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PHONON DISPERSION AND THERMODYNAMIC PROPERTIES OF YTTERBIUM, YB

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ABSTRACT
The phonon and thermodynamic properties of fccYtterbium (Yb) rare-earth metal is investigated by performing density functional theory (DFT) and density functional perturbation theory (DFTP) calculations within the quasi harmonic approximation (QHA). Phonon dispersion and phonon density of states (DOS) were computed as well as linear thermal expansion as a function of temperature and constant volume specific heat as a function of temperature. Our calculated lattice constant for Yb is in general agreement with both theoretical and experimental results. Our result for phonon dispersion curve is in good agreement with available experimental result. Specific heat capacity of 46.89 J/mol.K is predicted for rare earth fccYb metal based on the thermodynamic properties computed within QHA from phonon DOS.

Keywords: Ytterbium, DFPT, Phonon, DOS, Specific heat capacity

INTRODUCTION

Ytterbium (Yb) is a rare earth metal which belongs to the Lanthanide group, period six and f-block of the periodic table of elements (Winter, 2017). Yb has a 4f occupation ($4f^{14}$) such that only two electrons per atom contribute to the conduction bands, consequently the physical properties of this divalent elements are quite different from those of the trivalent rare-earth metals (Stassis *et al*., 1982). Yb is useful in various areas like fiber amplifier, fiber optic technologies and in different laser applications. Yb has a single dominant absorption band at 985nm in the infra-red making it useful in photocells application. When subjected to very high stresses, the electrical resistance of Yb metal increases thereby making a suitable material for in stress gauges for monitoring ground deformations from earthquakes and nuclear explosions. It is also used in thermal barrier system bond coatings on nickel, iron and other transitional metal alloy substrates. Yb has seven stable isotopes and two of them are used for medical and industrial purposes. Yb-168 is used for the production of Yb-169 and this radioisotope is used as a radiation source in gamma cameras. Yb-169 is also used in the medical field where it has been proposed as an alternative for I-125 and Pd-103 in the treatment of prostate cancer while it is also used for

diagnostics in the gastrointestinal tract. Isotopes Yb are useful in various applications like optical frequency standard and various experimental investigations (Americanelements, 2017). Yb is a Face Center Cubic (fcc) structure the belongs to the space group, Fm-3m with space group, Fm-3m. Its lattice parameters are: $a=b=c=5.4736$Å, $\alpha = \beta = \gamma = 90°$ (Winter, 2017; Harris and Raynor, 1969.). Phonon is a quantum mechanical description of a special type of vibrational motion, in which a lattice uniformly oscillates at the same frequency. Phonons play a major role in many of the physical properties of solids, including a material's thermal and electrical conductivities. Phonon dispersion arises from lattice vibration in crystals, which is an essential input to the calculation of thermodynamic quantities including the specific heat, the phonon density of state and the Debye temperatures (Zhang and Chen, 2012; Chepulskii and Curtarolo, 2009 and Krainyukova, 2011). Phonon dispersion can be measured both experimentally and theoretically (Zhang and Chen, 2012). Stassis *et al*. (1982) measured the phonon dispersion curves of the fccYb metal using neutron inelastic scattering. The vibrational free energy can be obtained using the quasi harmonic approximation (QHA), which takes into account the anharmonicity of the potential at first order. Vibrational properties can be understood in terms of the excitation of the non interacting phonon. QHA based on DFPT provided a reasonable description of the thermodynamic properties of many bulk materials below the melting point (Wang *et al*., 2012; Nie and Xie, 2007; Biernacki and Scheffler, 1989 and Togo *et al*., 2010). In this study, phonon dispersion of the rare-earth metal Yb was calculated within the quasi-harmonic approximation (QHA) based Density Functional Perturbation Theory (DFPT) was calculated along with phonon density of state (DOS) and specific heat at constant volume.

