Interplay of force constants in the lattice dynamics of disordered alloys: 
An ab-initio study

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A reliable prediction of interatomic force constants in disordered alloys is an outstanding problem. This is due to the need for a proper treatment of multisite (at least pair) correlation within a random environment. The situation becomes even more challenging for systems with large difference in atomic size and mass. We propose a systematic density functional theory (DFT) based study to predict the ab-initio force constants in random alloys. The method is based on a marriage between special quasirandom structures (SQS) and the augmented space recursion (ASR) to calculate phonon spectra, density of states (DOS) etc. bcc TaW and fcc NiPt alloys are considered as the two distinct test cases. Ta-Ta (W-W) bond distance in the alloy is predicted to be smaller (larger) than those in pure Ta (W), which, in turn, yields stiffer (softer) force constants for Ta (W). Pt-Pt force constants in the alloy, however, are predicted to be softer compared to Ni-Ni, due to large bond distance of the former. Our calculated force constants, phonon spectra and DOS are compared with experiments and other theoretical results, wherever available. Correct trend of present results for the two alloys pave a path for future studies in more complex alloy systems.

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I. INTRODUCTION

In spite of years of rigorous research, a reliable ab-initio theoretical model for structural and/or substitutional disordered alloys is still lacking. More importantly, the understanding of the problem of lattice dynamics (or phonons) in disordered alloys is still in its adolescence. This is mainly due to the presence of off-diagonal (multisite) disorder arising out of the force constant tensor \( D_{\mu\nu}(R_i - R_j) \) in the phonon problem. In addition the sum rule \( \sum_{R_j} D_{\mu\nu}(R_i - R_j) \) makes the disorder at a site depend upon its neighborhood or the so called environmental disorder. As such first principles method based on e.g. coherent potential approximation (CPA) is inapplicable in this problem. Within CPA, the atoms occupancy are assumed in an average sense embedded in a structure-less uniform average medium. This prohibits CPA to include structural relaxations, which contrasts from the experimental observations because bond distance between atomic pairs (e.g. A-A, B-B, and A-B in a binary alloy) are generally different. Various generalizations of CPA have been suggested over time, each has its own advantages and disadvantages. An striking approach, emerged in recent years, is the so called special quasirandom structure (SQS) proposed by Zunger et al. which carries the signature of configuration correlation with them. In particular, SQS is an ordered supercell which is constructed in such a way to mimic the most relevant pair and multisite correlation functions of the disordered phase. Unlike CPA and other related approaches, SQS is a local structural model which captures the most relevant microstates of disordered phase.

As far as the calculation of force constants for random alloys are concerned, three approaches are mainly utilized in the past. The first attempt was to fit an empirical set of force constants to match the available experimental phonon spectra. The second approach was to compute the force constants from selected ordered structures and then use them for random alloys. This is of course not a proper solution, because dynamical matrices are not directly transferable across the environment. In later studies, few SQS methods have been used, but only \( \leq 8 \)-atoms cell were used which is not enough to capture the detailed properties of phonons, as illustrated in the present work.

In addition to a reliable estimate of the force constants, equally important is the need for a method to perform configuration average over the disorder environment to get the phonon spectra, DOS etc. for the alloys. Augmented space formalism (ASF) is a powerful technique to do the same, and has been described in great details in many of our earlier papers. Interested readers are referred to articles for any details related to formalism. In the present rapid communication, we integrate a first principles SQS method with the ASF to demonstrate the interplay of force constants within a disorder environment. Unlike previous approaches, a systematic calculation of the force constants with increasing size of the SQS cell is made. Stress on the atomic sites are directly related to the force constant matrix and hence a small disturbance leads to a large change. To overcome this effect, we use the SQS cell in conjunction with the small displacement method to construct the dynamical matrix \( D_{\mu\nu} \). Based on the predicted bond length
distribution and the calculated force constants for each pair A-A, B-B, and A-B, it is concluded that a minimum of 32-atom SQS cell is needed to capture the important disorder correlations, and hence a reliable phonon dispersion. Two different alloy systems, bcc TaW and fcc NiPt, are chosen to demonstrate the reliability of the approach. Both the systems have inelastic neutron scattering data to compare our theoretical results. Ta and W belong to 5d-metal series with similar size and atomic masses, but quite different force constants. Ni and Pt on the other hand differ significantly in size (~ 12%), masses (Pt is 3-times heavier than Ni) as well as force constants (φ_{A-B} is 55% larger than φ_{Ni-Ni}). As such considerable differences are expected from the lattice dynamical properties of the two systems, with different interplay of force constant interactions. We compare our calculated dynamical matrices, phonon dispersion and DOS with existing experimental and theoretical data, wherever available.

