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ANALYTICAL AND FIRST PRINCIPLE CALCULATIONS OF THE LATTICE DYNAMICS OF CAESIUM (Cs) AND TUNGSTEN (W)

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Abstract

The phonon dispersion curves of Cs and W have been calculated from analytical (IFCs technique using Born – von Kármán model) with different numbers of interacting nearest-neighbours (NN) and computational approach (first principle using density functional theory) with the exchange correlation functionals. The different branches of the phonon band structure follow from the Eigen values after diagonalizing the dynamical matrix. The phonon frequencies in the first Brillouin zone were calculated along the directions of high symmetry, Γ → H, H → P, P → Γ and Γ → N. Obtain also are the thermodynamic properties from IFCs and first principle. It is observed that the phonon dispersion curve of Cs and W just like the first principle calculations, the IFCs calculation also gave a good agreement with experiment.

Keywords: Bcc Metals, Phonon, Interatomic Force Constants, Dynamical Matrix, Born – von Kármán.

1.0 INTRODUCTION

It is a fact that phonons play a vital role in several important phenomena in modern and classical solid-state physics. Thus, a vast number of physical properties hinge on the behaviour of their lattice dynamics and it follows that the force model, if given a good fit to the dispersion foretell brilliantly all other properties of the lattice dynamics [1, 2]. Currently, it is feasible to calculate specific properties of specific materials applying first principle techniques in quantum-mechanics in computational material science and condensed-matter theoretical physics with the chemical composition of the materials as its only input information. Accordingly, for a particular case of the properties of lattice dynamics, a considerable number of first principle calculations on the basis of the theory of linear response of the vibrations of lattice is feasible now by the success of density functional theory (DFT) [3, 4] coupled with the occurrence of density-functional perturbation theory (DFPT) [5, 6]. The DFPT is a technique used in employing the DFT in the heart of general theoretical architecture. Thus, making it feasible to produce accurately the dispersion curves of phonon on a smooth grating of wave vectors which encompass the whole Brillouin zone (BZ).

The first principle prediction of the dispersion curves of phonon of noble and transition metals have encountered challenges that still lack adequate solution from the generally used exchange correlation functional “local density approximation (LDA) and the generalized gradient approximation (GGA)” [4, 8, 9]. To improve on the first principle calculation results, the density functional theory was applied [10] with variation in the exchange and correlation functional being used, the dispersion curves can in some cases underestimate or overestimate when compared to experimental results. This brings us to the question, if the first principle (QUANTUM ESPRESSO) calculation [11, 12] is still having these challenges, is it also possible for us to tackle the phonon dispersion problem using the interatomic force constant technique as implemented in the Born-von Kármán model? The challenge here is to determine and improve on existing techniques employed to determine the lattice dynamics of Cs and W using analytical approach (interatomic force constants – IFCs) and computational approach (first principle or ab-initio – QUANTUM ESPRESSO) and compare with experiment. Also calculated are their thermodynamic properties.

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2.0 THEORETICAL FORMALISM

2.1 ANALYTICAL (IFCs) PROCEDURE

The Born-von Kármán theory was applied by assigning a force-constant matrix to each of the nearest neighbours of the atom considered, constructing the dynamical matrix from the individual force-constant matrices, and then solving the dynamical matrix for the phonon energies and the associated phonon polarizations.

INTERATOMIC FORCE CONSTANTS (IFCs)

The frequencies of the phonon of any material are typically somewhat a smooth function of the wave vector. Thus, for complete phonon dispersion an appropriate interpolation technique is needed. By Fourier analysis, the smoother the phonon dispersions considering the real space IFCs, the shorter the range of the real space:

$$\tilde{C}_{st}^{\alpha\beta}\left(\vec{R}\right)=\frac{1}{N_c}\sum e^{i\vec{q}.\vec{R}}\tilde{C}_{st}^{\alpha\beta}\left(\vec{q}\right) \qquad (1)$$

Thus, real space IFCs, i.e. the force constants between atoms of a system in a real space is easy and achievable using a set of matrix force constants computed and presented in a table on an even grid of points within a reciprocal space. The *fast Fourier transform* (FFT) technique [13] is the most effective way of computing numerically all these Fourier transforms. After obtaining the force constants between atoms of a system in real-space, then the dynamical matrices in reciprocal space (and, hence, vibrational) frequencies can be obtained at any wave vector (not necessarily contained in the original grid) by FFT. The shorter the range of real space force constants, the coarser will be the reciprocal space grid needed for such Fourier interpolation.

CONSTRUCTION OF THE DYNAMICAL MATRIX

The phonon frequencies are given by the solution of the secular determinant

$$\left|D_{\mathrm{ij}}(\vec{q})-m\omega^2 I\right|=0 \qquad (2)$$

Where m is the mass of the ion, ω is the phonon frequency, $D_{\mathrm{ij}}(\vec{q})$ is the dynamical matrix elements and I is a 3×3 unit matrix.The elements of the dynamical matrix are a matrix as shown below

$$D_{\mathrm{ij}}=\begin{pmatrix} D_{\mathrm{xx}}(\vec{q}) & D_{\mathrm{xy}}(\vec{q}) & D_{\mathrm{xz}}(\vec{q}) \\ D_{\mathrm{yx}}(\vec{q}) & D_{\mathrm{yy}}(\vec{q}) & D_{\mathrm{yz}}(\vec{q}) \\ D_{\mathrm{zx}}(\vec{q}) & D_{\mathrm{zy}}(\vec{q}) & D_{\mathrm{zz}}(\vec{q}) \end{pmatrix} \qquad (3)$$

Once the force constant matrices have been determined the elements of the dynamical matrix are evaluated. This gives for the diagonal matrix elements of the first nearest to eighth nearest neighbours dynamical matrix as:

$$D_{xx}(\vec{q})=\frac{1}{M}\left\{\begin{array}{l}
8\alpha_1+2\alpha_2+4\beta_2+8\alpha_3+4\beta_3+8\alpha_4+16\beta_4+8\alpha_5+2\alpha_6+4\beta_6+8\alpha_7+16\beta_7 \\
+8\alpha_8+8\beta_8+8\gamma_8+8\alpha_9+16\beta_9+8\alpha_{10}-8\alpha_1\cos\left(\frac{aq_x}{2}\right)\cos\left(\frac{aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right) \\
-2\alpha_2\cos(aq_x)-2\beta_2\cos(aq_y)-2\beta_2\cos(aq_z)-4\alpha_3\cos(aq_x)\cos(aq_y) \\
-4\alpha_3\cos(aq_x)\cos(aq_z)-4\beta_3\cos(aq_x)\cos(aq_y)-8\alpha_4\cos\left(\frac{3aq_x}{2}\right)\cos\left(\frac{aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right) \\
-8\beta_4\cos\left(\frac{aq_x}{2}\right)\cos\left(\frac{3aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right)-8\beta_4\cos\left(\frac{aq_x}{2}\right)\cos\left(\frac{aq_y}{2}\right)\cos\left(\frac{3aq_z}{2}\right) \\
-8\alpha_5\cos(aq_x)\cos(aq_y)\cos(aq_z)-2\alpha_6\cos(2aq_x)-2\beta_6\cos(2aq_y)-2\beta_6\cos(2aq_z) \\
-8\alpha_7\cos\left(\frac{aq_x}{2}\right)\cos\left(\frac{3aq_y}{2}\right)\cos\left(\frac{3aq_z}{2}\right)-8\beta_7\cos\left(\frac{3aq_x}{2}\right)\cos\left(\frac{3aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right) \\
-8\beta_7\cos\left(\frac{3aq_x}{2}\right)\cos\left(\frac{3aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right)-4\alpha_8\cos(2aq_x)\cos(aq_y)-4\alpha_8\cos(2aq_x)\cos(aq_z) \\
-4\gamma_8\cos(2aq_z)\cos(aq_y)-4\gamma_8\cos(2aq_y)\cos(aq_z)-4\beta_8\cos(aq_x)\cos(2aq_y) \\
-4\beta_8\cos(aq_x)\cos(2aq_z)
\end{array}\right\} \qquad (4)$$

