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LATTICE DYNAMICS OF GOLD (Au) AND NICKEL (Ni): IFC AND DFT APPROACH

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Abstract

Density functional theory (DFT) and interatomic force constant (IFC) have been applied to study the lattice dynamics of Gold and Nickel in order to determine which technique gives a better result when compared to experimental result. For the DFT calculation, GGA type of pseudopotential was used while the IFC technique requires extending the number of neighbours to the sixth neighbour. Since the IFC approach gives room for increase in the number of nearest-neighbors, it is observed that the results from IFC were in better agreement with experiment compared to results from DFT calculation.

Keywords: FCC metals, phonon dispersion, Density of states; thermodynamic properties

1. Introduction

The theory of lattice dynamics was originated by Born-Von Karman. Einstein and Debye [1] showed that the heat content of solids is dependent on the collective quantized modes of lattice vibrations associated with the little displacement of the basis ions from their equilibrium sites. Therefore, lattice dynamical studies generally seek to understand fully the nature of inter-atomic forces in solids and further to apply the understanding to related properties which include specific heat capacity, thermal and electrical conductivity, transmission of sound, superconductivity , Reflectivity of ionic crystals, crystallographic phase transitions etc [2]. Hence, lattice dynamical studies form a major component of research work done to access the properties of the condensed state. In the theory of lattice dynamics, there are two types of phonons. Acoustic and optical phonons, which have normal modes of lattice vibrations namely the longitudinal and the transverse modes defined in terms of the direction of propagation of lattice waves with respect to the source of vibration [3]. Solids greater than one atom per unit cell exhibits the two types of phonons while monoatomic solids with one longitudinal and two transverse modes passing through the origin exhibits only acoustic phonon. The measurement of phonon dispersion curves and fitting force-constant models to the measured frequencies has been of great interest for many years in the studies of lattice dynamics of metals. The force constants are understood to have a physical meaning and occasionally used to derive interpolation formulas for the calculations of phonon frequencies distributions and polarization vectors [4]. Certain relationships between some of the constants lead to good fit forces from remote neighbors and derived curves can give a very good fit in measured direction. Several authors have attempted theoretical calculations of the lattice dynamics of metals from first principles [5-7]. None of them has had marked success except for the alkaline metals. However, Harrison [7] has proved that, using two free parameters which can be evaluated from phonon measurements, that pseudopotential can be derived from a phenomenological model. Force constant analysis of the data for Pb has generally proved a failure. Models of several kinds with forces going out as far as the eighth neighbor have been tried without success[8]. Hanke [9] used the shell model to discuss the dynamics of Cu, Ni and some other metals. His idea was to use the shell-core concept to simulate polarization effects in the noble and transition metals. While the use of dipolar model for metals first seems inappropriate, Hanke has argued that the applicability of the model can be made plausible by microscopic consideration [10]. The prediction of phonon dispersion curve for noble metal have been a challenging problem (from the two commonly used exchange correlation functional, local density approximation (LDA) and generalized gradient approximation (GGA) although some researchers have explored other correlation functional to improve on the first

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principle calculation results) in recent years [11]. The density functional theory have been applied in this case . Depending on the exchange functionals used , the dispersion curves can in some cases overestimate or underestimate when compared to experimental results. The question now arises , if the first principle calculation is still having these challenges, is it also possible for us to tackle the phonon dispersion problem using the inter atomic force constant technique as implemented in the Born-Von Karman model? In this paper, a simulation software package is used to determine phonon dispersions curves and compared with the dispersions obtained analytically via inter-atomic force constants in order to ascertain which approach gives better results when compared to experimental results.