To calculate the force constants within a disorder environment, we first develop a structural model based on the SQS method. SQS is an N-atom periodic structure constructed in such a way that the associated set of correlation function of this structure mimic the ensemble average correlation functions of the random alloy. Different sized SQS-cells (8-atom, 16-atom, 32-atom and 64-atom) are used for both the fcc and bcc systems (See supplementary material for the SQS structures). We use Vienna ab-initio simulation package (VASP) with a pseudo-potential and a projected-augmented-wave (PAW) basis based on the local density approximation (LDA). The cut-off energy for the electronic wavefunctions is 500 eV. All the structures are fully relaxed until the energy converges to within 10^{-6} eV and the forces on each atom is less than 0.001 eV/Å. Such a relaxation, in a way, captures the effect of any static displacements that may be present in a real system. A Monkhorst-pack Brillouin zone (BZ) integration with a 8\times k-mesh is used for 8-atom SQS calculation. Convergence of D_{\mu\nu} as a function of k-points is checked, see below. Smaller k-meshes are used for larger supercells. Magnetic (non-magnetic) calculations are done for NiPt (Ta-W) systems. Relaxed lattice constants for 8-atom, 16-atom, 32-atom and 64-atom SQS calculation for fcc Ni_{50}Pt_{50} are 3.72, 3.72, 3.70, and 3.72 Å respectively, compared to the experimental value of 3.785 Å\(^{[13]}\). For bcc Ta_{50}W_{50}, they are 3.23 Å for all the structures, compared to 3.23 Å as observed\(^{[16]}\). To extract the force constant matrices, we use the fully relaxed SQS structures and apply the small displacement method using PHON package\(^{[12]}\) implemented within VASP. For 32-atom SQS, force fields are constructed by applying 48 displacements in fcc Ni_{50}Pt_{50} and 96 displacements in bcc Ta_{50}W_{50} along 3-cartesian axes, each of amplitude 0.04 Å.

Because of the low symmetry of the SQS-structures, the desired symmetry of the dynamical matrices for the underlying lattice (fcc and bcc in the present case) are lost. Lattice imposed symmetric dynamical matrices are required to perform a direct configuration average within the ASR scheme. These symmetric matrices are also directly comparable to the neutron scattering data and other theoretical results, if available. In order to resort to the symmetry of the underlying lattice, we followed two steps: (1) For a particular SQS-cell of a given lattice, one can see various atom-pairs along specific crystal directions followed by the occupancy number for each pair A-A, B-B, and A-B along those directions. This is shown in Fig. S1 of the supplementary material, where the occupancy number for each pair A-A, B-B, and A-B along various neighbor directions are displayed for 8-, 16- and 32-atoms SQS TaW (left panel) and NiPt (right panel) alloy. Depending on the occupancy number, the force constants are averaged for each configurations (i.e. A-A, B-B, and A-B pair) along every directions (up to first nearest neighbor [nn] for fcc and second neighbor [nnn] for bcc lattices). (2) Having done the directional averaging, we still lack the proper symmetry of the dynamical matrices for the underlying lattice. This is due to the relaxation effect, which modifies the atomic positions by δ. For example, a particular atom at (1/2,1/2,2/3) in a perfect fcc lattice moves to (1/2±δ_{1},1/2±δ_{2},2/3±δ_{3}) or atoms at (1/2,1/2,2/3) and (1,0,0) in a bcc lattice moves to (1/2±δ_{1},1/2±δ_{2},2/3±δ_{3}) and (1±δ_{1},±δ_{2},2/3±δ_{3}) respectively. In order to retrieve the desired symmetry of the dynamical matrix, we apply transformation operation on these average matrices to get the direction specific dynamical matrices e.g. φ_{111} = B_{1}φ_{−111}B_{1}^{T} along one of

| TABLE I. Dynamical matrices D_{\mu\nu}(l) \text{(Newton/meter)} for bcc Ta_{50}W_{50} (top) and fcc Ni_{50}Pt_{50} (bottom). N-atom represents the size of the SQS supercell, Other experimental \text{and theoretical data are given for comparison.} |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 8-atom          | 16-atom         | 32-atom         | 64-atom         | Expt.6,7        |
| **bcc Ta_{50}W_{50}** |                 |                 |                 |                 |
| Ta-Ta 27.707    | 25.103          | 22.324          | 22.872          | 16.983          | 111_{xx}       |
| W-W 28.934      | 24.568          | 21.063          | 21.069          | 23.000          | 111_{xx}       |
| Ta-Ta 27.734    | 26.071          | 23.192          | 21.783          | 23.984          | 111_{yy}       |
| W-W 6.655       | 8.348           | 9.418           | 11.156          | 19.200          | 111_{yy}       |
| Ta-Ta 11.504    | 15.727          | 16.120          | 17.599          | 21.201          | 111_{yy}       |
| W-W 5.855       | 13.080          | 13.668          | 13.984          | 17.603          | 111_{yy}       |
| Ta-Ta -0.009    | 9.114           | 25.937          | 17.180          | 1.182           | 200_{xx}       |
| W-W 0.016       | 17.693          | 36.233          | 41.915          | 47.300          | 200_{xx}       |
| Ta-W 16.448     | 13.442          | 30.733          | 29.367          | 24.803          | 200_{xx}       |
| Ta-Ta -0.001    | 3.105           | -2.909          | -0.598          | 1.423           | 200_{yy}       |
| W-W 0.008       | 2.755           | -1.648          | 0.244           | -0.800          | 200_{yy}       |
| Ta-W -1.634     | 3.656           | -2.163          | -0.620          | 0.181           | 200_{yy}       |

