Study Of Equation of State for Some Ionic Crystals

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Abstract: - An equation of state (EOS) is a fundamental framework in thermodynamics that expresses the relationship between the key thermodynamic variables that describe a system, such as pressure, volume, and temperature. We are utilizing an isothermal equation of state (EOS) to investigate the correlation between pressure (P) and volume compression under a specific temperature and also employed to examine the isothermal bulk modulus (B_T) and its pressure derivatives (B_T') and Gruneisen Parameter. This study delves into the analysis of the equation of state applied to an ionic crystal. In the present paper we have used 3 different, (I) Birch – Murnaghan EOS, (II) Vinet – Rydberg EOS, and (III) Brennan – Stacey EOS for Na-Cl which are Sodium Halide of ionic crystals. The comparison reveals that the all EOS yield very similar results.

Key Words: — ***Equation of state (EOS), Ionic crystals, Sodium Halides, Isothermal Bulk Modulus, Pressure derivatives of Isothermal Bulk Modulus.***

I. Introduction

Any crystallized solid's atoms are organized in a certain pattern, and the regularity of the surface matches the symmetry of the inside.[1] They have special physical and chemical characteristics due to their highly organized atomic or molecular structure. Crystals can be found in salts, minerals, gems, and even inorganic compounds, to mention a few.[2][3]
Ionically arranged ions in a lattice that is kept together by the electrostatic force of attraction make up ionic crystals, which are organic compounds or solids that are crystallized. Ions are these crystals' structural building blocks. Alternating positive and negative ions are found in equal amounts across the crystal lattice in such crystals.[3]
Positively charged sodium ions are drawn to negatively charged chloride ions, and vice versa, resulting in the formation of ionic bonds. Similar effect is shown in other alkali halides of crystals like NaBr, KBr, NaI etc. The 6:6 co-ordination of sodium chloride (NaCl) is unique. The intense interactions between the ions are reflected in the characteristics of NaCl, NaBr.

Manuscript revised August 11, 2023; accepted August 12, 2023. Date of publication August 13, 2023.

This paper available online at www.ijprse.com

ISSN (Online): 2582-7898; SJIF: 5.59

The strength of the interatomic forces in a solid substance determines its robustness and flexibility. As a result, putting a substance to pressure, which affects the space between its atoms, causes changes in its basic physical properties. This relationship between pressure and volume is known as the Equation of State, and it provides vital insights into understanding the material's particular physical properties.[4]
The size and magnitude of the charges on the ions that make up the lattice, which defines the physical characteristics of the crystal, have a significant impact on the strength of the attractive forces and the arrangement of ions inside the crystal. Positively charged ions (cations) and negatively charged ions (anions) bonded together by strong electrostatic forces form ionic crystals, a kind of crystalline substance.
A basic theoretical framework is constructed to examine how solids respond under high pressure conditions. This model is then utilized to calculate the pressure exerted on NaCl when subjected to significant compression. Additionally, the study compares the outcomes of this model with the Birch-Murnaghan, Vinet-Rydberg, and Brennan-Stacey equations of state (EOSs). The findings reveal that, in terms of the high-pressure compression behavior of NaCl, the current theoretical model and EOSs yield results that align with experimental data.

II. Method of Analysis

For the comparative study we have used three equations of states in the present paper as follows:

2.1 Birch-Murnaghan EOS

We have used third order (3rd- order) of Birch Murnaghan equation of state which has been derived using finite strain theory [5]

$$P = \frac{3}{2}K_0\left[x^{-7} - x^{-5}\right]\left[1 + \frac{3}{4}\left(K_0' - 4\right)\left(x^{-2} - 4\right)\right]$$

Where, $x = (V/V_o)^{1/3}$

This equation is a Birch – Murnaghan EOS

2.2 Vinet-Rydberg EOS

We have used Vinet-Rydberg EOS based on the universal relationship between binding energy and inter atomic separation for solids. [6][7]

$$P = 3K_0x^{-2}(1-x)\exp[\eta(1-x)]$$

Where, $x = (V/V_o)^{1/3}$ and and $n = 3/2(K_0'-1)$ [8][9]

