STUDY OF THERMOPHYSICAL PROPERTIES OF DIFFERENT CLASS OF SOLIDS UNDER HIGH PRESSURE AND HIGH TEMPERATURE

THESIS

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By

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Dedicated to
My Heart (Mother),
My Soul (Father)
And
My Inspiration (Advisor)

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Emotion cannot be adequately expressed in words, because then, emotions are transformed into merely formality, and formalities have to be completed. Acknowledgement in its true essence gives us an opportunity to remember and express our feeling for those whom we have and revere. When going get tough and tougher, the helping hands offered by all nearer and dear is always remembered with gratitude. Words may not be enough to express such feeling yet these lines are without any exaggeration, my expression of feeling.

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CERTIFICATE

This is to certify that the thesis entitled **"STUDY OF THERMOPHYSICAL PROPERTIES OF DIFFERENT CLASS OF SOLIDS UNDER HIGH PRESSURE AND HIGH TEMPERATURE"**, submitted in partial fulfillment of the requirements of the degree of the **Doctor of Philosophy** with major in **Physics** of the college of post graduate studies, G.B.Pant University of Agriculture and Technology, Pantnagar, is a record of bona fide research carried out by **Mr Kamal Devlal, Id.No. 27753,** under my supervision, and no part of the thesis has been submitted for any other degree or diploma.

The assistance and help received during the course of this investigation have been acknowledged.

Pantnagar
March 2005

(B.R.K.Gupta)
Chairman
Advisory Committee

CERTIFICATE

We, the undersigned, members of the Advisory Committee of **Mr Kamal Devlal, Id.No. 27753,** a candidate for the degree of **Doctor of Philosophy** with major in Physics, agree that the thesis entitled **"STUDY OF THERMOPHYSICAL PROPERTIES OF DIFFERENT CLASS OF SOLIDS UNDER HIGH PRESSURE AND HIGH TEMPERATURE",** may be submitted in fulfillment of the requirements for the degree.

(B.R.K.Gupta)
Chairman
Advisory Committee

(H.M.Agrawal)
Member

(Ajay)
Member

(M. C. Joshi)
Member

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Introduction

"Get good council before you begin
when you have decided out promptly"

CHAPTER 1 INTRODUCTION

Condensed matter physics is the branch of physics, which deal with solids consisting of atoms, ions or molecules very close together. Much of the physical world around us, and a large part of modern technology are based on the various solid materials. So it is interesting to study the behavior and thermophysical properties of different class of solids. In present work equations of state (EOS) are applied to study the thermophysical properties of three different classes of solids (i.e. inert gas solids, semiconductor and metals). The EOS is basically a pressure – volume – temperature relationship. The studies based on EOS are widely important not only in physics but also in chemistry and geophysics. The theoretical studies of EOS at high pressure and high temperature are of fundamental interest as they permit interpolation and extrapolation into the region in which the experimental data are sparse.

The present work describes the theoretical study of thermophysical properties especially compression, thermal expansion, bulk modulus, thermal expansion coefficient of different solids. The relation between pressure (P) and volume (V) at a constant temperature (T) is known as isothermal EOS while the relation between volume (V) and temperature (T) at fixed pressure is known as isobaric EOS. By applying the concept of thermal pressure we will derive some new isothermal EOS and isobaric EOS. A lot of EOSs are available in literature. In present study a comparative study of different EOSs and their modified forms are applied in three classes of solids viz. inert gas solids (Ne, Ar, Kr, Xe), semiconductors (Ge, Si, $FeSi_2$, SiC, SnS, MoN, MoN_2, AlN, GaN,) and metals (Mo, W, Ta, Os). Apart from these classes of solids we have also employed the EOS in FeSi and TiO_2 crystals, which are found into earth's core and lower mantle respectively and very important from earth and planetary science point of view. Brief information about these solids is presented in this chapter.

1.1. Inert Gas Solids

The inert gas solids (IGS) or Rare gas solids (RGS), neon, argon, krypton and xenon have been used as model substances for lattice dynamic calculations of thermodynamic properties.

These crystals are transparent, insulators, weakly bonded with very low melting points. Since the RGS have closed electronic shells unlike other solids, their thermodynamic properties such as bonding, thermal expansion, compression bulk modulus, thermal expansion coefficient, and heat capacity are entirely different than other class of solids (metals, semiconductors etc.). The crystal structure of these solids is fcc (**Kittel, 1995**). The combination of long range Van der Waal's attractive interaction (induced by dipole-dipole interaction) and short-range repulsive interaction (arises due to overlapping of charge distribution) gives the total energy of two atoms. The potential is well known Linnard- Jones potential (**Gupta, 1996**). Most of the theoretical calculations of RGS are based on the Linnard-Jones potential model. But in the present study a thermodynamic approach is used to calculate compression, expansion, bulk modulus etc. The detail descriptions of EOS are given in chapter 4. The major objective of theoretical calculation on the inert gas solids is to test the applicability of high-pressure and temperature equation of state upto their melting points on these solids.

Table 1.1: Some properties of inert gas solids at room temperature and zero pressure. (Kittel, 1996; Lee, 1996).

Inert Gas Solids	Cohesive Energy (KJ / Mole)	Melting points (K)	Structure
Ne	1.88	24	fcc
Ar	7.74	84	fcc
Kr	11.2	117	fcc
Xe	16.0	161	fcc

It can be noted from the table that these solids exist at very low temperature. Below the room temperature most of EOS fail to explain the bulk modulus, compression, and thermal expansion of these solids, however some equations of state i.e. Tait EOS (**Freund et al., 1989**), Singh-Gupta EOS (**Singh et al., 2003**) explain these properties satisfactorily. Since helium exists in liquid form we have not considered it in our present study of work.

1.2. Semiconductors

Semiconductors are materials whose electrical properties are intermediate between those of metals and insulators. The intermediate properties of these materials are determined by crystal structure and electronic energy bands. A lot of work has been done in the area of their electronic properties but not well understood about the thermophysical properties of these materials. In present work the thermophysical properties of some semiconductor materials (Ge, Si, $FeSi_2$, SnS, SiC, AlN, GaN, MoN, MoN_2) are investigated by using EOS models under high pressure and high temperature. The thermophysical properties of semiconductors are important not only from earth interior point of view but also from technological aspect. The brief introduction and importance of these materials are discussed below:

Germanium (Ge) is used mainly for making transistors and other semiconductor devices. It is transparent to infrared light and is therefore also used for making prism, lenses and window of infrared spectrometers and other scientific apparatus. The different structure phases of germanium are Ge I (Cubic diamond) and GeII (β Sn). The structures of Ge in different phase are discussed by Crain, A. D. Cicco and Qudri (**Cicco et al., 2003; Crain et al., 1995; Qadri, et al., 1983**).

Silicon (Si) is shinely blue–gray coloured and has almost metal like lusture. Electronic industry required a small quantity of pure silicon; most of silicon is used in iron industry. They are used as transistor and semiconductor device like computer chips. The structure of Si also exists in different phase i. e. diamond, β-Sn, BC8 and many others. (**Crain et al., 1995, Sze, 1983**)

Iron disilicide ($FeSi_2$) is an important semiconductor because of its wide applicability for optical devices like optical fibre communications. This material is also known as ecologically friendly semiconductor (**Makita, 1999; Mori et al., 2003**).

Silicon carbide SiC is very hard, chemically inert and dark purple coloured solid. SiC has a three dimensional structure of Si and C atoms and each atom tetrahedrally surrounded by four of other kind. There are a large number of different forms based on the diamond or wurtzite structure. The SiC has a number of structural phases at different pressures. At ambient conditions SiC can form in many different crystallographic modifications that originate from differences in the stacking sequences of Si-C pair lair. SiC undergoes a phase transition with a volume drop 20.3% from zinc-blende (B3) to rock salt around 100 GPa **(Yosida et al.,**

1993; Durandudru, 2004). It has wide potential for both structural and electronic applications suitable at high-pressure range (**Talwar, 2003**).

Tin sulfide (SnS) group IV-VI semiconductor, which is a promising material for optoelectronic devices. SnS crystallize in space group in the GeS (B16) type structure with lattice parameter a=11.200A, b= 3.987A and c= 4.334A (**Shalvoy et al., 1977; Trbojevic et al., 1981**). A structure phase transition from orthorhombic SnS to monoclinic SnS was observed at 18.15 GPa.

MoN and MoN_2 are members of transition metal carbide and nitride. These solids are characterized by high strength, high hardness with large value of cohesive energy. These materials are expected to highly incompressible. Transition metal nitride have structures that are based upon a hexagonal or cubic sublattice formed by the metal atom with interstitial sites that are fully or partially occupied by N atoms. Soignard Emmanuel described about its structure in detail (**Soignard et al., 2003**).

Similarly GaN and AlN are the semiconductor of III-V group. Group III nitrides AlN, GaN and InN are currently actively investigated in view of their promising potential for short wavelength electroluminescence devices (**Nakamura, 1997**). Despite the rapid progress of nitride uses in electronic devices, there is not much exploratory work in the field of thermal analysis (structural and thermodynamic characteristics) of these semiconductors. The GaN and AlN have been demonstrated as cubic zinc blende structure (**Brandt et al., 1995; Okumura et al., 1998**).

1.3. Metals

Metals can be considered to have a large number of free electrons called electron gas. This electron gas can be influenced and moved in magnetic and electric fields. The important anharmonic property of metal is the compression and thermal expansion. According to harmonic approximation the lattice vibrations leads to information such as no thermal expansion; the elastic constants are independent of pressure and temperature but in real sense none of above properties is satisfied perfectly. In the present work we have selected some d- block metals (Mo, W, Ta, Os) of periodic table, where a very few study has been explored. Some important properties of these metals are shown in Table 1.2.

Table 1.2: Some properties of metals at room temperature and zero pressure (Kittel, 1996; Lee, 1996).

Metals	Cohesive energy KJ / Mole	Melting points K	Structure
Mo	658	2895	bcc
W	859	3695	bcc
Ta	782	3293	bcc
Os	788	3306	hcp

Molybdenum (Mo) and tungsten (W) are very high melting point metals. Both Mo and W are alloyed with steel, gives very hard alloys, which are used to making steel. These alloys are used to make machine tools. Mo is also used as a catalyst in petrochemical industry. Tungsten is used to make tungsten carbide (extremely hard and used to make tip of drill machine) and filament of electric light lamps.

Tantalum (Ta) is a very important metal, which is used to make the capacitors for the electronic industry. Because human body does not reject it, thus it is valuable for making metal plates, screws and wire for repairing badly fractured bones. Tantalum carbide (TaC) is one of the highest melting point (4273^0 K) solid known. Osmium (Os) is also heavy transition metal located at middle of the periodic table. It has also highest density, large bulk modulus.

Rutile (TiO_2) and iron monosilide (FeSi) are two interesting solids for earth and planetary sciences. TiO_2 has an interesting properties of being a crystallographic analog of stishovite SiO_2, a significant high-pressure quartz phase in the Earth's lower mantle. The structure and thermophysical behavior of rutile at several P and T conditions is a subject of interest now a day. FeSi is also another important alloying solid for Earth and planetary sciences, which arises from the possibility that silicon might be an alloying element in the Earth's core. By using our modified EOS we will also explain thermophysical properties especially thermal expansion of these two solids (TiO_2 and FeSi).

Thus we are covering all main classes of solid from very weakly bonded inert gas solid to extremely hard solid to check the applicability of different EOSs. The Tait's and Murnaghan's EOS for compression and bulk modulus are the basic equation of state in literature (**Murnaghan, 1944; Freund et al., 1989**). Afterward a lot of EOS which involves the different approximations regarding the variation of bulk modulus B_T thermal expansion α, Anderson Gurneisen parameter δ_T and other related parameters with pressure and temperature are established. The widely used EOSs are Vinet EOS, Birch EOS (**Vinet et al., 1987; 1999; Gaurav et al., 2002**).

Recently Singh and Gupta (**Singh et al., 2003**) proposed a new integral form of equation of state which is based on the temperature dependence of δ_T. This equation describes the temperature dependence of thermal expansion and bulk modulus (B_T). In present work these equations are applied in inert gas solids first time. Also Tait's EOS and Murnaghan's EOS are used to study the compression and pressure dependence of bulk modulus of different class of solids. One step ahead in present work, these EOSs are modified by applying concept of thermal pressure. The modified new equations are temperature dependent however, the original equations are pressure dependent. The detail descriptions of modified EOSs are given in chapters 5.

The present thesis is divided in six chapters. The first chapter deals with the brief introduction about our study, materials (inert gas solids, semiconductors and metals) under investigations and EOSs. The review of literature is given in chapter two in which a critical survey of different equations of state and materials is given. In third chapter all main EOSs available in literature is collected. The fourth chapter deals with the mathematical formulism of some equation of states. The fifth chapter contains the results obtained by us and their comparison with available experimental data is shown. The results achieved in the present study are also well discussed.

Review of Literature

"The past can not be change
But future is yet in your power"

C. R. Tilford et al. [**Tilford et al., 1971**] studied the thermal expansion of solid Argon, Krypton and Xenon about 1K. In their experiment they applied three thermal capacitance techniques for measuring the thermal expansion. Thermal expansion data were obtained by taking simultaneous temperature and capacitance readings at a series of fixed temperature in a manner, which is very analogous to the heat pulse method in calorimeter.

M. S. Anderson et al. [**Anderson et al., 1975**] predicted an experimental equation of state for the inert gas solids. They determined the piston displacement equation for the inert gas solids Argon, Krypton and Xenon from reference temperature to the triple point. The predicted paper describe the thermal expansion in three heavier solid Argon, Krypton and Xenon, and indicate consistency between these results and other low-pressure experiment at all temperature below melting point.

S. B. Qadri et al. [**Qadri et al., 1983**] studied pressure induced phase transition in germanium (Ge). They reported that on increasing pressure at room temperature Ge transforms from its normal phase (diamond cubic phase Ge I) to tetragonal β – Sn phase (Ge II); on the releasing of pressure either a body centered tetragonal phase (Ge IV) or a body centered cubic phase (Ge IV) can be recovered. Depending on pressure and temperature conditions, the latter phase apparently requiring the high pressures. They also studied compressibility of Ge I phase.

P. Vinet et al. [**Vinet et al., 1986**] discovered a universal form of equation of state for pressure as well as a function of volume for all classes of solids in compression. They explained that in compression, wavefuntion overlap effects are significant for all classes of solids. Ionic and rare gas solids have been treated via overlap of atomic electronic densities; exchange and correlation energies had been computed in a local density electron approximation with some success. In 1987 [**Vinet et al., 1987**] they also reported an isothermal equation of state for solids in compression with a simple universal form. The various classes of solids (covalent, metallic, ionic and rare gas) can be distinguishable by their different types of interatomic separations. A general zero temperature EOS reported by Rose, et al. [**Rose et al., 1984**] which describes well the compression of metals in absence of phase transition. The EOS was derived from the cohesive energy, which was found essentially to depend exponentially on the EOS against high-pressure data from all class of solids within the experimental pressure range.

J. Freund et al. [**Freund et al., 1989**] described the isothermal inverted form of equations of state for compression (V/Vo) and bulk modulus (B). They found that total number of seven such equation in the literature i. e. Bridgman, Murnaghan, Tait, Borelius, Hayward, Schmidt, and, Huang and chow EOSs. [**Bridgman, 1952; Murnaghan, 1944; Hayward, 1967; Borelius, 1958; Schmidt, 1983; Huang et al., 1974**]. They applied all EOS to shock wave compression data of some basic solids viz. Li, Na, K, Ca, In, Pb, LiC ranging from zero to variable maximum pressure.

R. S. Hisxon et al. [**Hixson et al., 1992**] obtained new high-pressure shock wave data for molybdenum and tungsten. Data obtained by them had combined with previous data sets for those materials to extend the study by using two-stage light gas facility at Los Alamos National Laboratory Mexico.

In 1995 L. M. Thomas et al. [**Thomas et al., 1995**] studied a comparative study of NaCl by using different EOS. They showed the pressure dependence of bulk modulus and compression by various EOS and reported in literature. They compared the results with the corresponding values obtained by using interionic potential as well as experimental data. Values of bulk modulus as a function of pressure were also calculated. This work gives an idea about applicability of different EOS as available in literature.

J. Crain et al. [**Crain et al., 1995**] reported a detail study of germanium (Ge) and silicon (Si) semiconductors by the application and removal of high pressure. They showed the different phases of these semiconductors observed at different pressures, and crystallographic details of the BC8 and ST12 crystals structure. Kasper and Richards [**Kasper et al., 1963**] obtained the diffraction pattern of silicon which has been decompressurized from the metallic β – Sn phase. They will able to index their diffraction peaks on a body centered cubic unit cell have a lattice parameter a=6.636A. On the basis of density they suggested that there were 16 atoms per body centered cell and eight per primitive cell. This phase of silicon is referred as BC8 (body centered with eight atoms per primitive cell).

Feng et al. [**Feng, 1996; 1998**] have reported shock wave measurements to the strength and inelastic deformation of the crystalline SiC. X Ray diffraction (XRD) technique in conjugate with the diamond anvil cell have been used more extremely by several investigations to conduct pressure volume equation of state measurements on the different polytypes.

K. Karch et al. [**Karch et al., 1997**] performed the first principle calculations of structure and lattice dynamic properties of cubic GaN. They also discussed the detail about compression and bulk modulus and first pressure derivative at zero reference pressure obtained by different method of calculations as well as experiment.

J. M. Wagner [**Wagner et al., 2000**] presented the structural and lattice dynamical properties of wurtzite structure of GaN and AlN under hydrostatic pressure. They reported that the group III-V semiconductors are actively useful for electroluminecence devices. They calculate the compression at different pressure by density function theory and compared the results with experimental data.

M. Taravillo et al. [**Taravillo et al., 2002**] discussed a general method to include temperature effect into the equations of state of different solids. They predicted the pressure and temperature dependencies of the thermodynamic properties for a verity of solids viz. NaCl, LiF, KCl, Li, K ,Rb, Cs Al, Fe, Cu, Pt, Au and Pb. They reported pseudo-spinodal isothermal EOS, which express the bulk modulus as a power law characterized divergence pressure along the pseudo spinodal curve (PSC). This model was successfully applied to the general pressure behavior of dense matters. And a second model was subsequently derived to predict the temperature dependence of the thermodynamic properties at zero pressure.

S. Gaurav [**Gaurav et al., 2002**] has shown clearly that the Vinet equation of state (EOS) widely used in recent literature is not a new EOS. They have considered several EOSs to study the behavior of six solids viz. Ne, Ar, Cu, Al, LiH and MgO unto high compression. They found that the logarithmic EOS proposed by Poirier and Tarantola [**Poirier and Tarantola, 1998**] yield results, which are not consistent with the results, obtained from other equation of state for most of solids under study. Values of pressure (P), isothermal bulk modulus were calculated for the solids at different compressions had been to investigate the validity of various EOS.

L.Vocadlo [**Vocadlo et al., 2002**] determined the thermal expansion and cryatal structure of iron monosilicide (FeSi) by neutron diffraction between a temperature range from 4 K to 1173 K. They found that the average thermal expansion coefficient about room temperature was 4.85×10^{-5} K^{-1}. They also reported that the crystal structure to be found almost invariant with temperature. They determined the value of V_0 = $89.596A^3$, bulk modulus B_0 = 166.42 GPa, first pressure derivative of bulk modulus B_0' = 4.4. The electric and magnetic properties this material have a number of interesting and unusual features including the possibility of electric and magnetic transformation at very low temperature [**Paschen et al., 1997; Sluchnko et al., 1998**].

A. D. Cicco et al. [**Cicco et al., 2003**] investigate the high pressure and high temperature phase of Ge. They reported that the behavior of tetrahedral semiconductors under pressure and in particular that of germanium, has been found to be more complex than that expected due to the presence of several different polymorphs occurring usually upon decompression. The common phase of germanium are Ge I phase (cubic phase with β- Sn structure), Ge II (β- Sn with metallic phase) and Ge III (ST 12high pressure metallic phase). They reported the volume compression at different pressure for all three phase of Ge and bulk modulus, its pressure derivatives. More over no high temperature data for Ge solid stable and metastable phase under pressure are presently available in literature.

S. Q. Wang et al. [**Wang et al., 2003**] studied the first principle method on the lonsdaleite (hexagonal phase) of C, Si and Ge by using plane wave pseudopotential calculations in the scheme of density function theory and the local density approximation. Their results showed that the bulk moduli are quite similar between the diamond and lonsdaleite polytype of these elements. They reported the bulk modulus of lonsdaleite is higher than diamond. It was expected to replace diamond as the hardest material in the world. Their results also showed lansdaleite Ge as semimetal for its zero band gap at its triple point.

S. S. Kushwah et al. [**Kushwah et al., 2003**] calculated the volume of molybdenum and tungsten simultaneous changing pressure and temperature by using Shanker and Kushwah formulism. They obtained the results upto 300 GPa and upto 7000K. They reported that Shanker and Kushwah EOS is suitable approach for the materials for which B_0' are less than 4. However a heavy computational work is involved in the method followed by these workers.

Emmanuel Soignard et al. [**Soignard et al., 2003**] reported the compressibility of hexagonal phase of MoN that is a well-known hard material. They measured bulk modulus as B_0 = 345 GPa and B_0' =3.5. They also reported the cubic B1 structure MoN_2 phase that has a lower bulk modulus B_0 = 301 GPa and B_0' =4. The MoN and MoN_2 is expected as a highly incompressible. They described that the molybdenum nitride atom arranged in a fcc lattice and unto 50% of octahedral interstitials are filled with N atom. The MoN phase contains MoN atom arranged in a simple hexagonal (sh) pattern.

K. Y. Singh and B. R. K. Gupta [**Singh and Gupta, 2003**] reported a new integral form of equation to analysis the thermal expansion in minerals under effect of high temperature. The expression for the thermal expansion, bulk modulus and thermal expansion coefficient was obtained by assuming the fact that the Anderson parameter δ_T is temperature dependent parameter. In this work they obtained the results for the entire range from room temperature to melting temperature. The details about these EOSs are also given in chapter 4.

Baria et al. [**Baria et al., 2003**] did comprehensive study of lattice mechanical properties of some fcc transition metals. They proposed a model pseudo potential depending on an effective core radius, but otherwise parameter free to study the equation of state, binding energy, interatomic interaction, Phonon dispersion curves, Phonon density of state, Gruneisen parameter, frequencies and elastic constants of metals.

S. Gupta et al. [**Gupta et al., 2003**] derived expression for the isothermal bulk modulus and also their first and second order pressure derivatives for inert gas solids (Ne, Ar, Kr and Xe) and compared their results with available experimental data.

A. I. Karasevskii et al. [**Karasevskii et al., 2003**] reported EOS and thermodynamic properties of rare gas solids under high pressure. On the basis of imperical two body interactions they obtained the pressure dependence of Gurneisen parameter with a close agreement with experimental values. The basis for the theoretical description of the inert gas solids in this work was the statistical method recently proposed for the study of equilibrium properties of solids and successfully applied to the description of thermodynamic properties of Ar, Kr and Xe at ambient pressure. They compared the explicit result with the experimental data for Ar, Kr and Xe.

D. N. Talwar [**Talwar, 2003**] presented a rigid ion model at ambient and high pressure with a comprehensive study of lattice dynamic and thermodynamical properties of cubic III nitrides. He adopted Murnaghan's EOS for volume dependence of pressure. The theoretical results for specific heat and thermal expansion coefficients ware compared with available experimental data.

E. Francisco [**Francisco et al., 2003**] analyzed the P-V-T data of rutile phase of TiO_2. They presented a general computational scheme to extend their EOS for interpretation of the cell parameters response to hydrostatic pressure to orthogonal lattices. The main objectives of work was that to show

EOS can be easily extended to describe the behavior of linear structural parameters with pressure in orthogonal lattice and second objective was to analyze the performance of EOS in the description of high pressure and high temperature data of TiO_2.

Y. Mori et al. [**Mori et al., 2003**] investigated the high pressure X-ray and optical studies of iron diclicide ($FeSi_2$) unto 60.7 GPa. $FeSi_2$ is a promising material for optical applications. This is an ecofreindly semiconductor material. They determined the bulk modulus B_0 =243.46 GPa at zero pressure by Birch – Murnaghan's Equation of state [**Birch, 1952**].

A. K. Verma et al. [**Verma et al., 2004**] presented the hugoniots curves of Ta, Mo and W in their solids as well as liquid phases. The isotherm of the solids phases, which are necessary input for computation, had been obtained by full potential first principle calculations. They showed the 300K isotherms of Ta, Mo, and W by their models.

