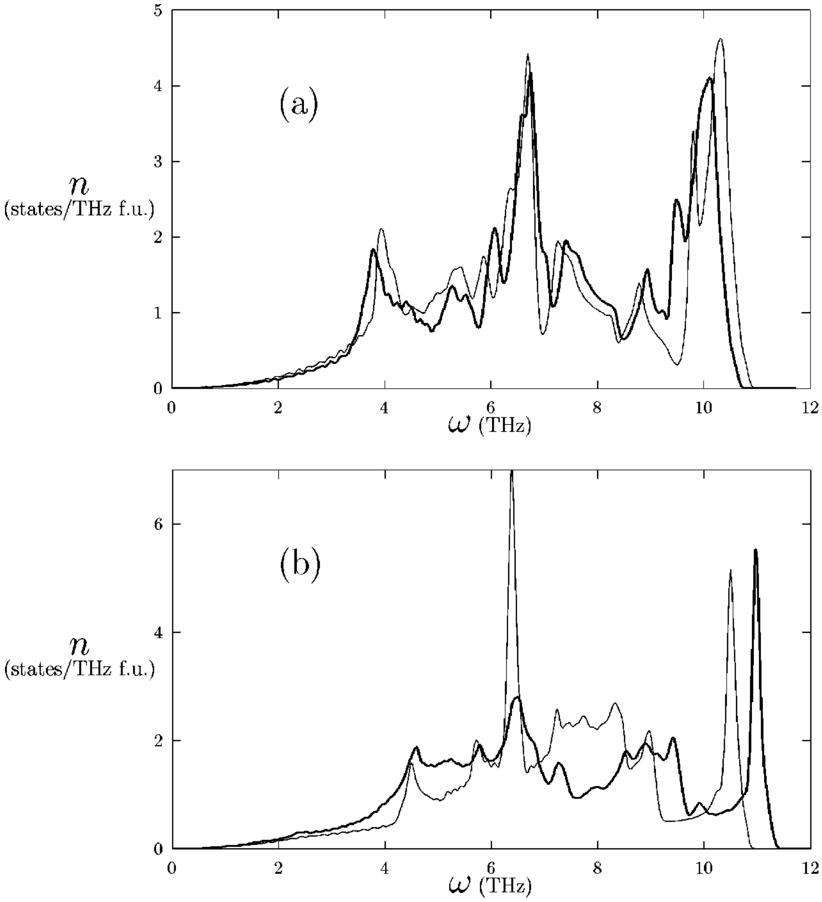

FIG. 5. Vibrational DOS (n) of the (a) $L1_2$ and (b) ''$Z4$'' structures. Thick line: as computed with CS FCs; thin line: as computed with CA FCs. Number of states is given per f.u, where f.u. is a formula unit Al_3Li.

is considerable compared to the electronic total energy difference. When the lattice parameters of various states of order differ, the vibrational free energy difference might be more significant still. As discussed elsewhere[1,42] the contribution of the vibrational free energy is related to the disorder in the FCs. In the present case the FCs relating to the Al-Li bonds differ much from the geometric mean of the FCs of the Al-Al and Li-Li bonds, as is readily apparent for the CA FCs in Fig. 2 where the Al-Li eigenvalues are not located midway between the corresponding Al-Al and Li-Li eigenvalues. Large deviations from the geometric mean result in a large configurational dependence of the vibrational free energy.[42]

The approximate linearity of ΔF_v with T in Fig. 6 indicates that the $T\Delta S_v$ term is dominant, but the argument deserves some care. At high temperature E_v, given by Eq. (19), is linear in T with a slope equal to the specific heat. The specific heat in turn, is not configuration dependent at high T, so that then ΔE_v vanishes. S_v, as a high temperature expansion of Eq. (20) shows, has a logarithmic temperature dependence,

$$\lim_{T\to+\infty} S_v = k_B N \log(T/T_o) + \text{const},$$

where T_o is some reference temperature, N is the number of vibrational states, and where the ''constant'' is configuration dependent. Therefore, at high temperature the vibrational entropy difference between two configurations, ΔS_v, approaches a constant value.

IV. CONCLUSION

The applicability of configuration independent FCs has been evaluated. It was argued that configuration independent FCs could be represented by configuration averaged (CA) FCs. The CA FCs were compared with FCs for specific configurations, and the physical properties that derive from FCs, such as the phonon dispersion, the elastic constants, the vibrational density of states, and vibrational free energy differences, were compared as well. Although strictly speaking, configuration independent FCs cannot exist because of unavoidable violations of the invariances, the configuration averaged (CA) FCs give reasonable results for some, but not all, physical properties.