COMPUTATIONAL METHODOLOGY

Density Functional Perturbation Theory (DFPT) has been used to investigate the phonon dispersions of the rare-earth metal Yb along major symmetry directions. The DFTP calculations were carried out with plane-wave norm conserving pseudopotentials to obtain the phonon dispersions via linear response approach. All computations were carried with the Quantum Espresso (QE) code (Giannozzi *et al*., 2009), using the Perdew and Zunger, PZ, parametrization of Local Density Approximation, LDA (Perdew and Zunger, 1981). Structural relaxation was done using the Broyden, Fletcher, Goldfarb, and Shannon (BFGS) method (Fletcher, 1987), as implemented in QE. Convergence tests were performed to determine the needed plane wave basis cut-off and zone sampling. The kinetic energy cutoff of plane wave was set to 15 Ry. Brillouin zone sampling was performed by using the Monkhorst–Pack scheme (Monkhorst and Pack, 1976) with a k-point grid of 8 x 8 x 8. Geometry optimization was considered to be performed when all components of all forces are smaller than 0.1 micro Ry. Structural data of (Harris and Raynor, 1969) were used as our initial geometry.

RESULTS

Geometry Optimization

Figure 1 shows the fcc crystal structure of Ytterbium as drawn using xcrysden (Kokalj, 2003). The equilibrium lattice constant was computed by fitting the total energy as a function of the volume to the Murnaghan equation of states (Murnaghan, 1944). Table 1 shows the calculated equilibrium lattice constant, a (Å) and the isothermal Bulk Modulus, B (GPa) at T=300Kin comparison with experimental and theoretical results. The calculated lattice constant for Ybis about 1% lesser than the experimental value, yet it compares better than other theoretical results. There is no experimental result for the bulk modulus of Yb but available results for bulk modulus, our calculated bulk modulus in the present study is about 18% higher than the theoretical value (Zhang and Chen, 2012).

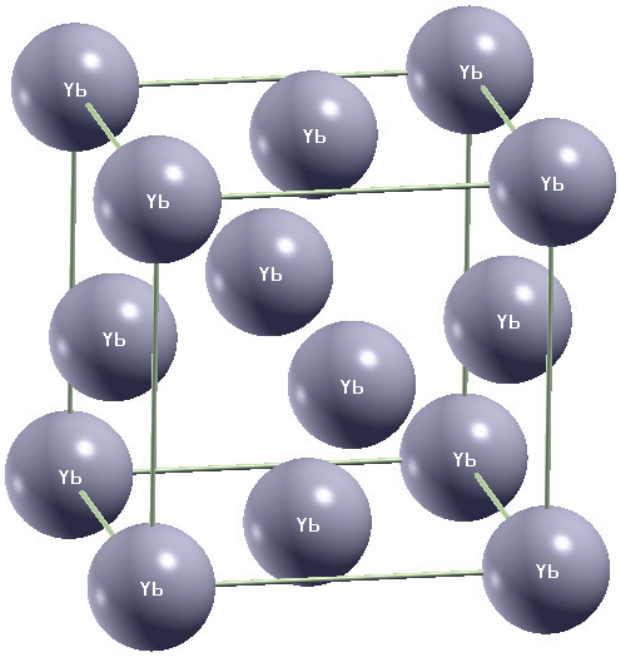

Figure 1: The crystal structure for fcc Ytterbium, Yb

Table 1: The equilibrium lattice constant, a (Å) and the isothermal Bulk Modulus, B (GPa) at T=300K in our calculation in comparison with experimental and theoretical results.

Material	a (Å)	B (GPa)	Reference
Yb	5.467	15.4	Present work
	5.4736	-	Experiment (Harris and Raynor, 1969.)
	5.45	13.1	MAEAM (Zhang and Chen, 2012)
	5.4847	31.0	(Winter, 2017)