Agnes Dewaele et al. [**Dewaele et al., 2004**] recently reported the volume of tantalum versus pressure accurately upto 101 GPa by single crystal X ray diffraction with helium as pressure transmitting medium. They observed a slight deviation from previous static determinations. They also calculated first principle calculation for showing a possible curve in P (V) relative to the experimental data. They show a nonhydrostatic pressure leads to overestimate the volume. They also compared the value of V_0, B_0 and B_0' for the EOS with the values obtained by X-ray diffraction measurement [**Cynn et al., 1999; Hanfland et al., 2002**], ultrasonic measurements [**Katahara et al., 1976**] and reduced shock wave measurements [**Wang et al., 2002**].

L. Ehm et al. [**Ehm et al., 2004**] investigated the thermophysical and structural behavior of SnS under high pressure by angular power diffraction unto 38.5 GPa. They observed a structural phase transition from orthorhombic SnS to monoclinic SnS at 18.5 GPa. They also calculated the bulk modulus at zero pressure B_0 =36.6 GPa and B_0' =5.5 for orthorhombic phase and B_0 =86.0 GPa and B_0' =4 for monoclinic.

George M. Amulete et al. [**Amulete et al., 2004**] determined the equation of state for monolithic silicon carbide (SiC) by high pressure ultrasonic and x-ray technique. SiC is very important semiconductor material because it's wide potential for both structural and electronic applications. SiC has high hardness, fracture toughness and high bulk modulus resulting in several technological application such as in ballastically superior armour ceramics and optical structural and wear resistant applications. They also obtained from the ultrasonic measurements as B_0 =216.5 GPa and B_0' =4.19.

Takemura Kenichi [**Kenichi, 2004**] carried high-pressure powder x-ray diffraction experiments on osmium (Os) at room temperature under quasihydrostatic conditions with a helium pressure medium. By fitting the pressure volume data upto 58 G Pa. and determined the bulk modulus B_0 and pressure derivative of B_0 as 395 GPa and B_0' =4.5. He carried out high-pressure powder X- ray diffraction experiment with diamond anvil cell DAC. The experiment was done upto 58 GPa.

A. K. Singh [**Singh, 2004**] reported that the diamond anvil cell has extensively used to generate pressure upto a few hundred GPa. A fine X-ray beam permits recording of diffraction pattern from the pressurized samples. Such high pressure was however not hydrostatic. Modeling of the stress state and resulting lattice strains in the sample give information on the compression behavior of solids.

Equation of State

"Use all methods analytical,
bring every detail into play planning to
the critical cause the team to win their way"

Equation of state is basically a relationship between thermodynamic variables i.e. pressure (P) volume (V) and temperature (T). The EOS may categorized in two forms, inverting and non-inverting. The inverting form represents V/V_0 as a function of pressure and non-inverting form represents P as a function of V/V_0. The EOSs are also categorized under two categories isotherm and isobaric. The relation between pressure (P), and volume V/V_0 at a given temperature is referred as an isotherm or isothermal EOS and the relation between temperature and volume at constant pressure is called isobaric EOS. In this chapter a brief introduction of important EOSs are presented. Some inverting EOSs are given here.

3.1. Murnaghan EOS

Murnaghan EOS is also a basic and widely used EOS [**Murnaghan, 1944**]. This EOS is based on the assumption that isothermal bulk modulus is a linear function of pressure.

$$B(P) = B_0 + B_0' P$$

We know that

$$B = -V\frac{dP}{dV}$$

combining above both equations

$$\frac{dV}{V} = -\frac{dP}{B_0 + B_0'P}$$

On integrating the above equation

$$\ln\left(\frac{V}{V_0}\right) = \frac{-1}{B_0'}\ln\left(1 + \frac{B_0'}{B_0}P\right)$$

$$\left(\frac{V}{V_0}\right) = \left(1 + \frac{B_0'}{B_0}P\right)^{-\frac{1}{B_0'}} \qquad (3.1)$$

above equation (3.) is Murnaghan's first order EOS for compression.

The Murnaghan EOS can also be generalized by extending the Taylor expansion of bulk modulus second order and final expressions is given as

$$\frac{V}{V_0} = \left[\frac{2B_0 - \left[\left(B_0'^2 - 2B_0B_0''\right)^{1/2} - B_0'\right]P}{2B_0 + \left[\left(B_0'^2 - 2B_0B_0''\right)^{1/2} + B_0\right]P}\right]^{\left(B_0'^2 - 2B_0B_0''\right)^{-\frac{1}{2}}} \qquad (3.2)$$

The first and second order equation for bulk modulus is expressed as

$$B(P) = B_0 + B_0' P \tag{3.3}$$

$$B(P) = B_0 + B_0' P + \frac{1}{2} B_0'' P^2 \tag{3.4}$$

3.2. Bridgman EOS

By using two parameters the simplest inverting EOS is power series given by Bridgman [**Bridgman, 1952**]

$$\frac{V}{V_0} = 1 - aP + bP^2 \tag{3.5}$$

By the definition of bulk modulus

$$B = -V \frac{dP}{dV}$$

$$\frac{dV}{dP} = -\frac{V}{B} \tag{3.6}$$

$$\frac{d^2V}{dP^2} = \frac{V}{B^2}\left(\frac{dB}{dP} + 1\right)$$

Taking their derivatives at P=0 and equating them with pressure derivative we get,

$a = \frac{1}{B_0}$ and $b = \frac{B_0' + 1}{2B_0^2}$.

3.3. Borelius Equation of State

Borelius [**Borelius, 1958**] is given as

$$\frac{V}{V_0}=1-\frac{aP}{b+P} \tag{3.7}$$

with $a=\frac{2}{B_0'+1}$ and $b=\frac{2B_0}{B_0'+1}$

3.4. Tait's Equation of State

The oldest EOS is the Tait's equation or linear secant (elastic) modulus equation followed by Hayward and Borelius [**Hayward, 1967; Borelius, 1958**]

$$\frac{V}{V_0}=1-a\ln(1+bP) \tag{3.8}$$

with $a=\frac{1}{B_0'+1}$ and $b=\frac{B'+1_0}{B_0}$

The Tait EOS is a simple and most useful non-linear isothermal equation of state. This equation gives good agreements in study of solids viz. Li, Na, K, Ca, Zn, Rb, Ag, In, Pb, LiCl, NaF, NaCl, NaBr etc. with pressure ranging from zero to variable maximum pressure. In the present thesis this equation as such and its modified form has been applied first time on inert gas solids, semiconductors, some metals and geological materials.

Similarly the expression for bulk modulus is given as [**MacDonald, 1969; Schlosser et al., 1989**]

$$B_T = B_0 \frac{V}{V_0}\left(1+\frac{B_0'+1}{B_0}P\right) \tag{3.9}$$

3.5. Schmidt Equation of State

Schmidt [**Schmidt, 1983**] proposed the following equation of state,

$$\frac{V}{V_0} = \exp\left[-\frac{1}{2B_0'}\int_0^P \frac{\ln\left(1-\frac{2B_0'}{B_0}P\right)dP}{P}\right] \tag{3.10}$$

In this equation integral in the bracket cannot be solved analytically and thus this equation could not to be used for calculation purpose.

3.6. Three Parameter Equations of State

The simplest three parameter EOS is the extension of the power series up to three terms of equation.

$$\frac{V}{V_0} = 1 - aP + bP^2 - cP^3 \tag{3.11}$$

Involving the third pressure derivative of volume

$$\frac{d^3V}{dP^3} = \frac{V}{B^2}\left(\frac{d^2B}{dP^2} - \frac{1}{B}\left(2\frac{dB}{dP}+1\right)\left(\frac{dB}{dP}+1\right)\right)$$

and the constants can be determined as before viz.

$$a = \frac{1}{B_0}\ ,\ b = \frac{B_0'+1}{2B_0^2}\cdot \text{ and } c = \frac{(2B_0'+1)(B_0'+1)}{6B_0^3} - \frac{B_0''}{6B_0^2}$$

The Murnaghan EOS can also be generalized by extending the Taylor expansion of bulk modulus second order and final expressions is given as

$$\frac{V}{V_0} = \left[\frac{2B_0 - \left[\left(B_0'^2 - 2B_0B_0''\right)^{1/2} - B_0'\right]P}{2B_0 + \left[\left(B_0'^2 - 2B_0B_0''\right)^{1/2} + B_0\right]P}\right]^{\left(B_0'^2 - 2B_0B_0''\right)^{-\frac{1}{2}}} \qquad (3.12)$$

3.7. Huang and Chow Equations of State

Huang and Chow [**Huang et al., 1974**] presented an EOS

$$\frac{V}{V_0} = 1 - a\left[1 - (1+bP)^{-c}\right] \qquad (3.13)$$

with $a = \dfrac{1+B_0'}{1+B_0'+B_0B_0''}$; $b = \dfrac{B_0'}{B_0} - \dfrac{B''}{B_0'+1}$

and $c = \dfrac{1+B_0'+B_0B_0''}{B_0'^2+B_0'-B_0B_0''}$

3.8. Birch's Equations of State

Most of the EOSs in literature are non-inverting form [**Stacey, 2001; 2004**]. The first main form of non-inverting EOS was obtained by Birch and therefore known as Birch equation of state [**Birch, 1952; 1978**]. The Birch EOS derived from the theory of finite strain by expanding the strain energy in a power series of Eulerian strain component f. The expression for the pressure is given as

$$P = 3B_0 f(1+2f)^{5/2}(1+af) \qquad (3.14)$$

Second Order is expressed as

$$P = 3B_0 f(1+2f)^{5/2}(1+af+bf^2) \qquad (3.15)$$

where,

$$f = \frac{1}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right] \qquad (3.16)$$

and

$$a = \frac{3}{2}(B_0' - 4)$$

$$b = \frac{1}{6}\left[9B_o B_0'' + 9B_0'^2 - 63B_0 + 143\right]$$

The expression for bulk moduli are given as

$$B = B_0(1+f)^{5/2}\left[1+(7+2a)f+9af^2\right] \tag{3.17}$$

$$B = B_0(1+f)^{5/2}\left[1+(7+2a)f+(9a+3b)f^2+11bf^3\right] \tag{3.18}$$

3.9. Vinet (Universal) Equations of State

Vinet et al. [**Vinet, 1987; 1999**] proposed a new EOS, which is found to be useful for all kind of solids. The final expression is given as

$$P = \frac{3(1-x)B_0\left[\exp\eta(1-x)\right]}{x^2} \tag{3.19}$$

where $x = \left(\frac{V}{V_0}\right)^{1/3}$

and $\eta = \frac{3}{2}(B_0' - 1)$

The expression for bulk modulus is obtained as

$$B = \frac{P}{3}\left[2+\eta x+\frac{x}{1-x}\right] \tag{3.20}$$

Other modified equation of state along with their derivations are described in chapter 4.

Mathematical Formulism

"Science mikes all its progress,
through the exact measurement of mathematical formulae"

In this chapter we have modified some equation of states derived earlier. Although a number of isothermal EOSs are available in literature, however, isobaric EOSs are limited and in some cases they are not applicable as such. There is no such equation of state, which could explain the thermophysical solids successfully. In the present study we have made an attempt to modify the isothermal EOS which can be used to study the thermal expansion in variety of solids. The isobaric equations of state have also been modified by introducing the concept of thermal pressure. The equation of state obtained earliar are first described and then modified in the present work of thesis.

4.1. Tait' EOS

The Tait EOS is a simple but most useful non-linear isothermal equation of state. Kumar [**Kumar, 1995**] presented a derivation of this EOS equation taking the product of the thermal coefficient of volume thermal expansion and bulk modulus to remain constant under the effect of pressure [**Birch, 1986**].

αB_T = constant (4.1)

Differentiation of equation (4.1) with respect to volume at constant temperature gives

$$\alpha\left(\frac{dB}{dV}\right)_T + B\left(\frac{d\alpha}{dV}\right)_T = 0 \tag{4.2}$$

or
$$\delta_T = \frac{V}{\alpha}\left(\frac{d\alpha}{dV}\right)_T = -\frac{V}{B}\left(\frac{dB}{dV}\right)_T \tag{4.3}$$

Where δ_T is Anderson-Gruneisen parameter.

$$\frac{dB}{B} = -\delta_T \frac{dV}{V} \tag{4.4}$$

Integrating equation (4.4) with $K=K_0$, when $V=V_0$. Assuming that δ_T is independent of V, we get

$$\frac{B}{B_0} = \left(\frac{V}{V_0}\right)^{-\delta_T} \tag{4.5}$$

Since

$B = -V\left(\frac{dP}{dV}\right)_T$ Then equation (4.5) becomes

$$-\frac{V}{B_0}\left(\frac{dP}{dV}\right) = \left(\frac{V}{V_0}\right)^{-\delta_T} \tag{4.6}$$

$$\text{or} \quad \frac{dV}{V^{\delta_T+1}} = -\frac{1}{B_0 V_0^{\delta_T}} dP \qquad (4.7)$$

The integration of equation (4.7) gives us the following relation

$$P = \frac{B_0}{B_0'}\left[\exp\left\{-B_0 \ln\frac{V}{V_0}\right\} - 1\right] \qquad (4.8)$$

The equation (4.8) can simplify by using different assumptions available in literature. Murnaghan approximation is that δ_T is independent of and $\delta_T = \left(\frac{dB}{dP}\right)_T = B_0'$. The more recent studies in high-pressure research demonstrate that the Anderson parameter δ_T is related to $\eta = V/V_0$ (where V_0 is the initial volume) as given below [**Anderson, 1992**].

$$\frac{(\delta_T + 1)}{\eta} = A \qquad (4.9)$$

Where A is a constant for given solid. Thus equation (4.3) takes the following form

$$\frac{dB}{B} = \left[-\frac{A}{V_0} + \frac{1}{V}\right] dV \qquad (4.10)$$

Integrating above equation we get

$$\frac{B}{B_0} = \frac{V}{V_0}\exp A\left[1 - \frac{V}{V_0}\right] \tag{4.11}$$

Since $B = -V\left(\frac{dP}{dV}\right)_T$ equation (4.9) may be rewritten as

$$\frac{B}{B_0}\exp A\left[1 - \frac{V}{V_0}\right]dV = -dP \tag{4.12}$$

On integration equation (4.12) gives

$$P = \frac{B_0}{A}\left[\exp A\left(1 - \frac{V}{V_0}\right) - 1\right] \tag{4.13}$$

Here K_0 is the zero pressure bulk modulus and the constant A is determined from the initial conditions, viz at $V=V_0$, $A=\delta_T^0+1$.

Equation 4.13 is thus the Tait Equation and can be written as follows

$$\frac{V}{V_0} = \left[1 - \frac{1}{B_0'+1}\ln\left\{1+\left(\frac{B_0'+1}{B_0}\right)P\right\}\right] \tag{4.14}$$

4.2. EOS for Isothermal Bulk Modulus B_0 and Thermal Expansion Coefficient (α_T) under pressure

By using eq. (4.11) we have [**Schlosser et al., 1989**]

$$B = B_0\frac{V}{V_0}\left(1+\frac{B_0'+1}{B_0}P\right) \tag{4.15}$$

from equation 4.14

$$1+\frac{B_0'+1}{B_0}P=\exp\left\{\left(1-\frac{V}{V_0}\right)\left(B_0'+1\right)\right\} \tag{4.16}$$

using equation 4.15 and 4.16 we get,

$$B=B_0\frac{V}{V_0}\exp\left\{\left(B_0'+1\right)\left(1-\frac{V}{V_0}\right)\right\} \tag{4.17}$$

The thermal expansion coefficient α, can be obtained by well known thermodynamic approximation [**Tallon, 1980; Birch, 1986; Shanker, 1993**] according to which under the effect of pressure the product of α and B_P remains constant. i. e.

$$\alpha B_P=\alpha_0 B_0 \tag{4.18}$$

Where α_0 and K_0 are the value of α and K at zero pressure. We have another approximation for Anderson- Gruneisen parameter [**Anderson et al., 1989; 1999**]

$$\delta_T=-\frac{1}{\alpha B}\left(\frac{dB}{dT}\right)_P=\frac{dB}{dP} \tag{4.19}$$

at P=0, we have $\delta_T^0=B_0'$. So the equation (4.15) with the help of equation (4.18) can be written as

$$\frac{\alpha}{\alpha_0} = \frac{B_0}{B} = \left(\frac{V}{V_0}\right)^{-1} \left\{1 + \frac{\delta_T^0 + 1}{B_0} P\right\}^{-1} \qquad (4.20)$$

or $$\alpha = \alpha_0 \left(\frac{V}{V_0}\right)^{-1} \exp\left\{-\left(B_0' + 1\right)\left(1 - \frac{V}{V_0}\right)\right\} \qquad (4.21)$$

Equation (4.21) is thus the final expression for thermal expansion coefficient.

4.3 Temperature Dependent form of Murnaghan EOS (Modified Murnaghan EOS)

The basic Murnaghan EOS is expressed as [**Murnagham, 1944**].

$$\frac{V}{V_0} = \left(1 + \frac{B_0'}{B_0} P\right)^{-1/B_0'} \qquad (4.22)$$

This is pressure dependent EOS at a constant temperature. Now if thermal pressure is taken in account then the effective pressure is reduced. The thermal pressure P_{Th} is expressed as [**Anderson et al., 1995**].

$$P_{Th} = \int_{T_0}^{T} \alpha_0 B_0 \, dT \qquad (4.23)$$

Where α_0 is thermal expansion coefficient and B_0 is bulk modulus at the zero reference pressure. By using eq. (4.23), the eq. (4.22) is modified as [**Devlal et al., 2004; 2005**].

$$\frac{V}{V_0}=\left(1+\frac{B_0'}{B_0}(P-P_{Th})\right)^{-1/B_0'} \tag{4.24}$$

On integrating eq. (4.23) and putting the value of thermal pressure in eq.(4.24) this equation can be expressed as

$$\frac{V}{V_0}=\left(1+\frac{B_0'}{B_0}\{P-\alpha_0 B_0(T-T_0)\}\right)^{-1/B_0'} \tag{4.25}$$

It may be considered that, if the reference pressure is zero then the eq. (4.25) can be expressed as

$$\frac{V}{V_0}=\{1-B_0'\alpha_0(T-T_0)\}^{-1/B_0'} \tag{4.26}$$

Similarly on inclusion of the concept of thermal pressure on the Murnaghan's first order equation for bulk modulus can be modified as follows

$$B_T=B_0+B_0'P \tag{4.27}$$

Again taking the account the effect of thermal pressure the above equation is written as

$$B_T = B_0 + B_0'(P - P_{Th})$$

on further simplification, we get

$$B_T = B_0 + B_0'\{P - B_0\alpha_0(T - T_0)\}$$

It may be considered that, if the reference pressure is zero then the eq. (4.25) can be expressed as

$$B_T = B_0 + B_0'\{P - B_0\alpha_0(T - T_0)\}$$

$$B_T = B_0[1 - B_0'\alpha_0(T - T_0)] \tag{4.28}$$

The eq. (4.26) and eq. (4.28) have been thus the final modified Murnaghan EOSs, which are temperature dependent expression for expansion and bulk modulus.

4.4. Temperature Dependent form of Tait's EOS (Modified Tait EOS)

The Tait EOS is expressed as

$$\frac{V}{V_0} = \left[1 - \frac{1}{B_0' + 1}\ln\left\{1 + \left(\frac{B_0' + 1}{B_0}\right)P\right\}\right] \tag{4.14}$$

This is pressure dependent EOS at a constant temperature. Now if thermal pressure is taken in account then the effective pressure is reduced as compared to the applied pressure due to thermal pressure [**Anderson et al., 1995; Kandpal et al., 2004**].

The thermal pressure P_{Th} is expressed as

$$P_{Th} = \int_{T_0}^{T} \alpha_0 B_0 dT \tag{4.23}$$

where α_0 is thermal expansion coefficient and B_0 is bulk modulus at the zero reference pressure. By using eq. (4.23), the eq. (4.22) is modified as

$$\frac{V}{V_0} = \left[1 - \frac{1}{B_0' + 1} \ln\left\{1 + \left(\frac{B_0' + 1}{B_0}\right)(P - P_{Th})\right\}\right] \tag{4.29}$$

On integrating eq. (4.23) and putting the value of thermal pressure in eq.(4.29) this equation can be expressed as

$$\frac{V}{V_0} = \left[1 - \frac{1}{B_0' + 1} \ln\left\{1 + \left(\frac{B_0' + 1}{B_0}\right)(P - \alpha_0 B_0 (T - T_0))\right\}\right] \tag{4.30}$$

It may be considered that, if the reference pressure is zero then the eq. (4.25) can be expressed as

$$\frac{V}{V_0} = \left[1 - \frac{1}{B_0' + 1} \ln\ \left\{1 - (B_0' + 1)\alpha_0 (T - T_0)\right\}\right] \tag{4.31}$$

Similarly on inclusion of the concept of thermal pressure on the Tait's equation for bulk modulus can be modified as follows.

$$B_T = B_0 \frac{V}{V_0}\left(1 + \frac{1 + B_0'}{B_0} P\right) \tag{4.32}$$

Again taking the account the effect of thermal pressure the above equation is written as

$$B_T = B_0 \frac{V}{V_0}\left(1 + \frac{1 + B_0'}{B_0} (P - P_{Th})\right) \tag{4.33}$$

on further simplification, we get

$$B_T = B_0 \frac{V}{V_0}\left(1 + \frac{1 + B_0'}{B_0} (P - B_0 \alpha_0 (T - T_0))\right) \tag{4.34}$$

It may be considered that, if the reference pressure is zero then the eq. (4.25) can be expressed as

$$B_T = B_0 \frac{V}{V_0} (1 - (1 + B_0')\alpha_0 (T - T_0)) \tag{4.35}$$

The eq. (4.31) and eq. (4.35) are the modified Tait's EOSs for thermal expression for expansion and bulk modulus as the function of temperature.

4.5. Temperature Dependent Integral form EOS (Singh-Gupta EOS)

4.5.1. Temperature Dependence of Volume Thermal Expansion Coefficient

Thermal expansion in solids is resulted due to the large amplitudes of lattice vibrations at high temperature and hence inter-atomic separation also increases on increasing temperature of the solid. The equation of state for the analysis of thermal expansion coefficient can also be derived in term of only the variable parameter temperature. Assuming that under the effect of temperature the product of thermal expansion coefficient and bulk modulus remains constant [**Anderson, 1967; Anderson et al., 1989**], i.e.

$$\alpha B_T = \text{constant} \qquad (4.36)$$

Where α is volume thermal expansion coefficient and B_T is bulk modulus.

On differentiating equation (4.36) with respect to T, at constant pressure, we have

$$\alpha\left(\frac{dB_T}{dP}\right)_P + B_T\left(\frac{d\alpha}{dT}\right)_P = 0 \qquad (4.37)$$

$$\left(\frac{dB_T}{dT}\right)_P = -\frac{B_T}{\alpha}\left(\frac{d\alpha}{dT}\right)_P \qquad (4.38)$$

The Anderson Gruneisen parameter δ_T is defined as

$$\delta_T = -\frac{1}{\alpha B_T}\left(\frac{dB_T}{dT}\right)_P \qquad (4.39)$$

Substituting the value of equation (4.38) in equation (5.39) we get

$$\delta_T = \frac{1}{\alpha^2}\left(\frac{d\alpha}{dT}\right)_P \qquad (4.40)$$

Here α is defined as

$$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P \qquad (4.41)$$

From equation (4.41) and (4.40) we get

$$\delta_T = \frac{V}{\alpha}\left(\frac{d\alpha}{dV}\right)_P \qquad (4.42)$$

The empirical temperature dependence of δ_T can be shown as follows [**Singh et al., 2003**]

$$\delta_T = \delta_T^0 x^k \qquad (4.43)$$

Where $X= (T/T_0)$, T_0 is reference temperature (room temperature) and δ_T^0 is the value of Anderson Gruneisen parameter (δ_T) at $T= T_0$ and k is new dimensionless thermo elastic parameter, whose value is calculated by the slope of the graph plotted between log (δ_T) and log (T/T_0) .

