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Phonon dispersions in random alloys: a method based on special quasi-random structure force constants

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Abstract

In an attempt to obtain reliable first-principles phonon dispersions of random alloys, we have developed a method to calculate the dynamical matrix, with respect to the wavevector space of the ideal lattice, by averaging over the force constants of a special quasi-random structure. Without additional approximations beyond standard density functional theory, the present scheme takes into account the local atomic position relaxations, the composition disorder, and the force constant disorder in a random alloy. Numerical results are presented for disordered Cu₃Au, FePd, and NiPd and good agreement between the calculations and the inelastic neutron scattering data is observed.

(Some figures may appear in colour only in the online journal)

1. Introduction

The phonon problem is well understood and has been formulated in terms of force constants in real space, a dynamical matrix in wavevector space, and derived phonon frequency for more than half a century [1, 2]. More excitingly, with the recent advances in computational methods and software within the framework of density functional theory (DFT) [3, 4], the phonon properties of many materials can now be calculated without invoking any adjustable parameters. Utilizing the repeated periodic structure of an ordered system, obtaining phonon frequencies involves a simple solution for the eigenvalues of a dynamical matrix with a dimension of just three times the total number of atoms in the primitive unit cell [1–4]. Indeed, excellent agreement between predicted and experimental phonon data has been obtained for many ordered systems [3–7].

The purpose of the present work is to extend the application of the existing method [1, 2] to the case of disordered systems. A disordered system possesses no periodicity in its structures. The quest to solve the phonon problem of a disordered system is thus to develop a method to calculate the dynamical matrix that properly utilizes the force constants corresponding to various pairs of chemical species

in the random chemical environment. Many theoretical attempts have been made [8–13], the majority being based on the coherent potential approximation (CPA) [8, 12, 13]. The CPA [14, 15] is a single-site, mean-field theory capable of dealing with composition disorder [16] and even anisotropic lattice distortions [17]. However, the physical framework of the CPA does not allow the atoms to deviate from their ideal lattice positions so that the CPA is unable to consider the effects of the local variations of bond lengths and force constants [18]. For example, in the random alloys of FePd and Cu₃Au it appears that the force constants calculated by the first-principles method were not appropriate for use as the input to CPA-based approaches [8, 9, 19]. To obtain good agreement with experimental data for these systems, the previous CPA-based calculations [8, 9, 12, 19] had to use the force constants obtained from the Born–von-Karman fitting of the experimentally measured phonon frequencies.

In comparison, an emerging method for calculating random alloys is the supercell approach, employing special quasi-random structures (SQS) with which one can calculate the effects of elastic relaxations on variations in both bond length and force constants with chemical composition by relaxing the positions of the atoms [18]. According to Zunger *et al* [20], a given structure is always characterized by a

set of correlation functions. An SQS is a supercell built with a number (16 and 32 in the present work) of ideal lattice sites among which the atomic distributions are set to mimic the most relevant pair and multisite correlation functions of a completely disordered phase [21]. Under the framework of standard DFT, the SQS approach is nothing but a general supercell approach. Therefore, it captures the key physics of force constant disorder in a random environment in a straightforward manner by calculating the variation in bond lengths with chemical composition and interaction force constants between the actual atoms in the SQS supercell. The SQS approach has been shown to give an excellent approximation of disordered structures [21–25].

A somewhat more theoretically demanding application of the SQS approach is the calculation of the phonon dispersions of a random alloy. The majority of experimental inelastic neutron scattering data [26–28] for phonons are reported in the form of phonon dispersions. However, there has been no prior attempt to use the SQS approach to interpret the phonon dispersions of a random alloy measured from inelastic neutron scattering experiments [26–28]. Because the existing publications treat the SQS supercell as a primitive unit cell of the ideal lattice, the existing SQS approach results in many more dispersion branches than inelastic neutron scattering that uses the crystal symmetry of the ideal lattice. This technicality makes comparison between the calculated phonon dispersions and the experimental inelastic neutron data extremely difficult. For example, the primitive unit cell of the ideal face-centered cubic (fcc) systems considered in the present work contains only one atom, $p = 1$, resulting in three acoustical phonon branches [1, 2], while an SQS treated as primitive cell results in many phonon branches. As an example of a case with no proper averaging, the SQS adopted in this work of $p = 16$ or more results in at least 48 branches.

2. Model and simulation methods

The main objective of this work is to propose a scheme to calculate the phonon frequencies of a random alloy within the SQS approach and to make the calculated dispersions comparable to inelastic neutron scattering data. One consideration that must be taken into account is that the phonon dispersions [26–28] measured from the inelastic neutron scattering experiments only represent the averaged vibrations of the ideal lattice. For the present work, an averaging method is provided to reduce the dimensions of the SQS supercell dynamical matrix to match the primitive unit cell of its corresponding ideal lattice for the calculation of the phonon frequencies, i.e. ‘unfolding the Brillouin zone’.

