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Thermodynamic properties of Al within the Density Functional Perturbation Theory based on the Quasi-Harmonic Approximation

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Abstract: We have performed self-consistent density functional perturtubation calculation using ab-initio LAPW method. From these and by considering QHA, we have determined the free Helmholtz energy in different volumes and for different temperatures in each volume. We have calculated some thermal properties of Al thermal expansion, linear coefficient of thermal expansion, entropy ,specific heat and the phonon density of states.

Key words: Density Functional Perturbation Theory, Quasi-Harmonic Approximation.

INTRODUCTION

Nevertheless, aluminum is today the second-most used metal, after steel. Aluminum is the thirteenth element in the periodic table that has a face centered cubic structure at room temperature. Aluminum displays excellent electrical and thermal conductivity, non-ferromagnetic, non-pyrophoric, non-toxic and has an attractive appearance in its natural finish. Aluminum is unrivalled as a packaging material for food and beverages, as well as pharmaceutical products. Due to the excessive use of aluminum, extensive studies is done on various properties of this material.

To evaluate the physical properties of a crystal, its total energy must first be determined. To calculate the total energy of the system, the many-body Schrödinger equation must be solved. The many-body systems Hamiltonian is very complex, so the approximation methods must be used (Baroni, S., 2009).

In the past, for the simulation of thermodynamic properties of materials Some approximations have been developed and applied. Quasi-harmonic approximation (QHA) is used recently to study the thermal properties of materials , In addition to being compatible with experience. greatly reduce the size and the computation time. In this approximation, the thermal properties of solids are returned to the system without interaction ,the phonon frequencies are related to the volume or other thermodynamic constraints (Srivastava, G.P., 1990).

Density functional perturbation theory (DFPT) (Giannozzi, P. and S. Baroni, 2005) allows the density functional theory (DFT) combined with QHA and we proved that this method is remarkably accurate in a large temperature range. In this paper The calculations were performed in the frame of density functional theory (DFT) using the full potentional linearized augmented plane wave (FP-LAPW) (Cottenier, S., 2004) method with the generalized gradient approximation (GGA) (Leeuwee, R.V., Kohn-Sham, 1999).

Computational Details:

The Helmholtz energy F at volume V and temperature T can be approximated as:

$$F(V,T) = E(V) + F_{vib}(V,T) \tag{1}$$

where E is the 0 K total energy, Fvib the vibrational energy of the lattice ions contribution to the free energy. Under quasi-harmonic approximation, Fvib can be calculated from phonon DOS by (Zhi-Gang Mei, 2009).

$$F_{vib}(V,T) = K_B T \int_0^\infty \ln\left(2\sinh\left[\frac{\hbar\omega}{2K_B T}\right]\right) g(\omega,V)\, d\omega \tag{2}$$

where ω represents the phonon frequency, and g(ω, V) the phonon DOS at frequency ω and volume V.

Phonon density of states (PDOS) in the framework of density functional perturbation theory (DFPT) calculated.

Density-functional calculations done within the generalized gradient approximation (GGA) Using the Perdew-Burke-Ernzerhof GGA for the exchange-correlation potential for all calculations.

In this study ower calculations have done by using Quantum Espresso QUANTUM ESPRESSO package (Quantum Espresso Home Page).

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Helmholtz free energy (F) in several different volumes and each volume to 100 different temperatures, in the range 0-500 ° K to 5 ° intervals were calculated. Considering the equation of state with constant pressure, the volume of the Helmholtz free energy is minimized at each temperature was obtained.

4-atom unit cell was considered .Dense k-point samplings in the first Brillouin zone were utilized 16 × 16 × 16 for total energy calculation and 8 × 8 × 8 for phonon calculation . dynamical matrix derived by 4 × 4 × 4 q wave vector In all cases the total energies were converged to 10^{-10} with a 50 Ry plane wave cutoff.

Results:

In Figure 1, the curve of energy versus lattice parameter is shown. Minimum point of the curve to the lattice parameter, Here is the 7/49 a.u., Which is in good agreement with experimental values measured (Jones, W. and N.H. March, 1985).