So the value of k is defined as

$$k = \left(\frac{\partial \ln \delta_T}{\partial \ln X} \right) \tag{4.44}$$

Substituting equation (4.43) in to equation (4.40) we get

$$\delta_T^0 X^k = \frac{1}{\alpha^2} \left(\frac{d\alpha}{dT} \right)_P$$

or

$$\delta_T^0 \left(\frac{T}{T_0} \right)^k = \frac{1}{\alpha^2} \left(\frac{d\alpha}{dT} \right)_P \tag{4.45}$$

Integrating equation (4.10)

$$\frac{\delta_T^0}{T_0^k} \left(\frac{T^{k+1}}{k+1} \right) = -\frac{1}{\alpha_T} + C \tag{4.46}$$

Where C is integrating constant, which can be calculated from initial condition at $T=T_0$ and $\alpha = \alpha_0$.

$$\frac{\delta_T^0}{T_0^k}\left(\frac{T_0^{k+1}}{k+1}\right) = -\frac{1}{a_0} + C$$

or $$C = \frac{\delta_T^0 T_0^{k+1}}{T_0^k(k+1)} + \frac{1}{a_0} \qquad (4.47)$$

Using equation (4.47) with (4.46) we have

$$\frac{\delta_T^0}{T_0^k}\left(\frac{T^{k+1}}{k+1}\right) - \frac{\delta_T^0}{T_0^k}\left(\frac{T_0^{k+1}}{k+1}\right) = \frac{1}{a_0} - \frac{1}{a_T}$$

Rearranging we get final expression for volume thermal expansion coefficient (a_T).

$$\frac{a_T}{a_0} = \left[1 - \frac{\delta_T^0 a_0}{T_0^k(k+1)}\left\{T^{k+1} - T_0^{k+1}\right\}\right]^{-1}$$

or $$a_T = a_0\left[1 - \frac{\delta_T^0 a_0}{T_0^k(k+1)}\left\{T^{k+1} - T_0^{k+1}\right\}\right]^{-1} \qquad (4.48)$$

This equation requires only three input parameters a_0, δ_T^0 and k at room temperature and the value of a_T is evaluated directly as a function of temperature. It should be emphasized that equation (4.48) is based on the assumption that δ_T is now the function of temperature unlike the previous studies [**Singh et al., 1991**].

4.5.2. Temperature Dependence of Bulk Modulus

If the empirical temperature dependence of δ_T is assumed as incase of metals equation (4.39) at P=0, may also rewritten as

$$-\left(\frac{dB_T}{dT}\right)=\alpha_0 B_0 \delta_T \tag{4.49}$$

using equation (4.43)

$$-\left(\frac{dB_T}{B_0}\right)=\alpha_0 \delta_T^0 \left(\frac{T}{T_0}\right)^k dT \tag{4.50}$$

Integrating above equation (4.50), i.e.

$$\int dB_T = -\frac{\alpha_0 B_0 \delta_T^0}{T_0^k}\int T^k dT$$

we get

$$B_T = -\frac{\alpha_0 B_0 \delta_T^0}{T_0^k}\left(\frac{T^{k+1}}{k+1}\right)+C \tag{4.51}$$

Where C is integrating constant, which can be calculated by initial conditions T=T_0, and B=B_0.

We get the final expression for bulk modulus B_T is

$$\frac{B_T}{B_0} = \left[1 - \frac{\alpha_0 \delta_T^0}{T_0^k (k+1)} \left\{T^{k+1} - T_0^{k+1}\right\}\right]$$

$$\text{or} \quad B_T = B_0 \left[1 - \frac{\alpha_0 \delta_T^0}{T_0^k (k+1)} \left\{T^{k+1} - T_0^{k+1}\right\}\right] \tag{4.52}$$

Here To refers to the room temperature or any other reference temperature value. Thus the value of bulk modulus B_T as a function of temperature can be calculated from equation (4.52). The beauty of this equation, it can be traced from the fact that the data of α(T) are not needed.

4.5.3. Temperature Dependence of Volume Thermal Expansion

The expression for the volume thermal expansion (V/V_0) can be similarly obtained by making use of the following equation

$$dB_T = -\delta_T B_T \frac{dV}{V} \tag{4.53}$$

Differentiating equation (4.52) with respect to temperature, we get

$$dB_T = -\frac{\alpha_0 B_0 \delta_T^0}{T_0^k} T^k dT \tag{4.54}$$

Using equation (4.54) with equation (4.53) we get

$$\frac{dV}{V} = \frac{a_0}{\left[1 - \frac{a_0 \delta_T^0}{T_0^k (k+1)} \left\{T^{k+1} - T_0^{k+1}\right\}\right]} dT \tag{4.55}$$

Integrating equation (4.55) we get the final expression for volume thermal expansion (V/V_0) as follows

$$\frac{V}{V_0} = \exp\left[\int_{T_0}^{T} \frac{a_0}{\left[1 - \frac{a_0 \delta_T^0}{T_0^k (k+1)} \left\{T^{k+1} - T_0^{k+1}\right\}\right]} dT\right]$$

or $$\frac{V}{V_0} = \exp\left[\int_{T_0}^{T} \frac{a_0}{\left[1 - A\left\{T^{k+1} - T_0^{k+1}\right\}\right]} dT\right] \tag{4.56}$$

where $$A = \frac{a_0 \delta_T^0}{T_0^k (k+1)}$$

The value of volume thermal expansion as a function of temperature for metals had been calculated by equation (4.56), which is known as Singh and Gupta's integral form of equation of state [**Singh et al., 2003**].

Results and Discussion

"Do not believe in any thing because it is presented so
It is said to you, unless and until you,
yourself, explore the truth"

In the present study of our research work we have analysed the thermophysical properties of variety of crystals by predicting their thermal expansion and bulk modulus by using the different EOS with their explanations. For this purpose two types of equations of state that is (1) isothermal equation of state; (2) isobaric equation of state are used to calculate the thermophysical properties of inert gas solids Ne, Ar, Kr, Xe, semiconductors Ge, Si, $FeSi_2$, SnS, SiC, MoN, MoN_2, AlN, GaN and some metals Mo, W, Ta, Os. The selected classes are entirely different to each other. Inert gas solids are very weakly bonded solids with very less bulk modulus. Semiconductors are relatively tightly bonded solids with high bulk modulus, while d-block metals are tightly bonded solids with high bulk modulus and melting point. Apart from these classes of solids we have also employed the EOS in FeSi and TiO_2 crystals which are found in earth's core and planetary system respectively.

The applications of these equations of state are thus fully tested by calculating their thermophysical properties cited above. The high-pressure compression in the solids is calculated by using isothermal equations (4.14) and (4.22); and bulk modulus at different pressure is calculated by using equations (4.17) and (4.27). The temperature dependent thermal expansion properties are calculated by using isobaric equations (4.31), (4.26) and (4.56); and bulk modulus by using equations (4.17), (4.28) and (4.52). The input parameters such as bulk modulus (B_0), first pressure derivative of bulk modulus (B_0') and the volume thermal expansion (α_0) at zero pressures and reference temperature are in given table 5.1 with their corresponding references.

The calculated values of thermal compression (V/V_0), thermal expansion (α) and bulk modulus (B_T) of inert gas solids are shown in tables 5.2 to 5.8. The experimental values are also given in these tables for the sake of comparison. Tables 5.2, 5.3, 5.5, 5.7, 5.9, 5.11, 5.13, 5.14, 5.16, 5.17, 5.18, 5.19, 5.20, 5.21, 5.22, 5.24, 5.26, 5.27, 5.28 and 5.30 contain the result calculated using the isothermal EOS while tables 5.4, 5.6, 5.8, 5.10, 5.12, 5.15, 5.23, 5.25, 5.29 and 5.31 show the theoretical results predicted under high temperature i.e. isobaric EOS. The isothermal compression and bulk modulus are calculated by the original Tait EOS and original Murnaghan EOS. It is found that the results achieved from Tait's equation of state are in better agreement with the available experimental data as compared to those obtained from Murnaghan EOS.

The isobaric thermal expansion, bulk modulus and thermal expansion coefficient are calculated by Singh-Gupta EOS, modified Tait EOS and Modified Murnaghan EOS. It is noted that the Singh-Gupta EOS gives better agreement with the available experimental data for inert gas solids. The comparisons of results obtained from different equations of state are also shown graphically in figures from 1.1 to 4.4. These equations of states are also employed to study the thermophysical properties of semiconductor and metals including FeSi and TiO_2 and the results calculated are reported in tables from 5.9 to 5.31. It is evident from these tables that in all cases the Tait's equation of state (isothermal EOS) explain the thermophysical properties more satisfactorily in comparison to the Murnaghan EOS.

Though, the original form of Tait's and Murnaghan's isothermal EOSs explain the thermophysical properties of the solids successfully, but these equations do not explain results under high temperature. We have therefore, modified the both Tait's and Murnaghan equations of state by including the concept of phonon pressure (thermal pressure) in order to explain the thermophysical properties satisfactorily in the range of high temperature particularly above their respective Debye temperatures.

These modified forms of equations, are, then employed to determine the thermal expansion and bulk modulus of variety of solid (inert gas solids, semiconductors and metals including FeSi and TiO_2) under high temperature. The values thus calculated from modified Tait's and Murnaghan's equations of state are reported in tables 5.4, 5.6, 5.8, 5.10, 5.12, 5.15, 5.23, 5.25, 5.28, 5.29 and 5.31 along with the available experimental data. In case of inert gas solids it is found that the modified form of Tait and modified Murnaghan equations predict the values very close to the experimental data and approximately also close to those obtained from Singh-Gupta equation of state. All results in tables are graphically represented in their corresponding figures.

On the basis of overall descriptions, it may thus be concluded that after the inclusion of thermal pressure term in original Tait's and Murnaghan's equations of state, these equations predict the results very close to the experimental values. Thus the phonon pressure term plays an important role to explain thermophysical properties of solid structure and also can be applied in more complex structure solids. It is also emphasized here that the modified isobaric Tait's EOS and Modified Murnaghan's EOS may be treated as the universal equations of state and at par to that of Singh-Gupta equation of state to analyse the anharmonic thermophysical properties of solid under high temperature.

Table 5.1: Input parameters with their corresponding references. The square brackets show the reference sources given below.

Solids	Structure	Reference Temp.(K)	B_0 (GPa)	B_0'	α 10^{-5} K
Ne	fcc		6.36[a]	7.61[a]	-
Ar	fcc	40	6.28[a] 2.18[b]	7.07[a] 7.5[b]	106.8 [b]
Kr	fcc	60	2.55[b]	7.3[b]	90.5[b]
Xe	fcc	60	3.67[c]	4.48[d]	60.0[e]
Ge	Cubic Diamond (Ge I)	295	74.9[f]	3.0[f]	1.8[g,h]
Si	Diamond	300	66.5[i]	5.46[i]	0.78[j]
FeSi$_2$	Base centered Orthorhombic	300	243.45[k]	3.24[k]	-
SiC	Zinc blend	300	217.0[m]	4.19[m]	-
SnS	α orthorhombic γ Monoclinic	300	36.6[n] 86.0[n]	5.5[n] 4.0[n]	-
MoN	Simple Hexagonal	300	345.0[p]	3.5[p]	-
MoN$_2$	fcc	300	301.0[p]	4.0[p]	-
AlN	wortzite	300	237.0[q]	4.7[q]	-
GaN	wortzite	300	215.8[r]	4.2[r]	-
Mo	bcc	293	268.0[s]	3.58[s]	1.50[s]
W	bcc	293	312.0[s]	3.68[s]	1.35[s]
Ta	bcc	300	194.0[t]	3.25[t]	-
Os	hcp	300	462.0[u]	2.4[u]	-
FeSi	CsCl type	300	166.42 [v]	404 [v]	4.85 [v]
TiO$_2$	rutile	300	210.0 [w]	6.7 [w]	2.25 [w]

Corresponding references of Table 5.1.

a [**Hama et al., 1996**]; b[**Wallace, 1970**] ; c [**Bell et al., 1976**]; d [**Gupta et al., 2003**]; e [**Venit et al., 1987**]; f [**Menoni, 1986**]; g [**Touloukian et al., 1975**]; h [**Cicco et al., 2003**]; i [**Borrnstein et al., 1987**]; j [**Sze, 1983**]; k [**Mori et al., 2003**]; m [**Amulete et al., 2004**]; n [**Ehm et al., 2004**]; p [**Soignard, 2003**]; q [**Ueno et al., 1994**]; r [**Borrnstein et al., 1987**]; s [**Kushwah et al., 2003**]; t [**Dewaele et al., 2004**]; u [**Belonoshka, 2004**]; v [**Vocadlo et al., 2002**]; w [**Francisco et al., 2003 Ming et al., 1979, Touloukian et. al., 1977**].

Table 5.2: Compression and bulk modulus behavior of Ne under high pressure.

P (G Pa)	V/V_0		B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS (eq 4.22)	Tait EOS (eq4.17)	Murnaghan EOS (eq 4.27)
0	1	1	6.36	6.36
5	0.7618	0.7746	37.66	44.41
10	0.6891	0.7141	63.72	82.46
15	0.6447	0.6793	87.37	120.51
20	0.6126	0.6553	109.45	158.56
25	0.5875	0.6370	130.29	196.61
30	0.5669	0.6224	150.12	234.66
35	0.5494	0.6102	169.14	272.71
40	0.5342	0.5998	187.46	310.76
45	0.5208	0.5908	205.11	348.81
50	0.5087	0.5829	222.34	386.86
55	0.4978	0.5757	238.98	424.91
60	0.4548	0.5908	255.24	462.96

Figure Captions

1. Figure 1.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for inert gas solid (Ne). Figure also shows the comparison between Tait's and Murnaghan's equations of state.

2. Figure 1.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for inert gas solid (Ne). Figure also shows the comparison between Tait's and Murnaghan's equations of state.

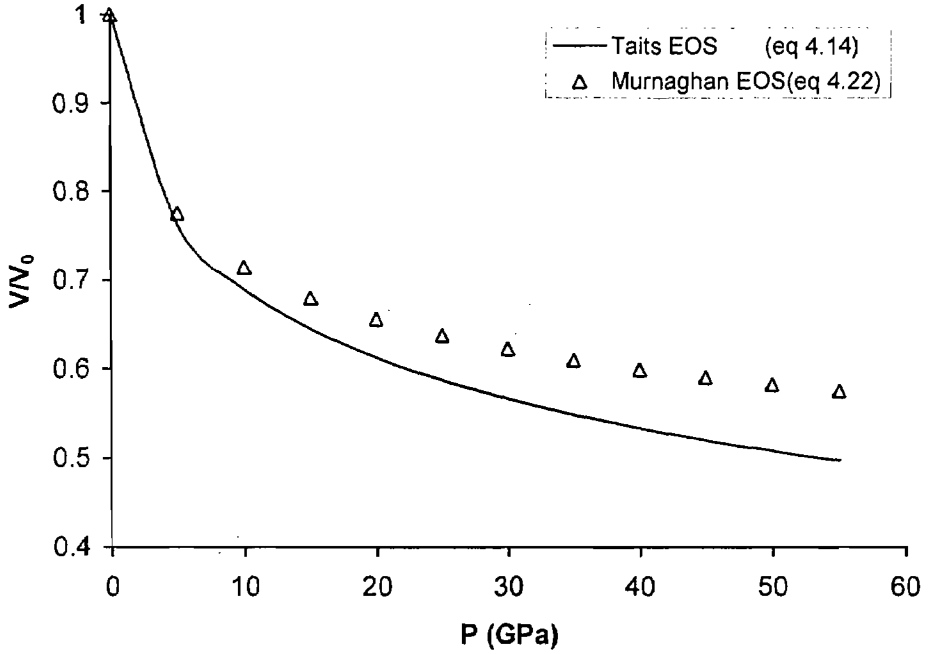


Fig. 1.1 Compression behavior of Ne

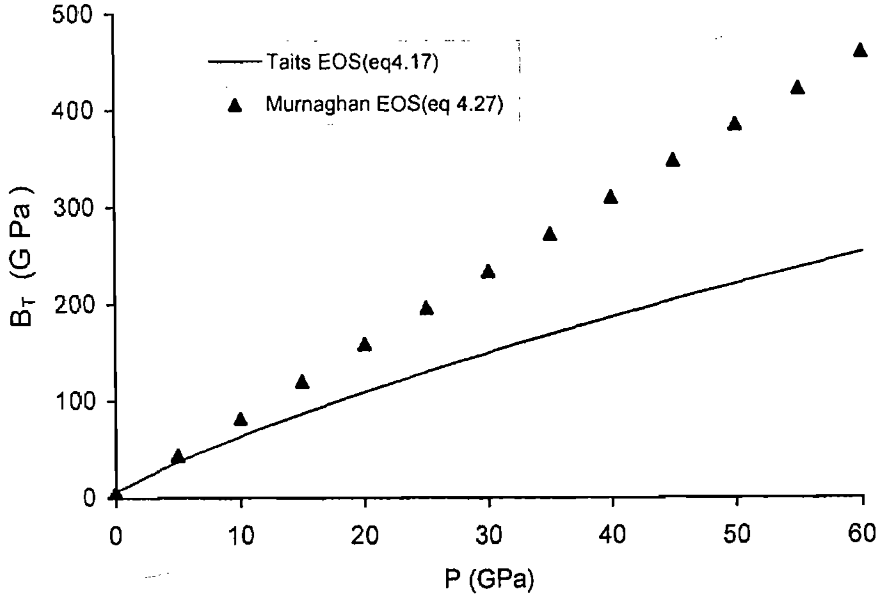


Fig. 1.2 Variation in bulk modulus with pressure

Table 5.3: Compression and bulk modulus behavior of Ar under high pressure with corresponding experimental data [a] Xu et al., 1985; Ross et al., 1986.

P (G Pa)	V/V_0			B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS(eq4.22)	Experimental [a]	Tait EOS(eq4.17)	Murnaghan EOS(eq 4.27)
0	1	1	1	6.28	6.28
5	0.7515	0.7652		35.06	41.63
10	0.6743	0.7015	0.674	58.65	76.98
15	0.6270	0.6650	0.655	79.89	121.33
20	0.5929	0.6397		99.47	147.68
25	0.5662	0.6206	0.563	117.84	183.03
30	0.5442	0.6053		135.26	218.38
35	0.5256	0.5926	0.517	151.79	253.73
40	0.5094	0.5817	0.494	172.33	289.08
45	0.4950	0.5723		183.00	324.43
50	0.4822	0.5640	0.471	197.67	359.78
55	0.4706	0.5564		211.85	395.13
60	0.4599	0.5499	0.448	225.70	430.48
65	0.4501	0.5438		239.07	465.83
70	0.4410	0.5382	0.425	252.09	501.18
75	0.4326	0.5330		264.63	536.53
80	0.4247	0.5282	0.413	276.90	571.88

Table 5.4: Thermal expansion behavior of Ar with corresponding experimental data [b] Anderson et al., 1975; [c] Wallace, 1970.

T (^{0}K)	V/V_0				B_T (G Pa)				α (10^{-5} K^{-1})	
	Modified Tait EOS (eq 4.31)	Modified Murnaghan EOS(eq 4.26)	Singh - Gupta (eq4.56)	Experimental [b]	Modified Tait EOS(eq4.17)	Modified Murnaghan EOS(eq 4.28)	Singh - Gupta (eq4.52)	Experimental [c]	Singh-Gupta (eq4.48)	Experimental [c]
40	1	1	1	1	2.18	2.18	2.18	2.18	106.8	106.8
45	1.0054	1.0054	1.0054	1.0087	2.09	2.09	2.07		111.42	
50	1.0112	1.0111	1.0112	1.0173	2.00	2.00	1.96	1.98	116.83	125.4
55	1.0172	1.0172	1.0174	1.0217	1.91	1.91	1.85		123.19	
60	1.0234	1.0235	1.0244	1.0304	1.82	1.83	1.72	1.75	130.69	145.0
65	1.0300	1.0302	1.0313	1.0369	1.73	1.74	1.59		139.64	
70	1.0370	1.0373	1.0391	1.0434	1.65	1.65	1.46	1.51	150.42	169.9
75	1.0449	1.0448	1.0479	1.0521	1.55	1.56	1.32		163.61	
80	1.0523	1.0528	1.0470	1.0630	1.47	1.48	1.17	1.20	180.04	203.1

Figure Captions

1. Figure 2.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for inert gas solid (Ar). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

2. Figure 2.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for inert gas solid (Ar). Figure also shows the comparison between Tait's and Murnaghan's equations of state.

3. Figure 2.3 shows the variation of Volume thermal expansion (V/V_0) with temperature (T) (in K) for inert gas solid (Ar). Figure also shows the comparison of the modified Tait's, modified Murnaghan's and Singh Gupta equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

4. Figure 2.4 shows the variation of Bulk modulus (B_T) (in GPa) with temperature (T) (in K) for inert gas solid (Ar). Figure also shows the comparison of modified Tait's, modified Murnaghan's and Singh Gupta equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

5. Figure 2.5 shows the variation of thermal expansion coefficient (α) (in 10^{-5} K^{-1}) with temperature (T) (in K) for inert gas solid (Ar). Figure also shows the comparison of Singh Gupta equation of state and experimental data. The square bracket with experimental values shows the reference given in table.

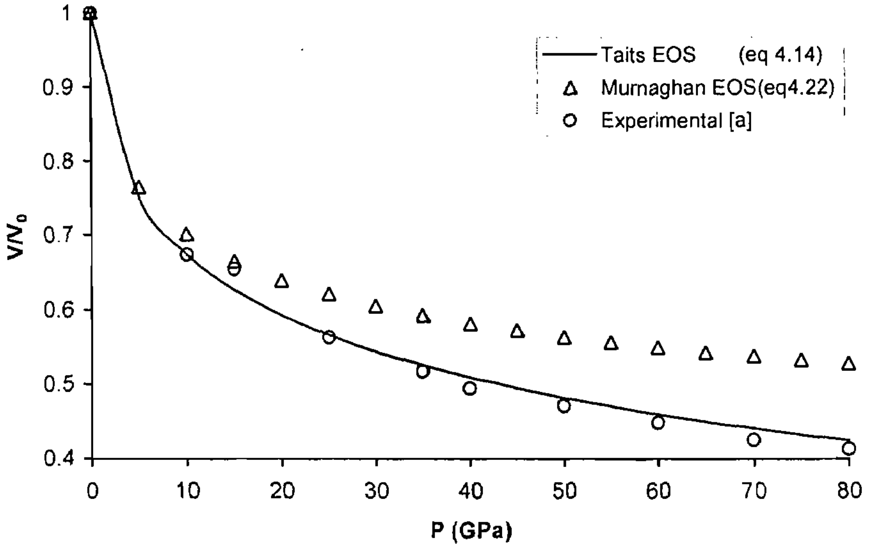


Fig. 2.1 Compression behavior of solid Ar

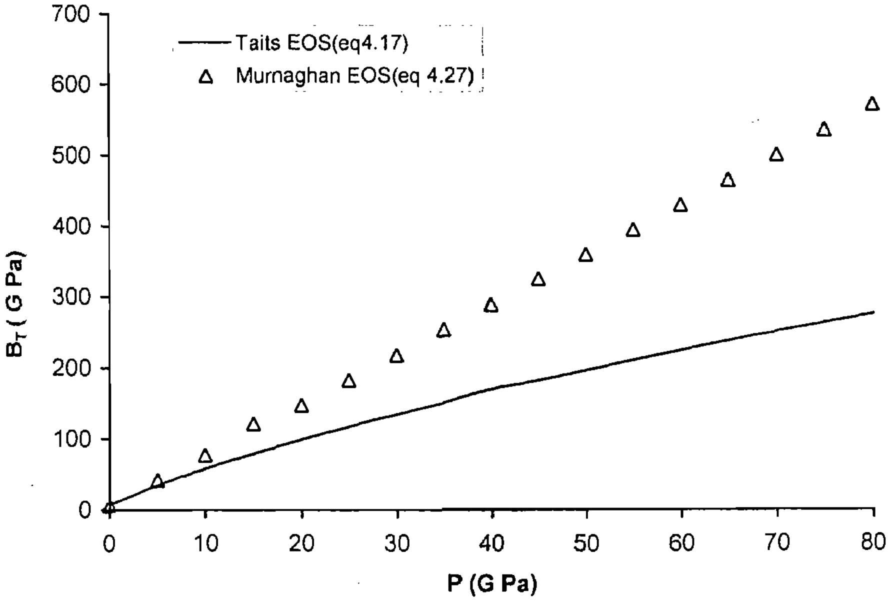


Fig. 2.2 Variation on bulk modulus with pressure of Ar

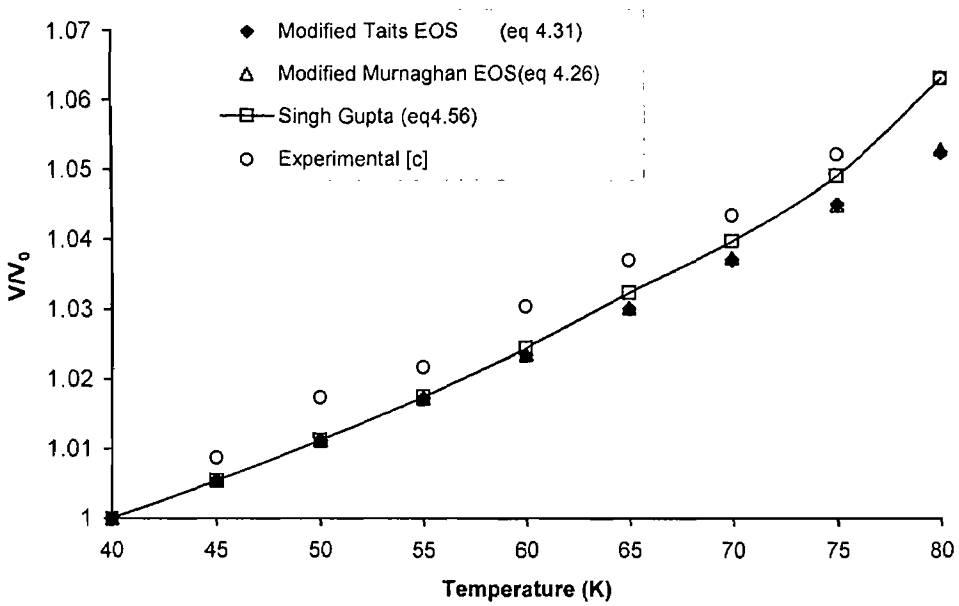


Fig. 2.3 Thermal expansion of solid Ar from reference temperature to melting temperature