$$D_{yy}(\vec{q})=\frac{1}{M}\left\{\begin{array}{l} 8\alpha_1+2\alpha_2+4\beta_2+8\alpha_3+4\beta_3+8\alpha_4+16\beta_4+8\alpha_5+2\alpha_6+4\beta_6+8\alpha_7+16\beta_7 \\ +8\alpha_8+8\beta_8+8\gamma_8+8\alpha_9+16\beta_9+8\alpha_{10}-8\alpha_1\cos\left(\frac{aq_x}{2}\right)\cos\left(\frac{aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right) \\ -2\alpha_2\cos(aq_y)-2\beta_2\cos(aq_x)-2\beta_2\cos(aq_z)-4\alpha_3\cos(aq_x)\cos(aq_y) \\ -4\alpha_3\cos(aq_y)\cos(aq_z)-4\beta_3\cos(aq_x)\cos(aq_z)-8\alpha_4\cos\left(\frac{aq_x}{2}\right)\cos\left(\frac{3aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right) \\ -8\beta_4\cos\left(\frac{3aq_x}{2}\right)\cos\left(\frac{aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right)-8\beta_4\cos\left(\frac{aq_x}{2}\right)\cos\left(\frac{aq_y}{2}\right)\cos\left(\frac{3aq_z}{2}\right) \\ -8\alpha_5\cos(aq_x)\cos(aq_y)\cos(aq_z)-2\alpha_6\cos(2aq_x)-2\beta_6\cos(2aq_y)-2\beta_6\cos(2aq_z) \\ -8\alpha_7\cos\left(\frac{3aq_x}{2}\right)\cos\left(\frac{aq_y}{2}\right)\cos\left(\frac{3aq_z}{2}\right)-8\beta_7\cos\left(\frac{aq_x}{2}\right)\cos\left(\frac{3aq_y}{2}\right)\cos\left(\frac{3aq_z}{2}\right) \\ -8\beta_7\cos\left(\frac{3aq_x}{2}\right)\cos\left(\frac{3aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right)-4\alpha_8\cos(2aq_y)\cos(aq_z)-4\alpha_8\cos(aq_x)\cos(2aq_y) \\ -4\gamma_8\cos(2aq_x)\cos(aq_z)-4\gamma_8\cos(2aq_x)\cos(aq_z)-4\beta_8\cos(2aq_x)\cos(aq_y) \\ -4\beta_8\cos(aq_y)\cos(2aq_z) \end{array}\right\} \tag{5}$$

$$D_{zz}(\vec{q})=\frac{1}{M}\left\{\begin{array}{l} 8\alpha_1+2\alpha_2+4\beta_2+8\alpha_3+4\beta_3+8\alpha_4+16\beta_4+8\alpha_5+2\alpha_6+4\beta_6+8\alpha_7+16\beta_7 \\ +8\alpha_8+8\beta_8+8\gamma_8+8\alpha_9+16\beta_9+8\alpha_{10}-8\alpha_1\cos\left(\frac{aq_x}{2}\right)\cos\left(\frac{aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right) \\ -2\alpha_2\cos(aq_z)-2\beta_2\cos(aq_x)-2\beta_2\cos(aq_y)-4\alpha_3\cos(aq_x)\cos(aq_z) \\ -4\alpha_3\cos(aq_y)\cos(aq_z)-4\beta_3\cos(aq_x)\cos(aq_y)-8\alpha_4\cos\left(\frac{aq_x}{2}\right)\cos\left(\frac{aq_y}{2}\right)\cos\left(\frac{3aq_z}{2}\right) \\ -8\beta_4\cos\left(\frac{3aq_x}{2}\right)\cos\left(\frac{aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right)-8\beta_4\cos\left(\frac{aq_x}{2}\right)\cos\left(\frac{3aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right) \\ -8\alpha_5\cos(aq_x)\cos(aq_y)\cos(aq_z)-2\alpha_6\cos(2aq_z)-2\beta_6\cos(2aq_y)-2\beta_6\cos(2aq_x) \\ -8\alpha_7\cos\left(\frac{3aq_x}{2}\right)\cos\left(\frac{3aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right)-8\beta_7\cos\left(\frac{aq_x}{2}\right)\cos\left(\frac{3aq_y}{2}\right)\cos\left(\frac{3aq_z}{2}\right) \\ -8\beta_7\cos\left(\frac{3aq_x}{2}\right)\cos\left(\frac{aq_y}{2}\right)\cos\left(\frac{3aq_z}{2}\right)-4\alpha_8\cos(aq_x)\cos(2aq_z)-4\alpha_8\cos(aq_y)\cos(2aq_z) \\ -4\gamma_8\cos(aq_x)\cos(2aq_y)-4\gamma_8\cos(2aq_x)\cos(aq_y)-4\beta_8\cos(2aq_x)\cos(aq_z) \\ -4\beta_8\cos(2aq_y)\cos(aq_z) \end{array}\right\} \tag{6}$$

And the off - diagonal matrix elements of the first nearest to eighth nearest neighbour dynamical matrix as:

$$D_{xy}=\frac{1}{M}\left\{\begin{array}{l} 8\beta_1\sin\left(\frac{aq_x}{2}\right)\sin\left(\frac{aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right)+4\gamma_3\sin(aq_x)\sin(aq_y) \\ +8\gamma_4\sin\left(\frac{3aq_x}{2}\right)\sin\left(\frac{aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right)+8\gamma_4\sin\left(\frac{aq_x}{2}\right)\sin\left(\frac{3aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right) \\ +8\delta_4\sin\left(\frac{aq_x}{2}\right)\sin\left(\frac{aq_y}{2}\right)\cos\left(\frac{3aq_z}{2}\right)+8\beta_5\sin(aq_x)\sin(aq_y)\cos(aq_z) \\ +8\gamma_7\sin\left(\frac{aq_x}{2}\right)\sin\left(\frac{3aq_y}{2}\right)\cos\left(\frac{3aq_z}{2}\right)+8\gamma_7\sin\left(\frac{3aq_x}{2}\right)\sin\left(\frac{aq_y}{2}\right)\cos\left(\frac{3aq_z}{2}\right) \\ +8\delta_7\sin\left(\frac{3aq_x}{2}\right)\sin\left(\frac{3aq_y}{2}\right)\cos\left(\frac{aq_z}{2}\right)+4\delta_8\sin(2aq_x)\sin(aq_y) \\ +4\delta_8\sin(aq_x)\sin(2aq_y) \end{array}\right\} \tag{7}$$