In the present work, the following procedure is proposed.

- (i) Make an SQS supercell based on the primitive unit cell of ideal lattice (fcc in the present work) to mimic the correlation functions of the random structure.
- (ii) Relax the SQS supercell with respect to the internal atomic positions while keeping the cell shape and volume fixed.

(iii) Make the phonon supercell by further enlarging the SQS supercell and calculate the force constants.

(iv) Calculate the dynamical matrix $D_{\alpha\beta}^{jk}(\mathbf{q})$, with the wavevector, \mathbf{q} , being defined from the primitive unit cell of the ideal lattice, through the following Fourier transformation [2]:

$$D_{\alpha\beta}^{jk}(\mathbf{q}) = \frac{1}{\mu} \frac{1}{N} \sum_{M,P} \phi_{\alpha\beta}^{jk}(M,P) \times \exp[i\mathbf{q} \cdot (\mathbf{R}(M,j) - \mathbf{R}(P,k))] \quad (1)$$

where $\phi_{\alpha\beta}^{jk}$ is the cumulative force constant [29] between the atom positioned at $\mathbf{R}(M,j)$ and the atom positioned at $\mathbf{R}(P,k)$, the indices j and k label the atoms in the primitive unit cell of the ideal lattice, and the indices M and P label the primitive unit cells of the ideal lattice in the phonon supercell. N is the supercell size in terms of the number of primitive unit cells of the ideal lattice.

We note here that in the above statement the concept of ‘the primitive unit cell of the ideal lattice’ may represent the distorted primitive unit cell of the ideal lattice after the atomic positions are relaxed. μ in equation (1) is the averaged atomic mass, which is calculated as the arithmetic average in the present work. It is noted that using the geometric average (not considered in the present work) to calculate μ is also acceptable, and it will result in slightly hardened phonon frequencies when compared to those calculated by the arithmetic average. The alternative method is to remove the prefactor $1/\mu$ and instead using the true atomic mass weight of $1/\sqrt{m(M,j)m(P,k)}$ inside the summation of equation (1). However, we find that if we do this while the calculated phonon dispersions are generally well away from the gamma point, in the vicinity of the gamma point the calculated phonon frequency does not go to zero, perhaps because the use of $1/\sqrt{m(M,j)m(P,k)}$ breaks the local symmetry or due to the finite size effect of the SQS supercell.

Equation (1) was originally derived to consider surface effects [2]. Otherwise, for an ordered phonon supercell, the summation over M can only result in a prefactor N since the translational invariance makes $\phi_{\alpha\beta}^{jk}$ depend on M and P only through the difference $\mathbf{R} = \mathbf{R}(P,k) - \mathbf{R}(M,j)$ [3]. For the present purpose, the summation over M serves as an average in the wavevector space over both the composition disorder and the force constant disorder.

It should be emphasized here that in calculating $D_{\alpha\beta}^{jk}$ in equation (1) we make use of all of the interaction force constants between the atoms within the supercell, as demonstrated by Parliński *et al* [29]. This implies that no intra-atomic interactions have been neglected except for those resulting from the phonon supercell size. The present approach is different from the approach in the alloy theoretic automated toolkit (ATAT) package [30] that we employed previously [21]. When using ATAT for the supercells in this work, a longer cutoff distance (beyond which the force constants are treated as zero) between the atoms must be defined to accurately fit the force constants.

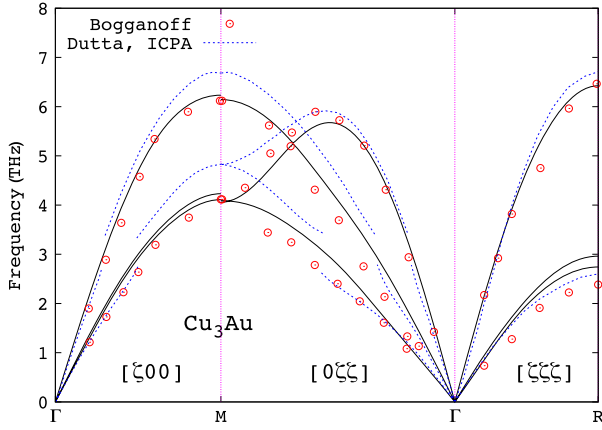


Figure 1. Phonon dispersions for random Cu_3Au . The solid (black) lines represent the present calculation and the open circles represent the inelastic neutron scattering data of Katano *et al* [27]. The dashed (blue) lines represent the calculated results using the *ab initio* transferable force constant model by Dutta *et al* [19].