The Phonon Dispersion Curve and Phonon DOS

The phonon dispersion curve as calculated based on DFPT using Quantum Espresso along high symmetry directions Γ-X-Γ-L-X-W-L of the Brillouin zone for fccYb is displayed in Figure 2. Our Phonon dispersion curve along special points in the first Brillouin zone of fcc lattice compares favorably with experimental result of Stassis *et al*. (1982) and the Modified Analytical Embedded Atom Method (MAEAM) numerical simulation results of Zhang and Chen (2012). Near lower frequency, the phonon dispersion curves reproduced very well the experimental results along major symmetry directions. In the high-frequency limit, it can be seen that the curves have a shape very similar to that obtained experimentally, though the actual degree of it varies somewhat. The maximum discrepancies of the frequency between experimental and calculated values are minimal. The discrepancies may be resulted from the fact that the current simulations are within harmonic approximation and adiabatic approximation, whereas, the measurements are obtained under conditions that the approximation effects are not negligible. Consequently, the above results indicate that DFPT using QUANTUM ESPRESSO provides a satisfactory description for the phonon dispersion in fcc metal Yb. Differences in the slopes may imply that fcc metal Yb is anisotropic with regard to the propagation of elastic waves. In addition, along the same symmetry directions, the successive increase of phonon frequencies for Yb, may be attributed to the successive decrease of atomic mass of these metals. At temperature above 935K, Yb undergoes a phase transformation to a body center cubic (bcc) phase. Figure 3 shows the phonon density of states (DOS) for fccYb which describes the number of states that are available in a system and is essential for determining the carrier concentrations and energy distribution within the system. The phonon DOS peaks are towards the high frequency spectrum.

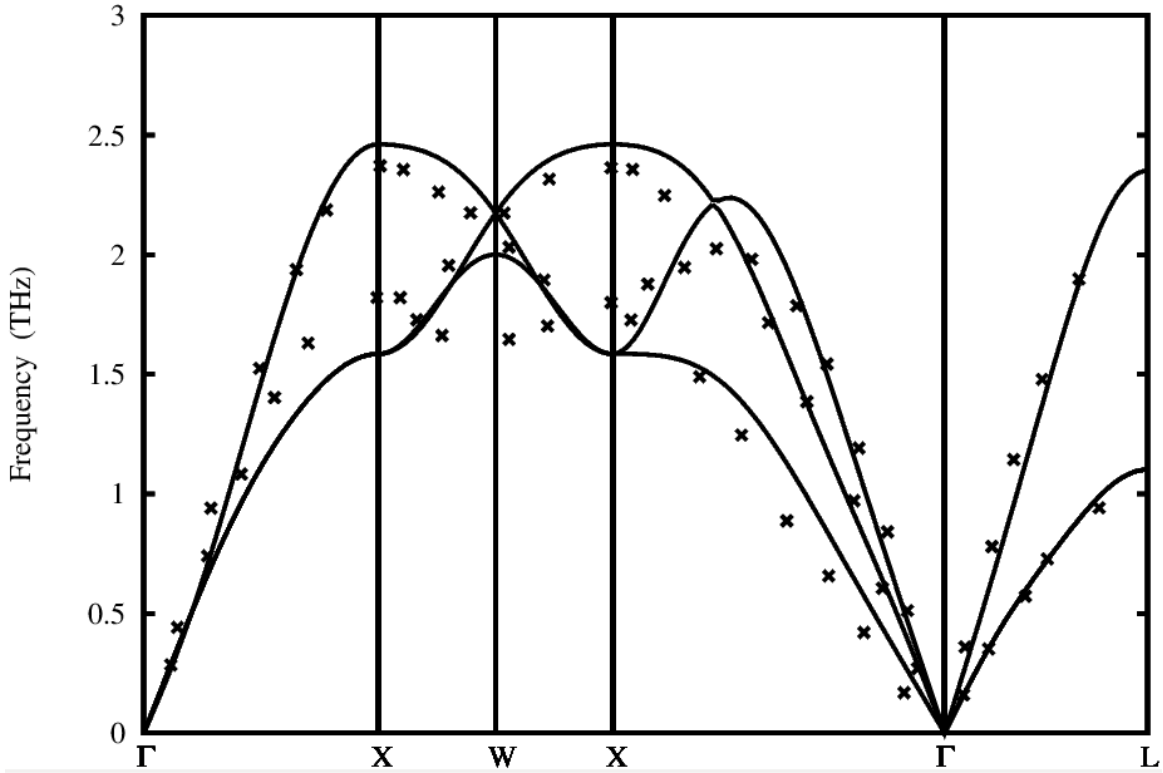

Figure 2: Phonon dispersion curves of Yb along five symmetry directions. The solid line represents the present calculation while the points are experimental data of Stassis *et al*. (1982)