$$D_{xz} = \frac{1}{M}\left\{\begin{array}{l} 8\beta_1 \sin\left(\frac{aq_x}{2}\right)\sin\left(\frac{aq_z}{2}\right)\cos\left(\frac{aq_y}{2}\right) + 4\gamma_3 \sin(aq_x)\sin(aq_z) \\ + 8\gamma_4 \sin\left(\frac{3aq_x}{2}\right)\sin\left(\frac{aq_z}{2}\right)\cos\left(\frac{aq_y}{2}\right) + 8\gamma_4 \sin\left(\frac{aq_x}{2}\right)\sin\left(\frac{3aq_z}{2}\right)\cos\left(\frac{aq_y}{2}\right) \\ + 8\delta_4 \sin\left(\frac{aq_x}{2}\right)\sin\left(\frac{aq_z}{2}\right)\cos\left(\frac{3aq_y}{2}\right) + 8\beta_5 \sin(aq_x)\sin(aq_z)\cos(aq_y) \\ + 8\gamma_7 \sin\left(\frac{aq_x}{2}\right)\sin\left(\frac{3aq_z}{2}\right)\cos\left(\frac{3aq_y}{2}\right) + 8\gamma_7 \sin\left(\frac{3aq_x}{2}\right)\sin\left(\frac{aq_z}{2}\right)\cos\left(\frac{3aq_y}{2}\right) \\ + 8\delta_7 \sin\left(\frac{3aq_x}{2}\right)\sin\left(\frac{3aq_z}{2}\right)\cos\left(\frac{aq_y}{2}\right) + 4\delta_8 \sin(2aq_x)\sin(aq_z) \\ + 4\delta_8 \sin(aq_x)\sin(2aq_z) \end{array}\right\} \quad (8)$$

$$D_{yz} = \frac{1}{M}\left\{\begin{array}{l} 8\beta_1 \sin\left(\frac{aq_y}{2}\right)\sin\left(\frac{aq_z}{2}\right)\cos\left(\frac{aq_x}{2}\right) + 4\gamma_3 \sin(aq_y)\sin(aq_z) \\ + 8\gamma_4 \sin\left(\frac{3aq_y}{2}\right)\sin\left(\frac{aq_z}{2}\right)\cos\left(\frac{aq_x}{2}\right) + 8\gamma_4 \sin\left(\frac{aq_y}{2}\right)\sin\left(\frac{3aq_z}{2}\right)\cos\left(\frac{aq_x}{2}\right) \\ + 8\delta_4 \sin\left(\frac{aq_z}{2}\right)\sin\left(\frac{aq_y}{2}\right)\cos\left(\frac{3aq_x}{2}\right) + 8\beta_5 \sin(aq_y)\sin(aq_z)\cos(aq_z) \\ + 8\gamma_7 \sin\left(\frac{aq_y}{2}\right)\sin\left(\frac{3aq_z}{2}\right)\cos\left(\frac{3aq_x}{2}\right) + 8\gamma_7 \sin\left(\frac{3aq_y}{2}\right)\sin\left(\frac{aq_z}{2}\right)\cos\left(\frac{3aq_x}{2}\right) \\ + 8\delta_7 \sin\left(\frac{3aq_y}{2}\right)\sin\left(\frac{3aq_z}{2}\right)\cos\left(\frac{aq_x}{2}\right) + 4\delta_8 \sin(2aq_y)\sin(aq_z) \\ + 4\delta_8 \sin(aq_y)\sin(2aq_z) \end{array}\right\} \quad (9)$$

Where M denotes the mass of the element, and $D_{\mathrm{xy}} = D_{\mathrm{yx}}$, $D_{\mathrm{xz}} = D_{\mathrm{zx}}$ and $D_{\mathrm{yz}} = D_{\mathrm{zy}}$. The elements α_1, β_1, … are the nearest neighbour parameters in a least-squares fit to the data. The force constants were also of great value as a simple mathematical description of the phonon spectrum [14] used this property in their method of calculating the phonon distribution function.

2.2 COMPUTATIONAL PROCEDURE

The DFT calculations were performed using QUANTUM ESPRESSO (opEn Source Package for Research in Electronic Structure, Simulation, and Optimization) [11, 12]. This code uses plane-wave and pseudopotential method to describe the electron-ion interaction. In this research work, the local density approximation (LDA), Generalized Gradient Approximation (GGA) with exchange and correlation functional described by Perdew-Burke-Ernzerhof (PBE) [10]. Also, PAW and PW91 method were used to generate the pseudopotentials for the elements in this work.

The convergence of the total electronic energy as computed in plane-wave pseudopotential codes is determined by two key computational parameters, namely the number of basis functions (plane-wave cut-off) and the number of k-points (k-spacing). In this research work, the number of basis functions was determined by running series of self-consistent calculations for different values of kinetic energy cut-off (ecutwfc) starting from (10 to 70) Ry at an interval of 5Ry. The converged values were found to be between 25 to 65 Ry. Also, the k-points values are in the range of 4 – 12 k-points meshes. All these assisted in determining accurately the electronic ground state properties of the systems studied in this work.

2.3 CALCULATION OF THE THERMODYNAMIC PROPERTIES OF BCC METALS

Thermodynamic functions of solids are determined by their vibrational degrees of freedom of their lattice [15]. Thus, for the calculation of these thermodynamic functions requires a complete knowledge of the vibrational spectrum, with adequate accuracy [16, 17, and 18]. The phonon contributions to the thermodynamic properties which include Helmholtz free energy ΔF, the internal energy ΔE, the constant-volume specific heat C_v, and the entropy S are computed for these bcc metals studied in this work within the temperature range of 0 – 800K with the following expressions:

For the Helmholtz free energy

$$\Delta F = 3nNK_BT\ln\left\{\begin{array}{l} 2\sinh\left(\frac{\hbar\omega_1}{2K_BT}\right)g(\omega_1)\Delta\omega_1 + 2\sinh\left(\frac{\hbar\omega_2}{2K_BT}\right)g(\omega_2)\Delta\omega_2 \\ +\ldots + 2\sinh\left(\frac{\hbar\omega_n}{2K_BT}\right)g(\omega_n)\Delta\omega_n \end{array}\right\} \tag{10}$$

For the internal energy we have

$$\Delta E = 3nN\frac{\hbar}{2}\ln\left\{\begin{array}{l} \omega\coth\left(\frac{\hbar\omega}{2K_BT}\right)g(\omega_1)\Delta\omega_1 + \omega\coth\left(\frac{\hbar\omega}{2K_BT}\right)g(\omega_2)\Delta\omega_2 \\ +\ldots + \omega\coth\left(\frac{\hbar\omega}{2K_BT}\right)g(\omega_n)\Delta\omega_n \end{array}\right\} \tag{11}$$

For the constant-volume specific heat we have

$$C_\upsilon = 3nNk_B\left\{\begin{array}{l} \left(\frac{\hbar\omega_1}{2K_BT}\right)^2 \operatorname{csc}h^2\left(\frac{\hbar\omega_1}{2K_BT}\right)g(\omega_1)\Delta\omega_1 \\ +\left(\frac{\hbar\omega_2}{2K_BT}\right)^2 \operatorname{csc}h^2\left(\frac{\hbar\omega_2}{2K_BT}\right)g(\omega_2)\Delta\omega_2 + \ldots \\ +\left(\frac{\hbar\omega_n}{2K_BT}\right)^2 \operatorname{csc}h^2\left(\frac{\hbar\omega_n}{2K_BT}\right)g(\omega_n)\Delta\omega_n \end{array}\right\} \tag{12}$$

