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Study of Thermodynamic Properties of Monoclinic Sulfur (Sβ) Under High Pressure Using Three Different Equations of State for the Treatment Scabies in Dermatology

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Abstract

Thermodynamic properties of monoclinic β-sulfur S_β under high pressure up to 20 Gpa have been studied, where Orthorhombic α-sulfur S_α changes to S_β at 94.4℃. The high pressure technology used to tackle the crystallization volume of sulfur S_β without changes in the chemical properties. Sulfur S_β can be used after the effect of high pressure in the development of the medicine used to treat scabies. The present study is performed to calculate the effects of high pressure on some important physical properties of the material such as (bulk modulus (B), compression volume ratio (V_P/V_o), Grüneisen parameter(γ), Debye temperature (θ_D) and phonon frequency spectrum (pfs). Three different equations of state EOS's (Birch- Murnaghan EOS, Vinet EOS and modified Lennard-Jones EOS) were implemented to analyze pressure-volume relationship and then combining calculated data with various expressions of volume dependence of the other thermodynamic properties that are; Bulk modulus, Grüneisen parameter, Debye temperature and phonon frequency spectrum. The behavior of any of these concepts were described in different figures. It was found that, relative volume, and Grüneisen parameter were decreased with high pressure, while the other considered parameters; Bulk modulus, Debye temperature and phonon frequency spectrum were expected to increase as a high pressure is applied.

Keywords: *Bulk modulus; volume compression ratio; lattice parameter; phonon frequency spectrum; isothermal equations of state.*

1. Introduction

In the present work, the bulk modulus (B), compression volume (V_P/V_o), lattice constant (a) and phonon frequency spectrum (pfs) of a S_β compound under the influence of high pressure were calculated using the "Birch-Murnaghan and modified Lennard-Jones" EOS. The calculated results have been compared with experimental data, which confirms the validity of the present equations of state. The Grüneisen parameter variation assumption has improved the results of phonon frequency spectrum under compression.

In this study, sulfur will be used to compress to make it smaller than its present in nature, where [1] observed that the materials in small size "Nano scale" can have more useful applications than their bulk counterpart.

Sulfur can be crystallized in some different lattices, the well-known orthorhombic structure of S_α comprising of S_8 rings [2], it is stable under high pressure up to (20-30) Gpa and became gradually amorphous on further compression [3, 4,5]. Recrystallization starts around 37 Gpa and fully completes only at 75 Gpa [6]. The structure of three solid allotropes as:

1.1 Orthorhombic α-Sulfur S_α

S_α is the stable form of Cycloocta-S. [7] has reported very accurate structure parameters. [8] established "the stacking of molecules", (Fig. 1a) show the "crankshaft" structure of this allotrope, is still erroneously assumed by many to contain coaxially stacked rings [7].

Lattice constants are "a = 10.4633 Å, b = 12.8786 Å, and c = 24.4784 Å, and the density is 2.069 g/cm^3 "[9], where its unit cell volume 3299.5 Å^3 [10].

1.2 Monoclinic β- Sulfur S_β

S_β forms at 94.4℃ from S_α [11], its structure determined by Trillat and Forestler [12], the unite cell contain six molecules S_8 i.e., 48 atoms, (Fig.1b), its lattice constant "a=10.778 Å, b=10.844 Å, and c=10.924 Å" [13], and its density is 1.94g/cm^3 [14], about 12% smaller than S_α, and its unit cell volume 1276.41Å^3 [15].

1.3 γ- Monoclinic Sulfur S_γ

The structure has been determined by [16], who confirmed the "sheared penny roll" staking, proposed by De Haan [17] (Fig. 1c). "The lattice constants are: a=8.44 Å, b=13.025Å, c=9.356Å" [16], four S_8 molecules occupy one unite cell and its density 2.19 g/cm^3 (larger than S_α and S_β-sulfur) [16-17].

The purpose of studying (sulfur S_β under high pressure), is for treating humans from some skin diseases specially (Scabies), where we note that its drug contains sulfur 5% for child and 10% for young people [19-20].

