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Theoretical Study of Thermo Elastic Properties of Hexagonal Close Packed Structure (HCP) of Iron (Fe) Under High Pressure

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***Abstract*- Evaluation of relative compression volume V_P/V_o, Isothermal Bulk modulus B_T and first Grüneisen parameter γ, for hcp Iron under high pressure have been achieved in this study by using equations of state (Dodson EOS, Vinet EOS and Birch-Murnaghan EOS). The constant parameters that are appeared in the equations of state are chosen from the literature. The obtained results from three equations of state are compared with each other and with other data published in literature. The data for V_P/V_o, B_T and γ_P, are found to be in good agreement with each other for whole pressure ranges. Some literature data are given in this study and agreedour results.**

***Keywords*- Equation of state (EOS), Dodson EOS, Vinet EOS, Birch- Murnaghan EOS, high pressure P and hcp Iron.**

I. INTRODUCTION

Iron is considered as an important material that has been observed, it is thought to be the main constituent in the Earth's core, at atmospheric pressure Iron is observed at body center cubic (bcc) phase, It transforms from bcc to face-center-cubic (fcc) structure at elevated temperature (~1150K at ambient pressure), and to hexagonal-close-packed (hcp) structure at increased pressure approximately up to ~11GPaat room temperature (Hemley*et al.*,1995). Bellow pressures of 20Gpa all phases (bcc, fcc, hcp and liquid) of Iron are observed. The hcp Iron is the most stable phase of iron up to high pressures, and temperatures, hcp Iron is the only solid phase observed up to at least 110 GPa, Only the hcp phase is evident between 50 and 110 GPa, in a wide range of temperatures at least to the meltingpoint (Hemley*et al.*,1995). It is likely that the bulk of the earth's solid inner core is composed of hcp iron(Hemley and Mao, 2001). Vast studies have been madeon hcp-Iron, (Yamazaki*et al*, 20012) determined the P-V-T equation of state of hcp- iron, in situ X-ray observations at pressures up to 80 GPa and temperatures up to 1900 K.The phonon density of states of hcp Iron with high statistical quality using nuclear resonant inelastic X-ray scattering and in situ X-ray diffraction experiments between pressures of 30 GPa and 171 GPa and at 300 K, was measured by (Chen*et al*. 2011). (Belonoshkot, 2010)has created the equation of state for hcp- Iron at high pressure by employing molecular dynamic simulations**.** (Miyagi *et al.*,2008) used the diamond anvil cell to observe the pressure change in a sample of bcc Iron up to pressures of about 220Gpa, In a run at ambient temperature, the sample was deformed to high pressure and started to convert to hcp phase at pressure of about 13 GPa, In a second run the sample was decompress back to the bcc phase, then upon heating the sample transformed to the fcc structure at temperature of about 1200K and ambient pressure, finally the fcc phase was converted to hcp by increasing pressure followed by deformation of the hcp phase at simultaneous high pressure and high temperature. The solid state is different from the gas, which has a general rule as it is known a general ideal gas rule (PV=nRT), Solid state can be described by more than one equations of state, the presence of lots of equation of state is returned to variation of methods in which equations of state are derived from.

II. THEORETICAL DETAILS

The pressure -volume- temperature relationship termed as equation of state (EOS), with the help of EOS, we can determine various properties of condensed phase physics, under varying conditions of pressures and temperatures. In order to find solutions to a variety of problems in earth science and condensed phase (solid state) physics, an equation of state (EOS) that accurately predicts solids behavior at high pressure and temperature is required. Also, the equations of state of some solids are used as pressure calibrations.

1. Equations of state (EOS)

There are enormous equations of state that have been derived based on different physical assumptions, for isothermal description of solids under strong compression: The following are some famous isothermal equations of state:

(i) Murnaghan EOS (Anderson,1995)

Murnaghan's EOScan is derived from the definition of the bulk modulus and the assumption made by Murnaghan that the bulk modulus (B) is linear with respect to pressure:

$$B_p = B_0 + B_0' P \text{ ……………………….(1)}$$

B_p:bulk modulus at high pressure P.
B_0: bulk modulus at ambient pressure.
B_0': First pressure derivative of bulk modulus.
P: Is pressure.