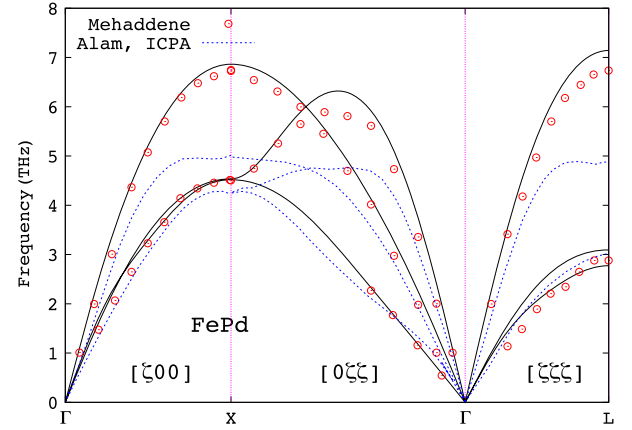


Figure 2. Phonon dispersions for random FePd . The solid (black) lines represent the present calculation and the open circles represent the inelastic neutron scattering data measured at 1020 K by Mehaddene *et al* [28]. The dashed (blue) lines represent the calculated results using DPFT within the ICPA [12] by Alam *et al* [8].

3. Computational details

This work chooses the random fcc alloys Cu_3Au , FePd , and NiPd as prototypes. The SQS supercells are built using the improved version [21, 31] of the ATAT package [30]. The generated SQS supercell sizes are 32, 16, and 16, for Cu_3Au , FePd , and NiPd , respectively. In the phonon calculations, we have chosen to use the fcc lattice constants of 3.750, 3.831, and 3.740 Å for Cu_3Au , FePd , and NiPd at 0 K, respectively. These values are within 1% of the measured lattice constants of random Cu_3Au (3.753 Å at 296 K [32]), FePd (3.831 Å at 1020 K [28]), and NiPd (3.720 Å [26] and ~ 3.750 Å [33]), respectively. The projector-augmented wave (PAW) method [34, 35] within the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [36] implemented in the VASP (version 5.2) package [34, 35] is employed. We use the linear-response approach together with the 128-atom phonon supercells and a Γ -centered $3 \times 3 \times 3$ k -mesh to calculate the real space force constants. The energy cutoffs for the phonon calculations are automatically determined by the setting of ‘PREC=A’ in VASP which gives 272.2, 267.9, and 269.5 eV for Cu_3Au , FePd , and NiPd , respectively. For the relaxations of the atomic positions of the SQS before the phonon calculations, the k -mesh is Γ -centered $7 \times 7 \times 7$ and the energy cutoffs are 1.25 times of those used in the phonon calculations. FePd and NiPd are treated with a ferromagnetic spin in all of the calculations.

4. Results and discussion

The calculated phonon dispersions, along the directions $(0\ 0\ \xi)$, $(0\ \xi\ \xi)$, and $(\xi\ \xi\ \xi)$, are compared with the inelastic neutron scattering data [26–28] in figures 1–3 for Cu_3Au , FePd , and NiPd , respectively. In the three cases presented, the transverse mode splits slightly for the dispersions of $(0\ 0\ \xi)$ and $(\xi\ \xi\ \xi)$. This is understandable since the dynamical matrix calculated using equation (1) does not completely

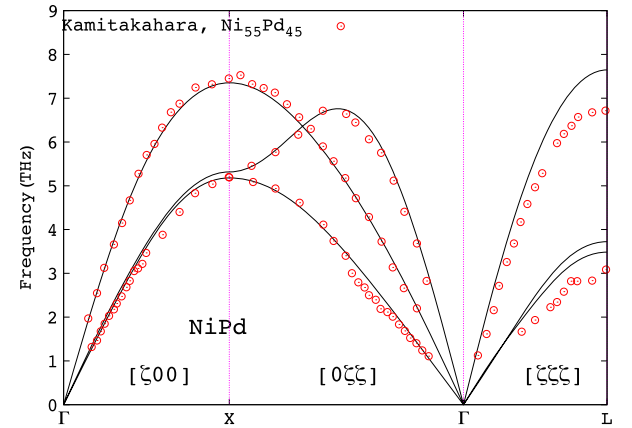


Figure 3. Phonon dispersions for random NiPd . The solid lines represent the present calculation and the open circles represent the inelastic neutron scattering data for $\text{Ni}_{55}\text{Pd}_{45}$ by Kamitakahara and Brockhouse [26].

satisfy the fcc symmetry that was broken within the SQS supercell to meet the correlation function requirements. For comparison with the previous CPA calculations, in particular for FePd , Alam *et al* [8] pointed out that the first-principles force constants used in the CPA calculations failed to capture the complexities of the force constant disorder in a random environment. In terms of agreeing with experiments, substantial improvements are seen in figure 2 of the present results over the previously calculated phonon dispersions using density functional perturbation theory (DPFT) within the itinerant coherent potential approximation (ICPA [12]) by Alam *et al* [8]. In fact, a combination of the transferable force constant model based on first-principles calculations in the ICPA also fails to reproduce the inelastic neutron scattering data for FePd [9] and Cu_3Au [19].