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In some cases, the treatment is time-consuming about (5-10) weeks or more. The reason, that sulfur is used in the treatment S_α type, which it has larger size than S_β and therefore does not enter the pores of the skin [21]. using high-pressure technology by three different equations of state to obtain a crystalline volume up to 0.65 of its original size after applying high pressure (about 20Gpa) to reach the skin pores size and grooves size that made by the Scabies germ. By comparing the dimensions of the pores with the grooves made by microscopic skin scabies under the skin, we will be able to make sulfur molecules interfere with skin
pores and then into grooves created by bacteria and then kill them. In addition, the sulfur acts on the adhesion on the eggs completely so that it drowns grooves and thus kills the larvae that are born after (3-5) days.

The human body can be disinfected by treating sulfur S_β under high pressure mixed with petrolatum ointment or Vaseline to be highly viscous [20].

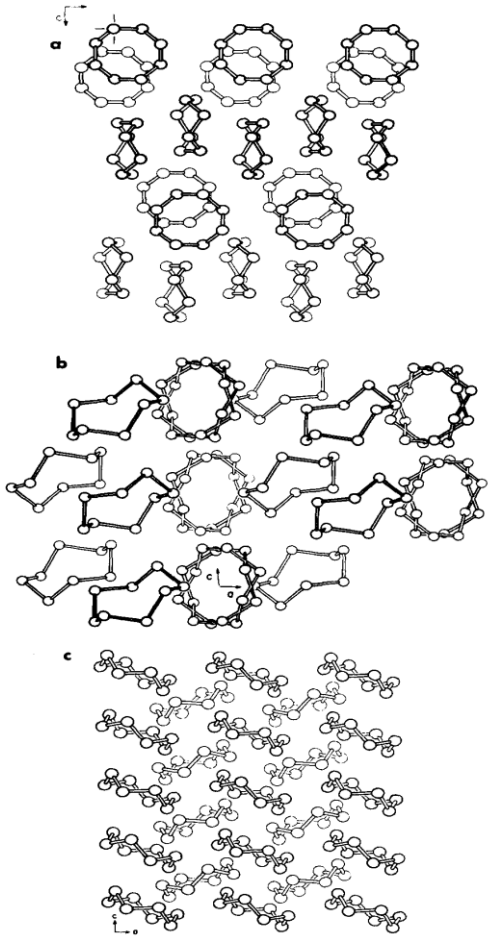

Figure1. The structure of the solid Figure 1 allotropes of Cycloocta S :(a) orthorhombic Sα, (b) monoclinic S_β, and (c) monoclinic S_γ. All views are perpendicular to the ***c*** *axis [17].*

2. Materials and Method of Study

Equation of state as a mathematical tool is used find relationship between fundamental properties of solid phase such as pressure and volume, without requirement of experimental methodology. Several equations of state have been developed to describe the behavior of solid materials under high pressure [22].

2.1. Birch–Murnaghan EOS [23,24]

$$P_{B\text{-}M} = \frac{3B_0}{2}\left(\eta^{-7/3}-\eta^{-5/3}\right)\left(1+\frac{3}{4}\left(B'_0-4\right)\left(\eta^{-2/3}-1\right)\right) \quad (1)$$

Where, $\eta = \frac{V_P}{V_0}$

2.2. Vinet EOS [25]

$$P_{Vinet} = 3B_o\left[\left(\frac{V_P}{V_o}\right)^{-2/3}\left\{1-\left(\frac{V_P}{V_o}\right)^{1/3}\right\}\right] \quad (2)$$
$$\exp\left[\left(\frac{3}{2}\right)\left(B'_o-1\right)\left\{1-\left(\frac{V_P}{V_o}\right)^{1/3}\right\}\right]$$

2.3. Modified Lennard-Jones EOS [26]

$$P_{mL-J} = \frac{B_o}{n}\left(\frac{V_o}{V_P}\right)^n\left[\left(\frac{V_o}{V_P}\right)^n - 1\right] \quad (3)$$