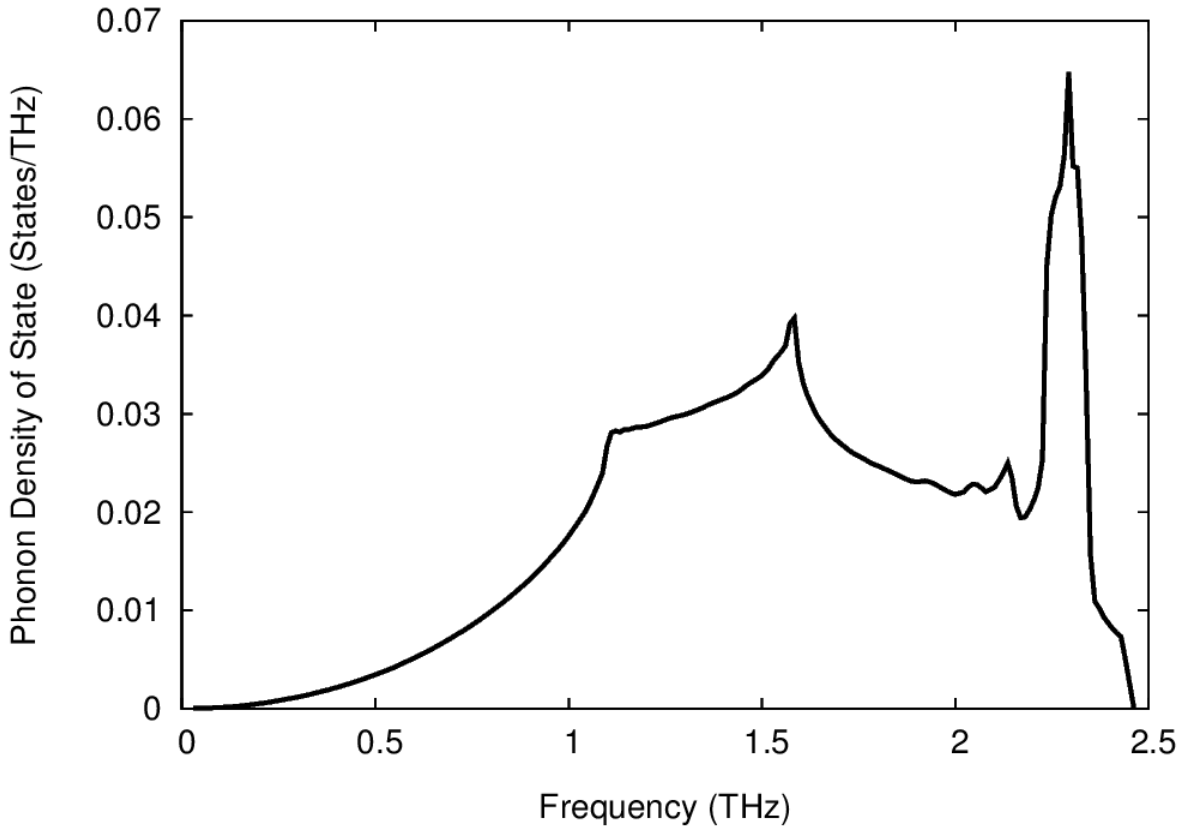

Figure 3: Computed Phonon density of state for Yb

Thermodynamic Properties

In thermodynamics, the energy contained within the system is refer to as the internal energy of that system which exclude the kinetic energy and the potential energy of the system as a whole due to external force fields. The Helmholtz free energy within QHA is given as (Adetunji *et al*., 2016; Eryigit and Gurel, 2010).

$$F(V,T) = U_{stat}(V) + k_B T \sum_{q\lambda} In\left(2sinh\left[\frac{\hbar\omega_{q\lambda}(V)}{2k_B T}\right]\right) + F_{el}(V,T) \qquad (1)$$