2.0 Methodology

2.1 Analytical Procedure

The phonon dispersion curve from IFC approach can be computed from the dynamical matrix D(q) at the wave vector q given below.

$$D^{\alpha\beta}(q) = \left(\frac{1}{\sqrt{m_i m_{i'}}}\right)\sum_{i'} \phi_{\alpha\beta}(0i, l'i')exp[iq.(r_l'_{i'} - r_{0i})] \quad (1)$$

where mi is the mass of the ith atom. Phonon frequencies ω(q) and mode eigenvectors X(q) at q are obtained by using the eigenvalue equation[12]:

$$D(q) - \omega^2 I|X(q)=0 \quad (2)$$

Where ω, D(q) and I have their usual meanings. The elements of the dynamical matrix is a 3×3 matrix as sh

2.2 Computational procedure

The calculations are carried out within the local density approximation (LDA)[13] and generalized gradient approximation (GGA) [14] for the exchange and correlation energy with quantum espresso code. The kinetic energy cut off (Ecut) of 55Ryd and 35Ry were used for Au and Ni respectively. The integration over the Brillouin zone were performed in the reciprocal space with uniform K-point meshes 11 x 11 x 11 and 12 x 12 x 12 for LDA and GGA respectively while 8 x 8 x 8 K-point mesh was used for Ni in both LDA and GGA. The self consistency calculation was assumed to have converged when the difference in energy between subsequent iteration was 1.0 x 10Ryd. The optimized lattice constants were obtained by fitting the total energy vs lattices constant curve with the Birch Munanghan equation of states. The lattice dynamics of both Au and Ni were computed immediately self-consistency calculation is achieved.

3.0 Results and Discussion

3.1 PHONON DISPERSION OF GOLD (Au)

The phonon dispersion of Au calculated from quantum espresso code and inter atomic force constants (IFCs) compared with experimental inelastic neutron scattering data data [15] are shown in Figures 1 and 2. The experimental results are shown as black circles, the red line are the dispersions calculated by GGA functional whereas the green lines are the LDA dispersion. The density functional theory DFT calculations carried out for Au, the electron-ion was treated by using ultrasoft pseudopontential, within the applied self-consistent method. In gold (Au) the phonon dispersion of LDA functional at equilibrium lattice constant are close to experiment while the phonon dispersion of the GGA functional decreases the experiment. The theoretical LDA decreases the lattice parameter by 1.6% while the GGA increases it by 1.9%.The analytical calculated phonon dispersions curves of Au using IFCs approach of the 1-2NN, 1-5NN and 1-6NN are shown in Figure 2. The red, green and blue lines represents the nearest neighbours (NN) respectively. The force constants employed for the calculations are shown on Table 1. IFCs computed of the phonon dispersion curves of Gold showed that 1-6NN dispersions computed was found to be in better agreement with experimental data at symmetry points W_T and L_L with a percentage error of 2.5% and 0.6% respectively compared to 1-5NN which gave 2.9% and 0.7% respectively. Therefore, in Au the phonons of the IFCs gave a better agreement with experimental phonons than those of Quantum Espresso. The Density of states (DOS) of Quantum Espresso and analytical are shown in Figures 3 and 4.

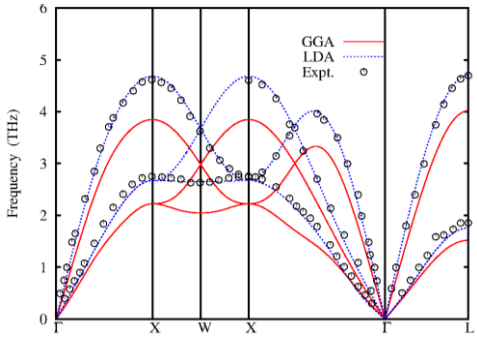

Figure 1: Calculated phonon dispersions for fcc-Au compared to inelastic neutron scattering data (black circles) [15]

Table 1: Frequencies calculated from Quantum espresso at selected points of the BZ for Au. All frequencies are in THz

Au	a(a.u)	X_T	X_L	W_T	W_L	L_T	L_L
EXP (b)	7.34	2.7578	4.6163	2.6379	3.6271	1.8585	4.7062
LDA(c)	7.65	2.6728	4.6849	2.6489	3.6683	1.7583	4.7061
GGA(c)	7.90	2.2229	3.8482	2.0468	2.9825	1.5185	4.0178

