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First-principles based investigation on effects of magnetism on lattice dynamics in $Fe_{72}Pd_{28}$ alloy

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ABSTRACT

A first-principles based investigation of influence of magnetism on lattice dynamics of $Fe_{72}Pd_{28}$ system near the Invar composition has been carried by computing the pressure dependence of the phonon frequencies, the Gruñeisen parameters, the disorder-induced widths and the elastic shear constant using a combination of transferable force constant model, density functional perturbation theory and the itinerant coherent potential approximation, an analytic tool for performing configuration averaging in disordered alloys. We find that with increasing pressure and collapse of magnetic moment, the TA_1[110] phonon frequencies harden along with the elastic shear constant. We do not observe any significant variation of the mode Gruñeisen parameter with change in magnetic moment. These results indicate that there is no magneto-volume effect on the lattice dynamics and the experimentally observed phonon softening with increasing magnetization has to be associated with the martensitic instability.

1. Introduction

Fe based alloys such as FePt, FeNi and FePd, in both ordered and disordered phases have been the subject of extensive theoretical and experimental investigations for over three decades [1–8]. The interest in these systems stem out of the anomalously low thermal expansion coefficient, the "Invar" property, of these materials for Fe-rich compositions. The focus of the research on these systems, therefore, has been the pursuit for understanding the mechanism behind the Invar behavior. The Invar characteristics are observed for alloys near $Fe_{75}X_{25}$ (X = Pt, Ni, Pd) compositions and thus these systems have been subjects of extensive investigations. The Invar behavior in these systems is understood in terms of the instability of the magnetic moment i.e. the magneto-volume effect [9–11]. During the last two decades, the lattice dynamical behavior of these systems was also studied in detail [12–18]. Neutron-scattering measurements in these systems reveal that there is an anomalous softening of the TA_1[110] phonon branch upon cooling below the magnetic transition temperature, along with a softening of the elastic shear modulus. This anomaly in lattice dynamics was interpreted in terms of enhanced electron–phonon interactions [19]. However, since these systems also undergo a martensitic transformation around the temperatures where measurements were done, attempts were also made to understand whether the anomalous softening in lattice dynamical properties is related to the instability of the system prior to martensitic transformation. That this could be the case and no coupling between lattice dynamics and magnetism is responsible for the anomaly in case of Fe_3Pt was established by subjecting the system under pressure so that it undergoes a transition from a high-volume high-spin state to a low-volume low-spin state [20]. Similarly, for Fe_3Ni, band structure calculations attributed the phonon softening upon cooling the system, to pre-martensitic transition only [21].

In comparison to FePt and FeNi systems, results on the Fe–Pd system, particularly for the disordered phase are much less in number. There haven't been any significant investigation of the system near the Invar composition exploring the inter-relations between magnetism and lattice dynamics. Fe_3Pd, like Fe_3Pt and Fe_3Ni, also undergoes a spin moment collapse upon volume contraction, as has been observed in first-principles electronic structure calculations [22,23]. The only extensive study exploring the effect of magnetism on lattice dynamics in this system was performed on $Fe_{72}Pd_{28}$ and $Fe_{63}Pd_{37}$ alloys over a wide temperature range by neutron-scattering experiments [24]. The measurements showed that the TA_1[110] branch undergoes an anomalous softening near the zone center upon cooling below the magnetic transition temperature. A consequent softening of the elastic shear modulus is also observed. The investigation was however, inconclusive about the origin of this anomaly, partly because the measurements couldn't be done near the martensitic fcc–fct

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transformation temperature which the system undergoes. The understanding of the phonon anomaly in view of change in magnetic ordering upon cooling was, thus, incomplete.

In this work, we investigate the inter-relations between magnetism and lattice dynamics in $Fe_{72}Pd_{28}$. The motivation was to explore the possibility of anomalous behavior in lattice dynamics upon collapse of magnetic moment so that a possible connection between the anomaly in lattice dynamics and magneto-volume effect can be established. To our knowledge, a theoretical investigation of this aspect has never been carried out for this system. The reasons could be two fold: first, the computations of lattice dynamics at finite temperatures based upon accurate first-principles electronic structure methods are expensive and second, the lack of a suitable analytic, self-consistent theory for addressing the force constant and environmental disorders in the context of lattice dynamics in disordered compositions. In this work, the second difficulty is appropriately taken care of by a combination of first-principles based transferable force constant (TFC) approach [25] and the Itinerant Coherent Potential Approximation (ICPA) [26]for configuration averaging. The understanding of the anomaly in phonon spectra with change in magnetic moment has been addressed by computing the lattice dynamics at various pressures so that the collapse of the magnetic moment to a low-spin low-volume state from a high-spin high-volume state can be incorporated. Such an approach, as was done in case of neutron-scattering measurements on Fe_3Pt, is useful because it helps in gaining insight into the impact of spin collapse on the lattice dynamics which in turn can help in understanding the experimental observations.

