Vol. 4 Issue No. 2, April-June 2022
e-ISSN 2456-7701
Journal of Science and Technological Researches
A Peer Reviewed Journal
Origin of Innovation
Domain: www.jstr.org.in, Email: editor@jstr.org.in

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Date of Received	**17 April, 2022**
Date of Revised	**22 May, 2022**
Date of Acceptance	**5 June, 2022**
Date of Publication	**30 June, 2022**

DOI : https://doi.org/10.51514/JSTR.4.2.2022.1-5

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ABSTRACT

The Debye characteristic temperature is of considerable importance to scientists because it correlates the elastic properties with the thermodynamic properties (such as phonons, thermal expansion, thermal conductivity, specific heat, and lattice enthalpy) of the solids. After examining the experimental data of the volume dependence of Debye temperature for ε-Fe, we have considered a relation for Debye temperature as a function of compression i.e. $\theta_D = A + B \exp\, C\left(\frac{V}{V_0}\right)$, where A, B and C are adjustable parameters. The results from the proposed relation for Debye temperature, shear sound velocity and thermal expansivity associated with a new equation of state recently reported by Singh et al. are agreed well with experimental data.

Keywords: *Debye temperature, shear velocity, equation of state, thermal expansivity, high pressure, ε-Fe.*

INTRODUCTION

Fundamentally, the temperature of the highest normal mode of vibration of a crystal is known as the Debye temperature. In other words, the Debye temperature relates elastic properties to thermodynamic properties such as phonons, thermal expansion, thermal conductivity, specific heat, and lattice enthalpy. However, the behavior of the equation of state does not depend on the structure of the solids. On the other hand, the shear moduli of the material are dependent on the structure of the solids under the compression limit. The Shear moduli are directly connected with numerous key physical quantities, for example, seismic velocities, anisotropy, Cauchy's deviation, thermal conductivity, Debye temperature, interatomic potentials, etc [1]. Shear moduli play a crucial role in understanding the seismic observation of Earth's mantle and core under high pressures and temperatures [1-2].

The volume, pressure, Debye temperature, vibrational Grüneisen parameter, and thermal expansivity for hcp-iron (ε-Fe) were measured experimentally in-situ in the diamond cell by Anderson et al. [3]. The Bulk modulus, its pressure derivative, and shear sound velocity were calculated by using the measured parameters and the Birch-Murnaghan equation of state. A set of experimental data for Debye temperature (θ_D) versus volume (V) was also presented by Dubrovinsky et al. [4]. The experimental data [3-4] and theoretical analysis results [5-8] for ε-Fe reflect the Debye temperature is an exponential function of compression. Therefore, we have considered a relation such as $\theta_D = a_0 + a_1 \exp\, a_2\left(\frac{V}{V_0}\right)$, where a_0, a_1 and a_2 are adjustable parameters. Theoretical computations exist on a variety of thermodynamic properties of ε-Fe under the high pressure and high temperature range [5-15] but little is known about the pressure dependence of the Debye temperature.

Therefore, the aim of this paper is to give a detailed description of the behavior of thermoelastic properties of ε-Fe under high pressure. We make use of the new analytical equation of state based on the Eulerian finite strain scheme recently reported by Singh et al [16-18]. This equation of state based on *n*-th power of edge length by compression was used to investigate the pressure, pressure dependence bulk moduli of ε-Fe. The calculated Debye temperature at different isothermal compression ranging 1 to 0.6 has been compared with experimental data and other theoretical results. The calculated results of bulk modulus, shear sound velocity and thermal

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expansivity at different isothermal compression ranges have also been compared with experimental data and other theoretical results. The excellent agreement with experimental data explains substantially the validity of the present work.

THEORETICAL ANALYSIS

In order to explain the behavior of thermoelastic properties of ε-Fe, we have used a new equation of state based on Eulerian finite theory based on n-th power of edge length by compression recently reported by Singh et al. [16-18] and it may be written as follow

$$P = 3K_{T0} f_n (1 + n f_n)^{\frac{3}{n}+1} \left\{1 + \frac{3}{2}\left(K'_{T0} - (n+2)\right) f_n\right\} \quad \ldots(1)$$

Where the f_n be Eulerian finite strain and expressed as

$$f_n = \frac{1}{n}\left[\left(\frac{V_0}{V}\right)^{\frac{n}{3}} - 1\right] \quad \ldots(2)$$

where V_0 is the lattice volume at $P = 0$ and $T = 300\,K$.