Finally, for the entropy we have

$$S = 3nNk_B\left\{\begin{array}{l} \left[\frac{\hbar\omega_1}{2K_BT}\coth\frac{\hbar\omega_1}{2K_BT} - \ln\left(2\sinh\frac{\hbar\omega_1}{2K_BT}\right)\right]g(\omega)d\omega_1 \\ +\left[\frac{\hbar\omega_2}{2K_BT}\coth\frac{\hbar\omega_2}{2K_BT} - \ln\left(2\sinh\frac{\hbar\omega_2}{2K_BT}\right)\right]g(\omega)d\omega_2 \\ +\ldots+\left[\frac{\hbar\omega_n}{2K_BT}\coth\frac{\hbar\omega_n}{2K_BT} - \ln\left(2\sinh\frac{\hbar\omega_n}{2K_BT}\right)\right]g(\omega)d\omega_n \end{array}\right\} \tag{13}$$

Note: $\coth = \frac{1}{\tanh}$, $\operatorname{csc}h = \frac{1}{\sinh}$

Where K_B is the Boltzmann's constant, $\hbar$ is reduced Planck's constant

3.0 RESULTS AND DISCUSSION

3.1 Lattice dynamics

Fig. 1, shows the phonon dispersion curve of Caesium (Cs) from IFCs calculated up to fifth nearest neighbours implemented by Born – von Kármán model and matched with data from experiment. The data from experiment is presented in blue, green and red circles with the red solid line calculations from IFCs. Fig. 2, the blue solid curve is the dispersion calculated using the generalized gradient approximation (GGA-PBE), with the experimental data in blue, green and red circles. Tables 1a and 1b show that the 5th nearest neighbours dispersions calculated with (MAE 0.0241THz, MARE 3.43%), did not improve the results when matched with experiment, but gave a better result when compared with that of the DFT using GGA (PAW) which gave (MAE 0.0796THz, MARE 11.32%). Also, the lattice constant given by GGA (PAW) is 0.04% above that of the experiment. Fig. 3, shows the phonon dispersion curve of Tungsten (W) from IFCs calculated up to eighth nearest neighbours implemented into Born – von Kármán model and matched with data from experiment. The data from experiment is presented in blue, green and red circles with the red solid line calculations from IFCs. Fig. 4. The experimental data is shown as blue, green and red circles; the black and red solid curves are the dispersion calculated using GGA-PBE and PW91 respectively. In tables 2a and 2b, IFCs calculations of the lattice dynamics of Tungsten (W) showed that the 8th nearest neighbour dispersions calculated with (MAE 0.1208THz), percentage error (MARE 2.19%) improve on the experimental results. Whereas, the density functional theory (DFT) using GGA (PBE) and PW91 gave a larger MAE and

MARE as (MAE 2.8305THz, MARE 51.32%) and (MAE 0.5076THz, MARE 9.20%) respectively. In the first principle calculations using DFT, the PW91functional gave a better result when compared to GGA (PBE) functional. Also, the PW91 and GGA (PBE) gave the same percentage error to the lattice constant by 0.81% slightly above experiment. Details of the extension of the force constants will be discussed in details somewhere else.

3.2 Thermodynamic properties

Figs. 5 and 9, shows an increase in the internal energy as temperature increases and also at 0K it is above zero. Figs. 6 and 10, shows a decrease in the free energy with increase in temperature whereas in Figs. 7 and 11, shows an increase in the entropy with an increase in temperature. In Figs. 8 and 12, the heat capacity on the other hand shows a rapid increase with temperature and approaches the Dulong-Petit limit at high temperature and at low temperature the graph obeys the T^3 and at very low temperature the graph obeys the linear law as can be found in literature.

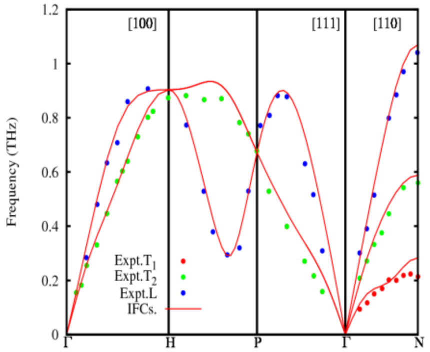

Fig 1: Caesium dispersion curves. The Red curves correspond to eighth nearest neighbours fit (IFCs). The experimental results [19]are shown by the symbols ● ●and ●

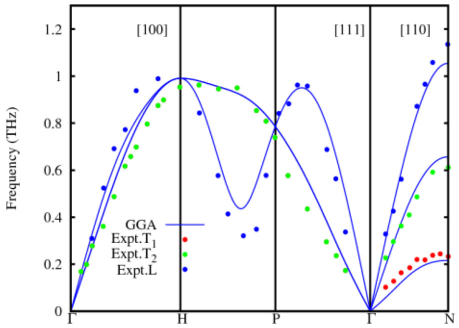

Fig 2: Caesium dispersion curves. GGA results from QUANTUM ESPRESSO calculations. The experimental results [19] are shown by the symbols ● , ● and ●

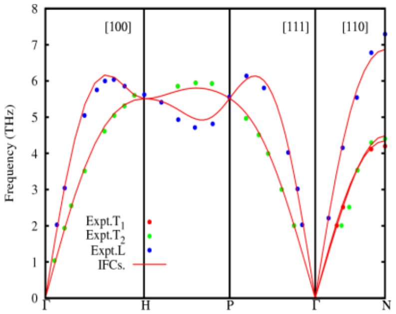

Fig 3: Tungsten dispersion curves. The Red curves correspond to fifth nearest neighbours fit (IFCs). The experimental results from the inelastic neutron scattering data [20] are shown by the symbols ● , ● and ●

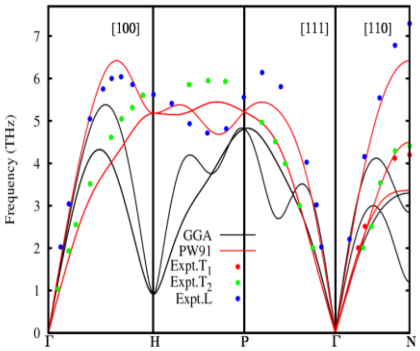

Fig 4: Tungsten dispersion curves. GGA(PBE) and PW91 results. The experimental results from the inelastic neutron scattering data [20] are shown by the symbols ●, ● and ●

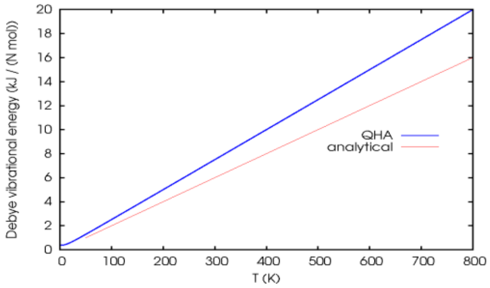

Fig 5: The internal energies ΔE of Caesium. Analytical (IFCs) calculated values in the pink line; First principle (QUANTUM ESPRESSO) calculated values in blue line