For the purpose of showing the force constant disorder and atomic position distortion obtained from the SQS approach, figure 4 shows the spring model [18, 24] of the

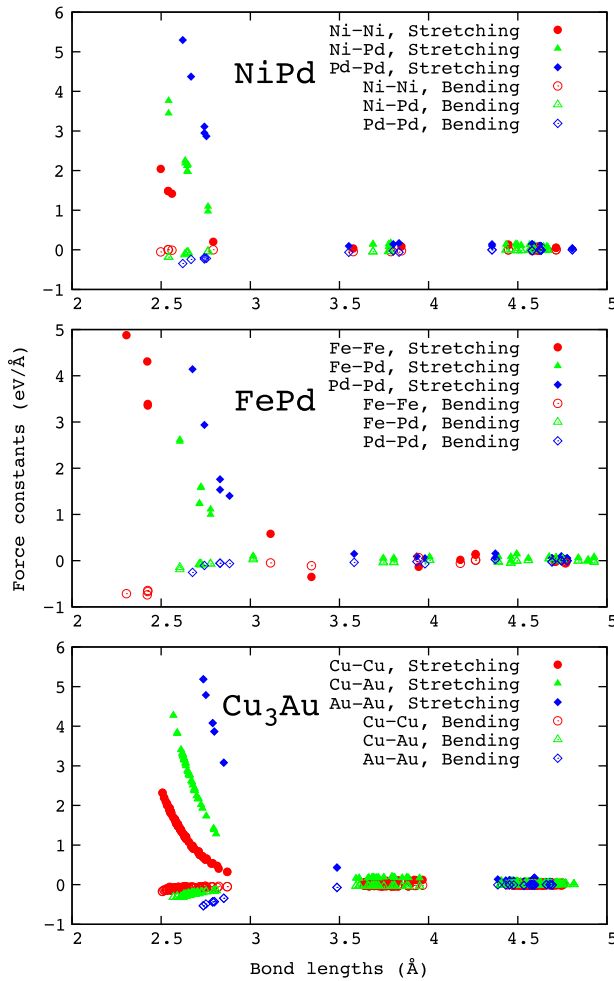


Figure 4. Variations in bond lengths and force constants versus atom pair type.

stretching and bending force constants as a function of the bond length between atoms up to third nearest neighbors in the measured ideal lattice. In this model, the ‘stretching force constant’ is derived by projecting a force constant tensor into the direction joining the two atoms in question. The ‘bending force constant’ is derived by an average over the two projected force constants whose directions are perpendicular to the stretching direction. For Cu₃Au and NiPd, it is clearly seen that the bond lengths are partitioned into three groups corresponding to the first, second, and third nearest neighbors within the confines of the ideal lattice. For FePd, in contrast, the partition is not clearly seen, implying that the variations of bond lengths are rather large for FePd. It is observed that the first nearest neighbor stretching force constants are strongly dependent on the atom pair types as observed in the previous work [18], showing the success of considering the force constant disorder with the SQS approach. For the first nearest neighbor interaction in NiPd and Cu₃Au, it is observed that the Pd–Pd and Au–Au stretching force constants are several times larger than the Ni–Ni and Cu–Cu stretching force constants, implying that the Pd–Pd and Au–Au pairs prefer longer bond lengths than the Ni–Ni and Cu–Cu pairs. For NiPd and Cu₃Au, the values of the first nearest neighbor

stretching force constants correlate reasonably well to both the bond length and atom pair type. This, in turn, means that for a given atom pair type in NiPd and Cu₃Au, the first nearest neighbor stretching force constants are found to lie on a single curve [18, 24]. However, in contrast to NiPd and Cu₃Au, the values of the first nearest neighbor stretching force constants in FePd cannot reasonably be sorted by the types of atom pair.

5. Conclusion

In summary, we have presented a scheme which makes it possible to calculate the phonon dispersions of random alloys using the SQS approach within standard DFT, while considering the disorder in composition, bond length, and the force constant. As examples, phonon dispersions of random Cu₃Au, FePd, and NiPd fcc SQS are calculated, and good agreements with experiments are obtained. In particular, within the framework of using first-principles force constants as an input, substantial improvements over the previous CPA-based approach are seen for FePd and Cu₃Au.

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