Where the first term and second term on the right-hand side of equation (1) are the static internal energy at volume V and the vibrational free energy as a result of phonon contribution. Static internal energy can be easily determined from standard density functional theory (DFT) calculations. The sum is over all phonon branches λ and over all wave vectors q in the first Brillouin zone,$\hbar$ is the reduced Planck constant, and $\hbar\omega_{q\lambda}$(V) is the frequency of the phonon with wave vector q and polarization λ, evaluated at constant volume V . The last term is the thermal electronic contribution to free energy. Usually, it is assumed that the electronic contribution to total free energy can be negligible (Adetunji *et al*., 2016; Eryigit and Gurel, 2010). The vibrational specific heat $C_V$at constant volume in the QHA is given as;

$$C_V^{vib} = \sum_{q\lambda} k_B \left(\frac{\hbar\omega_{q\lambda}(V)}{2k_BT}\right)^2 cosh^2\left(\frac{\hbar\omega_{q\lambda}(V)}{2k_BT}\right)^2 \quad (2)$$

The electronic specific heat can be obtained from;

$$C_V^{el} = T\left(\frac{\partial S_{el}}{\partial T}\right)_V \quad (3)$$

and the total specific heat at constant volume is then $C_V = C_V^{ph} + C_V^{el}$. The specific heat at a constant pressure, C_p, is different from the specific heat at a constant volume, C_v due to anharmonicity. C_v goes to a constant which is given by classical equipartition law: $C_V = 3Nk_B$ where N is the number of atoms in the system and k_B is the Boltzmann's constant. The knowledge of heat capacity of a substance provides crucial information on its vibrational properties and applications (Adetunji *et al*., 2016; Belaroussi *et al*., 2008).The constant volume heat capacity, C_V tends to the Petit and Dulong limit at high temperature, C_V is proportional to T^3 (Adetunji $et\ al.,2016$) PDe12 \l 1033 (Debye, 1912). The volume thermal expansion coefficient and the linear thermal expansion are given by equations (4) and (5); (Wang *et al*., 2012)

$$\propto (T) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_r \quad (4)$$

$$\epsilon(T) = \left(\frac{a(T)-a(T_c)}{a(T_c)}\right) \quad (5)$$

where $a(T_c)$ is the equilibrium lattice constant and $a(T) = [V(T)]^{1/3}$ at $T_c = 300K$.

The linear thermal expansion, ϵ as defined in equation (5) for Yb is shown in Figure 4. It shows the calculated linear thermal expansion for Yb. Temperature dependence specific heat for fccYb is displayed in figure 6, at low temperature, C_v obeys T^3 law. Calculated C_v for Yb at 300K is 48.69J/mol.K and it is tending towards the asymptotic limit of 50 J/mol.K.