Using Eq. (1) and the definition of isothermal bulk modulus, the expression for isothermal bulk modulus may be written as follows:

$$K_T = K_{T0}(1 + n f_n)^{\frac{3}{n}+1}\left\{1 + (3 + 2n) f_n + \frac{3}{2}\{K'_{T0} - (n+2)\}\{2 f_n + 3(n+1) {f_n}^2\}\right\} \quad ..(3)$$

The proposed formulation (Eq. (1)) can be used to yield a variety of equations of states by choosing the value of n. For instance, it may yield the first power Eulerian EOS for $n = 1$, the Birch-Murnaghan EOS for $n = 2$ and the third power Eulerian EOS for $n = 3$ recently reported by Katsura and Tange [19].

By contrast, Anderson et al. [20] and Chopelas et al. [21] have proposed an expansion behavior that is incompatible with infinite pressure. Because of expression proposed by Chopelas et al. [21] gives $\alpha \to \infty$ while Anderson et al. [20] gives the finite value of α in the limit of extreme compression. According to Stacey et.al [22-23], the Thermal expansivity α should be zero at the extreme limit of compression. After examining the various studies [22-30], we present a simple straightforward theoretical model for the behavior of thermal expansivity with pressure. Therefore, we chose a simple polynomial relationship α that satisfied the Stacey criteria $\left(\frac{P}{K}\right)_\infty^{-1} = K'_\infty$ and may be written as

$$\alpha = \left(A_0 + A_1 \frac{P}{K} K'\right)^m \quad \ldots(4)$$

Where A, B and m are material dependent constants.

$A_0 = {\alpha_0}^{\frac{1}{m}}$ and $A_1 = -{\alpha_0}^{\frac{1}{m}}$. The subscript 0 represents the value at zero pressure.

Thus, eq. (1) written as

$$\alpha = \alpha_0 \left(1 - \frac{P}{K} K'\right)^m \quad \ldots(5)$$

The value of m is slightly greater than one, which depends upon materials. From Eq. (4) the value of α tends α_0 at zero pressure and zero at infinite pressure. The proposed expression for α follows the Stacey criteria [23].

After refining the experimental and theoretical results [3-8] for ε-Fe, we have been proposed a relation for the Debye temperature as a function of the compression. Thus

$$\theta_D = a_0 + a_1 \exp\ a_2 \left(\frac{V}{V_0}\right) \quad \ldots(6)$$

where a_0, a_1 and a_2 are adjustable parameters.

According to the quasi-harmonic approximation, the Debye-temperature can be defined in terms of sound velocity as [1]

$$\theta_D = 251.2\ V^{-1/3} v_m \quad \ldots(7)$$

Where v_m is the mean sound velocity. The value of v_m is heavily weighted by, the shear sound velocity v_s.

Anderson [12] pointed out that the Poisson ratio of the majority of materials lies between 0.15 and 0.3 so that within an approximation of a few percentages and gave the following relation

$$v_s = 0.9\ v_m \quad \ldots(8)$$

Therefore,

$$v_s = \frac{\theta_D V^{1/3}}{276.3} \quad \ldots(9)$$

Where all symbols are having their usual meanings.

RESULTS AND DISCUSSION

The volume variation of ε-Fe with pressure at room temperature (300 K) is described by Eq. (1) with choosing the values of $n = 1, 1.5, 2$ and 3. The pressure has been calculated at different isothermal compression ranging 1 to 0.6 ($V =$ 6.73 to 4.0 $cm^3\ mol^{-1}$). Where $V_0 = 6.73\ cm^3\ mol^{-1}$ at $P = 0$ and $T =$

e-ISSN 2456-7701
Vol. 4 Issue No. 2, April-June 2022

$300\,K$ of ε-Fe. The input parameters used in calculation are taken $K_{T0} = 164\,GPa$ and $K'_{T0} = 5.81$ from Anderson et al. [3]. We have obtained a similar trend as compression $\left(\frac{V}{V_0}\right)\rightarrow 0$ and pressure P→∞ with respect to Eq. (1) for $n = 1, 1.5, 2$ and 3. These Equations follow the basic thermodynamic conditions as well as the Stacey criteria. The results of Eq. (1) for the value of $n = 1.5$ are very compatible with experimental data [3] shown in Fig. 1. While results from the first power Eulerian EOS ($n = 1$), the Birch-Murnaghan EOS ($n = 2$), and the third power Eulerian EOS ($n = 3$) show inconsistency from the experimental results [3]. Thus, the excellent compromise with experimental data of the proposed model of the equation of state for $n = 1.5$ shows the validity of the present work.