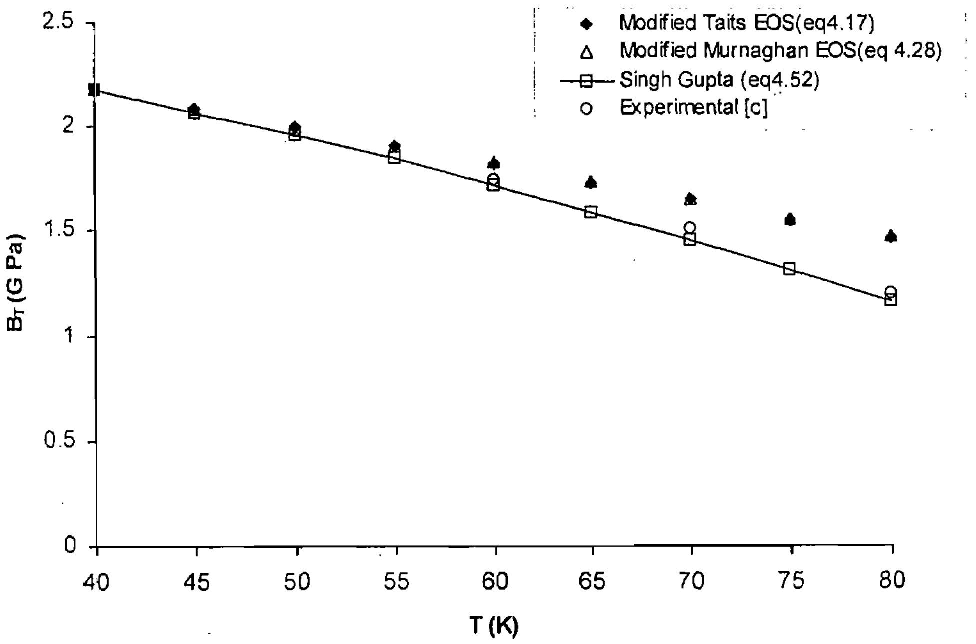


Fig. 2.4 Variation in bulk modulus of Ar with temperature

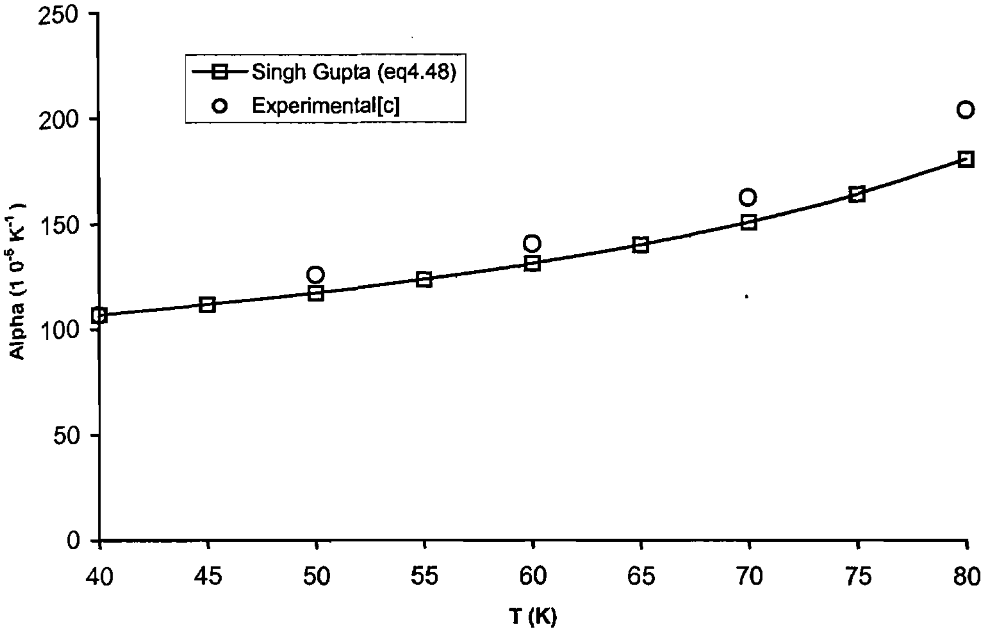


Fig 2.5 Variation in thermal expansion coefficient of Ar with temperature

Table 5.5: Compression and bulk modulus behavior of Kr under high pressure.

P (G Pa)	V/V_0		B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS(eq4.22)	Tait EOS(eq4.17)	Murnaghan EOS(eq 4.27)
0	1	1	2.55	2.55
5	0.6567	0.6881	22.94	39.05
10	0.5767	0.6286	49.35	75.55
15	0.5290	0.5955	67.26	112.05
20	0.7950	0.5730	82.46	148.55
25	0.4685	0.5560	98.42	185.05
30	0.4468	0.5424	112.39	221.55
35	0.4284	0.5312	125.54	258.05
40	0.4124	0.5217	138.02	294.55
45	0.3983	0.5134	149.85	331.05
50	0.3857	0.5061	161.11	367.55
55	0.3743	0.4996	171.86	404.05
60	0.3639	0.4883	182.15	440.55

Table 5.6: Thermal expansion behavior of Kr with corresponding experimental data [c] Wallace, 1970.

T	V/V_0			B_T (G Pa)				α (10^{-5} K^{-1})	
(^{0}K)	Modified Tait EOS (eq 4.31)	Modified Murnaghan EOS(eq 4.26)	Singh - Gupta (eq4.56)	Modified Tait EOS(eq4.17)	Modified Murnaghan EOS(eq 4.28)	Singh - Gupta (eq4.52)	Experimental [c]	Singh- Gupta (eq4.48)	Experimental [c]
60	1	1	1	2.55	2.55	2.55	2.55	90.50	90.5
65	1.0046	1.0046	1.0046	2.46	2.46	2.46		93.56	
70	1.0094	1.0094	1.0094	2.38	2.38	2.37	2.30	97.12	98.7
75	1.0144	1.0143	1.0144	2.29	2.29	2.27		101.13	
80	1.0196	1.0196	1.0197	2.20	2.21	2.18	2.05	105.68	107.3
85	1.0250	1.0250	1.0252	2.12	2.12	2.07		110.86	
90	1.0307	1.0307	1.0310	2.03	2.04	1.97		116.79	
95	1.0367	1.0366	1.0372	1.94	2.96	1.86		123.62	
100	1.0430	1.0429	1.0439	1.86	1.87	1.75		131.56	
105	1.0497	1.0495	1.0510	1.77	1.79	1.63		140.80	
110	1.0567	1.0564	1.0587	1.68	1.70	1.51		151.99	
115	1.0642	1.0638	1.0675	1.59	1.62	1.39		165.36	
120	1.0721	1.0716	1.0764	1.50	1.53	1.26		181.78	

Figure Captions

1. Figure 3.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for inert gas solid (Kr). Figure also shows the comparison between Tait's and Murnaghan's equations of state.

2. Figure 3.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for inert gas solid (Kr). Figure also shows the comparison between Tait's and Murnaghan's equations of state.

3. Figure 3.3 shows the variation of Volume thermal expansion (V/V_0) with temperature (T) (in K) for inert gas solid (Kr). Figure also shows the comparison among the modified Tait's, modified Murnaghan's and Singh Gupta equations of state.

4. Figure 3.4 shows the variation of Bulk modulus (B_T) (in GPa) with temperature (T) (in K) for inert gas solid (Kr). Figure also shows the comparison of modified Tait's, modified Murnaghan's and Singh Gupta equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

5. Figure 3.5 shows the variation of thermal expansion coefficient (α) (in 10^{-5} K^{-1}) with temperature (T) (in K) for inert gas solid (Kr). Figure also shows the comparison between Singh Gupta equations of state and experimental data. The square bracket with experimental values shows the reference given in table.

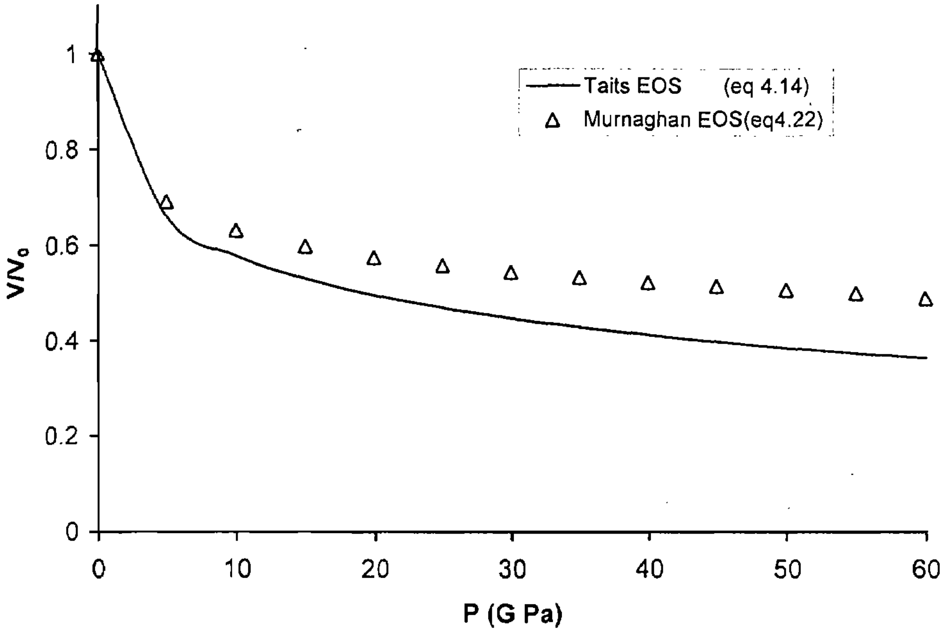


Fig. 3.1 compression behavior of Kr at different pressures

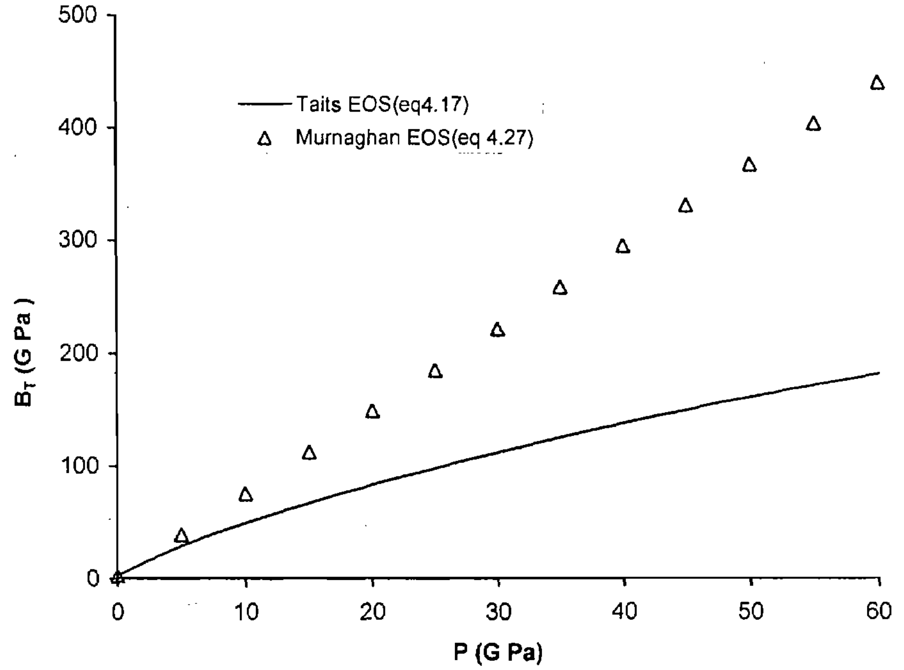


Fig. 3.2 Variation of bulk modulus of Kr with pressure

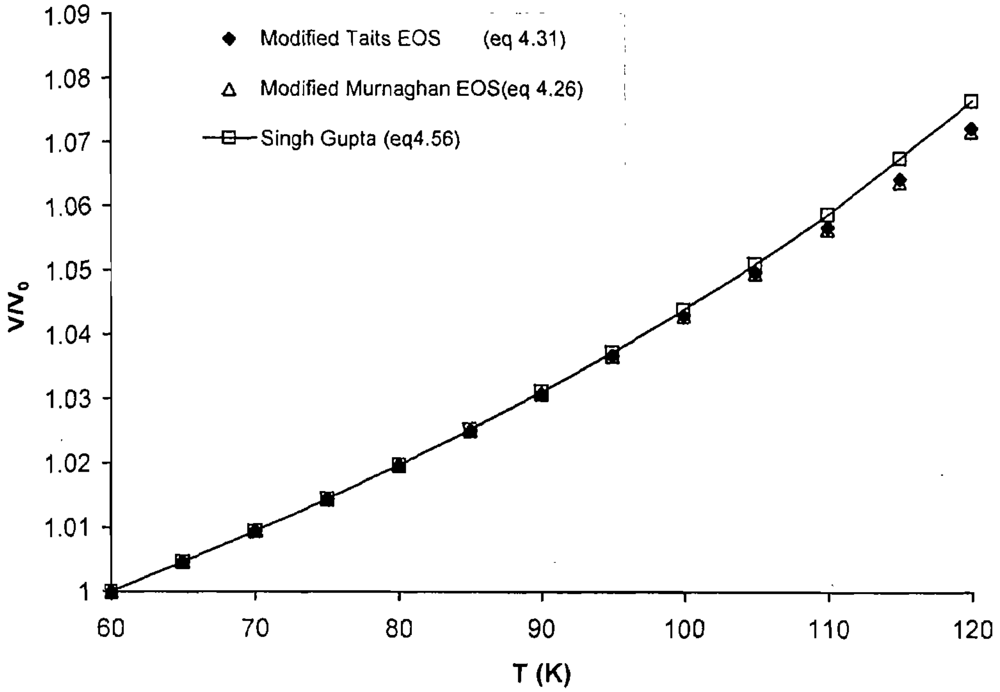


Fig. 3.3 Thermal expansion of Kr

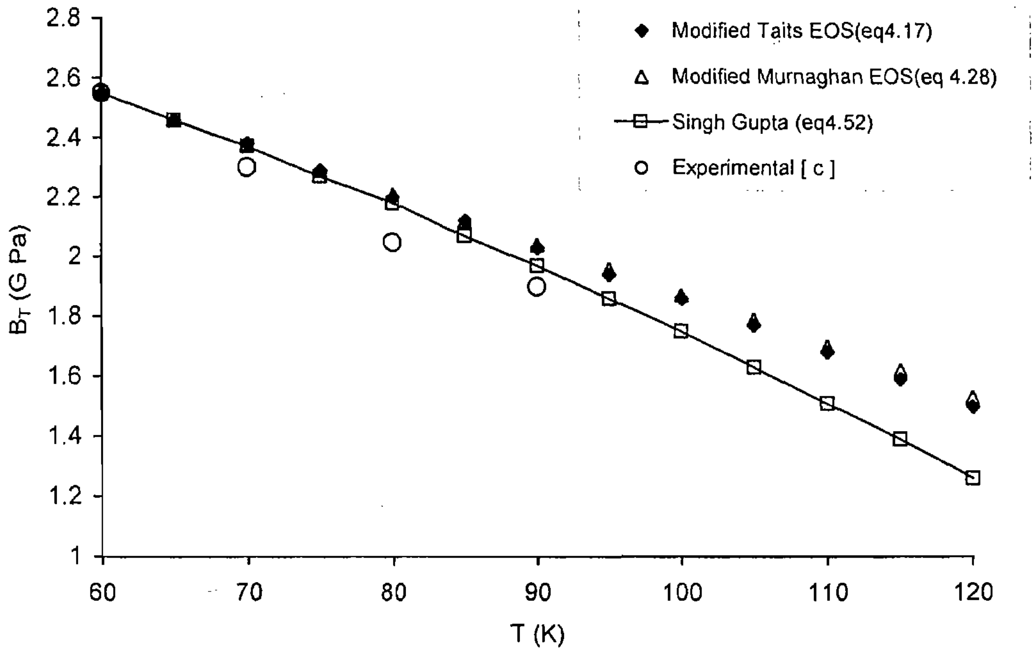


Fig. 3.4 Variation in bulk modulus with temperature of Kr

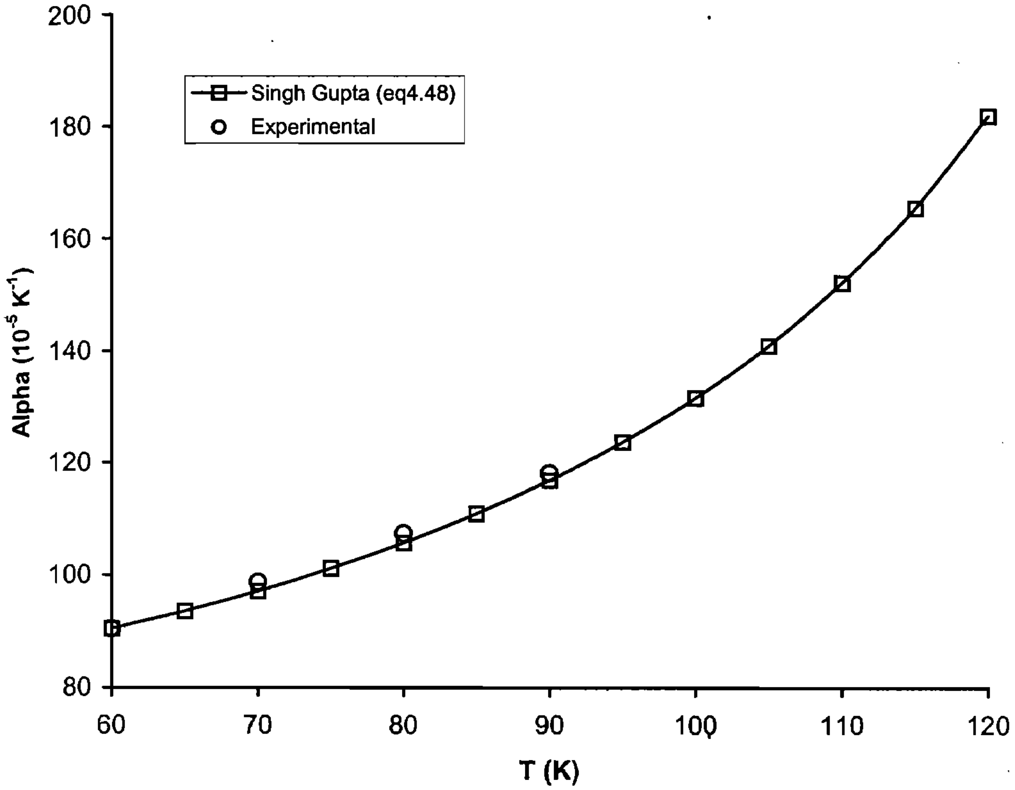


Fig. 3.5 Variation in thermal expansion coefficient with temperature of Kr

Table 5.7: Compression and bulk modulus behavior of Xe under high pressure with corresponding experimental data [d] Zisman et al.,1985.

P (G Pa)	V/V_0			B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS(eq4.22)	Experimental [d]	Tait EOS(eq4.17)	Murnaghan EOS(eq 4.27)
0	1	1	1	3.67	3.67
5	0.7222	0.7420	0.74	36.90	46.07
10	0.6529	0.6870	0.66	64.35	88.47
15	0.6115	0.6560	0.81	89.24	130.87
20	0.5818	0.6347	0.58	112.51	173.27
25	0.5587	0.6185	0.54	134.50	215.67
30	0.5397	0.6055	0.52	155.57	258.07
35	0.5236	0.5948	0.51	175.81	300.0
40	0.5097	0.5856	0.48	195.25	342.87
45	0.4974	0.5776	0.47	214.10	385.27
50	0.4864	0.5705	0.46	232.38	427.67
55	0.4764	0.5642		250.24	470.07
60	0.4673	0.5585		267.57	512.47

Table 5.8: Thermal expansion behavior of Xe.

T (⁰K)	V/V₀ Modified Tait EOS (eq 4.31)	V/V₀ Modified Murnaghan EOS (eq 4.26)	V/V₀ Singh-Gupta (eq4.56)	B_T (G Pa) Modified Tait EOS (eq4.17)	B_T (G Pa) Modified Murnaghan EOS (eq 4.28)	B_T (G Pa) Singh-Gupta (eq4.52)
60	1	1	1	3.02	3.02	3.02
70	1.0061	1.0061	1.0617	2.87	2.87	2.87
80	1.0126	1.0126	1.0127	2.73	2.73	2.71
90	1.0195	1.0195	1.0197	2.59	2.59	2.53
100	1.0269	1.0269	1.0273	2.44	2.45	2.39
110	1.0348	1.0347	1.0356	2.30	2.31	2.15
120	1.0433	1.0431	1.0448	2.15	2.17	1.94
130	1.0524	1.0520	1.0503	2.00	2.03	1.72
140	1.0623	1.0619	1.0672	1.85	1.88	1.49
150	1.0732	1.0726	1.0813	1.70	1.74	1.25
160	1.0853	1.0842	1. 890	1.54	1.60	1.00

Figure Captions

1. Figure 4.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for inert gas solid (Xe). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

2. Figure 4.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for inert gas solid (Xe). Figure also shows the comparison between Tait's and Murnaghan's equations of state.

3. Figure 4.3 shows the variation of Volume thermal expansion (V/V_0) with temperature (T) (in K) for inert gas solid (Xe). Figure also shows the comparison among the modified Tait's, modified Murnaghan's and Singh Gupta equations of state.

4. Figure 4.4 shows the variation of Bulk modulus (B_T) (in GPa) with temperature (T) (in K) for inert gas solid (Xe). Figure also shows the comparison among the modified Tait's, modified Murnaghan's and Singh Gupta equations of state.