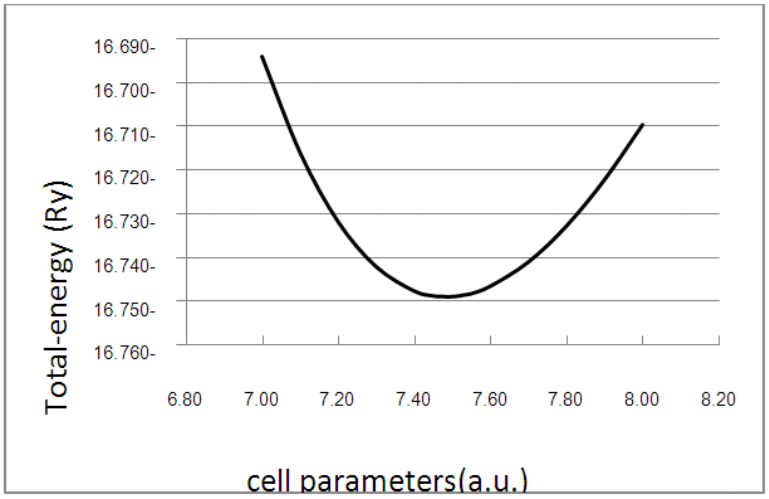

Fig. 1: Total energy curves in terms of cell parameters.

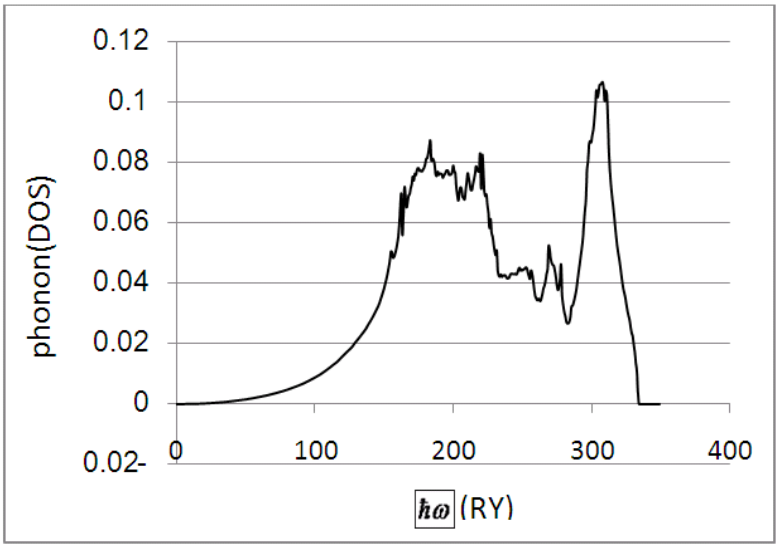

Fig. 2: The curve of phonon density of states (PDOS).

Phonon density of states, Entropy, vibrational contribution of Helmholtz free energy and Heat capacity (Lubarda, V.A., 2003) obtained for each volume, But due to the large number of curves, the results for only the Volume of the crystal lattice that minimizes the total energy, are reported (7/49 a.u. lattice parameter).

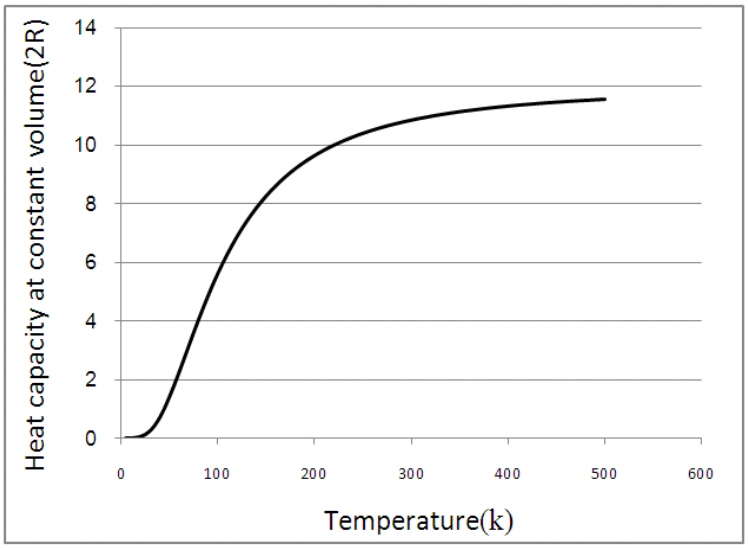

Fig. 3: Heat capacity curves in terms of temperature in constant volume.