| **fcc Ni_{50}Pt_{50}** |                 |                 |                 |                 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 8-atom          | 16-atom         | 32-atom         | 64-atom         | Other8,9        |
| Ni-Ni 6.289     | 8.433           | 9.813           | 9.107           | 8.231           | 110_{xx}       |
| Pt-Pt 13.755    | 34.576          | 36.317          | 26.747          | 33.494          | 110_{xx}       |
| Ni-Pt 12.421    | 17.387          | 21.210          | 17.200          | 17.868          | 110_{xx}       |
| Ni-Ni 3.791     | 8.845           | 11.115          | 9.712           | 9.580           | 110_{yy}       |
| Pt-Pt 9.008     | 36.546          | 43.377          | 31.426          | 39.655          | 110_{yy}       |
| Ni-Pt 8.026     | 18.287          | 25.091          | 19.416          | 20.740          | 110_{yy}       |
| Ni-Ni 5.394     | 0.946           | -1.845          | -0.0423         | -0.525          | 110_{zz}       |
| Pt-Pt 9.487     | 2.310           | -8.351          | -4.199          | -6.854          | 110_{zz}       |
| Ni-Pt 8.785     | 1.035           | -4.124          | -1.141          | -2.820          | 110_{zz}       |
the nearest neighbor direction of bcc lattice, where $B_i$ is the transformation matrix. A list of transformation matrices along specific directions for both fcc and bcc lattices are given in Table S1 of the supplement (See [12]).

The calculated dispersion in the occupancy for each pair reflects the sensitivity of the bond distances on the local environment. The calculated nearest neighbor (next nearest neighbor) average bond distances for three pairs $d_{Ta-Ta}$, $d_{W-W}$, and $d_{Ta-W}$ are 2.837 (3.220), 2.775 (3.226), and 2.788Å (3.235Å) respectively for 64-atom SQS Ta$_{50}$W$_{50}$. The nn-bond distance for Ta-Ta in the alloy is found to be $\sim$ 0.8% smaller compared to that in pure Ta, while W-W bond distance in the alloy is $\sim$ 1.7% larger than that in pure W. The calculated dynamical matrices (up to 2nd neighbor) for 8-, 16-, 32- and 64-atom SQS Ta$_{50}$W$_{50}$ are shown in the upper part of Table I. Note that, experimental force constants for Ta-Ta and W-W pairs are not for the alloy, but for pure Ta and pure W respectively. Force constants for Ta-W pair, however, are indeed for the alloy. Notably our calculated Ta-Ta force constants in the alloy are stiffer compared to those in pure Ta. On the other hand, the calculated W-W force constants are softer than those in pure W. This prediction actually jibe with the calculated bond lengths between these two pairs. Alloying shrinks (expands) the Ta-Ta (W-W) bond lengths making the springs relatively stiffer (softer). As far as the force constants for Ta-W pair goes, 64-atom SQS results are our best numbers to compare with the experiment. Experimental force constants are computed using a polynomial fit to their measured dispersion. Keeping in mind the sensitivity of the estimates, both on the theoretical and experimental front, the overall agreement between the 64-atom SQS results and the experiment for Ta-W force constants is fairly well.

The calculated average bond lengths for Ni-Ni, Pt-Pt and Ni-Pt pairs are 2.573, 2.692 and 2.604Å respectively for 64-atom SQS Ni$_{50}$Pt$_{50}$. Ni-Ni (Pt-Pt) bond length in the alloy is $\sim$ 3.3% larger ($\sim$ 2.8% smaller) than those in pure Ni (Pt). As such, Ni-Ni (Pt-Pt) force constants in the random alloy is expected to get softer (stiffer) compared to those in pure Ni (Pt). The calculated ab-initio force constants for the three pairs in disordered Ni$_{50}$Pt$_{50}$ alloy are shown in the lower panel of Table I. As before, results are shown for 8-, 16-, 32- and 64-atom SQS. Because these calculations are done for ferromagnetic NiPt, a one to one comparison with the experiment requires observed data at very low temperature, which we were unable to find in the literature. We have also performed non-magnetic calculations for NiPt, and found similar results for $D_{\mu\nu}$. In Table I, the force constants under the column labeled Other are the results from a recent calculation on Ni$_{50}$Pt$_{50}$ alloy by Granas et al. [15] These force constants for each pair (Ni-Ni, Pt-Pt and Ni-Pt) are within the disordered environment, and agree fairly well with ours within a few percent. Calculated force constants for Ni-Ni (Pt-Pt) pairs in the alloy are found to be softer (stiffer) compared to those in pure Ni (Pt) (See Ref. [21] for the force constants of pure Ni and Pt). This, again, goes in accordance with the bond lengths of respective pairs in the alloy vs. those in pure elements.