Where B_O: Isothermal bulk modulus at atmospheric pressure
B'_o: First pressure Derivative of bulk modulus
Vo: Volume at ambient condition.
Vp: Volume under high pressure P

$$n = \frac{1}{3}B'_o \quad ; \quad B'_o = \frac{dB}{dp}$$

2.4. Bulk Modulus (*B*)

The Bulk modulus (*B*) relates the fraction change in volume to the change in the applied pressure as [27]:

$$B = -V\left(\frac{dP}{dV}\right)_T \quad (4)$$

On volume derivation of equations (1, 2, 3) and substituting in eq. (4) we can express the bulk modulus at pressure (p) as:

$$B_{B-M} = \frac{3B_o}{2}\left[\left(\frac{7}{3}\right)\eta^{-7/3} - \frac{5}{3}\eta^{-5/3} - \frac{9}{4}\left(B'_o-4\right)\eta^{-3} + \frac{7}{2}\left(B'_o-4\right)\eta^{-7/3} + \frac{5}{4}\left(B'_O-4\right)\eta^{-5/3}\right] \quad (5)$$

$$B_{Vinet} = \left[2B_o\left(\eta^{-2/3}-\eta^{-1/3}\right) + B_o\eta^{-1/3} + \frac{3}{2}B_o\left(B'_o-1\right)\left(\eta^{-1/3}-1\right)\right]$$
$$\exp\left[\left\{\frac{3}{2}\left(B'_o-1\right)\right\}\left(1-\eta^{1/3}\right)\right] \quad (6)$$

$$B_{mL-J} = B_o\left(\frac{V_o}{V}\right)^n\left[2\left(\frac{V_o}{V}\right)^n - 1\right] \quad (7)$$

2.5. First Grüneisen Parameter (γ)

The relation that describe (γ) is given as [28,29]:

$$\gamma_P = \gamma_0\left(\frac{V_P}{V_0}\right)^q \quad (8)$$

Where γ_o: First Grüneisen parameter at atmosphere pressure.
γ_P : First Grüneisen parameter under high pressure (P).

q: Second Grüneisen parameter.
q Has been considered as equal to unity or a constant value [25].

2.6. Debye Temperature (θ_D)

θ_D is a key parameter that determines the thermal transport dynamic properties. [30] Expressed Debye temperature under high pressure as:

$$\theta_{DP} = \theta_{Do}\left(\frac{V_o}{V_P}\right)^{\gamma} \quad (9)$$

θ_{Do}: Debye temperature at atmospheric pressure
θ_{DP}: Debye temperature at pressure (P).

2.7. Phonon Frequency Spectrum (PFS)

$$\upsilon_P = \upsilon_o\left(\frac{V_P}{V_o}\right)^{-\gamma} \quad (10)$$

The physical properties of solids can vary under high pressure, where the frequency of mode densities depend on specific volume eq. (10) [31]. The changes in the distribution function of the frequencies under high pressure expressed by eq. (11) [32].

$$g\left(\upsilon_P, V_P\right) = \left(\frac{V_P}{V_o}\right)^{\gamma} g\left[\upsilon_o\ , V_o\right] \quad (11)$$

υ_o : Frequency at atmospheric pressure

υ_P : Frequency under high pressure (P)

3. Calculations and Results

3.1. Compression Volume V_P/V_0

Table (1) values of bulk modulus (B_o), its derivative (B_o') and first Grüneisen parameter γ for S_β compared with Sα taken from its original references.