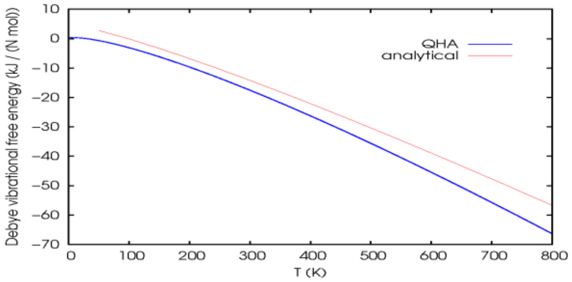

Fig 6: The Helmholtz free energies ΔF of Caesium. Analytical (IFCs) calculated values in the pink line; First principle calculated values in blue line

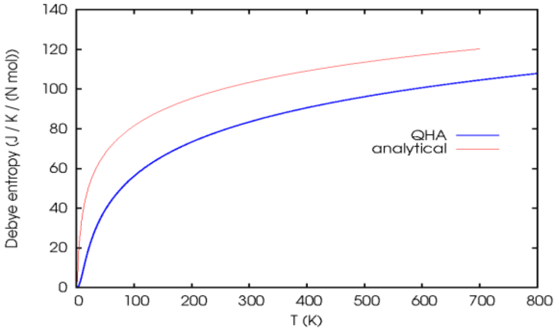

Fig 7: The entropy of Caesium. Analytical (IFCs) calculated values in the pink line; First principle calculated values in blue line

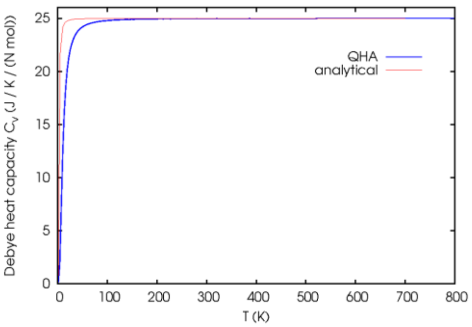

Fig 8: The C_v for Caesium. Analytical (IFCs) in the pink line dispersion; First principle calculated values in blue line

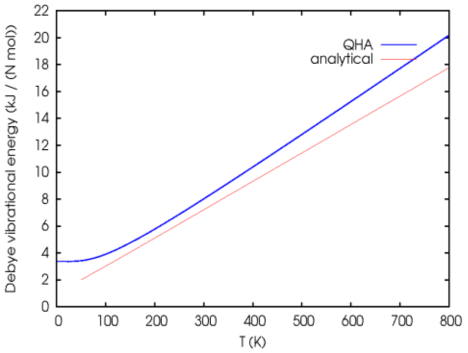

Fig 9: The phonon contribution to the internal energies ΔE of Tungsten. Analytical (IFCs) calculated values in the pink line; First principle calculated values in blue line

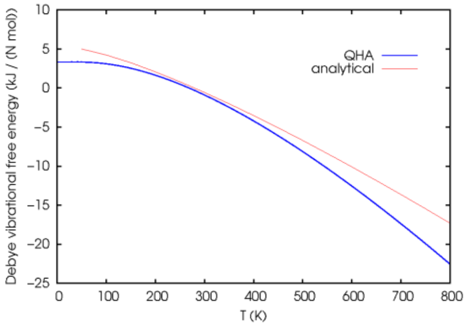

Fig 10: The phonon contribution to the Helmholtz free energies ΔF of Tungsten. Analytical (IFCs) calculated values in the pink line; First principle calculated values in blue line

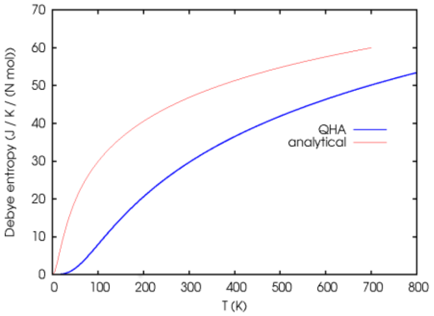

Fig 11: The entropy of Tungsten. Analytical (IFCs) calculated values in the pink line; First principle calculated values in blue line

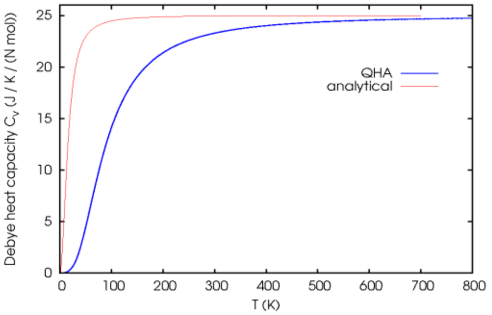

Fig 12: The C_v for Tungsten. Analytical (IFCs) in pink line; First principle calculated values in blue line

Table 1: (a) Frequencies and calculated percentage errors at some high symmetry points for Caesium (Cs). (b) Calculated MAE and MARE for Caesium.

(a)

	a_T	FREQUENCY(THz)						
	$(a.u)$	H_L	H_T	P_L	P_T	N_L	N_{T_1}	N_{T_2}
GGA(PBE)	11.61	0.9908	0.9908	0.7858	0.7858	1.0543	0.2162	0.6564
IFCs	-	0.9037	0.9037	0.6725	0.6725	1.0686	0.2828	0.5881
Expt. [a]	11.605	0.9068	0.8739	0.6505	0.6775	1.0405	0.2136	0.5602
			$\%\ Error$					
GGA(PBE)	0.04	9.26	0.13	20.80	15.99	1.33	1.22	17.17
IFCs	-	0.34	3.41	3.38	0.74	2.70	32.40	4.98

(b)

	TOTAL	AVERAGE	$\pm(work - expt.)$(THz)	MAE (THz)	MARE (%)
GGA(PBE)	5.4801	0.7815	0.5571	0.0796	11.32
IFCs	5.0919	0.7274	0.1689	0.0241	3.43
Expt. [a]	4.9230	0.7033	-	-	-

[a][19] (Experiment)

Table 2: (a) Frequencies and calculated percentage errors at some high symmetry points for Tungsten (W). (b) Calculated MAE and MARE for Tungsten.

(a)

	a_T	**FREQUENCY(THz)**						
	$(a.u)$	H_L	H_T	P_L	P_T	N_L	N_{T_1}	N_{T_2}
GGA(PBE)	6.03	0.9116	0.9116	4.8143	4.8143	3.2995	1.2000	2.8443
PW91	6.03	5.1784	5.1784	5.2130	5.2130	6.4183	3.3601	4.4943
IFCs	-	5.5104	5.5104	5.5200	5.5200	6.8691	4.3471	4.4860
Expt. ^{b}	5.981	5.6215	5.6039	5.5557	5.9287	7.2935	4.1997	4.4059
			$\%\ Error$					
GGA(PBE)	0.81	83.78	83.73	13.34	18.80	54.76	71.43	35.44
PW91	0.81	7.88	7.59	6.57	12.07	12.00	19.99	14.06
IFCs	-	1.98	1.67	0.64	6.89	5.82	3.51	1.82

(b)

	TOTAL	AVERAGE	$\pm(work - expt.)$ (THz)	MAE (THz)	MARE (%)
GGA(PBE)	18.7956	2.6851	19.8133	2.8305	51.32
PW91	35.0555	5.0079	3.5534	0.5076	9.20
IFCs	37.7630	5.3947	0.8459	0.1208	2.19
Expt. ^{p}	38.6089	5.5156	-	-	-

^{b} [20] (Experiment).