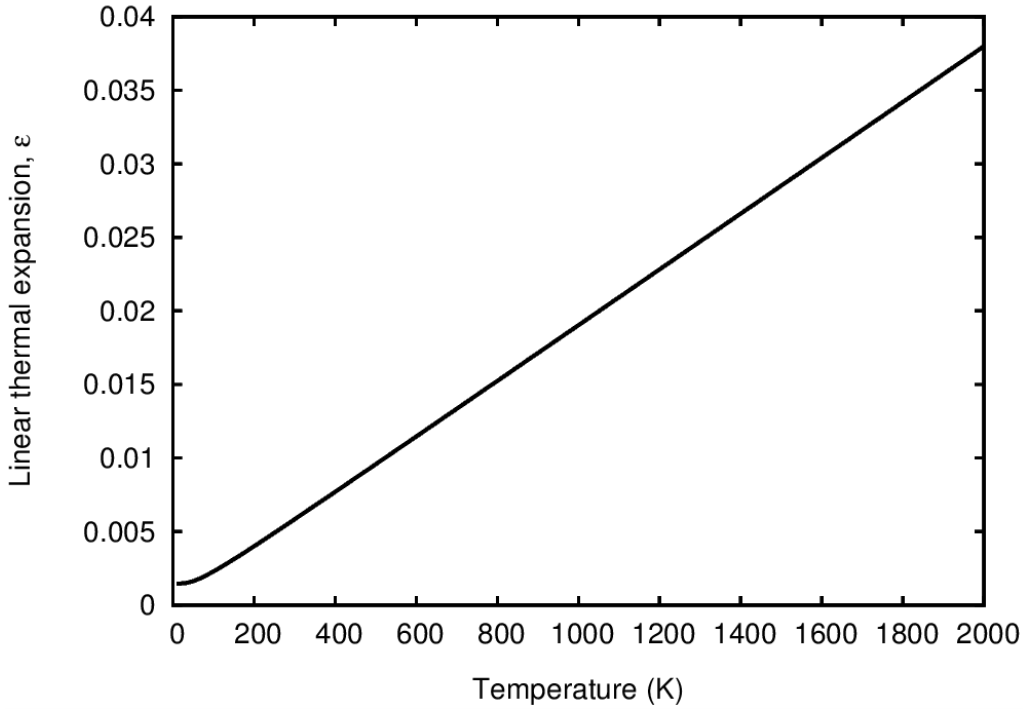

Figure 4: Computed linear thermal expansion as a function of temperature for Yb

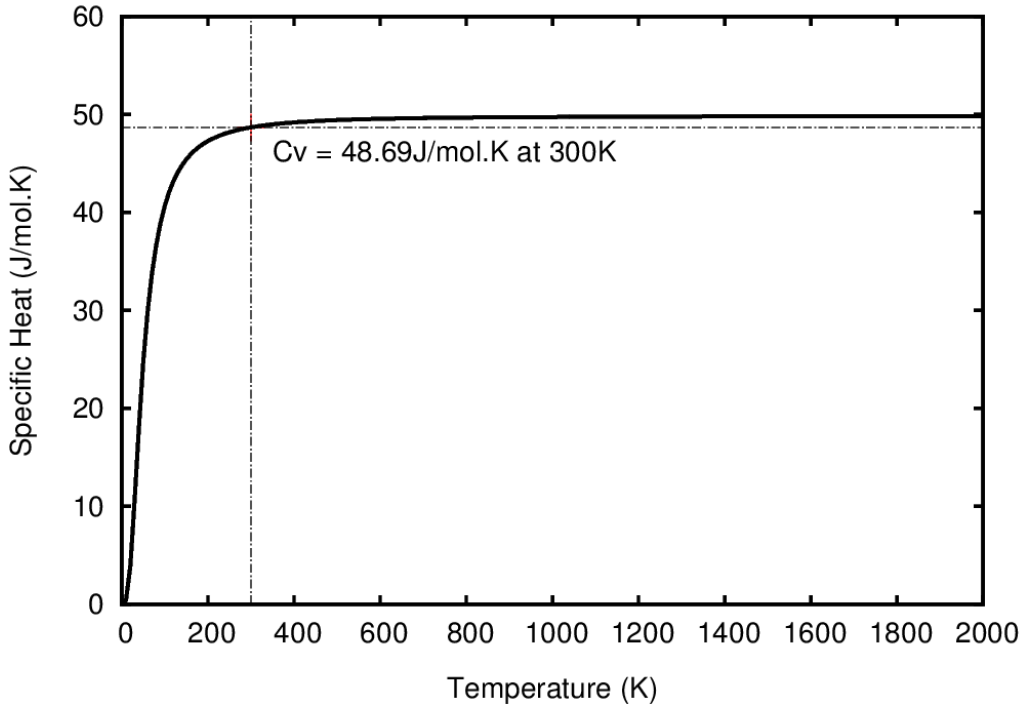

Figure 5: Calculated specific heat at constant volume as a function of temperature

Conclusion

The phonon and thermodynamic properties computation have been carried out within DFT and DFTP within the QHA for the rare – earth fccYb metal, phonon dispersion, phonon DOS, linear thermal expansion as a function of temperature and constant volume specific heat were calculated. Our calculated lattice constant is in good agreement with both theoretical and experimental values. Our result for phonon dispersion curve is in good agreement with available experimental result. Our DOS peaks are located towards the high frequency spectrum of the phonon frequencies. Base on the thermodynamic properties computed within QHA from phonon DOS, specific heat capacity of 46.89 J/mol.K is predicted for rare earth fccYb metal.

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