Keeping in mind the sensitivity of dynamical matrices to finer details of calculation, we have checked the convergence of various components of $D$ with respect to the number of k-points used in BZ integration. This is shown in Fig. 1 and 2 for 8-atom SQS Ta$_{50}$W$_{50}$ and Ni$_{50}$Pt$_{50}$ respectively. Different colors indicate different pairs of force constants while various components of $D$ are distinguished by different symbols. One can notice that ALL the components of $D$ for both the systems are well converged by 6$^2$ k-points.

Figure 3 shows the calculated phonon dispersion (left) and the configuration averaged phonon DOS (right) for bcc Ta$_{50}$W$_{50}$. Dispersion curves are calculated using the force constants of 32-atom SQS, as listed in Table I.
Phonon DOS, however, are shown with three sets of force constants, i.e., 8-, 16-, and 32-atom SQS, for comparison. Error bars in the dispersion curve indicate the full widths at half maxima (FWHM). Our calculated phonon dispersion and DOS using 64-atom SQS force constants are very similar to those using 32-atom SQS ones (also true in case of NiPt, see below). As such it is intuitively expected that, with increasing size of the supercell, the force constant matrix D converges in a collective manner. Finally, note that our calculated dispersion compares fairly well with the experiment [shown by square symbol].

Figure 4 (left) shows the phonon dispersion for Ni50Pt50 alloy calculated using the force constants of 32-atom SQS cell (see Table I). Unlike TaW, NiPt alloy shows interesting split band behavior along each symmetry direction. This is due to the strong disorder in both mass and force constants, giving rise to resonant modes, and has been evidenced in previous studies. Error bars with solid circles indicate the calculated FWHM. Error bars with square symbol along \( \langle \zeta 00 \rangle \) direction indicate the neutron scattering data. The panel on the right shows the configuration averaged phonon DOS with three sets of calculated force constants. Square symbols indicate the generalized phonon DOS derived from inelastic incoherent scattering. Notice that the calculated band edge increases with increasing the SQS cell size, and compare better with experiment. The integral value under each phonon DOS, however, remain the same. It is important to emphasize that the experimental phonon DOS is only shown for reference. A one to one comparison between our calculated DOS and the experimental DOS is not feasible. In inelastic neutron scattering, phonon DOS can be represented as \( N(\omega) = \sum_j (b_j/M_j)n_j(\omega) \), where \( b_j, M_j \) and \( n_j(\omega) \) are the inelastic scattering cross section, atomic mass, and the partial phonon DOS of atom \( j \) respectively. Although the calculated DOS from the force constants of 32-atom (or 64-atom, not shown here) SQS cell resembles maximally with the experimental DOS, the calculated band edge is still less than the measured one. This is an inherent problem of LDA-based calculations, which usually underestimates the band edge of the calculated DOS and are also reflected via the bulk modulus.

In summary, we propose a systematic first principles calculation of the interatomic force constants for disordered alloys. SQS structures of different cell size are used to capture the effects of random environment at different length scales. Two alloy systems with very different intrinsic properties (i.e., lattice type, masses, force constants etc.) are investigated. In bcc Ta50W50 alloy, Ta-Ta force constants are predicted to be stiffer compared to those in pure Ta, however W-W force constants behave oppositely. In fcc Ni50Pt50 alloy, Ni-Ni (Pt-Pt) force constants within the disordered environment behave softer (stiffer) than those in pure Ni (Pt). Calculated average bond lengths between each pair of atoms are found to closely dictate the nature of force constants. For both the alloys, the prediction of bond length distribution and the force constants are found to improve with increasing size of the SQS-cell; in particular, the 32-atom and 64-atom SQS cell for bcc Ta50W50 yields force constants which agree fairly well with experiment. Ab-initio prediction of force constants in random alloys is one of the key thrust of the present work. Calculated phonon dispersion and the DOS also compare reasonably well with available experimental data. We propose the present method as a potential solution to the microscopic understanding of force constants in disordered alloys. Future studies on more complex alloys, addressing the effects of magnetic order, lattice mismatch etc. on force constants, are ongoing which will provide an even more stringent test of the present methodology.

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