Table 3: Eighth nearest neighbours general force models fit for Caesium and Tantalum.

Position of neighbour	**Force constant (dyn/cm)**	**Eightnearest neighbours fit (Cs)**	**Eighth nearest neighbours fit (W)**	**Nearest neighbours**
$\frac{a}{2}(1,1,1)$	α_1	462.9	16983	First
$\frac{a}{2}(1,1,1)$	β_1	601.3	11201	First
$\frac{a}{2}(2,0,0)$	α_2	486.8	1182	Second
$\frac{a}{2}(2,0,0)$	β_2	-109.3	1423	Second
$\frac{a}{2}(2,2,0)$	α_3	20.6	3546	Third
$\frac{a}{2}(2,2,0)$	β_3	11.4	-5427	Third
$\frac{a}{2}(2,2,0)$	γ_3	-75	1943	Third
$\frac{a}{2}(3,1,1)$	α_4	-41.5	3577	Fourth
$\frac{a}{2}(3,1,1)$	β_4	-3.7	-718	Fourth
$\frac{a}{2}(3,1,1)$	γ_4	-37	983	Fourth
$\frac{a}{2}(3,1,1)$	δ_4	-3	-1728	Fourth

$\frac{a}{2}(2,2,2)$	α_5	**-43.1**	**-493**	**Fifth**
$\frac{a}{2}(2,2,2)$	β_5	-16.2	812	Fifth
$\frac{a}{2}(4,0,0)$	α_6	-25.7	-3705	Sixth
$\frac{a}{2}(4,0,0)$	β_6	25.8	134	Sixth
$\frac{a}{2}(1,3,3)$	α_7	5.7	558	Seventh
$\frac{a}{2}(1,3,3)$	β_7	12.7	-237	Seventh
$\frac{a}{2}(1,3,3)$	γ_7	4.3	-683	Seventh
$\frac{a}{2}(1,3,3)$	δ_7	-3	106	Seventh
$\frac{a}{2}(4,2,0)$	α_8	-1	70	Eighth
$\frac{a}{2}(4,2,0)$	β_8	1	-170	Eighth
$\frac{a}{2}(4,2,0)$	γ_8	0	100	Eighth
$\frac{a}{2}(4,2,0)$	δ_8	-0.2	-30	Eighth

Table 4: Force-constant matrices $\emptyset(\mathbf{0},\boldsymbol{l})$ corresponding to the first nearest to eighth nearest neighbours of the atom at the origin

Atomic Pair	$\phi(0,l)$	Atomic Pair	$\phi(0,l)$	Atomic Pair	$\phi(0,l)$
$0-1\ \frac{a}{2}(1,1,1)$ $\frac{a}{2}(-1,-1,-1)$	$-\begin{pmatrix}\alpha_1 & \beta_1 & \beta_1\\ \beta_1 & \alpha_1 & \beta_1\\ \beta_1 & \beta_1 & \alpha_1\end{pmatrix}$	$0-2\ \frac{a}{2}(-1,1,1)$ $\frac{a}{2}(1,-1,-1)$	$-\begin{pmatrix}\alpha_1 & -\beta_1 & \beta_1\\ -\beta_1 & \alpha_1 & -\beta_1\\ \beta_1 & -\beta_1 & \alpha_1\end{pmatrix}$	$0-3\ \frac{a}{2}(1,-1,1)$ $\frac{a}{2}(-1,1,-1)$	$-\begin{pmatrix}\alpha_1 & -\beta_1 & \beta_1\\ -\beta_1 & \alpha_1 & -\beta_1\\ \beta_1 & -\beta_1 & \alpha_1\end{pmatrix}$
$0-4$ $\frac{a}{2}(-1,-1,1)$ $\frac{a}{2}(1,1,-1)$	$-\begin{pmatrix}\alpha_1 & \beta_1 & -\beta_1\\ \beta_1 & \alpha_1 & -\beta_1\\ -\beta_1 & -\beta_1 & \alpha_1\end{pmatrix}$	$0-5\ \frac{a}{2}(2,0,0)$ $\frac{a}{2}(-2,0,0)$	$-\begin{pmatrix}\alpha_2 & 0 & 0\\ 0 & \beta_2 & 0\\ 0 & 0 & \beta_2\end{pmatrix}$	$0-6\ \frac{a}{2}(0,2,0)$ $\frac{a}{2}(0,-2,0)$	$-\begin{pmatrix}\beta_2 & 0 & 0\\ 0 & \alpha_2 & 0\\ 0 & 0 & \beta_2\end{pmatrix}$
$0-7\ \frac{a}{2}(0,0,2)$ $\frac{a}{2}(0,0,-2)$	$-\begin{pmatrix}\beta_2 & 0 & 0\\ 0 & \beta_2 & 0\\ 0 & 0 & \alpha_2\end{pmatrix}$	$0-8\ \frac{a}{2}(2,2,0)$ $\frac{a}{2}(-2,-2,0)$	$-\begin{pmatrix}\alpha_3 & \gamma_3 & 0\\ \gamma_3 & \alpha_3 & 0\\ 0 & 0 & \beta_3\end{pmatrix}$	$0-9$ $\frac{a}{2}(-2,2,0)$ $\frac{a}{2}(2,-2,0)$	$-\begin{pmatrix}\alpha_3 & -\gamma_3 & 0\\ -\gamma_3 & \alpha_3 & 0\\ 0 & 0 & \beta_3\end{pmatrix}$
$0-10\ \frac{a}{2}(0,2,2)$ $\frac{a}{2}(0,-2,-2)$	$-\begin{pmatrix}\beta_3 & 0 & 0\\ 0 & \alpha_3 & \gamma_3\\ 0 & \gamma_3 & \alpha_3\end{pmatrix}$	$0-11$ $\frac{a}{2}(0,-2,2)$ $\frac{a}{2}(0,2,-2)$	$-\begin{pmatrix}\beta_3 & 0 & 0\\ 0 & \alpha_3 & -\gamma_3\\ 0 & -\gamma_3 & \alpha_3\end{pmatrix}$	$0-12\ \frac{a}{2}(2,0,2)$ $\frac{a}{2}(-2,0,-2)$	$-\begin{pmatrix}\alpha_3 & 0 & \gamma_3\\ 0 & \beta_3 & 0\\ \gamma_3 & 0 & \alpha_3\end{pmatrix}$
$0-13\ \frac{a}{2}(-2,0,2)$ $\frac{a}{2}(2,0,-2)$	$-\begin{pmatrix}\alpha_3 & 0 & -\gamma_3\\ 0 & \beta_3 & 0\\ -\gamma_3 & 0 & \alpha_3\end{pmatrix}$	$0-14\ \frac{a}{2}(3,1,1)$ $\frac{a}{2}(-3,-1,-1)$	$-\begin{pmatrix}\alpha_4 & \gamma_4 & \gamma_4\\ \gamma_4 & \beta_4 & \delta_4\\ \gamma_4 & \delta_4 & \beta_4\end{pmatrix}$	$0-15\ \frac{a}{2}(-3,1,1)$ $\frac{a}{2}(3,-1,-1)$	$-\begin{pmatrix}\alpha_4 & -\gamma_4 & -\gamma_4\\ -\gamma_4 & \beta_4 & \delta_4\\ -\gamma_4 & \delta_4 & \beta_4\end{pmatrix}$