From the definition of the isothermal Bulk modulus B

$$B = -V \frac{dP}{dV} \qquad \text{……………..(2)}$$

On the basis of pressure integral form of eq.(2), becomes:

$$\frac{V_P}{V_o} = \exp\left[-\int_{po}^{p} \frac{dP}{B(P)} \right] \text{…………….(3)}$$

Inserting eq.(1), in to eq.(3.), the following equation is obtained:

$$\left(\frac{V_P}{V_o} \right) = \left(1 + \frac{B_o'}{B_o} P \right)^{-\frac{1}{B_o'}} \text{ ……………(4)}$$

Where $V_P$and V_o are volume at high pressure and atmospheric pressure respectively.

(ii) Birch-Murnaghan EOS(Anderson, 1995)

The most famous EOSs for solids is the Birch-Murnaghan equation. The Birch–Murnaghan EOS is developed from the internal potential energy in a solid, based on finite strain theory and pressure derivative of internal potential energy, also from the definition of the bulk modulus. Birch–Murnaghan EOS is:

$$\mathrm{P}_{B-M} = \frac{3}{2} B_o \left[\left(\frac{V_P}{V_o} \right)^{-7/3} - \left(\frac{V_P}{V_o} \right)^{-5/3} \right] \times$$
$$\left\{ 1 - \frac{3}{4} \left(4 - B_o' \right) \left[\left(\frac{V_P}{V_o} \right)^{-2/3} - 1 \right] \right\} \text{……………………..(5)}$$

The Dodson EOS can be written as:

$$P_D = \frac{27}{8} B_o B_o'^{\,2} \left[\begin{array}{l} \left(\frac{V_p}{Vo} \right)^{-2/3} - 1 + 4 \left\{ 1 - \frac{2}{3B_o'} \right\} \times \\ \left\{ 1 - \left(\frac{V_p}{V_o} \right)^{-1/3} - \frac{1}{6} \left(1 - \frac{2}{3B_o'} \right) Ln \left(\frac{V_P}{V_o} \right) \right\} \end{array} \right] \text{…………(6)}$$

(iii) Vinet EOS (Vinet, 1987)

The Vinet EOS is based on a relationship between the binding energies and the interatomic spacing. And pressure derivative of binding energies, the Vinet EOS is:

$$P_V = 3B_o \left(\frac{V_P}{V_o} \right)^{\frac{-2}{3}} \times \left(1 - \left(\frac{V_P}{V_o} \right)^{\frac{1}{3}} \right) \times$$
$$exp\left(\left(\frac{3}{2} \left(B_o' - 1 \right) \times \left(1 - \left(\frac{V_P}{V_o} \right)^{\frac{1}{3}} \right) \right) \right) \text{………….(7)}$$

2. Isothermal Bulk modulus

The Isothermal bulk modulus of a substance measures the substance's resistance to uniform compression, at room temperature.

It is defined as the pressure increase needed to cause a given relative decrease in volume. Its unit is Pascal. The isothermal bulk modulus B_T can be formally defined by the equation:

$B_T = - V \partial P/\partial V$ ……………… (8)

In order to test the validation of the isothermal EOSs, the bulk modulus for each of them is calculated with eq.(8).

3. Gruneisen Parameterγ

Grünesein parameter is an important quantity in condensed matter, as it appears in equations which describe, thermodynamic properties, under high pressure. The Grünesein parameter has two definitions, a microscopic and a macroscopic definition. The microscopic definition states, that the vibrational frequencies of individual atoms in a solid, varies with the volume V, via a relation:

$$\gamma_i = -\frac{\partial \ln \omega_i}{\partial \ln V}$$

Where, ω_i is the frequency of the ith mode of vibration.