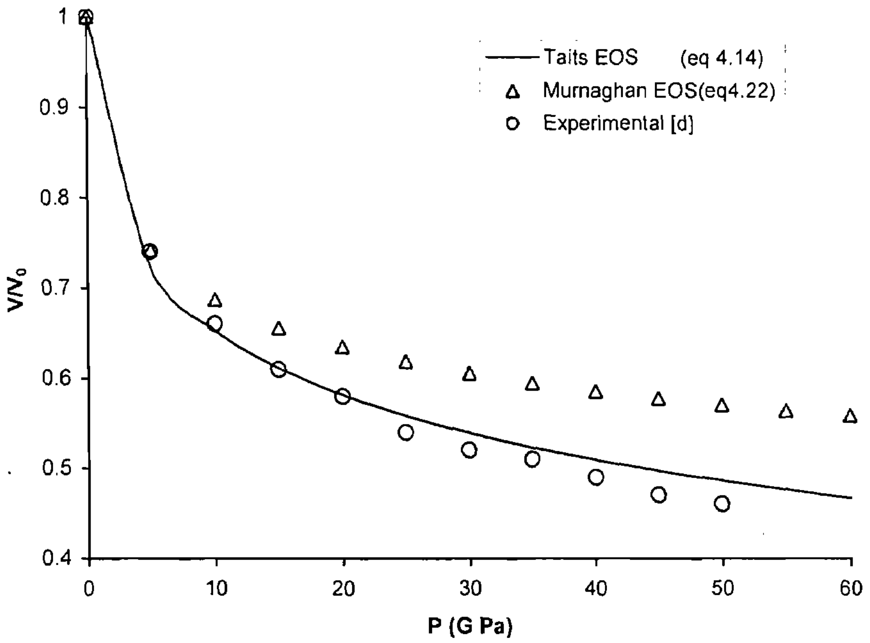


Fig.4.1 Compression behavior of Xe at different pressure

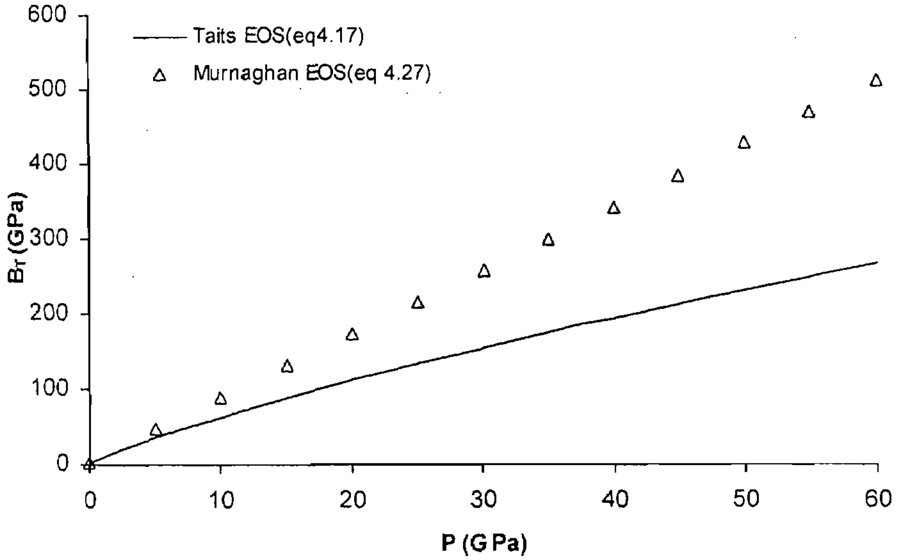


Fig. 4.2 Variation in bulk modulus with pressure for Xe

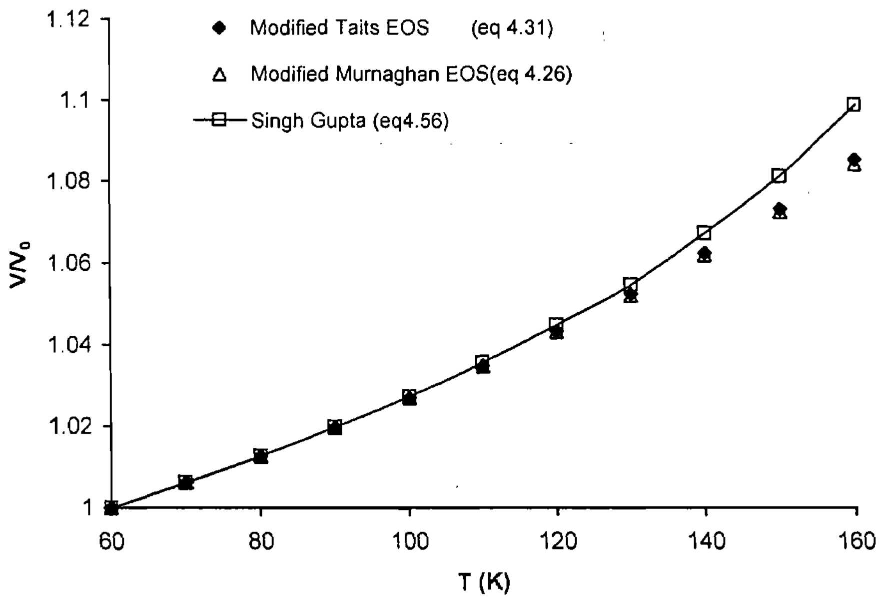


Fig. 4.3 Thermal expansion of Xe at different temperature

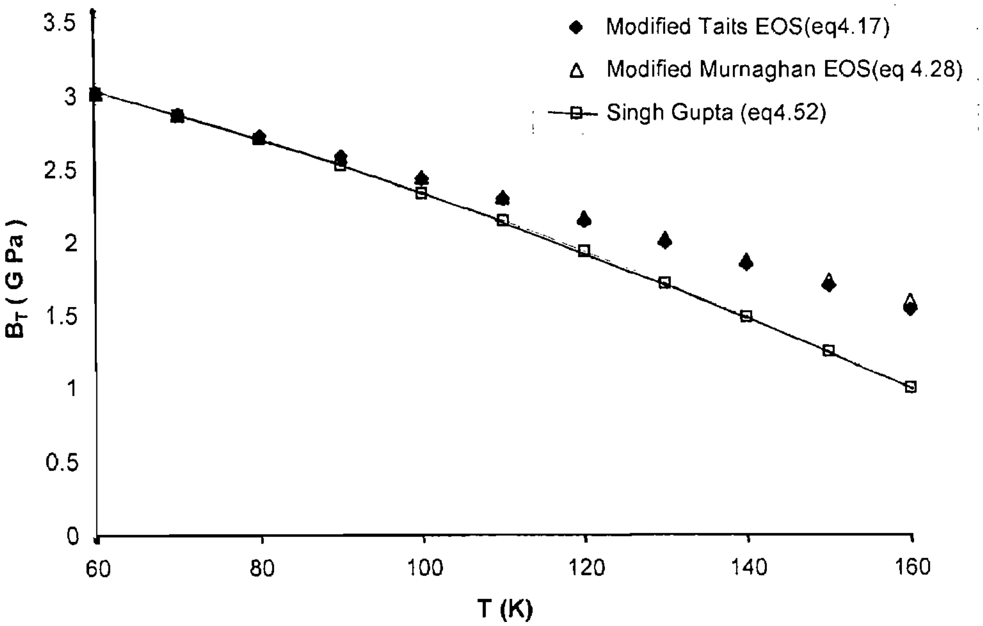


Fig. 4.4 Variation in bulk modulus with temperature

Table 5.9: Compression and bulk modulus behavior of Ge under high pressure with corresponding experimental data [e] Cicco et al.,12003.

P (GPa)	V/V$_0$			B_T (G Pa)	
	Tait EOS (eq4.14)	Murnaghan EOS (eq4.22)	Experimental [e]	Tait EOS (eq4.17)	Murnaghan EOS (eq 4.27)
0	1	1	1	74.9	74.9
2	0.9746	0.9667	0.972	81.2	80.9
4	0.9516	0.9376	0.951	86.5	86.9
6	0.9330	0.9115	0.932	92.5	92.9
8	0.9110	0.8880	0.92	97.79	98.9
10	0.8930	0.8600	0.90	102.6	104.9
12	0.8762	0.8470	0.875	108.0	110.9

Table 5.10: Thermal expansion behavior of Ge.

T (^{0}K)	V/V_0		B_T (G Pa)	
	Modified Tait EOS (eq4.31)	Modified Murnaghan EOS (eq4.26)	Modified Tait EOS (eq4.17)	Modified Murnaghan EOS (eq4.28)
300	1	1	74.9	74.9
400	1.0018	1.0018	74.49	74.49
500	1.0036	1.0036	74.09	74.09
600	1.0054	1.0054	73.69	73.68
700	1.0073	1.0073	73.27	73.28
800	1.0091	1.0091	72.88	72.87
900	1.011	1.011	72.48	72.47
1000	1.0129	1.0129	72.05	72.06
1100	1.0148	1.0148	71.63	71.66
1200	1.0167	1.0167	71.23	71.25

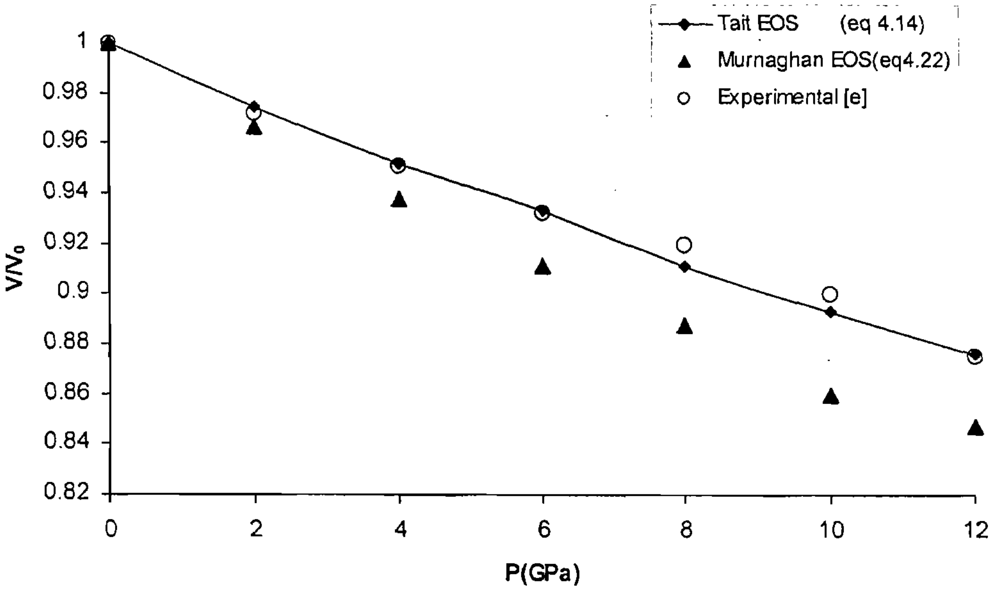
Figure Captions

1. Figure 5.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for semiconductor (Ge in phase1). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

2. Figure 5.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for semiconductor (Ge in phase1). Figure also shows the comparison between Tait's and Murnaghan's equations of state.

3. Figure 5.3 shows the variation of Volume thermal expansion (V/V_0) with temperature (T) (in K) for semiconductor (Ge in phase1). Figure also shows the comparison between the modified Tait's and modified Murnaghan's.

4. Figure 5.4 shows the variation of Bulk modulus (B_T) (in GPa) with temperature (T) (in K) for semiconductor (Ge in phase1). Figure also shows the comparison between the modified Tait's and modified Murnaghan's.



5.1 Compression behavior of Ge in phase 1

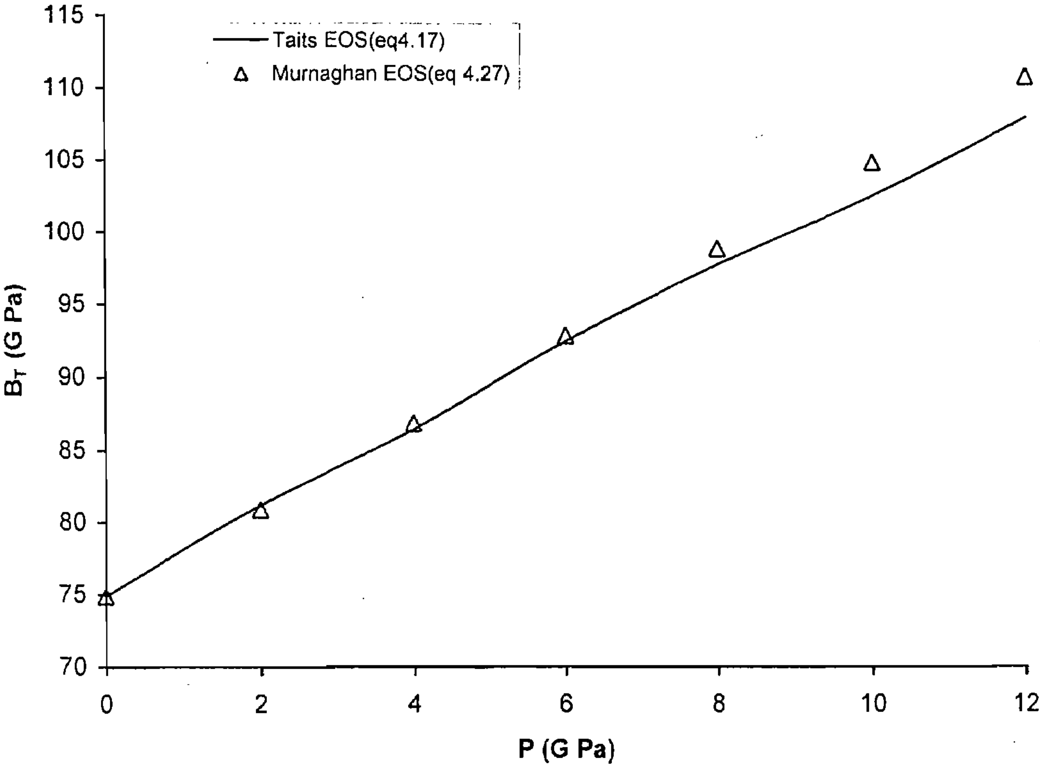


Fig. 5.2 Variation in bulk modulus with pressure of Ge in Phase I

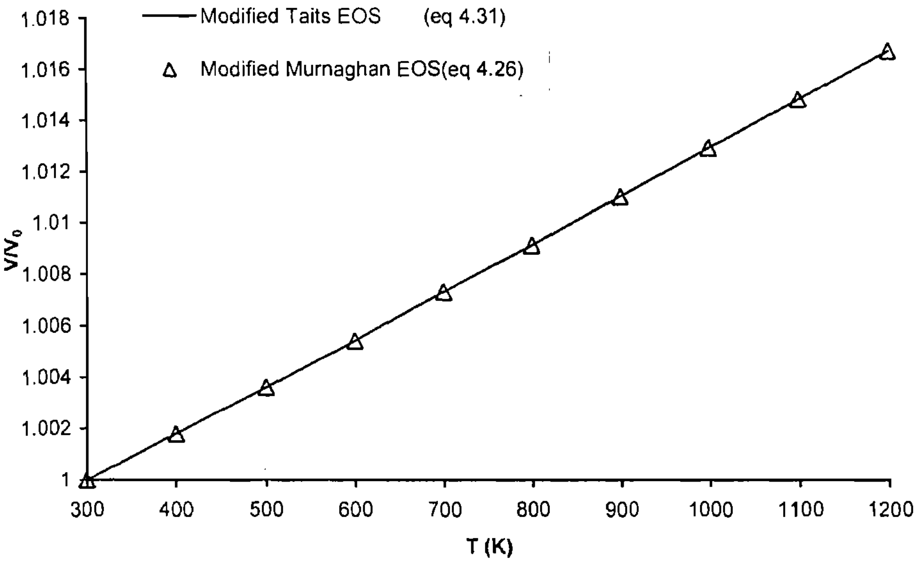


Fig 5.3 Thermal Expansion of Ge in phase I

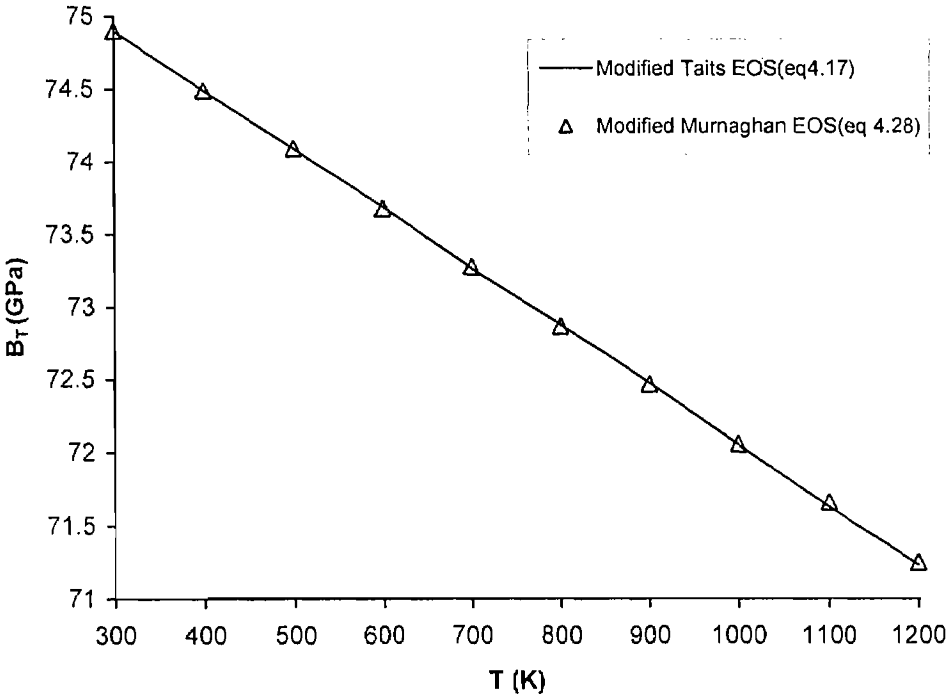


Fig. 5.4 Variation in Bulk modulus with temperature of Ge

Table 5.11: Compression behavior of Si under high pressure.

P (G Pa)	V/V0		B_T (G Pa)	
	Tait EOS (eq .14)	Murnaghan EOS(eq4.22)	Tait EOS(eq4.17)	Murnaghan EOS(eq 4.27)
0	1	1	66.25	66.25
5	0.9385	0.9387	97.31	93.55
10	0.8946	0.8957	128.81	120.58
15	0.8604	0.8629	158.77	148.15
20	0.835	0.8366	190.22	175.45
25	0.8088	0.8147	220.1	202.75
30	0.7881	0.7961	249.59	230.05
35	0.7702	0.7799	278.53	257.35
40	0.7539	0.7656	307.16	284.65
45	0.7392	0.7529	335.27	311.95
50	0.7258	0.7414	363	339.25

Table 5.12: Thermal expansion behavior of Si.

T (^{0}K)	V/V_0		B_T (G Pa)	
	Modified Tait EOS (eq 4.31)	Modified Murnaghan EOS(eq 4.26)	Modified Tait EOS(eq4.17)	Modified Murnaghan EOS(eq 4.28)
300	1	1	66.25	66.25
400	1.00078	1.00078	65.96	65.96
500	1.00156	1.0016	65.67	65.68
600	1.00235	1.0023	65.38	65.4
700	1.00315	1.00315	65.1	65.12
800	1.0039	1.00394	64.85	64.83
900	1.0047	1.00475	64.57	64.55
1000	1.0055	1.00555	64.28	64.27
1100	1.0063	1.0063	64.0	63.99
1200	1.0072	1.0072	63.69	63.71
1300	1.008	1.008	63.41	63.42
1400	1.0088	1.0088	63.13	63.14
1500	1.0096	1.00965	62.86	62.86
1600	1.0104	1.01048	62.58	62.58

Figure Captions

1. Figure 6.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for semiconductor (Si). Figure also shows the comparison between Tait's and Murnaghan's equations of state.

2. Figure 6.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for semiconductor (Si). Figure also shows the comparison between Tait's and Murnaghan's equations of state.

3. Figure 6.3 shows the variation of Volume thermal expansion (V/V_0) with temperature (T) (in K) for semiconductor (Si). Figure also shows the comparison between the modified Tait's and modified Murnaghan's equations of state.

4. Figure 6.4 shows the variation of Bulk modulus (B_T) (in GPa) with temperature (T) (in K) for semiconductor (Si). Figure also shows the comparison between the modified Tait's and modified Murnaghan's equations of state.

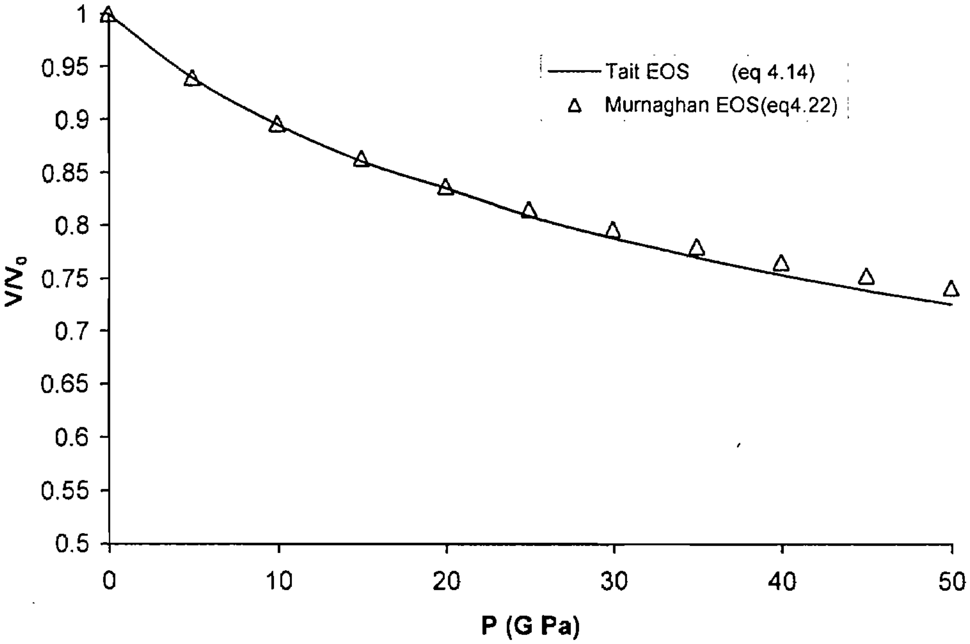


Fig. 6.1 Compression behavior of Si

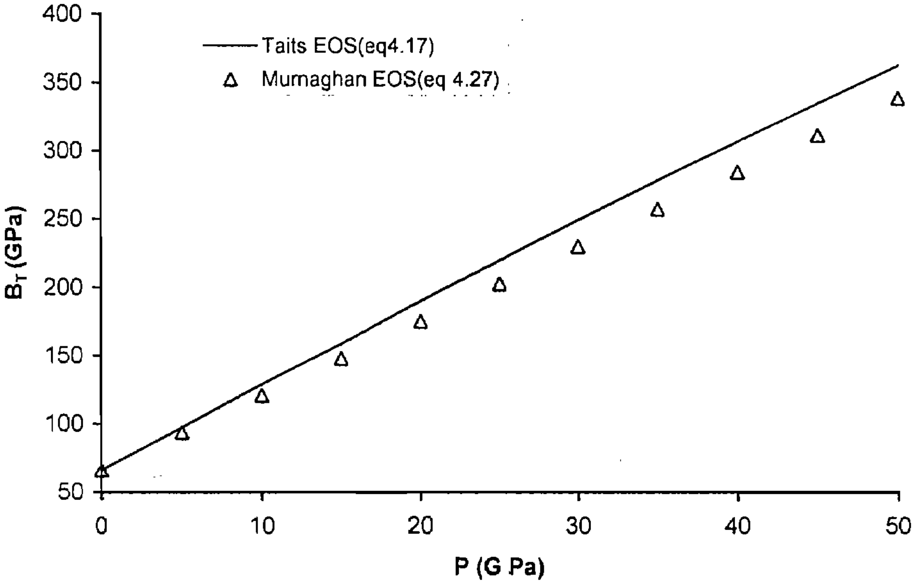


Fig 6.2 Variation in bulk modulus with pressure of Si

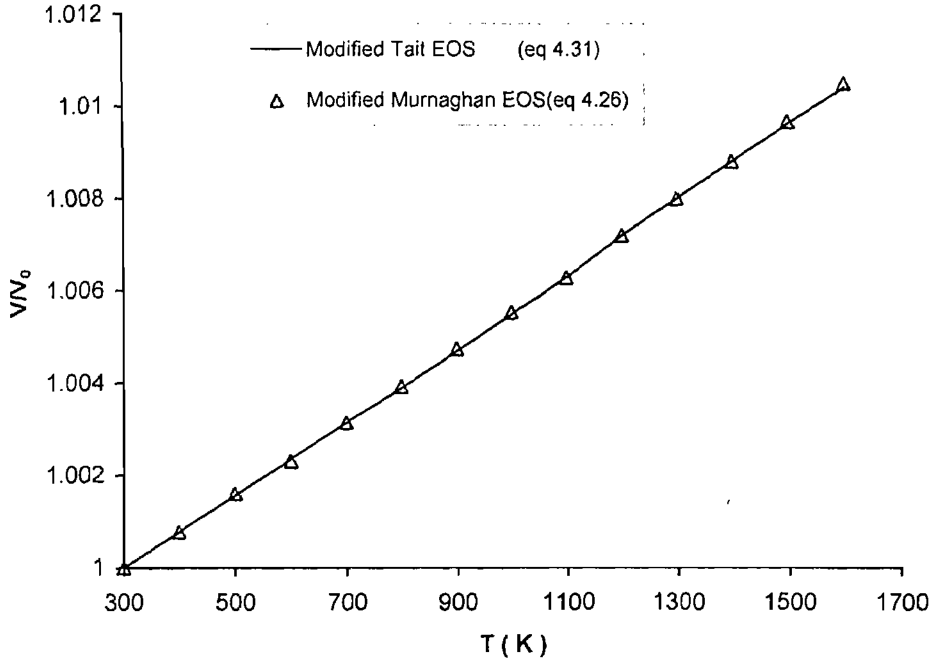


Fig 6.3 Thermal expension behavior of Si

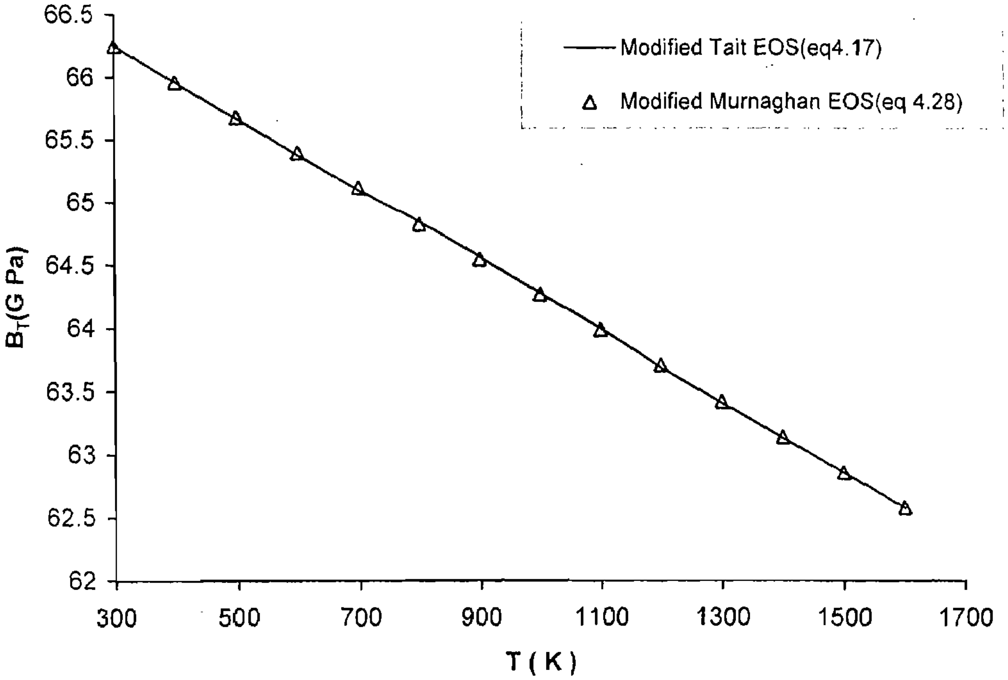


Fig. 6.4 Bulk modulus of Si at different temperature

Table 5.13: Compression behavior of $FeSi_2$ under high pressure with corresponding experimental data [f] Mori et al., 2003.