It was shown that only the largest elements in the FC matrices of the nearest neighbor shells were rather similar across configurations, other elements could differ both in sign and in magnitude. Nevertheless, the elastic constants computed with CA FCs agreed rather well with those obtained from CS FCs. The CA FCs computed at a particular composition appear to work well for computing the elastic constants and phonon dispersion at other compositions as well. However, the CA results are not reliable for predicting the highest or lowest C_{ij} among competing configurations.

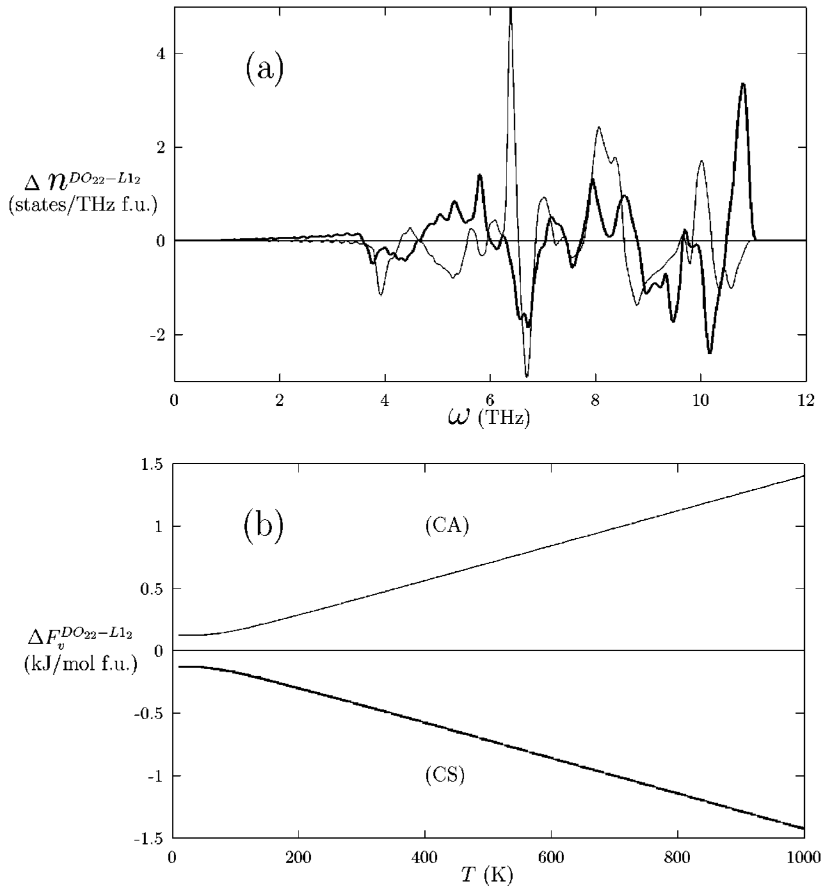

FIG. 6. Differences between DO_{22} and $L1_2$ structures as computed with CS FCs (thick line) and as computed with CA FCs (thin line); (a) difference of VDOS $\Delta n = n(DO_{22}) - n(L1_2)$, (b) vibrational free energy difference $\Delta F_v = F_v(DO_{22}) - F_v(L1_2)$ as a function of temperature (T) in kJ/mol f.u.

When the forces on atoms are known, the FCs can be used to compute relaxations and relaxation energies. Both CA and CS FCs appear to give rather accurate results, so that it might be possible to use one set of CA FCs to guess relaxation effects in a variety of configurations. The CA FCs predicted a relaxation of the position which was about 73% of the *ab initio* value, and the predicted relaxation energy was about 67% of the *ab initio* result. Although this may appear rather inaccurate, it was not much worse than what was obtained with the CS FCs. This hints at strong anharmonic effects in crystals where internal degrees of freedom exist.

The phonon dispersion too, is generally well reproduced by the CA FCs, but flatness of certain branches leads to incorrect peaks in the vibrational density of states of some structures. These inaccuracies in the density of states were responsible for the failure of the CA FCs to give the correct sign of the DO_{22}–$\mathrm{L}1_2$ vibrational free energy difference.

The calculations here suggest that the vibrational free energy difference of ordered configurations at the same lattice parameter can be comparable to the electronic total energy difference. When the lattice parameter displays a strong dependence on the state of order, the vibrational free energy might play an even more significant role.

In spite of the apparent success for the prediction of elastic constants and relaxations, and to a lesser extend for the phonon dispersions, the configuration independent–configuration averaged FCs are not accurate enough for a description of the coupling of configurational and vibrational free energy contributions in the context of alloy theory. This result implies that vibrational entropy differences associated with order-disorder transformations as computed with configuration independent FCs are probably not reliable.[20]

The configuration averaged FCs fail to correctly reproduce the vibrational free energy difference in the idealized model system studied here. This failure should be expected to be even more pronounced in real alloys where competing structures differ not only in atomic configuration, but also in terms of the lattice parameter and the cell internal degrees of freedom.

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