And, the macroscopic or thermodynamic formulation of the Grüneisen parameter (γ) is given by the following relation (Vocadlo and Price, 1994).

$$\gamma = \frac{\alpha V B_T}{C_v}$$

Where, C_v is the specific heat of solid at constant volume and α is thermal expansion and B_T is the isothermal bualk modulus:

4. Gruneisen parameter under high pressure $\boldsymbol{\gamma_p}$

(Boehler and Ramakrishnan 1980) expressed the relation of the volume dependence of the Grüneisen parameter as written bellow:

$$\gamma_p = \gamma_o \left(\frac{V_P}{V_O}\right)^q \quad \text{……………….(9)}$$

Where,

γ_o ,γ_P : Grüneisen parameter at atmospheric pressure and under high pressurerespectively. q is a second Grüneisen parameter.

(Agnon and Bukowiniski, 1990), has suggested that *q* could be changed under high pressure as

$$q = q_o \left(\frac{V_P}{V_o}\right)^n \quad \text{……..…………… (10)}$$

q_o and q are second Grüneisen parameter at atmospheric pressure and under high pressure respectively, with (*n*) is equal unity.

III. METHOD OF STUDY

Equations of state (EOS), Offer us to find the behavior of solid materials under high pressure. Three equations of state (Birch-Murnaghan **,** Dodson and Vinet) EOS**,** are used in this study, to determine the volume compression ratio V_p/V_o, the Isothermal bulk modulus $B_T$and Grunesien parameter of hcp Iron uder high pressures and room temperature. The constant parameters that appear in the EOS's and have been used in this study are shown in Table I. The results are shown in figures, compared to each other and to literature data. The obtained data will show the validity of the equations of state.

Table I

Values of the input parameters of hcp-Iron, at ambient pressure and room temperature, used in the present work.

Parameters	Values	References
Bulk modulus B_o	174Gpa	Belonoshko, 2010
First pressure derivative of Bulk modulus B'_o	5.29	Belonoshko, 2010
1st Grüneisen parameter γ_o	1.71 1.83	Xing*et al*., 2008 Vijay, 2011
Second Grüneisen parameter q_o	0.8	Murphy*et al*., 2011

IV. CALCULATIONS AND RESULTS

1- Evaluation of pressure (P) - V_p/V_o of hcp iron using EOSs:

On substituting the constant parameters, B_o and B'_o from Table I in the equations of state EOSs, equations (5 , 6,7), We have calculated pressures (P) at different relative compression volume(V_P /Vo) ranging from 1-0.65 , by the present EOSs, the result is shown, either in Table II and fig. 1, in comparison with literature data.

Table II

Calculated Pressure P at different V_P/V_o for hcp Iron, byusing Birch –M EOS, Dodson EOS and Vinet EOS.

V_P/V_o	Pressure(GPa)		
	Birch –M EOS	Dodson EOS	Vinet EOS
1	0	0	0
0.97	5.7447	5.7399	5.7427
0.94	12.6820	12.6381	12.6637
0.93	15.3014	15.2287	15.2712
0.90	24.2314	23.9893	24.1310
0.88	31.2045	30.7470	31.0147
0.85	43.4941	42.4709	43.0691
0.81	64.0915	61.5916	63.0475
0.77	90.9440	85.5877	88.6872
0.73	126.1972	115.6722	121.7075
0.7	159.9260	143.1502	152.6868
0.67	201.7888	175.7353	190.3939
0.65	235.3201	200.7801	220.0613

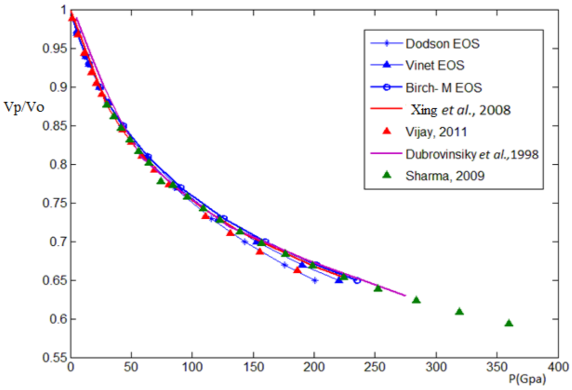


Fig. 1. Variation of V_p/V_o with high Pressure P for hcp-Iron, by usingBirch-M., Dodson and Vinet EOSs, in Comparison with Data Published in Literature.