[15] This work

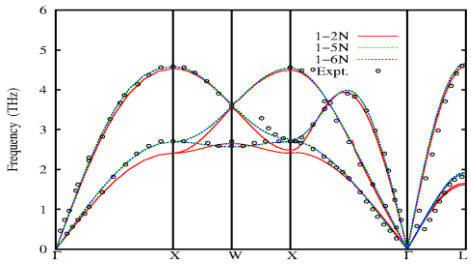

Figure 2: Calculated phonon dispersions for fcc-Au from analytical approach using IFCs up to 6th neighbour

Table 2: Frequencies calculated analytically using IFCs up to 6thneighbour at selected points of the BZ for Au. All frequencies are in THz

Au	X_T	X_L	W_T	W_L	L_T	L_L
EXP(a)	2.7578	4.6163	2.6379	3.6271	1.8585	4.7062
1-2N(b)	2.4117	4.5349	2.6531	3.6078	1.6593	4.6046
1-5N(b)	2.6988	4.5852	2.5617	3.6262	1.9268	4.6720
1-6N(c)	2.6988	4.5852	2.5713	3.6330	1.9397	4.6773

(a)[15] (b) This work

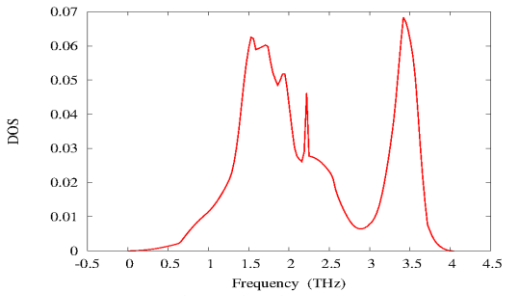

Figure 3: The density of state of Au from Quantum espresso code

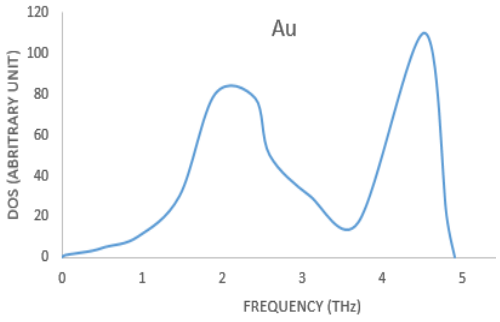

Figure 4: The density of state of Au from Analytical approach using IFCs up to 6th Neighbour

3.2 PHONON DISPERSION OF NICKEL (Ni)

The phonon dispersion of Ni calculated from quantum Espresso code and inter atomic force constant (IFCs) compared with experimental results [16] are shown in figures 5 and 6 respectively. The results are shown as blue squares, the red lines are the dispersions calculated by GGA functional and the green lines are the LDA dispersions, in density functional theory

(DFT) calculations carried out for Ni the electron-ion was treated by using ultrasoft and norm-conserving ab initio pseudopotential, within the applied self consistent method. In this work, the LDA and GGA overestimates the experiment, giving their frequencies higher than experiment. The overestimation of the frequencies of GGA functional show discrepancies with other studies. The work of *Hatt et al* [17] discovered a big amount of temperature effect and was of the opinion that GGA underestimate and LDA overestimate the frequencies. The LDA lattice parameter of Nickel has an error of -2.7% and GGA resolves this error correcting it to 0.2%. The analytical calculated phonon dispersions of Ni using IFCs approach of the 1-2NN, 1-5NN and 1-6NN are shown in Figure 6. The red, green and blue lines represents the nearest neighbours respectively and experimental inelastic neutron scattering represented by blue stars. The force constants employed for the calculations are shown on Table 4. IFCs computed phonon curves of Nickel showed that 1-6NN dispersions gave a slightly better agreement with experimental results at symmetry points W_T and L_L with a percentage error of 0.5% and 0.27% respectively compared to 1-5NN which gave 0.6% and 0.3% respectively. Therefore, in Nickel, the phonons dispersions of IFCs gave better agreement with the experimental phonons than those from quantum espresso code. The DOS from Quantum Espresso Code and analytical are shown Figures 7 and 8.