The above Equation is a Vinet-Rydberg EOS

2.3 Brenan-Stacey EOS

We have used brennan stacey EOS which is derived using thermodynamic formulation for Grüneisen parameter. [10][11]

$$P = \frac{3K_0x^{-4}}{(3K_0' - 5)}\left[\exp\left\{\frac{(3K_0' - 5)(1 - x^3)}{3}\right\} - 1\right]$$

Where, $x = (V/V_0)^{1/3}$

This Equation is Known as Brennan-Stacey EOS[12]

Where V is the volume at pressure P and V0 is the volume at zero pressure, K0 is isothermal bulk modulus at zero pressure and K0 ’ first pressure derivative of isothermal bulk modulus at zero pressure

Here, K_T is the isothermal bulk modulus which is calculated by using this formula:

$K_T = -V(\partial P/\partial V)_T$

And K_T’ is the first order pressure derivative of bulk modulus can be calculated by the formula:

$K_T' = (\partial K_T/\partial P)_T$

The value of Grüneisen parameter (γ) can be calculated by using the formula given by Borton and Stacey [13]

$$\gamma = \frac{\left(\frac{1}{2}\right)K' - \frac{1}{6} - \frac{f}{3}\left[1 - \frac{1}{3}\left(\frac{P}{K_T}\right)\right]}{1 - \left(\frac{4}{3}\right)\left(\frac{P}{K_T}\right)}$$

Where, f = 2.35

III. Result and Analysis

Understanding an ionic crystal's thermodynamic characteristics, phase transitions, and mechanical behavior all depend critically on its equation of state.

In the following paper for the purpose of calculating pressure(P), isothermal bulk modulus (K_T), first pressure derivative of isothermal bulk modulus (K_T'), and grüneisen parameter at various values, we have described the work and graph comparison of all three equations of state, namely Birch-Murnaghan EOS,Vinet Rydberg EOS and Brennan Stacey EOS from equations stated above.

Table.1. The input values for NaCl and NaI are shown in

Material	Ko (GPa)	Ko’	References
NaCl	24.0	5.39	[14]

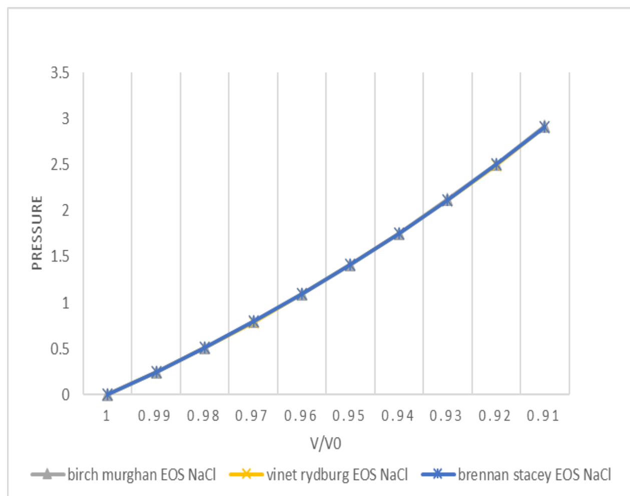

Fig.1. Graph between Pressure(P)versus Compression(V/V_o) For Nacl

From Figure. 1 it is clear that on increasing pressure(P), the value of compression(V/V0) increasing for. Alkali Halides of ionic material Na-Cl, all the three EOS corresponds well with each other and co-incident at every point upto compression range ($V/V_0 = 0.91$) at pressure (14Gpa)