2. Evaluation of Isothermal Bulk modulus B_T under high pressure for hcp Iron

On deriving the equations 5,6 and 7 (Birch - M. EOS, Dodson EOS and Vinet EOS) with respect to volume and substituting them in to equation(8), we obtained expressions of the Isothermal Bulk modulus B_T as a function of relative compression volume V_p/V_o , due to Birch – M. EOS, Dodson EOS and Vinet EOS respectively, as in the following:

$$B_T B-M = \frac{B_0}{2}\left[7\eta^{\frac{-7}{3}} - 5\eta^{\frac{-5}{3}}\right] +$$

$$\frac{3}{8} B_0 \left(B' - 4\right)\left(9\eta^{\frac{-9}{3}} - 14\eta^{\frac{-7}{3}} + 5\eta^{\frac{-5}{3}}\right)$$

……………………………….(11)

where $\eta = \frac{V_P}{V_o}$

$$B_T Dodson = \frac{27}{8} B_o B_o'^{2} \left[\frac{\frac{2}{3}\eta^{\frac{-2}{3}} - 4\left(1 - \frac{2}{3B'_o}\right)}{\left\{\frac{1}{3}\eta^{\frac{-1}{3}} - \frac{1}{6}\left(1 - \frac{2}{3B'_o}\right)\right\}}\right] \quad ....(12)$$

$$B_{T-Vinet} = B_o\eta^{\frac{-2}{3}}\left[1 + \left(\frac{3}{2}\left(B'_o - 1\right)\eta^{\frac{1}{3}} + 1\right)\left(1 - \eta^{\frac{1}{3}}\right)\right] \times$$

$$\exp\left(\left(B'_o - 1\right)\left(1 - \eta^{\frac{1}{3}}\right)\right) \quad ....(13)$$

Using the parameters from Table I, and substituting V_P/V_odata in Table II into equations (11, 12 and 3), we obtain the variation of the bulk modulus B_T for hcp Iron under high pressure, The result is shown in figure (2), in comparison with the data obtained by (Cohen *et al*., 1999).

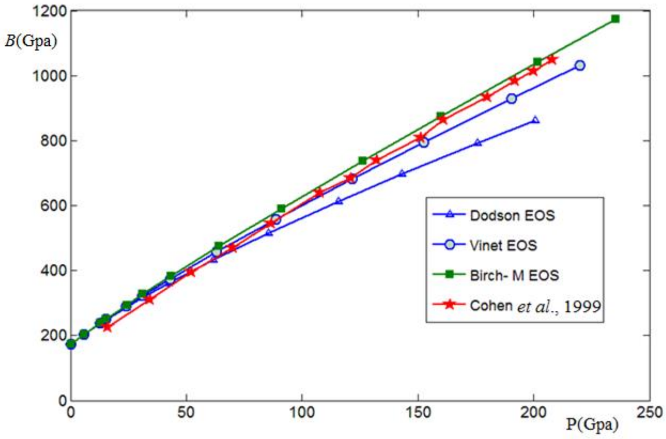
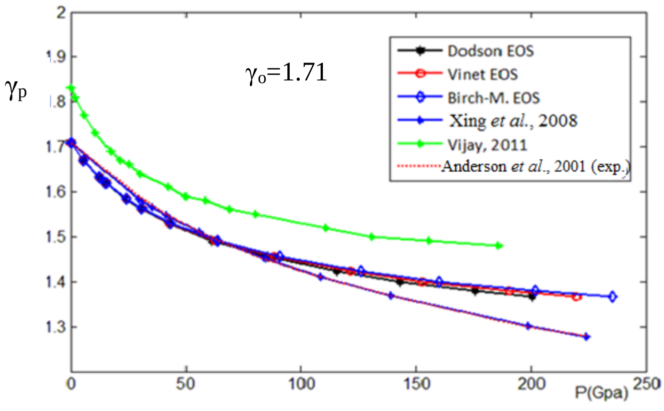