Sulfur-type	B_oGpa	B_o'	Ref.	γ	Ref.
Sα	7.692	5.433	[32]	0.54	[33]
Sβ	7.046	5.597	[32]	0.54	[33]

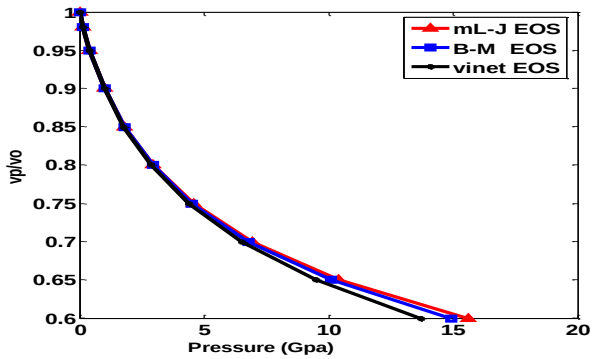

Figure 2. Variation of V_P/V_o for S_β at different values of pressure, using" mL- J, B-M & Vinet" EOSs.

By using data in Table (1) and using equations (1), (2) and (3) we get results for variations of V_P/V_0 with high pressure for S_β which are shown in fig.(1).

3.2. Bulk Modulus

By substituting values of B_o, B_o' for S_β from Table (1) and V_P/V_o rom Fig.(1) in equations (5),(6) and (7), we got the results of bulk modulus (B_{B-M}, B_{mL-J}, and B_{Vinet}) at different value of high pressure, and the results are shown in Fig. (3).

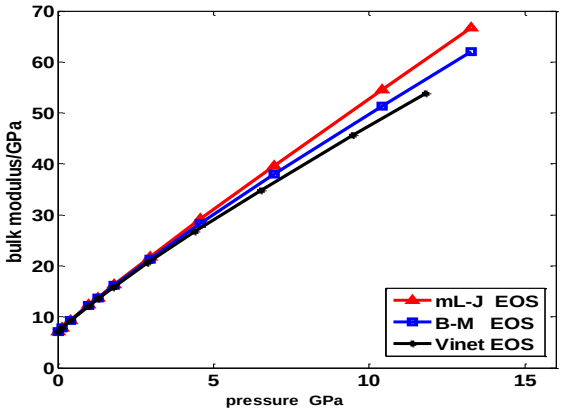

Figure 3. Variation of bulk modulus B_o for S_β at different values of pressure, using "mL- J, B-M & Vinet" EOSs.

3.3. First Grüneisen Parameter

First Grüneisen parameter γ belongs to the most important physical characteristics of crystal lattice dynamics [34]. Where γ is assumed to be volume dependent [35,36].

Fig.(4) show results for variation of (γ_P/γ_0) for sulfur S_β under high pressure using data of V_P/V_0 which is given from three equations (1), (2) and (3) at different value of pressure, and substituting it in eq.(8). Fig.4 shows a slightly reduction in Grüneisen parameter with increasing pressure from nearly 0.55 to just under 0.35.

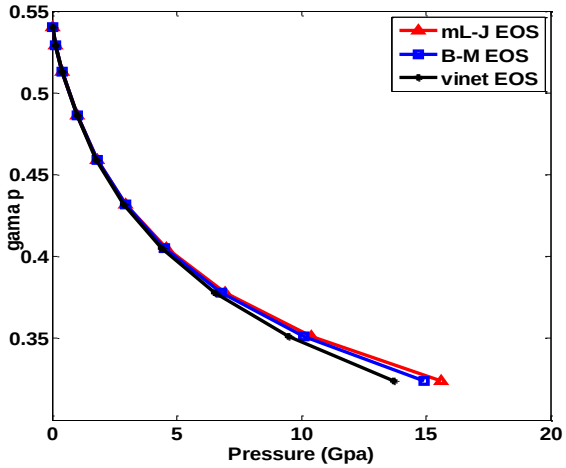

Figure 4. Variation of (γ_P/γ_0) mL- J, B-M & Vinet" EOSs.

3.4. Debye's Temperature

Figure (5) Shows results of variation of $(\theta_{D_P}/\theta_{D_0})$ with high pressure for S_β using equations (1), (2) and (3), when use V_P/V_0 values from Fig. (2) and substituting it in Eq. (9).