0 – 16 $\frac{a}{2}(3,1,-1)$ $\frac{a}{2}(-3,-1,1)$	$-\begin{pmatrix}\alpha_4 & \gamma_4 & -\gamma_4\\ \gamma_4 & \beta_4 & -\delta_4\\ -\gamma_4 & -\delta_4 & \beta_4\end{pmatrix}$	0 – 17 $\frac{a}{2}(3,-1,1)$ $\frac{a}{2}(-3,1,-1)$	$-\begin{pmatrix}\alpha_4 & -\gamma_4 & \gamma_4\\ -\gamma_4 & \beta_4 & -\delta_4\\ \gamma_4 & -\delta_4 & \beta_4\end{pmatrix}$	0 – 18 $\frac{a}{2}(1,3,1)$ $\frac{a}{2}(-1,-3,-1)$	$-\begin{pmatrix}\beta_4 & \gamma_4 & \delta_4\\ \gamma_4 & \alpha_4 & \gamma_4\\ \delta_4 & \gamma_4 & \beta_4\end{pmatrix}$
0 – 19 $\frac{a}{2}(1,-3,-1)$ $\frac{a}{2}(-1,3,1)$	$-\begin{pmatrix}\beta_4 & -\gamma_4 & -\delta_4\\ -\gamma_4 & \alpha_4 & \gamma_4\\ -\delta_4 & \gamma_4 & \beta_4\end{pmatrix}$	0 – 20 $\frac{a}{2}(1,3,-1)$ $\frac{a}{2}(-1,-3,1)$	$-\begin{pmatrix}\beta_4 & \gamma_4 & -\delta_4\\ \gamma_4 & \alpha_4 & -\gamma_4\\ -\delta_4 & -\gamma_4 & \beta_4\end{pmatrix}$	0 – 21 $\frac{a}{2}(1,-3,1)$ $\frac{a}{2}(-1,3,-1)$	$-\begin{pmatrix}\beta_4 & -\gamma_4 & \delta_4\\ -\gamma_4 & \alpha_4 & -\gamma_4\\ \delta_4 & -\gamma_4 & \beta_4\end{pmatrix}$
0 – 22 $\frac{a}{2}(1,1,3)$ $\frac{a}{2}(-1,-1,-3)$	$-\begin{pmatrix}\beta_4 & \delta_4 & \gamma_4\\ \delta_4 & \beta_4 & \gamma_4\\ \gamma_4 & \gamma_4 & \alpha_4\end{pmatrix}$	0 – 23 $\frac{a}{2}(1,1,-3)$ $\frac{a}{2}(-1,-1,3)$	$-\begin{pmatrix}\beta_4 & \delta_4 & -\gamma_4\\ \delta_4 & \beta_4 & -\gamma_4\\ -\gamma_4 & -\gamma_4 & \alpha_4\end{pmatrix}$	0 – 24 $\frac{a}{2}(-1,1,3)$ $\frac{a}{2}(1,-1,-3)$	$-\begin{pmatrix}\beta_4 & -\delta_4 & -\gamma_4\\ -\delta_4 & \beta_4 & \gamma_4\\ -\gamma_4 & \gamma_4 & \alpha_4\end{pmatrix}$
0 – 25 $\frac{a}{2}(1,-1,3)$ $\frac{a}{2}(-1,1,-3)$	$-\begin{pmatrix}\beta_4 & -\delta_4 & \gamma_4\\ -\delta_4 & \beta_4 & -\gamma_4\\ \gamma_4 & -\gamma_4 & \alpha_4\end{pmatrix}$	0 – 26 $\frac{a}{2}(2,2,2)$ $\frac{a}{2}(-2,-2,-2)$	$-\begin{pmatrix}\alpha_5 & \beta_5 & \beta_5\\ \beta_5 & \alpha_5 & \beta_5\\ \beta_5 & \beta_5 & \alpha_5\end{pmatrix}$	0 – 27 $\frac{a}{2}(-2,2,2)$ $\frac{a}{2}(2,-2,-2)$	$-\begin{pmatrix}\alpha_5 & -\beta_5 & -\beta_5\\ -\beta_5 & \alpha_5 & \beta_5\\ -\beta_5 & \beta_5 & \alpha_5\end{pmatrix}$
0 – 28 $\frac{a}{2}(2,-2,2)$ $\frac{a}{2}(-2,2,-2)$	$-\begin{pmatrix}\alpha_5 & -\beta_5 & \beta_5\\ -\beta_5 & \alpha_5 & -\beta_5\\ \beta_5 & -\beta_5 & \alpha_5\end{pmatrix}$	0 – 29 $\frac{a}{2}(2,2,-2)$ $\frac{a}{2}(-2,-2,2)$	$-\begin{pmatrix}\alpha_5 & \beta_5 & -\beta_5\\ \beta_5 & \alpha_5 & -\beta_5\\ -\beta_5 & -\beta_5 & \alpha_5\end{pmatrix}$	0 – 30 $\frac{a}{2}(4,0,0)$ $\frac{a}{2}(-4,0,0)$	$-\begin{pmatrix}\alpha_6 & 0 & 0\\ 0 & \beta_6 & 0\\ 0 & 0 & \beta_6\end{pmatrix}$
0 – 31 $\frac{a}{2}(0,4,0)$ $\frac{a}{2}(0,-4,0)$	$-\begin{pmatrix}\beta_6 & 0 & 0\\ 0 & \alpha_6 & 0\\ 0 & 0 & \beta_6\end{pmatrix}$	0 – 32 $\frac{a}{2}(0,0,4)$ $\frac{a}{2}(0,0,-4)$	$-\begin{pmatrix}\beta_6 & 0 & 0\\ 0 & \beta_6 & 0\\ 0 & 0 & \alpha_6\end{pmatrix}$	0 – 33 $\frac{a}{2}(1,3,3)$ $\frac{a}{2}(-1,-3,-3)$	$-\begin{pmatrix}\alpha_7 & \gamma_7 & \gamma_7\\ \gamma_7 & \beta_7 & \delta_7\\ \gamma_7 & \delta_7 & \beta_7\end{pmatrix}$
0 – 34 $\frac{a}{2}(-1,3,3)$ $\frac{a}{2}(1,-3,-3)$	$-\begin{pmatrix}\alpha_7 & -\gamma_7 & -\gamma_7\\ -\gamma_7 & \beta_7 & \delta_7\\ -\gamma_7 & \delta_7 & \beta_7\end{pmatrix}$	0 – 35 $\frac{a}{2}(1,3,-3)$ $\frac{a}{2}(-1,-3,3)$	$-\begin{pmatrix}\alpha_7 & \gamma_7 & -\gamma_7\\ \gamma_7 & \beta_7 & -\delta_7\\ -\gamma_7 & -\delta_7 & \beta_7\end{pmatrix}$	0 – 36 $\frac{a}{2}(1,-3,3)$ $\frac{a}{2}(-1,3,-3)$	$-\begin{pmatrix}\alpha_7 & -\gamma_7 & \gamma_7\\ -\gamma_7 & \beta_7 & -\delta_7\\ \gamma_7 & -\delta_7 & \beta_7\end{pmatrix}$