In what follows, we have calculated the variations of phonon spectra, the disorder-induced widths, the Gruñeisen parameters and the elastic shear modulus as a function of volume (spin state) for $Fe_{72}Pd_{28}$. In the following section we briefly discuss the methodologies adopted followed by the results. The concluding remarks are presented at the end.

2. Methodology and computational details

Incorporating the randomness of the inter-atomic force constants in a disordered alloy environment is the most challenging task for computation of phonon spectra and related properties. The ICPA method, although, addresses this off-diagonal disorder in random alloys, in an analytic and self-consistent way, it requires accurate information of inter-atomic force constants between various pair of chemical species for being applicable to realistic alloys. The most reliable sources of such information are the first-principles electronic structure methods. However, modeling the random alloy environment in first-principles techniques requires construction of large supercells, thus, increasing the computation time manifold. This problem is recently alleviated by the TFC model. This model is constructed upon the observation that the relation between the stiffness of a given bond connecting a given species pair and the bond distance itself, is transferable across compositions [25]. The advantage of this observation is that it provides a very simplistic and computationally feasible way to determine the force constants as the force constants versus bond distance relationships can be determined from a relatively small number of first-principles calculations on select configurations and then can be transferred to determine the force constants for other atomic configurations, once the relevant bond lengths are known. The TFC has found to be extremely successful in computing the vibrational entropies for a number of alloys [25,27,28]. Recently, we have devised a first-principles based approach for computation of complete phonon spectra of random binary alloys by combining the TFC model with the ICPA. The computed phonon spectra and elastic constants for various concentrations of Pd_xFe_{1-x} alloys had excellent agreement with the experimental results [29], thus validating the accuracy of this method. In this work, we have, therefore, used this approach to extract the inter-atomic force constants of various pairs of species at various volumes for disordered $Fe_{72}Pd_{28}$ and used as inputs to the ICPA calculations for computation of phonon spectra and related quantities.

For construction of the transferability relation between the bond stiffness and bond distances, we have used the first-principles Quantum-Espresso code [30], based upon a Plane wave-Pseudopotential implementation of the density functional perturbation theory [31]. Force constants for $L1_2$ Fe_3Pd and $FePd_3$, $L1_0$ FePd and fcc Fe and fcc Pd structures at their respective equilibrium and experimental lattice parameters have been used for construction of the transferability relation. Ultrasoft pseudopotentials [32] with nonlinear core corrections [33] were used. Perdew–Zunger parametrization of the local density approximation [34] was used for the exchange-correlation part of the potential. Plane waves with energies up to 55 Ry are used in order to describe electron wave functions and Fourier components of the augmented charge density with cutoff energy up to 650 Ry are taken into account. The Brillouin-zone integrations are carried out with Methfessel–Paxton smearing [35] using a $12 \times 12 \times 12$ **k**-point mesh. The value of the smearing parameter is 0.02 Ry. These parameters are found to yield phonon frequencies converged to within 5%.

After achieving the desired level of convergence for the electronic structure, the force constants are conveniently computed in reciprocal space on a finite **q**-point grid and Fourier transformation is employed to obtain the real space force constants [36]. The number of unique real-spaced force constants and their accuracy depend upon the density of the **q**-point grids: the closer the **q**-points are spaced, the more accurate the force constants are. In this work, we have used a $4 \times 4 \times 4$ **q**-point mesh for all structures.

The required configuration averaging is performed by employing the ICPA method. The disorder in the force constants was considered for nearest neighboring shell only and the calculations were done on 400 energy points. A small imaginary frequency part of -0.05 was used in the Green's functions. The Brillouin-zone integration was done over 356 **q**-points in the irreducible Brillouin zone. The simplest linear-mixing scheme was used to accelerate the convergence. The number of iterations ranged from 5 to 15 for all the calculations. The phonon frequencies are obtained from the peaks of the coherent scattering structure factors and the disorder-induced widths are obtained from the full-width at half-maxima (FWHM) of the structure factors.

3. Results and discussions

3.1. Magnetic properties

We first look at the magnetic properties of the ordered Fe_3Pd alloy. Fig. 1 presents the variation of the total magnetic moment per atom with reduced volume V/V_0, where V_0 is the volume of the ferromagnetic ground state calculated using the Plane wave-Pseudopotential (PW-PP) technique as implemented in the Quantum-Espresso code. The equilibrium lattice constant (volume) and the total magnetic moment are in good agreement with the experiment and the results of the LMTO calculations [22]. The qualitative behavior of magnetic moment with contraction in volume is also in good agreement with the LMTO results. The results show that with increasing pressure (decreasing volume) there is a sudden collapse of the total magnetic moment for $V/V_0 \sim 0.83$. To explore this behavior in more detail, we calculated the total energy variations with volume and spin states using the fixed-spin moment method [37]. Fig. 2 presents the results for the variation of total energy with volume for the two spin branches.