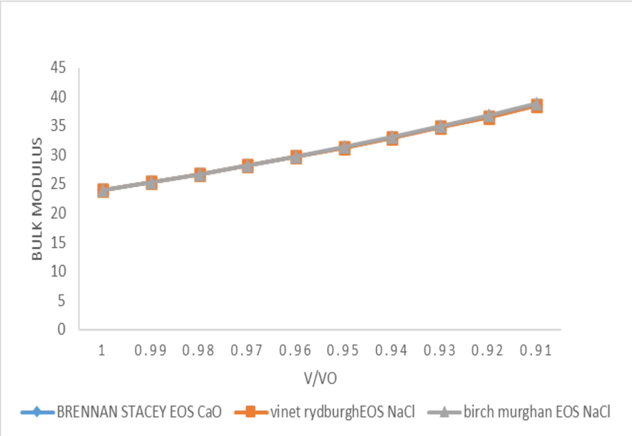

Fig.2. Graph for isothermal bulk modulus (B_T)versus compression(V/V_o) for NaCl

Studying From Figure. 2 it is clear that on increasing bulk modulus (K_T), the value of compression(V/V0) increases for. alkali halide of ionic material NaCl, all the three EOSs corresponds well with each other and co-incident at every point upto compression range (V/V_0 = 0.91) at upto pressure (40Gp)[15]

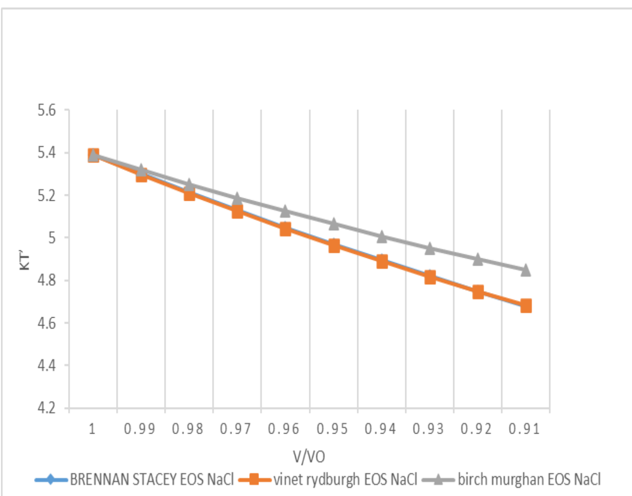

Fig.3. Graph For First Pressure Derivative of Isothermal Bulk Modulus (K_T') Versus Compression(V/V_o) For Nacl

Now studying Figure 3 it is clear that on decreasing the first pressure derivative of isothermal bulk modulus, the value of compression increases for NaCl. Further here the Brennan-Stacey EOS and VinetRydberg EOS corresponds well with each other but the BirchMurnaghan EOS starts deviating below compression range V/V0=0.99 at first pressure derivative of isothermal bulk modulus 5.32 with other two EOS.

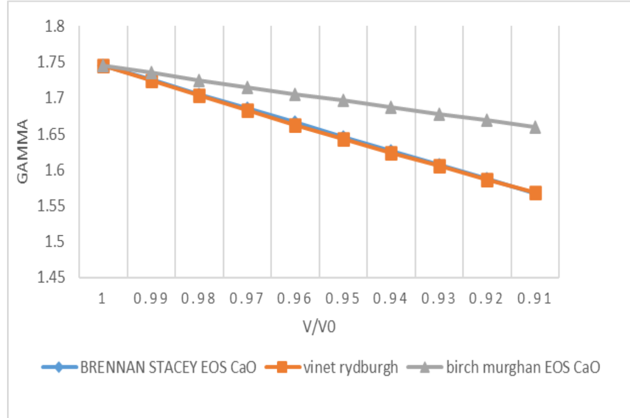

Fig.4. Graph for grüneisen parameter versus compression(V/V_o) for NaCl

Lastly the graph between grüneisen parameter and compression is plotted, here studying Figure 4 it is clear that on decreasing the grüneisen parameter the value of compression increases for NaCl. Further here the Brennan-Stacey EOS and VinetRydberg EOS corresponds well with each other but the BirchMurnaghan EOS starts deviating below compression range V/V0=0.99 at value 1.73 for grüneisen parameter with other two EOS.[16]

IV. Conclusion

Thus, studying all three graphs we can conclude that at various compression ratios (V/V0), all three EOSs produce pressure that is very comparable, and almost 3 GPa of pressure is required to compress the material to 90% of its starting value.
Additionally, whereas the pressure derivative of the bulk modulus drops as compression rises, the bulk modulus grows constantly.
Also, it evaluates that on decreasing the Gruneisen parameter, the value of compression increases for high-temperature superconductors [17].

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