P (G Pa)	V/V0			B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS (eq4.22)	Experimental [f]	Tait EOS (eq4.17)	Murnaghan EOS(eq 4.27)
0	1	1	1	243.46	243.48
5.5	0.9748	0.9803	0.9756	265.06	261.28
13.0	0.9518	0.9518	0.9523	284.26	285.58
21	0.9264	0.9266	0.9302	308.14	311.5
27	0.9091	0.9094	0.909	325.4	330.94
35	0.8877	0.884	0.8888	347.92	356.86
40	0.8753	0.8763	0.8733	361.58	373.06
51	0.85	0.8518	0.851	390.89	408.7
60	0.8312	0.8338	0.8333	413.96	437.86

Figure Captions

1. Figure 7.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for semiconductor ($FeSi_2$). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

2. Figure 7.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for semiconductor ($FeSi_2$). Figure also shows the comparison between Tait's and Murnaghan's equations of state.

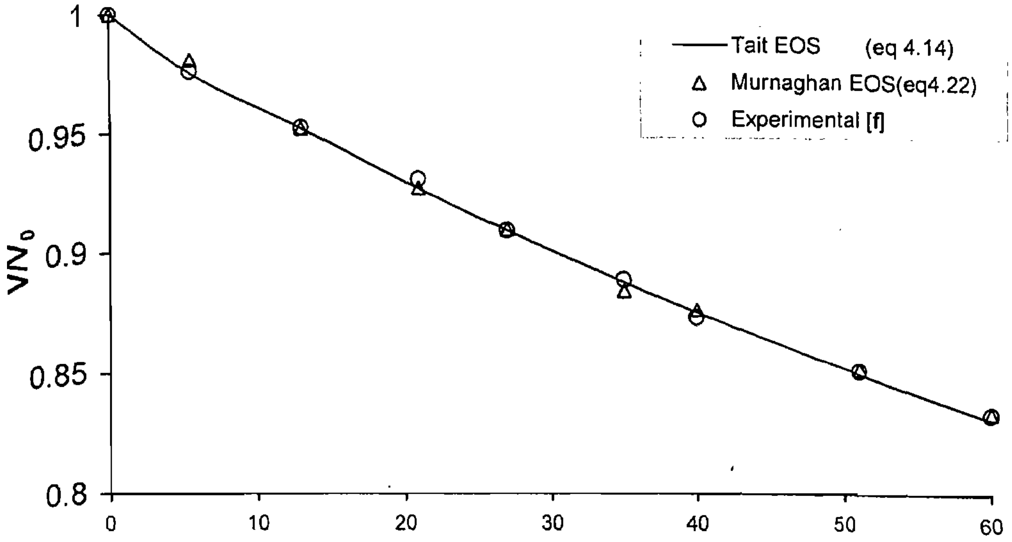


Fig. 7.1 Compression behavior of $FeSi_2$

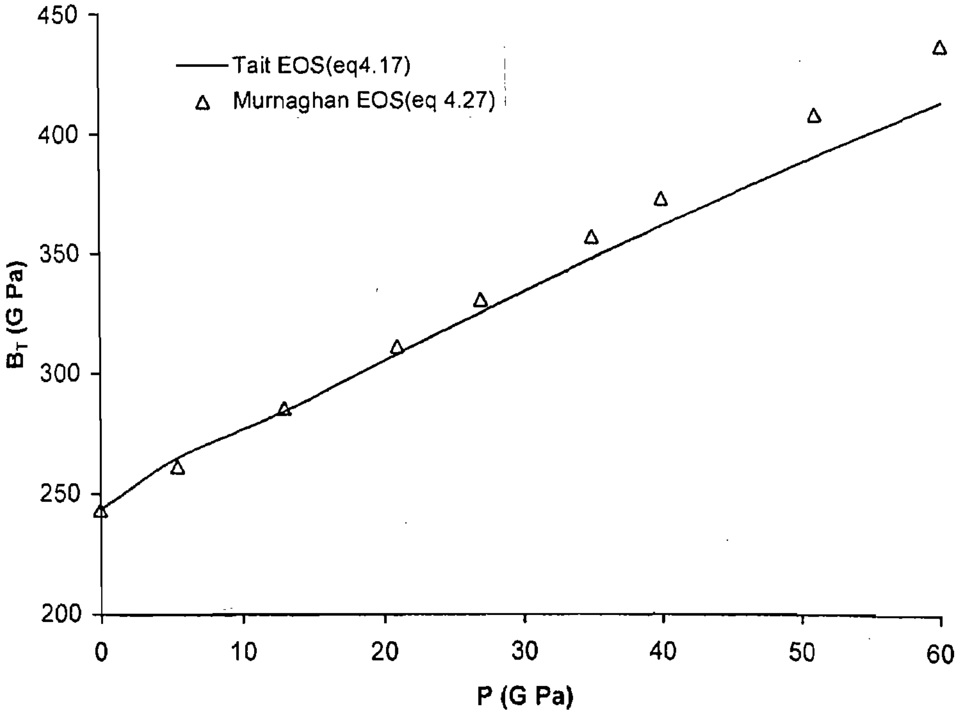


Fig. 7.2 Bulk modulus of $FeSi_2$ at different pressure

Table 5.14 : Compression and bulk modulus behavior of SiC under high pressure with corresponding experimental data [g] Amulele et al., 2003.

P (G Pa)	V/V₀			P (G Pa)	B_T (G Pa)		
	Tait EOS (eq 4.14)	Murnaghan EOS (eq4.22)	Experimental [g]		Tait EOS (eq4.17)	Murnaghan EOS (eq 4.27)	Experimental [g]
0	1	1	1	0	217	217.0	-
10	0.9587	0.9588	0.958	2	225.74	225.0	-
20	0.9247	0.9251	0.91	4	234	233.76	235.0
30	0.8959	0.8968	0.89	5	238.13	237.95	239.0
40	0.8708	0.8725	0.87	6	242.13	242.14	241.8
50	0.8486	0.8512	0.83	7	246.2	246.33	244.0
60	0.8287	0.8324	0.82	8	250.22	250.52	250.0
70	0.8106	0.8156	-	9	254.31	254.71	252.0
80	0.7942	0.8003	-	10	258.37	258.09	256.0
90	0.779	0.7865	-	11	262.23	263.09	260.0
100	0.7649	0.7738	0.735	12	266.28	267.28	265.8
200	0.6621	0.6858	0.64	-	-	-	-
300	0.5954	0.6332	0.56	-	-	-	-
400	0.546	0.5965	0.51	-	-	-	-
500	0.5067	0.5687	0.48	-	-	-	-

Table 5.15: Thermal expansion behavior of SiC.

T (^{0}K)	V/V_0		B_T (G Pa)	
	Modified Tait EOS (eq 4.31)	Modified Murnaghan EOS(eq 4.26)	Modified Tait EOS (eq4.17)	Modified Murnaghan EOS(eq 4.28)
300	1	1	217.4	217.4
400	1.001	1.001	216.49	216.44
500	1.0021	1.0021	215.49	215.48
600	1.0031	1.0032	214.59	214.53
700	1.0042	1.0042	213.6	213.57
800	1.0053	1.0053	212.62	212.61
900	1.0064	1.0064	211.64	211.66
1000	1.0074	1.0074	210.75	210.70
1100	1.0085	1.0085	209.78	209.74
1200	1.0096	1.0096	208.82	208.79
1300	1.0107	1.0108	207.85	207.83
1400	1.0119	1.0119	206.81	206.87
1500	1.0130	1.0130	205.85	205.92
1600	1.0141	1.0141	204.9	204.96

Figure Captions

1. Figure 8.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for semiconductor (SiC). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

2. Figure 8.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for semiconductor (Si). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

3. Figure 6.3 shows the variation of Volume thermal expansion (V/V_0) with temperature (T) (in K) for semiconductor (Si). Figure also shows the comparison between the modified Tait's and modified Murnaghan's equations of state.

4. Figure 6.4 shows the variation of Bulk modulus (B_T) (in GPa) with temperature (T) (in K) for semiconductor (Si). Figure also shows the comparison between the modified Tait's and modified Murnaghan's equations of state.

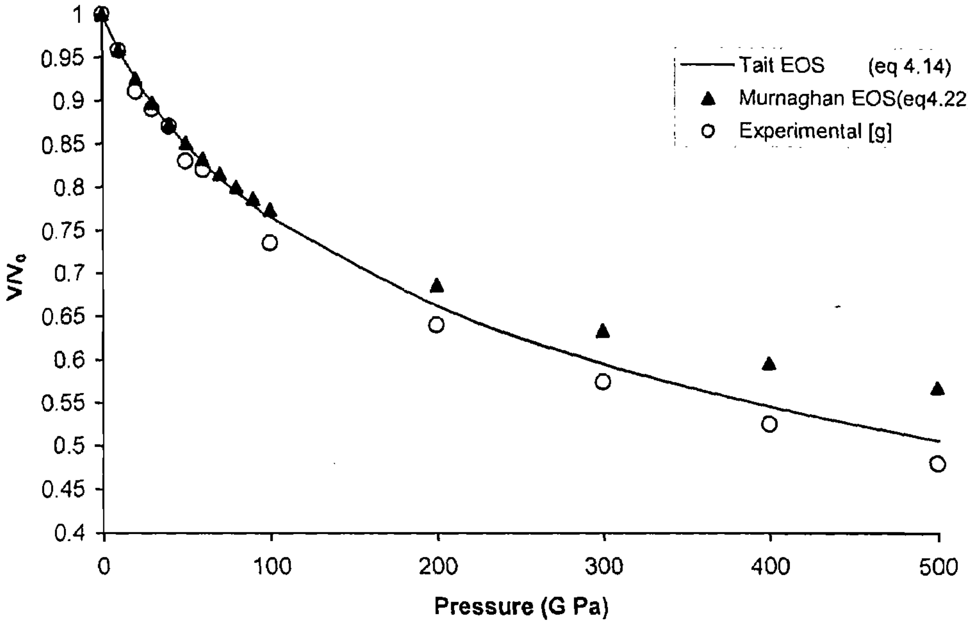


Fig. 8.1 Compression behavior of SiC

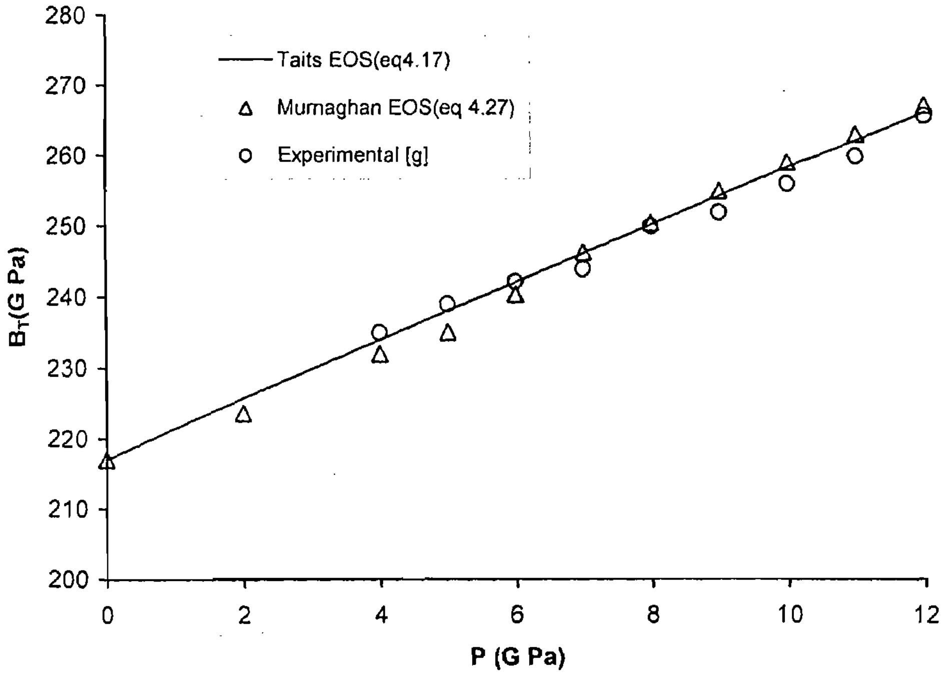


Fig. 8.2 Bulk modulus of SiC at different pressure

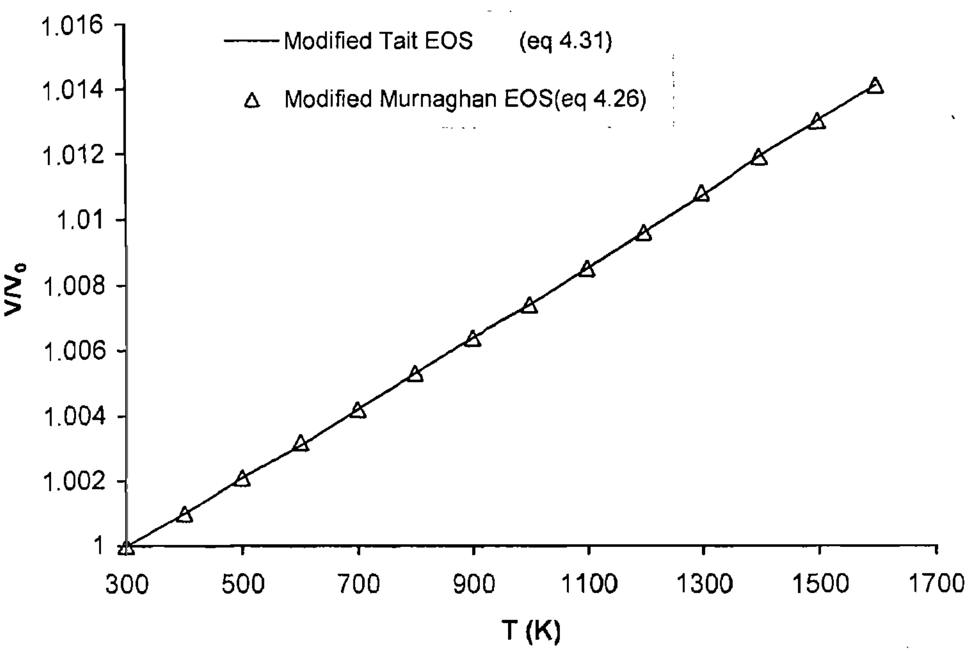


Fig. 8.3 Thermal Expansion of SiC

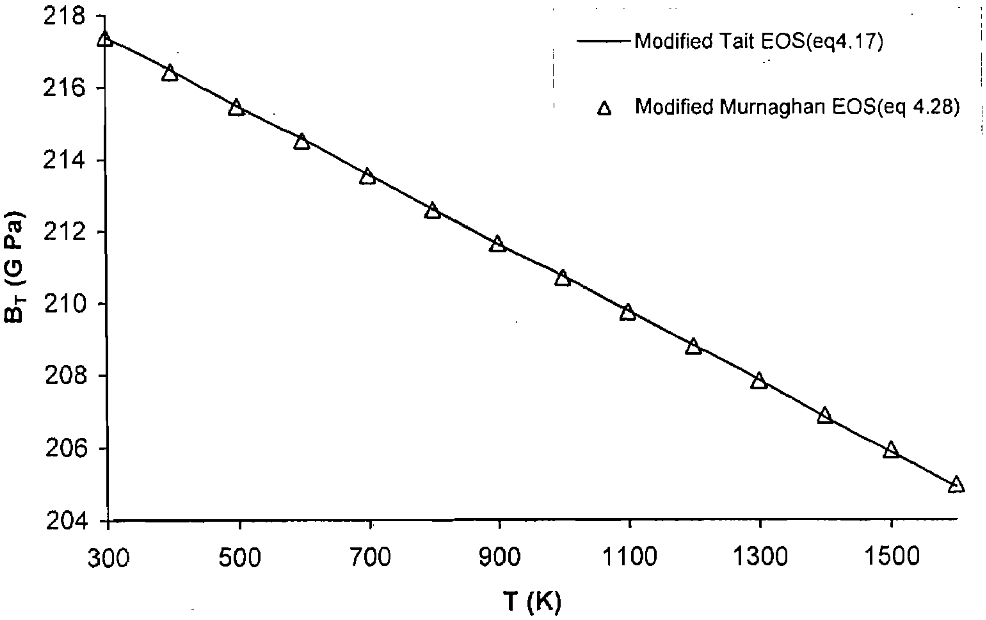


Fig. 8.4 Bulk modulus of SiC at different temperature

Table 5.16: Compression and bulk modulus behavior of α SnS under high pressure with corresponding experimental data [h] Ehm et al., 2004.

P (G Pa)	V/V₀			B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS(eq 4.22)	Experimental [h]	Tait EOS (eq4.17)	Murnaghan EOS(eq 4.27)
0	1	1	1	36.6	36.60
1.18	0.9705	0.9706	0.9750	43.02	43.12
1.86	0.9560	0.9556	0.9640	46.57	46.85
3.05	0.9330	0.9337	0.9410	52.66	53.39
5.25	0.8986	0.8996	0.9200	63.57	65.47
5.93	0.8893	0.8905	0.8910	66.84	69.22
7.45	0.8700	0.8723	0.8730	74.00	77.57
7.62	0.8682	0.8703	0.8682	74.84	78.58
10.50	0.8380	0.8417	0.8433	87.90	94.39
11.86	0.8255	0.8302	0.8368	93.92	101.83
13.56	0.8113	0.8170	0.8158	101.23	111.17
15.27	0.7983	0.8051	0.8106	108.39	120.58
15.93	0.7934	0.8007	0.7980	112.20	124.21

Table 5.17: Compression and bulk modulus behavior of γ SnS under high pressure with corresponding experimental data [i] Ehm et al., 2004.

P (G Pa)	V/V_0			B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS (eq 4.22)	Experimental [i]	Tait EOS (eq4.17)	Murnaghan EOS (eq 4.27)
17.5	0.8596	0.8616	0.85	149.16	156
20	0.8457	0.8483	0.843	157.31	166
22.5	0.8327	0.8360	0.8375	165.3	176
24	0.8253	0.8290	0.8250	170.00	182
26.8	0.8121	0.8168	0.8125	178.70	193.2
28	0.8067	0.8118	0.8060	182.37	198
30.5	0.7959	0.8018	0.7937	189.91	208
33.5	0.7837	0.7907	0.7812	198.76	220
36	0.7741	0.7819	0.7750	205.98	230
38	0.7667	0.7753	0.7625	211.70	238

Figure Captions

1. Figure 9.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for semiconductor (SnS in alpha phase). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

2. Figure 9.2 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for semiconductor (SnS in gamma phase). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

3. Figure 9.3 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for semiconductor (SnS in alpha phase). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

4. Figure 9.4 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for semiconductor (SnS in gamma phase). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

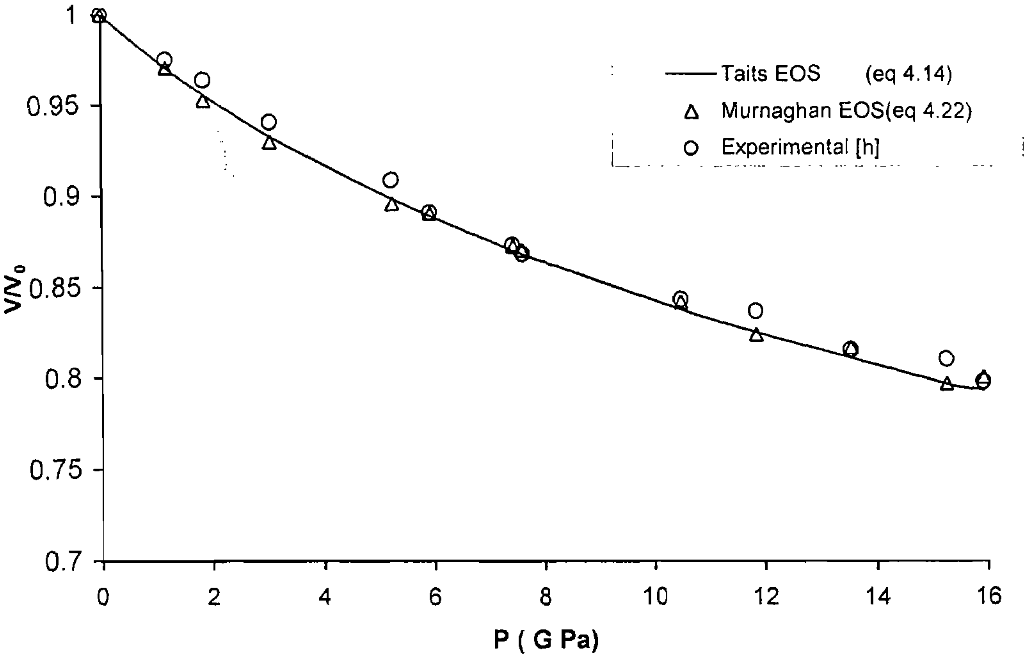


Fig. 9.1 Compression behavior of SnS in alpha phase.