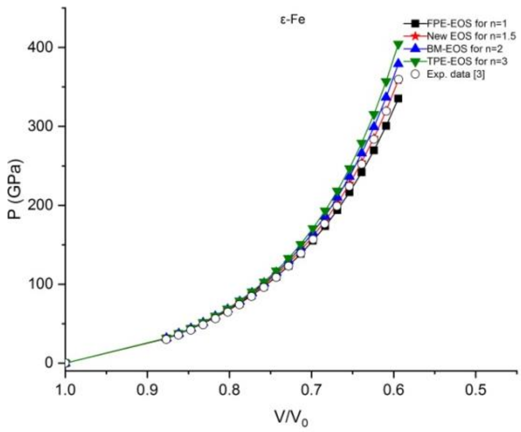

Fig. 1: Volume-pressure variation for different values of n of the equation of state for ε-Fe. The figure compare the calculated results and other models (filled symbols) with experimental data (open symbols).

The computed bulk moduli (K_T) as functions of pressure for ε-Fe using Eq. (2) are shown in Fig. 2. It may be noticed from Fig. 2, the value of K_T increases with the increase of pressure. However, it may be pointed out from Fig. 2 that experimental values of K_T using 3rd order and 4th order BM-EOS [3] intermediate lie between Eq. (2) for $n = 1.5$ and Eq. (2) for $n = 2$ (BM-EOS). While Eq. (2) for n=1.5 and 2 agrees well with experimental data [3] up to about 190 GPa pressure and is much better than results *ab initio* technique reported by Krasilnikov et.al [31]. However, the results obtained by Eq. (2) for $n = 1$ and 3 do not agree well with experimental data [3]. In fact, the results calculated by Eq. (2) for $n = 2$ i.e. BM-EOS are similar to Experimental results by 3rd order and 4th order BM-EOS [3] because of same analysis. However, the results from Eq. (2) for $n = 1.5$ are very close to experimental data [3].

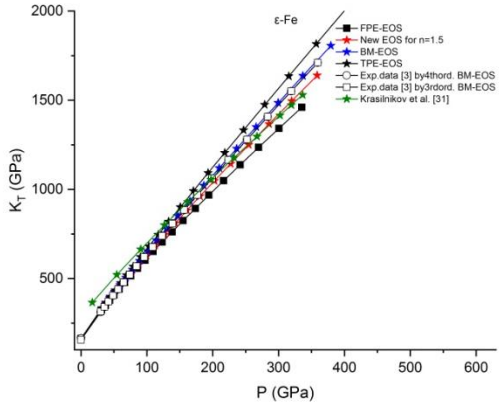

Fig. 2: Pressure dependence of bulk moduli for hcp-iron (ε-Fe). The figures compare the calculated results and other models (filled symbols) with experimental data (open symbols).

The thermal expansivity for ε-Fe has been calculated using Eq. (5). The required variables: P, K and K' and the input values: $\alpha_0 = 7.83 \times 10^{-5} K^{-1}$ [3] and $m = 1.51$ have been used in the calculation of α. The calculated results of α associated with considered EOS have been plotted as their function of pressure along with experimental data [3] which is shown in Fig. 3. As it can be observed from Fig. 3, our theoretical calculations based on Eq. (1) follows the similar trend of the experimental data [3]. The calculated values of α for TPE-EOS yield better agreement with experimental data [3] up to the high-pressure limit, while the results from the new EOS (n=1.5) are matched only at higher pressure. The results from other considered equations of state have slightly diverged from experimental data [3]. Consequently, the polynomial relationship of α follows the Stacey criteria [23] and yields results that is compatible with experimental data.

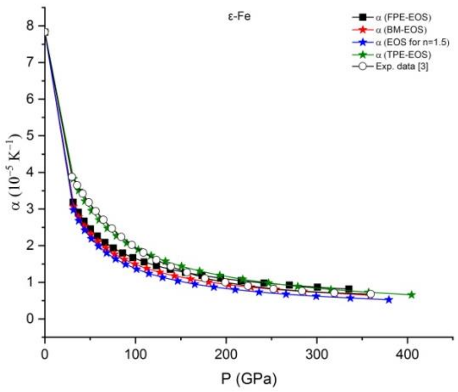

Fig. 3: Pressure dependence of thermal expansivity for hcp-iron (ε-Fe). The figures compare the calculated results and other models (filled symbols) with experimental data (open symbols).