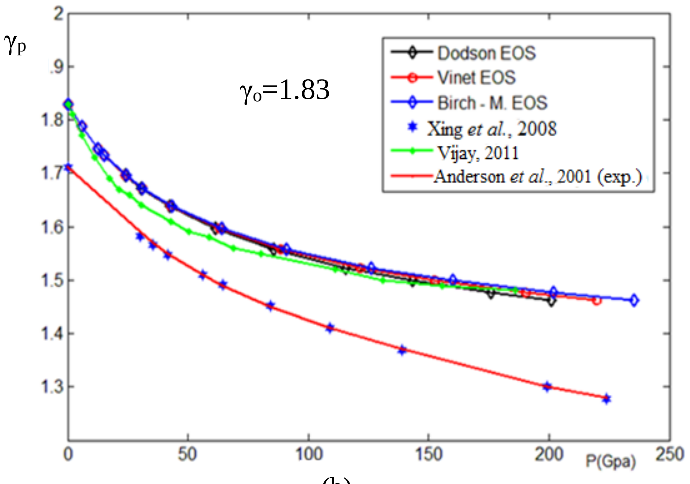
Fig.2. Variation of Bulk modulus at high pressure, using the present EOSs, in comparison with literature data.

3. *Evaluation of Grüneisen Parameter (γ_p) variation of hcp Iron under high pressure*

Considering pressure dependent of the second Grüneisen parameter q, and from Table I choosing ($q_o = 0.8$, γ_o=1.71 one time and 1.83 a second time).Then combining the equations 9 and 10 with V_p/V_o values in Table II, we have obtained the variation of $\boldsymbol{\gamma_P}$ with high pressure *P*, as shown in figure (3***a*** and ***b***), and compared with literature.



(*a*)



(b)

Fig. 3. Variation of Grüneisen parameter $\gamma_p$at high pressure, taking (*a*): γ_o=1.71 and (*b*): γ_o=1.83,The result is shown to be compared with the literature data.

The present work for determining the equation of state of hcp Iron, is important, in testing and showing the accuracy of the equations of state that have been used.

In evaluating pressures at different V_P/V_o, all EOSs gave good results through all pressure, as shown in fig. 1. Beyond the pressure of 100Gpa the results of Birch and Vinet EOS's more agreed with the literature data, than that obtained by Dodson EOS.

The result for the isothermal bulk B_T under high pressure, shows that the bulk modulus increases continuously with increasing pressure, as shown in the fig. 2.The result indicated that up to 80Gpa are found to be in good agreement with each other and with the data obtained by (Cohen *et al.*,1999), but beyond this range the results diverge from each other for the three EOS's.

The obtained data of P- V/V_o and B_T by Birch- M. and Vinet EOSs, are better than that given by Dodson EOS.

On evaluation of Grüneisen parameter under high pressure, the obtained results with the three EOSs, are in good agreement with each other, in the whole pressure ranges.

Taking the first Grüneisen parameter γ_o=1.71, gives results of $\gamma_p$that is agreed with the result found by (Xing et al, 2008). While using γ_o=1.83, our results by EOSs, are satisfied with the data obtained by (Vijay, 2011).

(ii) *Conclusion*

In this work, three EOSs are used, It is concluded that the results obtained for hcp Iron, using the parameters, in Table I, for Pressure P, bulk modulus B_T and Grüneisen parameter γ_P at different values of V_P/V_o from 1 to 0.65, are reported in Table II and fig. 1,2 and 3. All the obtained data are in agreement with each other up to pressures of about 80Gpa. The constant parameters B_o, B_o' and γ_o ,have large effect, in results of the equation of states. Since there are difference calculated values of these parameters, that they should be chosen so clearly.

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VII. REFRERENCES

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