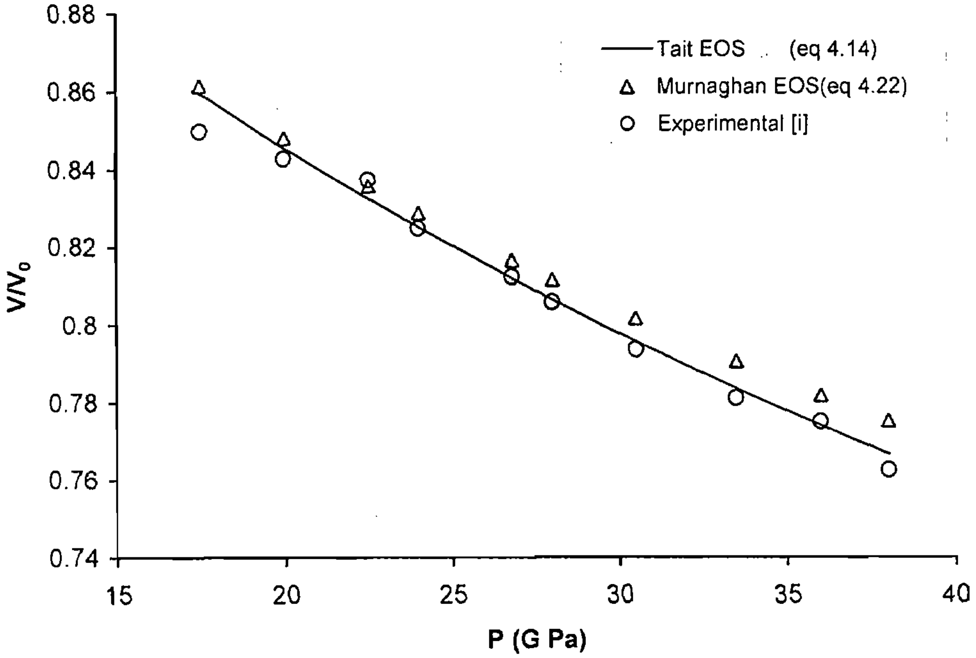


Fig. 9.2 Compression behavior of SnS in gama phase

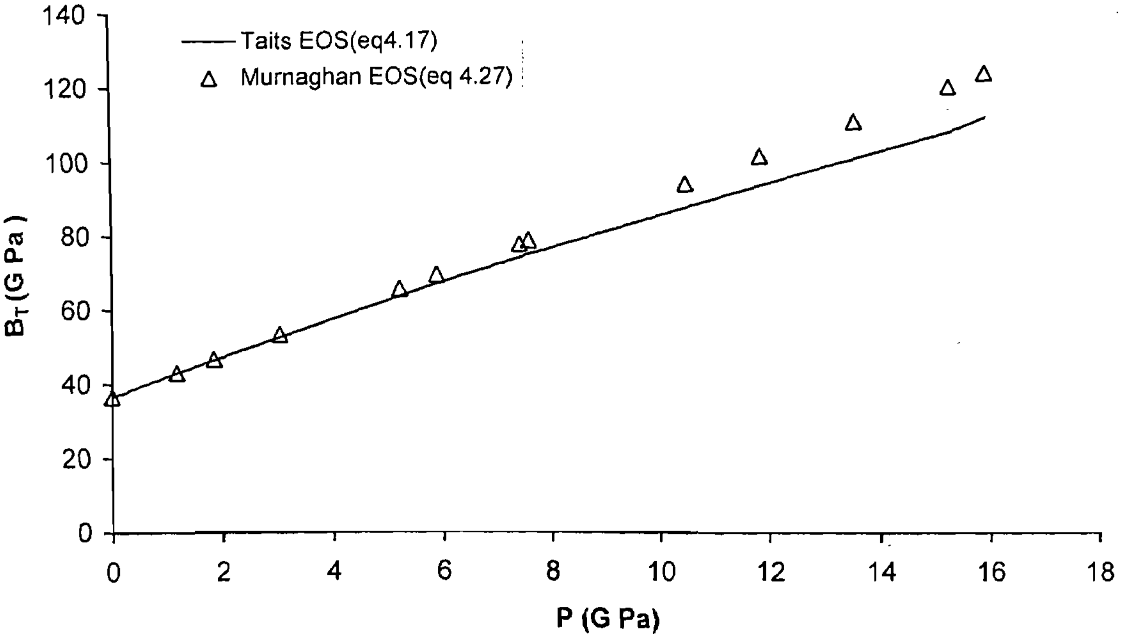


Fig. 9.3 Bulk modulus behavior of SnS in alpha phase

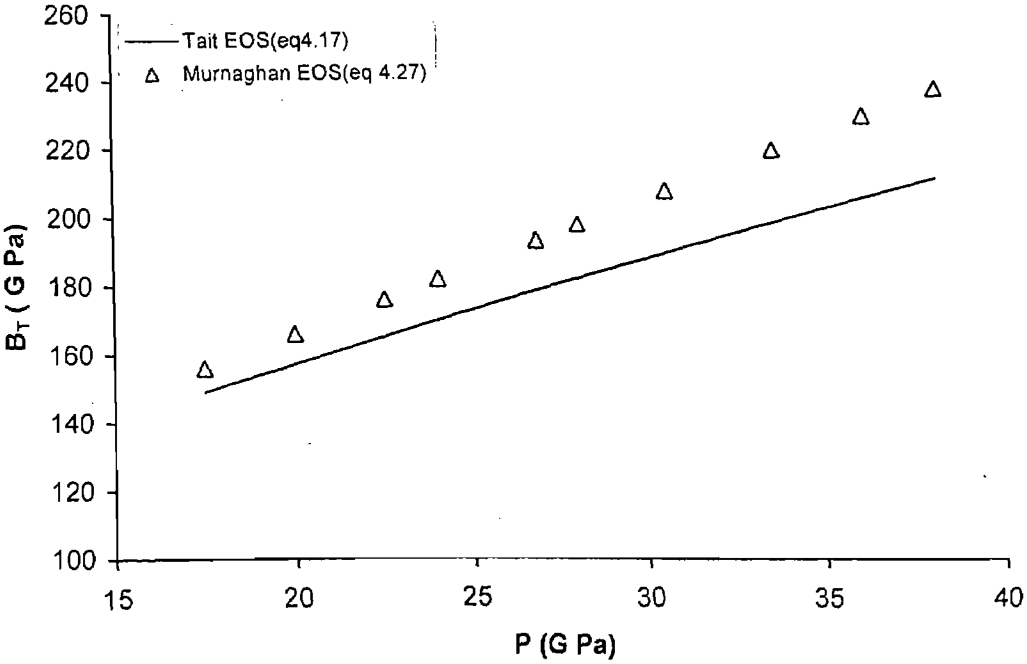


Fig. 9.4 Bulk modulus behavior of SnS (beta phase)

Table 5.18: Compression and bulk modulus behavior of MoN under high pressure with corresponding experimental data [j] Soignard et al., 2003.

P (G Pa)	V/V0			B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS(eq 4.22)	Experimental [j]	Tait EOS (eq4.17)	Murnaghan EOS(eq 4.27)
0	1	1	1	345	345
11	0.9702	0.9702	0.97	382.7	383.5
17	0.9554	0.9555	0.956	402.8	404.5
25	0.9372	0.9374	0.936	428.92	432.5
32	0.9224	0.9228	0.924	451.22	457
40	0.9066	0.9072	0.908	476.17	485
46	0.8955	0.8963	0.896	494.43	506
50	0.8884	0.8893	0.888	506.44	520
56	0.8781	0.8793	0.878	524.31	541
64	0.8651	0.8667	0.866	547.67	569
67	0.8604	0.8662	0.86	556.34	579.5
72	0.8528	0.8549	0.856	570.61	597
74	0.8498	0.8521	0.85	576.33	604
80	0.8411	0.8438	0.844	593.2	625
90	0.8274	0.8308		620.6	660
100	0.8144	0.8186		647.7	695

Figure Captions

1. Figure 10.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for semiconductor (MoN). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

2. Figure 10.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for semiconductor (MoN). Figure also shows the comparison between Tait's and Murnaghan's equations of state.

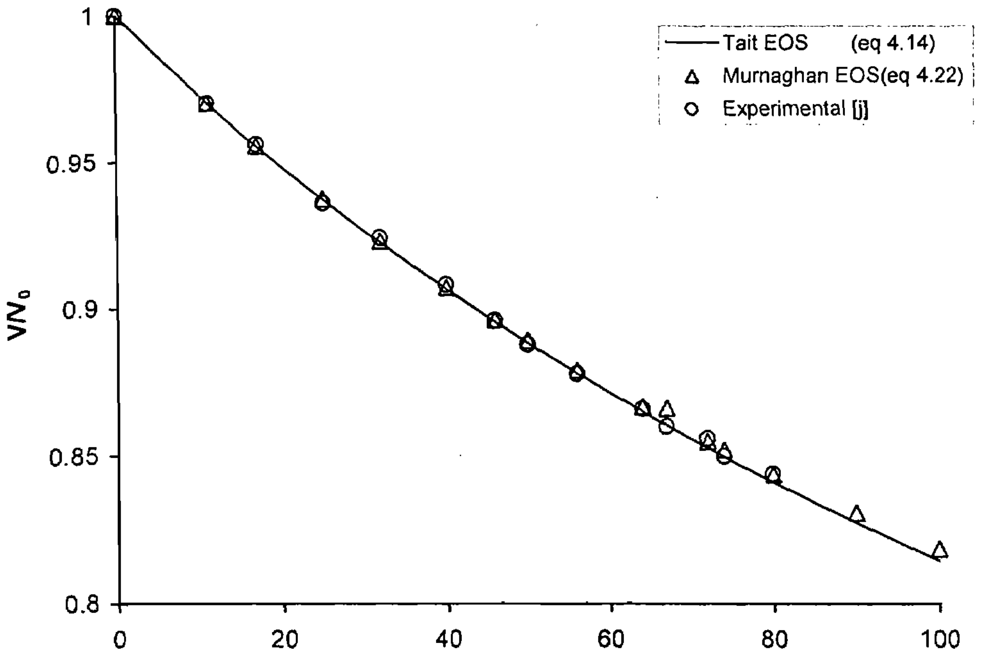


Fig. 10.1 Compression behavior of MoN

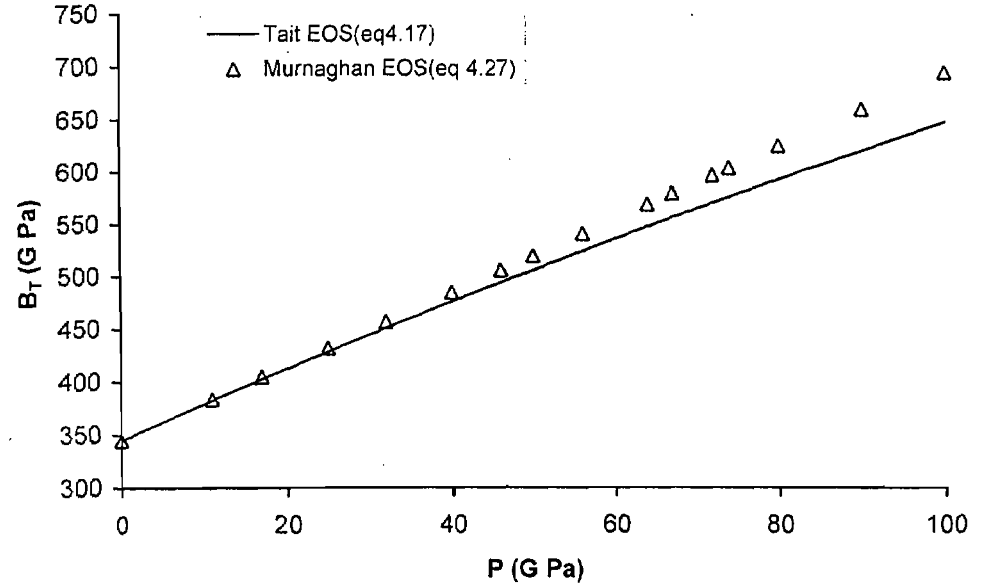


Fig. 10.2 variation in bulk modulus of MoN with pressure

Table 5.19: Compression and bulk modulus behavior of MoN_2 under high pressure with corresponding experimental data [k] Soignard et al., 2003.

P (G Pa)	V/V_0			B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS (eq 4.22)	Experimental [k]	Tait EOS (eq4.17)	Murnaghan EOS (eq 4.27)
0	1	1	1	301	301
3	0.9902	0.9902	0.98	313	313
8	0.975	0.975	0.974	332.5	333
10	0.9692	0.9692	0.968	340.3	341
12	0.9636	0.9636	0.96	347.9	349
16	0.9528	0.9529	0.956	363.1	365
20	0.9426	0.9427	0.946	378	381
23	0.9352	0.9354	0.942	389.2	393
25	0.9305	0.9307	0.924	396.5	401
27.5	0.9247	0.9262	0.924	405.6	411
30	0.9191	0.9195	0.914	414.6	421
33	0.9125	0.9131	0.908	425.4	433
35	0.9083	0.9089	0.9	432.4	441
40	0.8981	0.8989		449.9	461
45	0.8883	0.8894		467.4	481
50	0.879	0.8804		484.5	501

Figure Captions

1. Figure 11.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for semiconductor (MoN_2). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

2. Figure 11.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for semiconductor (MoN_2). Figure also shows the comparison between Tait's and Murnaghan's equations of state.

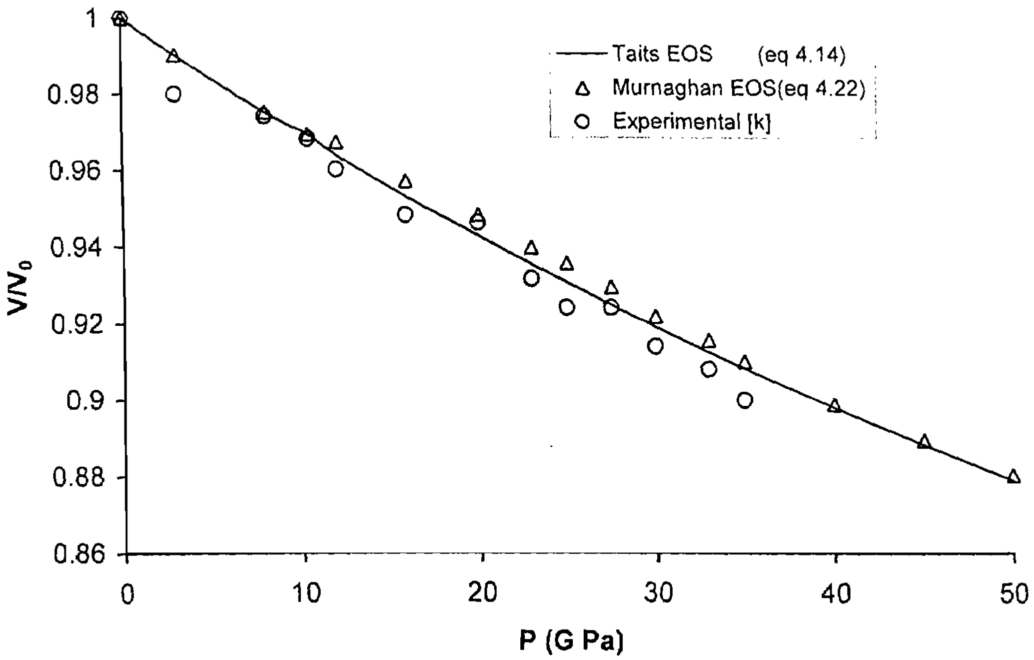


Fig. 11.1 Compression behavior of MoN_2

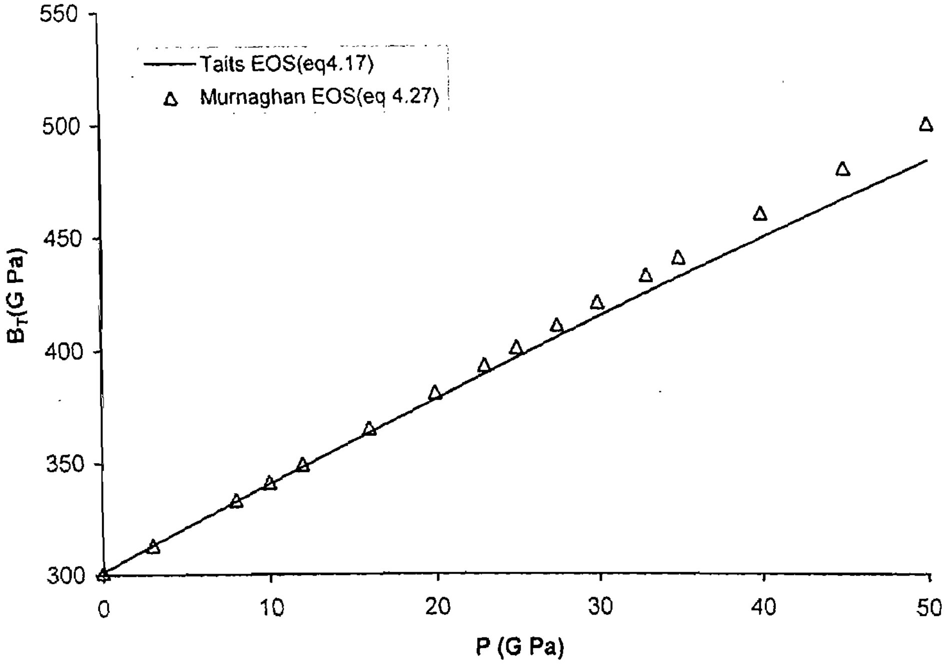


Fig. 11.2 Variation of bulk modulus of MoN_2 with pressure

Table 5.20: Compression and bulk modulus behavior of AlN under high pressure with corresponding experimental data [k] Ueno et al., 1992.

P (G Pa)	V/V_0			B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS (eq 4.22)	Experimental [n]	Tait EOS (eq4.17)	Murnaghan EOS (eq 4.27)
0	1	1	1	215.8	215.8
2	0.9909	0.9909	0.99	224.19	223.6
4	0.9823	0.9823		232.41	232
6	0.974	0.974	0.975	240.61	240.4
7	0.970	0.970	0.97	244.66	244.6
10	0.9584	0.9585	0.96	256.77	257.2
12	0.9511	0.9512		264.67	265.6
15	0.9406	0.9408	0.94	276.44	278.2
17	0.9339	0.9312	0.93	284.2	286.6
20	0.9243	0.9247		295.67	299.2
22.5	0.9167	0.9171	0.92	305.06	309.7
25	0.9093	0.9099		314.47	320.2
30	0.8953	0.8962		333.01	341.2

Figure Captions

1. Figure 12.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for semiconductor (AlN). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

2. Figure 12.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for semiconductor (AlN). Figure also shows the comparison between Tait's and Murnaghan's equations of state.

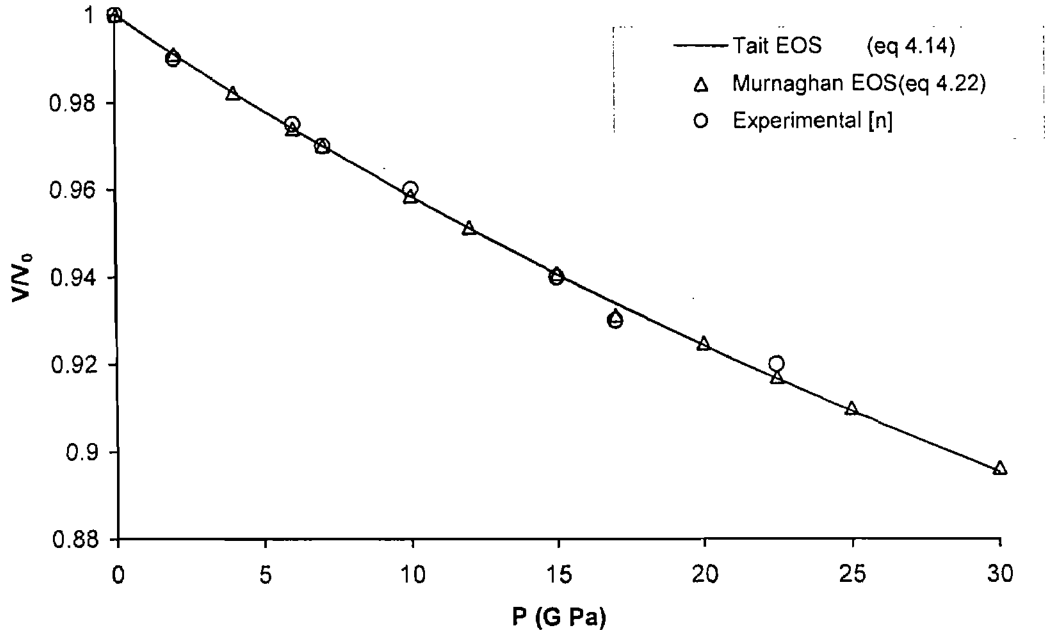


Fig. 12.1 Compression behavior of AlN

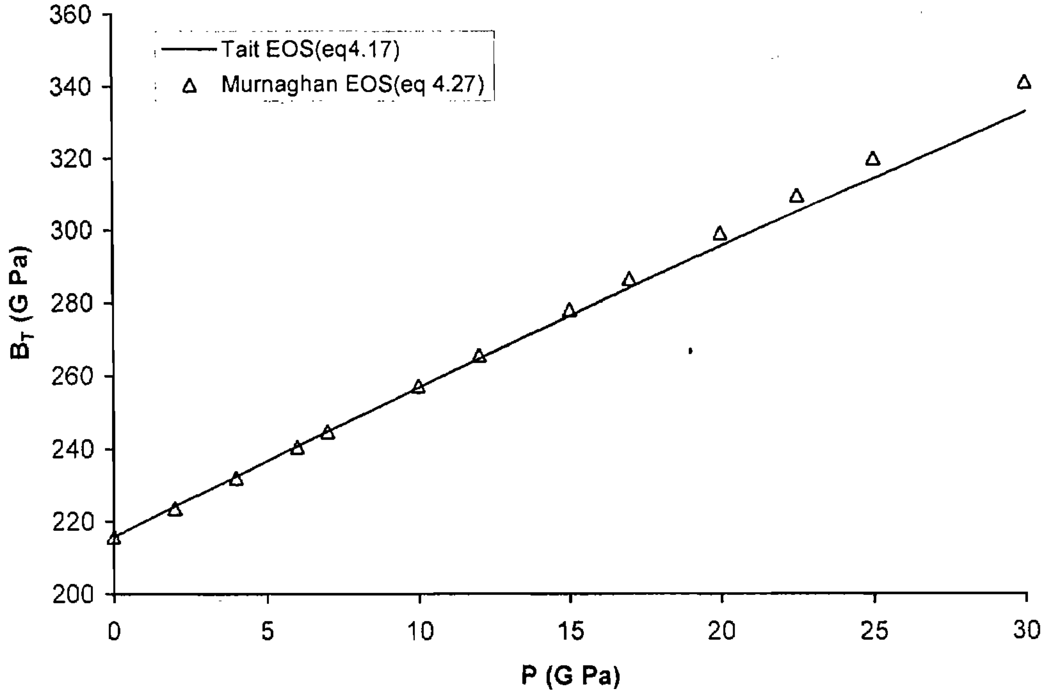


Fig. 12.2 Variation of bulk modulus with pressure of AlN

Table 5.21: Compression and bulk modulus behavior of GaN under high pressure with corresponding experimental data [m] Ueno et al. 1994.

P (G Pa)	V/V0			B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS(eq 4.22)	Experimental [m]	Tait EOS (eq4.17)	Murnaghan EOS(eq 4.27)
0	1	1	1	241.72	241.7
1	0.9958	0.9958	0.99	260.3	260.5
5	0.9800	0.9800	0.975	278.68	279.3
9	0.9654	0.9656		292.37	293.4
12	0.9551	0.9555	0.95	296.9	298.1
13	0.9518	0.9523		319.34	321.6
18	0.9361	0.9371	0.918	328.18	331
20	0.9302	0.9313		350.09	354.5
25	0.9162	0.9178	0.905	358.9	363.9
27	0.9108	0.9128	0.918	371.84	378
30	0.9031	0.9054		401.78	410.9
37	0.8862	0.8895		414.45	425
40	0.8794	0.8831	0.885	439.53	453.2
46	0.8665	0.8711	0.875	464.34	481.4
52	0.8544	0.860	0.85	496.91	519
60	0.8394	0.8463		241.72	241.7

Figure Captions

1. Figure 13.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for semiconductor (GaN). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

2. Figure 13.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for semiconductor (GaN). Figure also shows the comparison between Tait's and Murnaghan's equations of state.

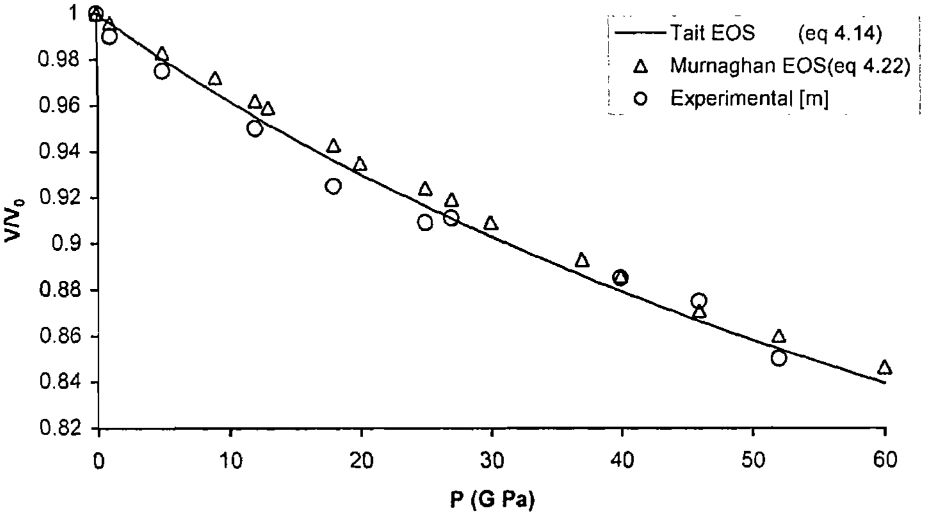


Fig. 13.1 Compression behavior of GaN

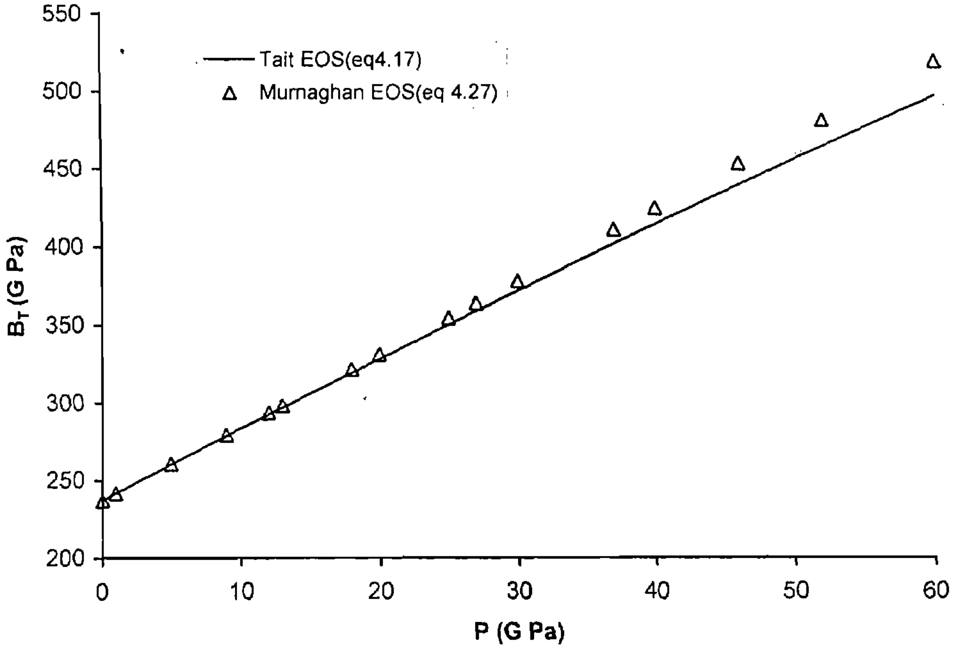


Fig. 13.2 Variation in bulk modulus with pressure of GaN

Table 5.22: Compression and bulk modulus behavior of Mo under high pressure with corresponding experimental data [p] Hixson et al., 1992.