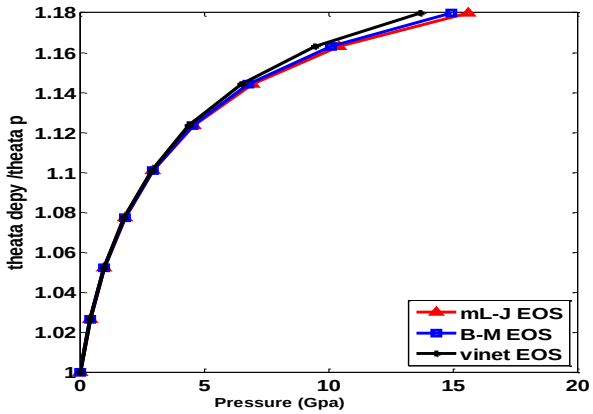

Figure 5. Variation of $(\theta_{D_P}/\theta_{D_0})$ *for* S_β *at different values of pressure, using" m.L-J, B-M & Vinet" EOSs.*

3.5. Phonon Frequency Spectrum (pfs)

In the present work, the change in density of state (DOS) from (pfs) for sulfur is observed as expected by eq. (11). Fig. (6) show calculated pfs from literature [37]. by using values of V_P/V_0 under high pressure from Fig.(1) and compiling in eq.(10) and eq.(11) for the three equations (1), (2) and (3) which give the results of pressure effect on pfs and illustrated in Figs (7, 8 and 9).