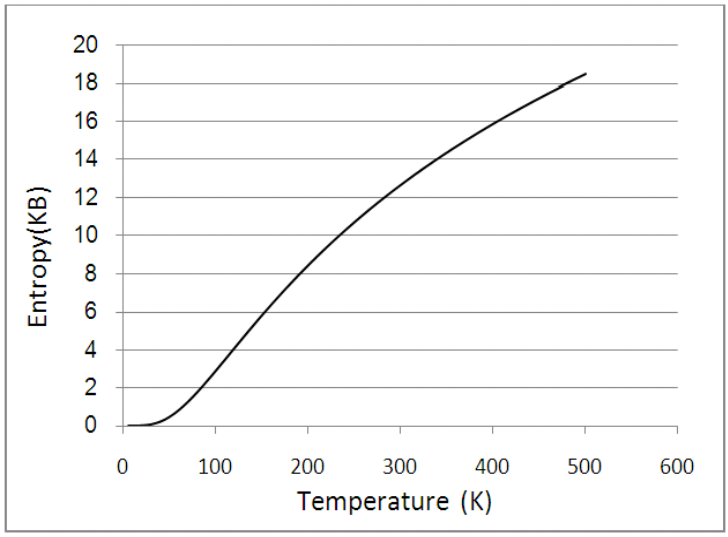

Fig. 4: Entropy curves in terms of temperature in 7/49 a.u. lattice parameter.

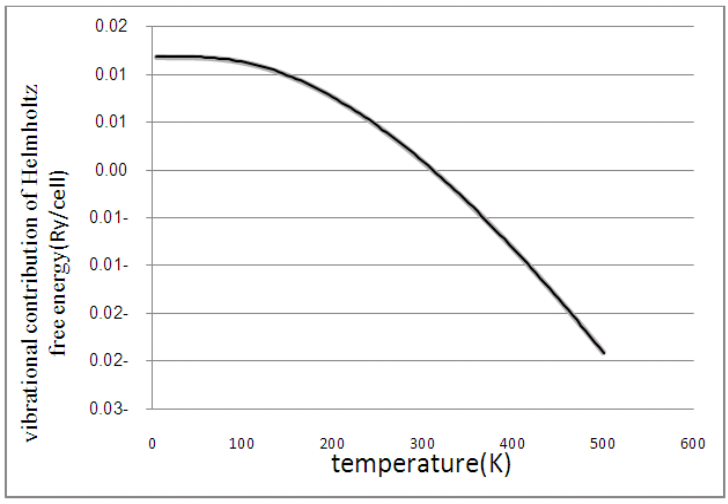

Fig. 5: Vibrational contribution of Helmholtz free energy as a function of temperature in 7/49 a.u. lattice parameter.

Helmholtz free energy was calculated from equation 1. Volume that gives the minimum free energy at each temperature, were determined. the diagram of the lattice parameter (related volumes) plotted versus temperature, Which gave the lattice thermal expansion curve.

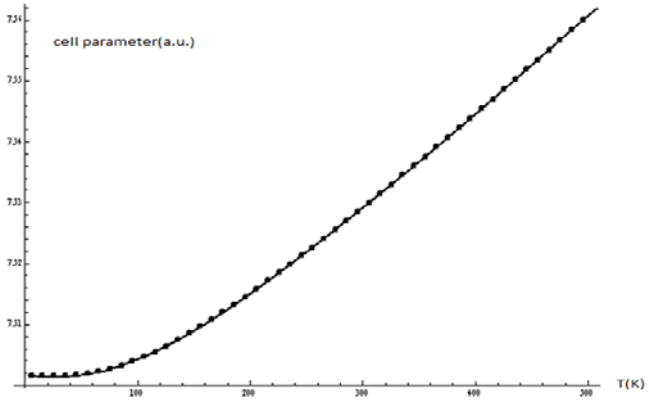

Fig. 6: Lattice thermal expansion curve in the quasi-harmonic approximation.

The Linear thermal expansion coefficient was calculated according to equation:

$$\alpha = \frac{1}{a}\left(\frac{\partial a}{\partial T}\right) \tag{3}$$

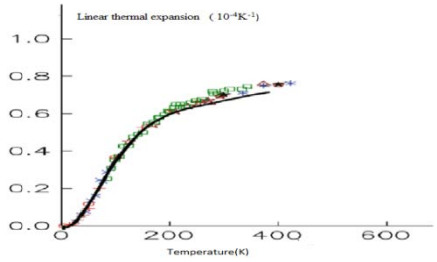

Fig. 7: The linear thermal expansion coefficient (α) versus temperature. The calculated results are plotted as solid. The experimental datas (Jacobs, M.H.G. and R. Schemid-Fetzer, 2010) are plotted as open symbols.

In this calculation, the linear expansion coefficient at low temperatures showed good compatibility with experimental datas. At temperatures above 300 K, the results are somewhat distanced from the experimental values. Due to the anharmonic effects at the quasiharmonic level increase with increasing temperature.

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