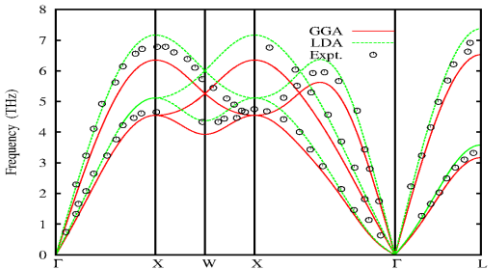

Figure 5: Computed phonon dispersions for Ni from Quantum Espresso compared to experimental results. (black circles) [16]

Table 3: Frequencies calculated from quantum espresso at selected symmetry points for Ni in THz.

Ni	a(a.u)	X_T	X_L	W_T	W_L	L_T	L_L
EXP (a)	6.65	6.2650	8.5432	6.2050	7.4940	4.2266	8.8729
LDA(b)	6.47	6.5013	8.8952	6.2480	7.6748	4.3437	9.3829
GGA(b)	6.66	6.4619	8.8850	6.3015	7.5064	4.6039	8.8850

(a)[16]
(b)This work

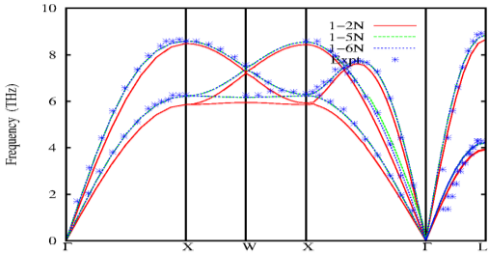

Figure 6: Computed phonon dispersions for Ni from analytical approach using IFCs up to 6th neighbor compared to experimental results. (blue stars) [16]

Table 4: Frequencies computed analytically using ifcs up to 6th neighbour at selected symmetry points for Ni in THz.

Ni	X_T	X_L	W_T	W_L	L_T	L_L
EXP (a)	6.2650	8.5432	6.2050	7.4940	4.2266	8.8729
1-2N (b)	5.8536	8.4830	5.9454	7.2600	3.9440	8.6569
1-5N (b)	6.2263	8.5919	6.2263	7.4330	4.2397	8.8464
1-6N (c)	6.2263	8.5919	6.1698	7.4357	4.2445	8.8487

(a)[16]
(b)[18]
(c)This work

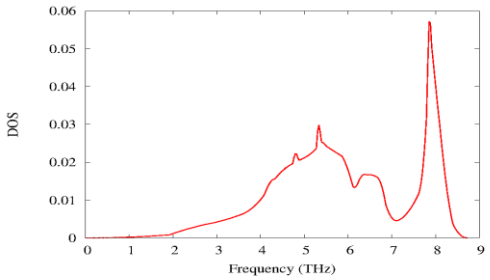

Figure 7 : The density of states of fcc-Ni from Quantum espresso code

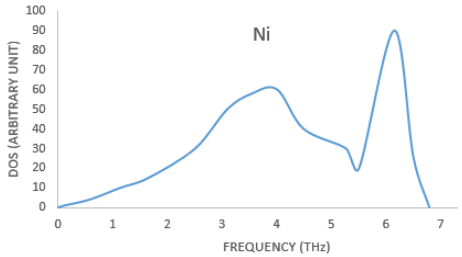

Figure 8: The density of states of fcc-Ni from Analytical approach using IFCs up to 6th Neighbour

4.0 Conclusion

Phonon dispersion curve gives an insight on the nature of lattice vibrations in the FCC metals. The phonon dispersions and density of states(DOS) Gold(Au) and Nickel(Ni) were calculated successfully using two techniques. The interatomic force constants (IFCs) technique based on Born von Karman model and first principle technique based on the density functional theory (DFT) implemented by Quantum espresso. The phonon dispersions were computed along high symmetry points of the Brillouin Zone(BZ). Results obtained from the two techniques were compared with experiment. Gold(Au) and Nickel(Ni) at some symmetry points were in better agreement with experiment than those in Literature.

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