By examining the experimental data [3], the adjustable parameters $a_0, a_1,$ and a_2 for eq. (6) are fitted suitable found 230, 3560, and -2.825 to calculate the Debye temperature. Thus the proposed model of Debye temperature (Eq. (6)) yields the value $\theta_{D0} = 441\ K$ at zero pressure and $T = 300\ K$. The calculated results for Debye temperature (θ_D) as a function of the pressure from newly EOS (Eq. (1) for $n = 1.5$) along with experimental data have been shown in Fig. 4. The results of pressure dependence of the Debye temperature reflect a similar trend as experimental data [3]. The calculated values of θ_D for $K'_{T0} = 5.81$ yield better agreement with experimental data [3] up to the high-pressure limit, while the results for $K'_{T0} = 5.35$ does not agree well.

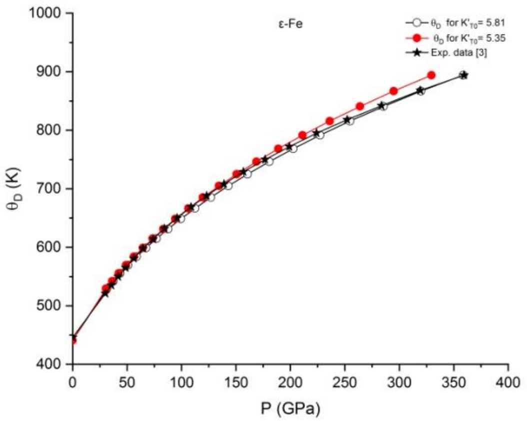

Fig. 4: Pressure dependence of Debye temperature for hcp-iron (ε-Fe). The figures compare the calculated results and other models (filled symbols) with experimental data (open symbols).

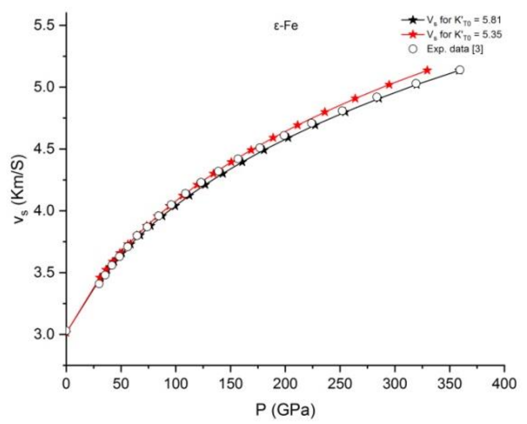

Fig. 5: Pressure dependence of shear Sound velocity for hcp-iron (ε-Fe). The figures compare the calculated results and other models (filled symbols) with experimental data (open symbols).

The results extracted by Eq. (9) for shear sound velocity (v_s) and the pressure from newly EOS (Eq. (1) for $n = 1.5$) dependence of shear sound velocity have been shown in Fig. 5. The shear sound velocity increases with increase of pressure. The results of shear sound velocity for $K'_o = 5.81$ along with experimental data [3] indicates a better agreement while the results for $K'_o = 5.35$ does not agree well with experimental data [3]. An excellent agreement with experimental data explores the validity of present work.

CONCLUSION

The results from proposed EOSs are very satisfactory and agree well with experimental data follow the basic thermodynamic conditions as well as Stacey criteria. The formulation of proposed EOSs is based on the Eulerian finite stain scheme using the nth power of edge length by compression. The proposed EOSs (Eq. (1)) for the value $n = 1.5$ indicate the better agreement with the experimental data [3]. Therefore, we have further studied other parameters isothermal bulk moduli, thermal expansivity, Debye temperature and the shear velocity as function of pressure extracted by newly EOS (Eq. (1) for $n = 1.5$). Although the results for ε-Fe from Equation. (3), (5), (6) and (9) for $K'_o = 5.91$ correspond well with experimental results.

ACKNOWLEDGMENTS

Authors are grateful to Dr. Pushpa Kashyap, Principal, Dr. B. R. Ambedkar Government Degree College, Mainpuri (UP) for facilitating the necessary amenities. S. P. Singh acknowledges the Uttar Pradesh Government grant under *the scheme* '*Research and Development'* for financial support. We are also grateful to the reviewer for his valuable and constructive suggestions which have been very useful in revising the manuscript

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