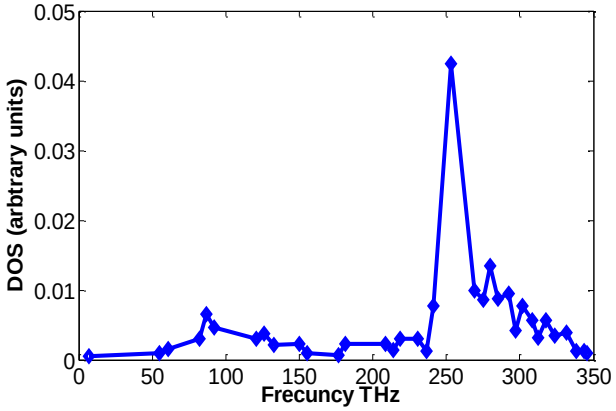

Figure 6. phonon frequency spectrum of S_β *at ambient condition[36].*

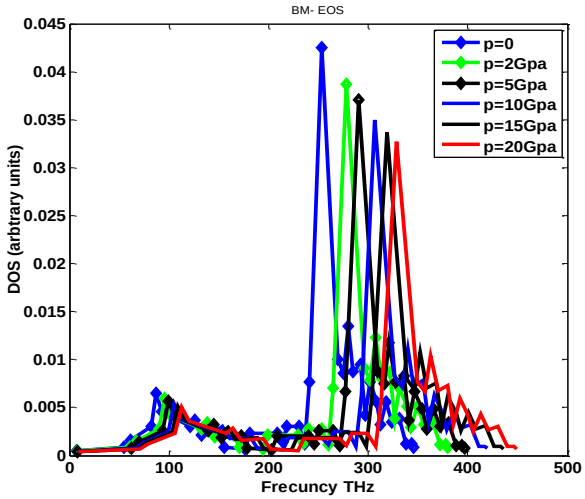

Figure 7. (pfs) for S_β *at different value of high pressure using (B-M EOS).*

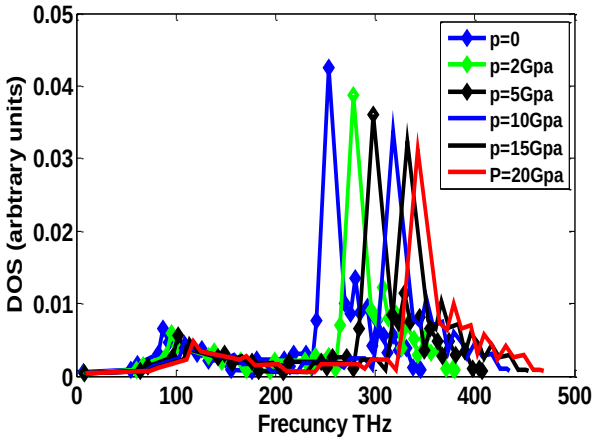

Figure 8. (pfs) for S_β *at different value of high pressure using (mL-J EOS).*

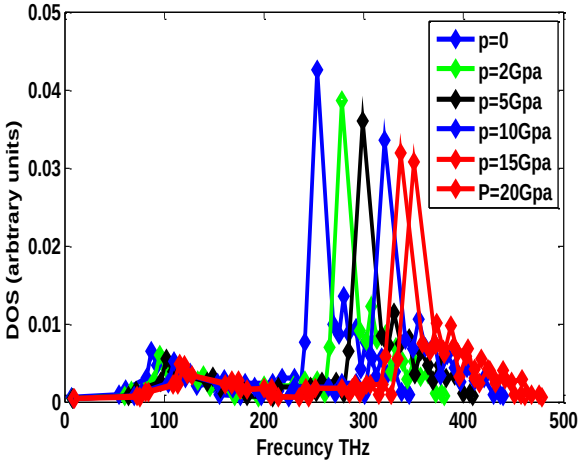

Figure 9. (pfs) for S_β *at different value of high pressure using (Vinet EOS).*

4. Results and Discussions

The aim of this study is to develop a medicine uses to treat the germ of scabies, of which its size is (0.25mm), and lives under the skin, we advise international pharmaceutical companies to use S_β treated under high pressure, less than "20Gpa" mixtures of Vaseline instead of S_α, by comparing volume under high pressure for S_β with germs size and grooves size that germs make, we found that S_β molecules are able to get into the grooves through skin pores (50μm) and thus killing larvae when the eggs are hatching, unlike S_α that remains on the surface of the skin and does not enter the grooves because of its large size compared to S_β. To establish this purpose, the present work reviewed some important physical properties of sulfur S_β have been studied under the effect of high pressure. Using three equations of state, its relative volume was observed under high pressure reaching 0.65 of its original size at pressures between (9 -11) GPa. Implementing the mathematical equations (1-11), the most important physical properties of sulfur were analyzed under high pressure up to 20 Gpa. The results were obtained and shown in Figures (1-8). The results in figs. 4-5 show an increasing trend for both bulk modulus and Debye temperature with increasing pressure. In fig. 5, it is noted that at lower pressure there is a more dramatic increase in Debye temperature, while as the pressure is increased more and more, the Debye temperature curve shifts up slowly, this can be attributed as a result of electrical repulsive force between adjacent atoms and molecules. On the other hand, the

Grüneisen parameter and phonon density of state decreased with the application of high pressure. Regarding to the volume of S_β particles, high pressure up to 16Gpa results in a dramatic change. Therefore, the present characteristics under strong compression results in only slight changes in other properties, with no change in chemical properties. All the studied properties gave excellent results for two equations (B-M EOS and mL-J EOS) more than (Vinet EOS), but when we study the (pfs), equations (Vinet EOS and mL-J EOS) give better results than (B-M EOS).

5. Conclusion

High pressure effects on some vital thermo-elastic properties of sulfur S_β material are analyzed such as relative volume, Grüneisen parameter, bulk modulus and phonon frequency spectrum. We have used some EOSs to derive formula for bulk modulus dependence on high pressure as given in Eqs. 5-7. Results in figs. 6-8 illustrate shifts in the energy of the modes (states) that high pressure causes exciting many new modes of vibration.

Nomenclature

V_P/V_0	Volume compression ratio
V_0	Volume at ambient condition
V_P	Volume under high pressure
EOS	Equation of state
$P_{B\text{-}M}$ EOS	Birch–Murnaghan equation of state
$P_{mL\text{-}J}$ EOS	Modified Lennard-Jones equation of state
γ_o	First Grüneisen parameter
γ_P	Grüneisen parameter under pressure
B_o	Bulk modulus
υ_o	Frequency under ambient condition
υ_P	Frequency under high pressure
θ_{Do}	Debye temperature at atmospheric pressure
θ_{DP}	Debye temperature under high pressure

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