0 – 37 $\frac{a}{2}(3,1,3)$ $\frac{a}{2}(-3,-1,-3)$	$-\begin{pmatrix}\beta_7 & \gamma_7 & \delta_7\\ \gamma_7 & \alpha_7 & \gamma_7\\ \delta_7 & \gamma_7 & \beta_7\end{pmatrix}$	0 – 38 $\frac{a}{2}(3,-1,-3)$ $\frac{a}{2}(-3,1,3)$	$-\begin{pmatrix}\beta_7 & -\gamma_7 & -\delta_7\\ -\gamma_7 & \alpha_7 & \gamma_7\\ -\delta_7 & \gamma_7 & \beta_7\end{pmatrix}$	0 – 39 $\frac{a}{2}(3,-1,3)$ $\frac{a}{2}(-3,1,-3)$	$-\begin{pmatrix}\beta_7 & -\gamma_7 & \delta_7\\ -\gamma_7 & \alpha_7 & -\gamma_7\\ \delta_7 & -\gamma_7 & \beta_7\end{pmatrix}$
0 – 40 $\frac{a}{2}(3,1,-3)$ $\frac{a}{2}(-3,-1,3)$	$-\begin{pmatrix}\beta_7 & \gamma_7 & -\delta_7\\ \gamma_7 & \alpha_7 & -\gamma_7\\ -\delta_7 & -\gamma_7 & \beta_7\end{pmatrix}$	0 – 41 $\frac{a}{2}(3,3,1)$ $\frac{a}{2}(-3,-3,-1)$	$-\begin{pmatrix}\beta_7 & \delta_7 & \gamma_7\\ \delta_7 & \beta_7 & \gamma_7\\ \gamma_7 & \gamma_7 & \alpha_7\end{pmatrix}$	0 – 42 $\frac{a}{2}(3,-3,-1)$ $\frac{a}{2}(-3,3,1)$	$-\begin{pmatrix}\beta_7 & -\delta_7 & -\gamma_7\\ -\delta_7 & \beta_7 & \gamma_7\\ -\gamma_7 & \gamma_7 & \alpha_7\end{pmatrix}$
0 – 43 $\frac{a}{2}(3,3,-1)$ $\frac{a}{2}(-3,-3,1)$	$-\begin{pmatrix}\beta_7 & \delta_7 & -\gamma_7\\ \delta_7 & \beta_7 & -\gamma_7\\ -\gamma_7 & -\gamma_7 & \alpha_7\end{pmatrix}$	0 – 44 $\frac{a}{2}(3,-3,1)$ $\frac{a}{2}(-3,3,-1)$	$-\begin{pmatrix}\beta_7 & -\delta_7 & \gamma_7\\ -\delta_7 & \beta_7 & -\gamma_7\\ \gamma_7 & -\gamma_7 & \alpha_7\end{pmatrix}$	0 – 45 $\frac{a}{2}(4,2,0)$ $\frac{a}{2}(-4,-2,0)$	$-\begin{pmatrix}\alpha_8 & \delta_8 & 0\\ \delta_8 & \beta_8 & 0\\ 0 & 0 & \gamma_8\end{pmatrix}$
0 – 46 $\frac{a}{2}(4,-2,0)$ $\frac{a}{2}(-4,2,0)$	$-\begin{pmatrix}\alpha_8 & -\delta_8 & 0\\ -\delta_8 & \beta_8 & 0\\ 0 & 0 & \gamma_8\end{pmatrix}$	0 – 47 $\frac{a}{2}(4,0,2)$ $\frac{a}{2}(-4,0,-2)$	$-\begin{pmatrix}\alpha_8 & 0 & \delta_8\\ 0 & \gamma_8 & 0\\ \delta_8 & 0 & \beta_8\end{pmatrix}$	0 – 48 $\frac{a}{2}(4,0,-2)$ $\frac{a}{2}(-4,0,2)$	$-\begin{pmatrix}\alpha_8 & 0 & -\delta_8\\ 0 & \gamma_8 & 0\\ -\delta_8 & 0 & \beta_8\end{pmatrix}$
0 – 49 $\frac{a}{2}(0,2,4)$ $\frac{a}{2}(0,-2,-4)$	$-\begin{pmatrix}\gamma_8 & 0 & 0\\ 0 & \beta_8 & \delta_8\\ 0 & \delta_8 & \alpha_8\end{pmatrix}$	0 – 50 $\frac{a}{2}(0,2,-4)$ $\frac{a}{2}(0,-2,4)$	$-\begin{pmatrix}\gamma_8 & 0 & 0\\ 0 & \beta_8 & -\delta_8\\ 0 & -\delta_8 & \alpha_8\end{pmatrix}$	0 – 51 $\frac{a}{2}(0,4,2)$ $\frac{a}{2}(0,-4,-2)$	$-\begin{pmatrix}\gamma_8 & 0 & 0\\ 0 & \alpha_8 & \delta_8\\ 0 & \delta_8 & \beta_8\end{pmatrix}$
0 – 52 $\frac{a}{2}(0,-4,2)$ $\frac{a}{2}(0,4,-2)$	$-\begin{pmatrix}\gamma_8 & 0 & 0\\ 0 & \alpha_8 & -\delta_8\\ 0 & -\delta_8 & \beta_8\end{pmatrix}$	0 – 53 $\frac{a}{2}(2,4,0)$ $\frac{a}{2}(-2,-4,0)$	$-\begin{pmatrix}\beta_8 & \delta_8 & 0\\ \delta_8 & \alpha_8 & 0\\ 0 & 0 & \gamma_8\end{pmatrix}$	0 – 54 $\frac{a}{2}(2,-4,0)$ $\frac{a}{2}(-2,4,0)$	$-\begin{pmatrix}\beta_8 & -\delta_8 & 0\\ -\delta_8 & \alpha_8 & 0\\ 0 & 0 & \gamma_8\end{pmatrix}$
0 – 55 $\frac{a}{2}(2,0,4)$ $\frac{a}{2}(-2,0,-4)$	$-\begin{pmatrix}\beta_8 & 0 & \delta_8\\ 0 & \gamma_8 & 0\\ \delta_8 & 0 & \alpha_8\end{pmatrix}$	0 – 56 $\frac{a}{2}(2,0,-4)$ $\frac{a}{2}(-2,0,4)$	$-\begin{pmatrix}\beta_8 & 0 & -\delta_8\\ 0 & \gamma_8 & 0\\ -\delta_8 & 0 & \alpha_8\end{pmatrix}$		

4.0 CONCLUSION

The dispersion curves and thermodynamic properties of Cs and W were calculated successfully using two techniques; the interatomic force constants (IFCs) technique employing the Born – von Kármán model and the first principle technique based on DFT implemented by QUANTUM ESPRESSO. The phonon dispersions were computed along the principal symmetry directions of the BZ. The results obtained from both techniques were matched with data from experiment. We conclude that the phonon dispersion curve of Cs and W from IFCs calculation shows good agreement with experiment just like that of the first principle calculations.

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