P (G Pa)	V/V_0			B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS (eq 4.22)	Experimental [p]	Tait EOS (eq4.17)	Murnaghan EOS (eq 4.27)
0	1	1	1	268	268
20	0.9358	0.9359		336.52	339.6
40	0.8862	0.8872	0.88	399.96	411.2
50	0.8651	0.8668	0.858	430.05	447
90	0.7960	0.8020	0.82	543.02	590.2
100	0.7824	0.7890	0.78	568.04	626
120	0.7564	0.7655	0.76	618.61	697.6
140	0.7332	0.7448	0.74	666.86	769.2
160	0.7123	0.7266		712.93	840.8
180	0.6931	0.7102	0.698	757.48	912.4
220	0.6593	0.6818	0.66	841.18	1055.6
240	0.6442	0.6694		880.77	1127.2
260	0.6300	0.6580	0.62	919.24	1198.8
280	0.6167	0.6474		956.35	1270.4
300	0.6042	0.6376	0.61	992.17	1342

Table 5.23: Thermal expansion behavior of Mo.

T (^{0}K)	V/V_0		B_T (G Pa)	
	Modified Tait EOS(eq 4.31)	Modified Murnaghan EOS (eq 4.26)	Modified Tait EOS (eq4.17)	Modified Murnaghan EOS (eq 4.28)
300	1	1	268	268
600	1.0045	1.0045	263.71	263.68
900	1.0091	1.0091	259.39	259.36
1200	1.0139	1.0139	254.96	255.04
1500	1.0187	1.0187	250.6	250.73
1800	1.0237	1.0237	246.13	246.41
2100	1.0288	1.0288	241.64	242.09
2400	1.034	1.0339	237.15	237.77
2700	1.0393	1.0392	232.65	233.77
3000	1.0447	1.0447	228.14	229.14

Figure Captions

1. Figure 14.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for metal (Mo). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

2. Figure 14.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for metal (Mo). Figure also shows the comparison of Tait's and Murnaghan's equations of state.

3. Figure 14.3 shows the variation of Volume thermal expansion (V/V_0) with temperature (T) (in K) for metal (Mo). Figure also shows the comparison of modified Tait's and modified Murnaghan's equations.

4. Figure 14.4 shows the variation of Bulk modulus (B_T) (in GPa) with temperature (T) (in K) for metal (Mo). Figure also shows the comparison of Tait's and Murnaghan's equations of state.

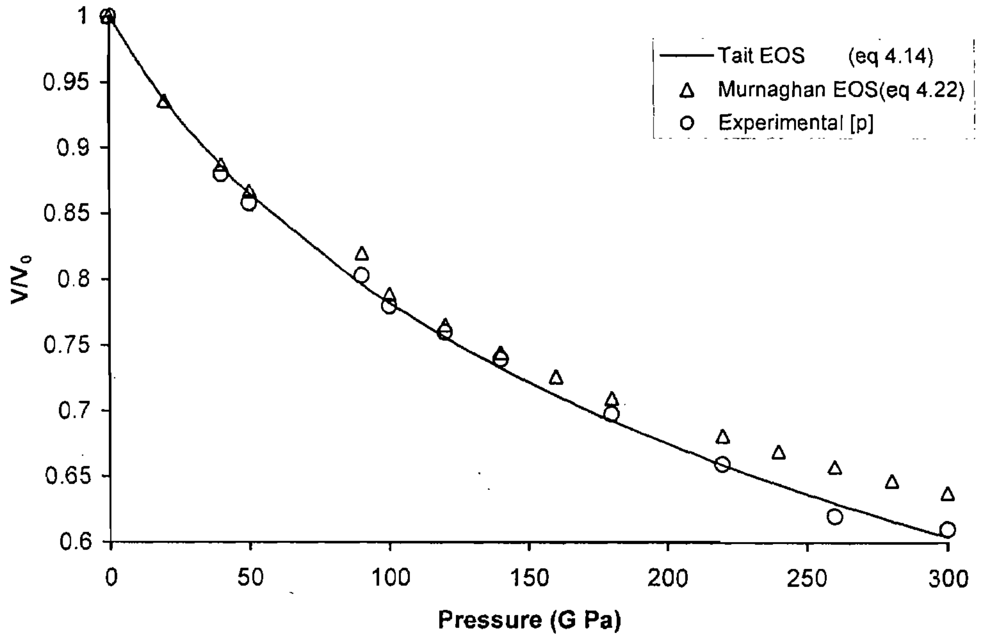


Fig. 14.1 Compression behavior of Mo

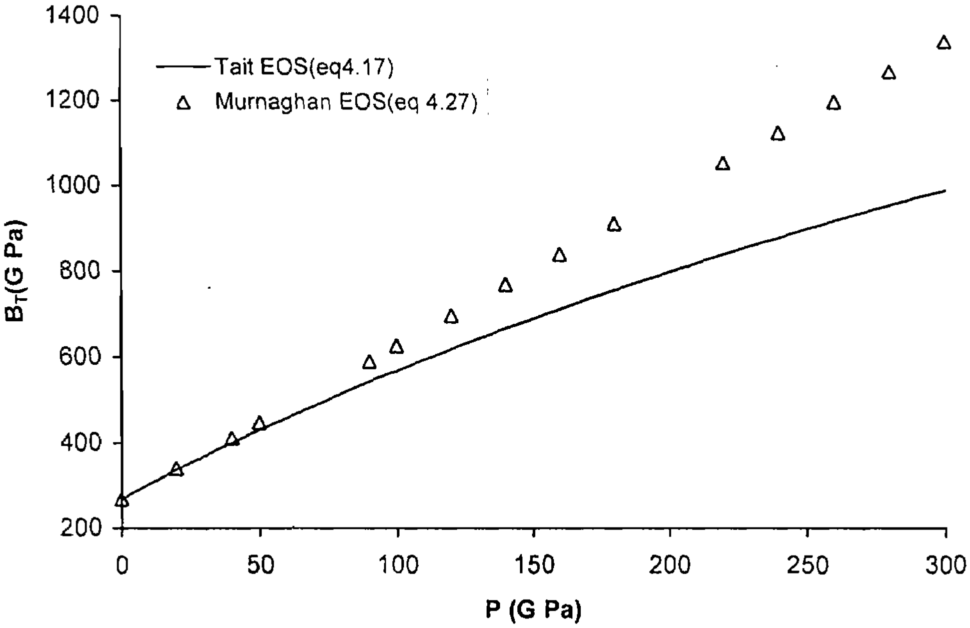


Fig. 14.2 Variation in bulk modulus of Mo with pressure

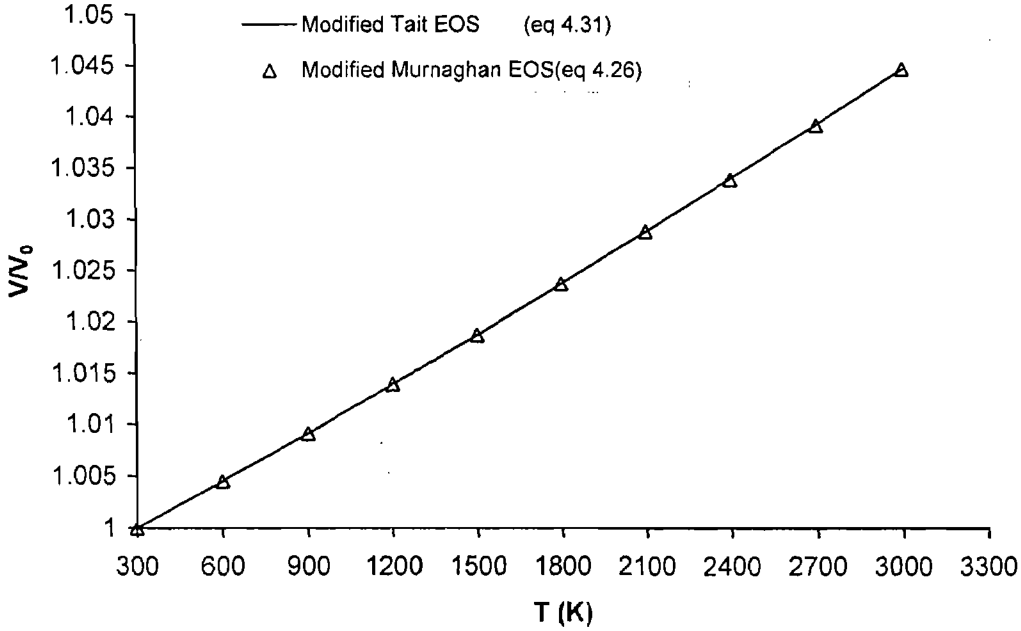


Fig. 14.3 Thermal expansion of Mo with temperature

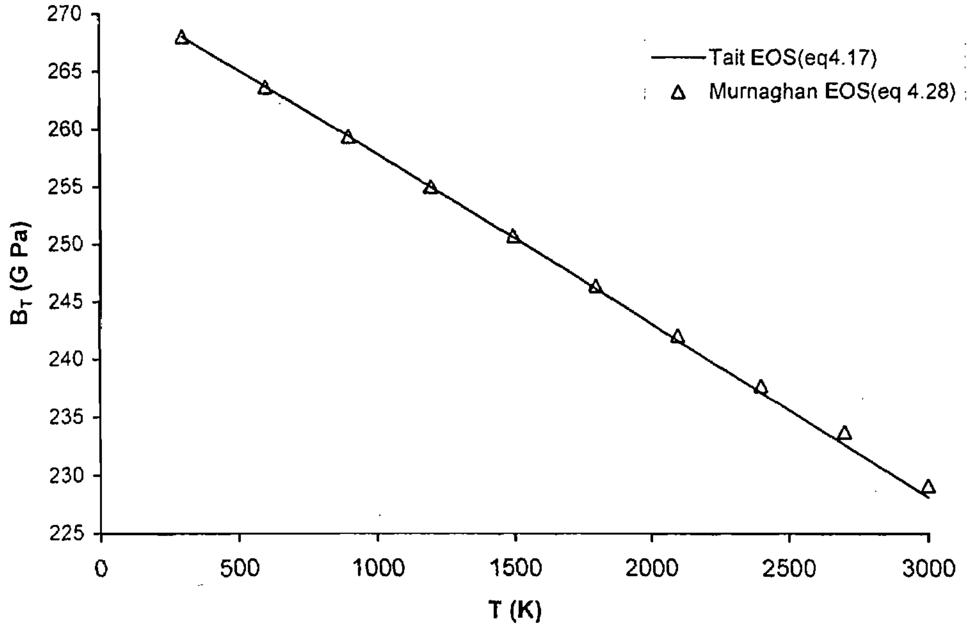


Fig. 14.4 Variation in bulk modulus of Mo with temperature

Table 5.24: Compression and bulk modulus behavior of W under high pressure with corresponding experimental data [q] Hixson et al., 1992.

P (G Pa)	V/V$_0$			B$_T$ (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS (eq 4.22)	Experimental [q]	Tait EOS (eq4.17)	Murnaghan EOS (eq 4.27)
0	1	1	1	312	312
25	0.9319	0.9321	0.95	399.88	404
50	0.8804	0.8816	0.885	480.75	496
70	0.8466	0.8491	0.84	541.52	569.6
100	0.8042	0.8092	0.81	627.3	680
110	0.7900	0.7976	0.79	658.57	716.8
150	0.7481	0.7582	0.75	758.75	864
180	0.7200	0.7338	0.73	832.88	974.4
200	0.7037	0.7194	0.7	878.55	1048
270	0.6539	0.6777	0.675	1030.65	1305
300	0.6335	0.6629	0.65	1098.52	1416

Table 5.25: Thermal expansion behavior of W.

T (^{0}K)	V/V$_0$		B_T (G Pa)	
	Modified Tait EOS (eq 4.31)	Modified Murnaghan EOS (eq 4.26)	Modified Tait EOS (eq4.17)	Modified Murnaghan EOS (eq 4.28)
300	1	1	312	312
600	1.004	1.004	307.43	307.28
900	1.0082	1.0082	302.71	302.57
1200	1.0125	1.0125	297.95	297.86
1500	1.0168	1.0168	293.25	293.15
1800	1.0212	1.0212	288.52	288.43
2100	1.0257	1.0257	283.75	283.72
2400	1.0304	1.0304	278.85	279.01
2700	1.0351	1.0351	274.02	274.3
3000	1.0399	1.0399	269.18	269.59

Figure Captions

1. Figure 15.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for metal (W). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

2. Figure 15.2 shows the variation variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for metal (W). Figure also shows the comparison of Tait's and Murnaghan's equations of state.

3. Figure 15.3 shows the variation of Volume thermal expansion (V/V_0) with temperature (T) (in K) for metal (W). Figure also shows the comparison of modified Tait's and modified Murnaghan's equations.

4. Figure 15.4 shows the variation of Bulk modulus (B_T) (in GPa) with temperature (T) (in K) for metal (W). Figure also shows the comparison of Tait's and Murnaghan's equations of state.

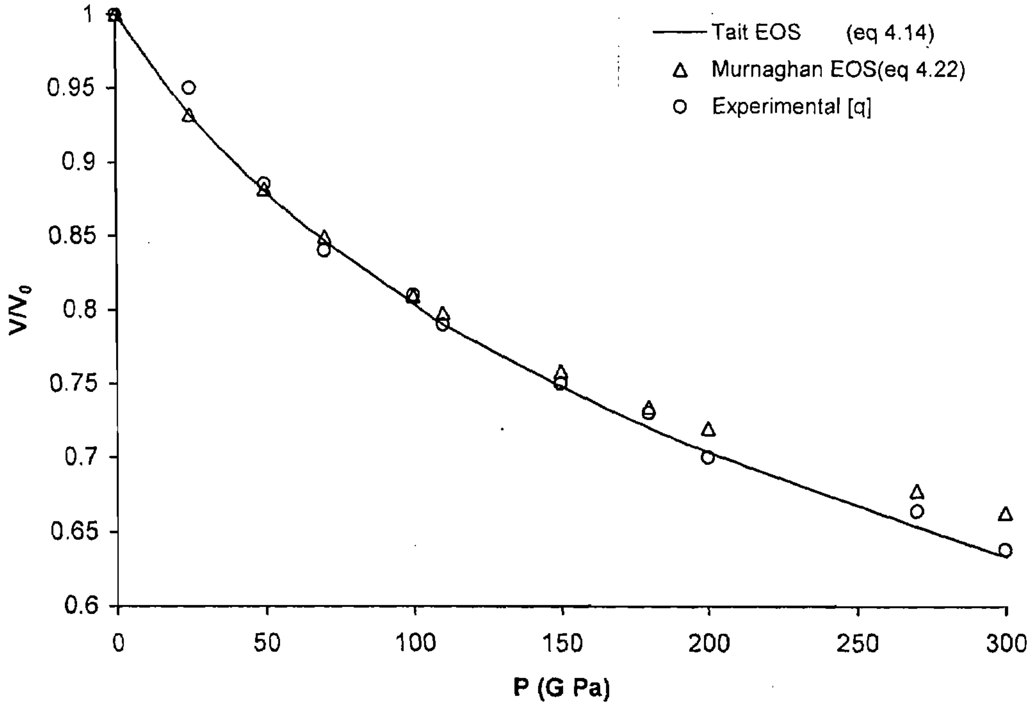


Fig. 15.1 Compression behavior of W

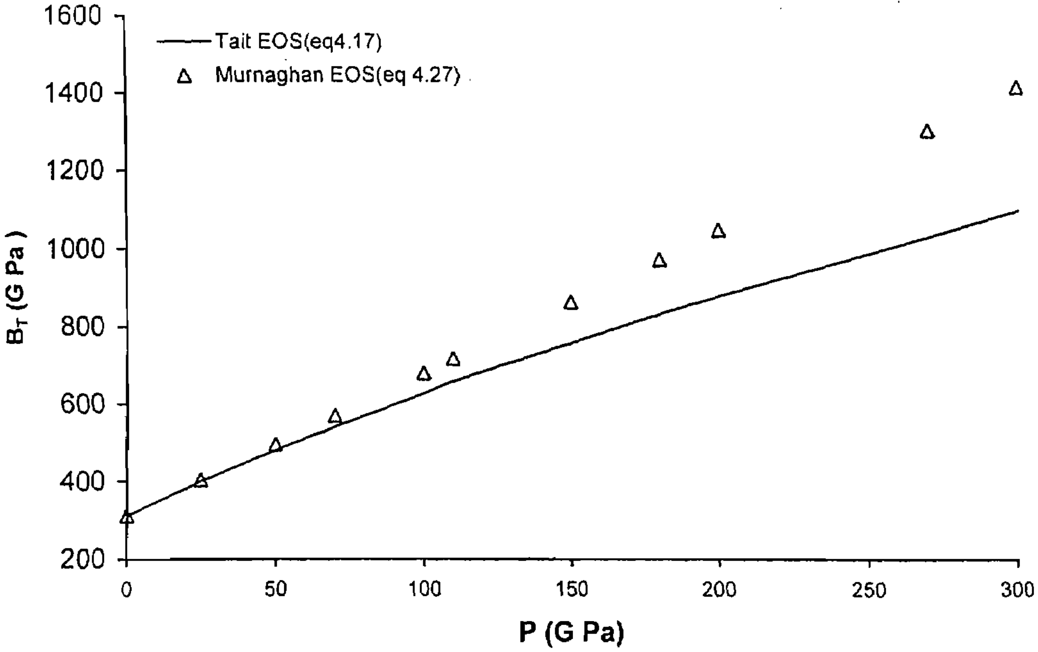


Fig.15.2 Variation in bulk modulus with pressure for W

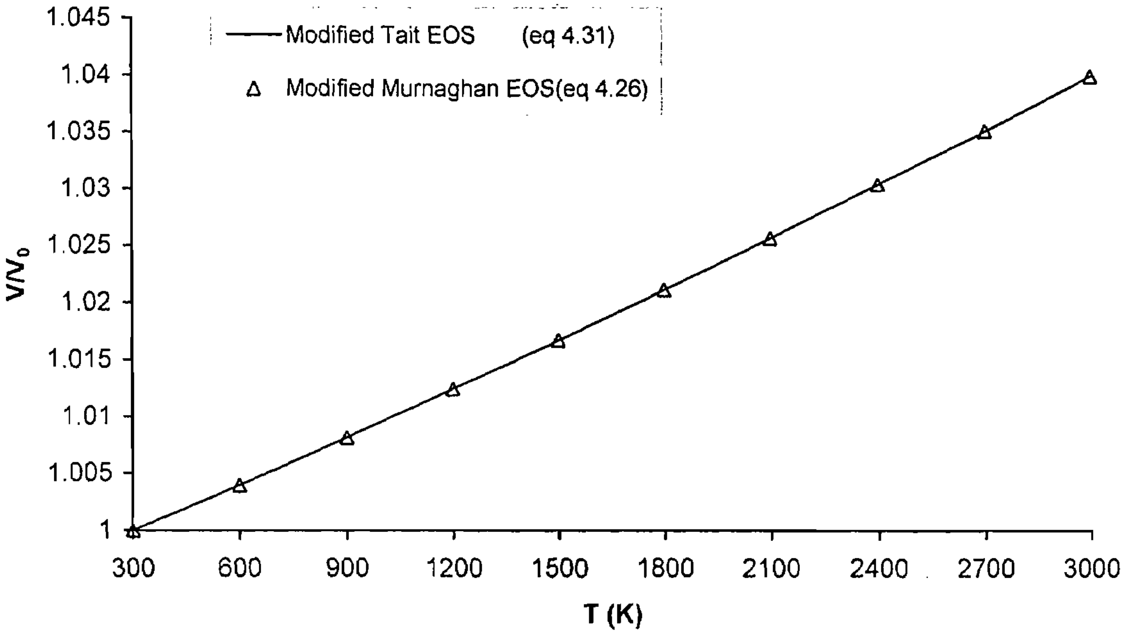


Fig. 15.3 Thermal expansion behavior of W

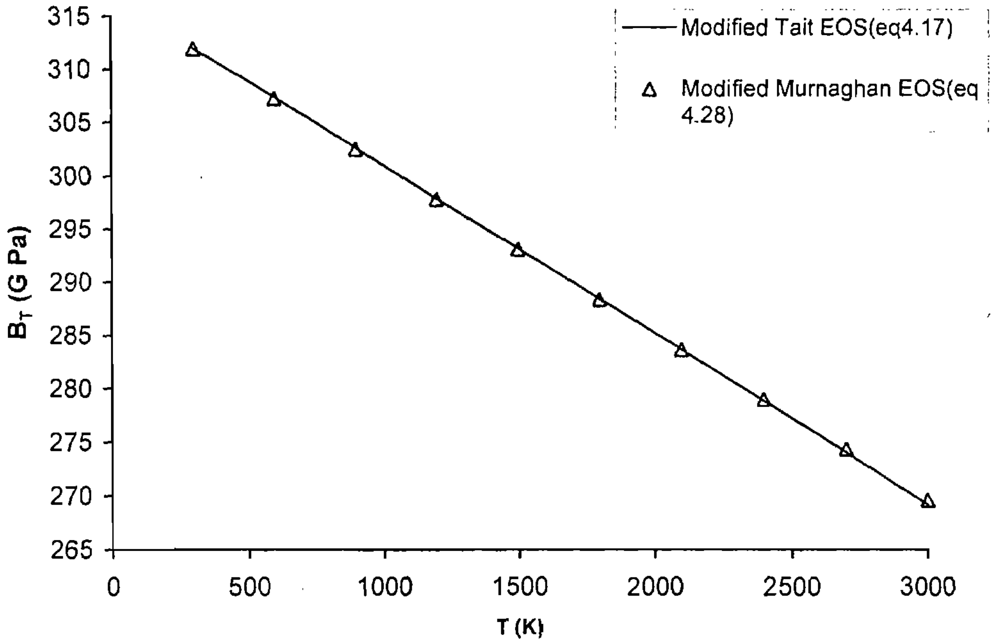


Fig. 15.4 Variation of bulk moduluswith temperature of W

Table 5.26: **Compression and bulk modulus behavior of Ta under high pressure with corresponding experimental data [r] Dewaele et al., 2004.**

P (G Pa)	V/V_0			B_T (G Pa)	
	Tait EOS (eq4.14)	Murnaghan EOS (eq4.22)	Experimental [r]	Tait EOS (eq4.17)	Murnaghan EOS (eq4.27)
0	1	1	1	194	194
5	0.9755	0.9755	0.9751	210.01	210.25
10.9	0.9496	0.9497	0.9505	228.22	229.42
15	0.9331	0.93333	0.9324	240.55	242.75
20.6	0.9123	0.9128	0.9134	256.92	260.95
25.8	0.8945	0.8953	0.8971	271.71	277.85
31.3	0.8771	0.8783	0.8806	286.87	295.72
36	0.8631	0.8648	0.8625	299.6	311
41.5	0.8478	0.8501	0.8512	314.06	328.87
51.4	0.8225	0.826	0.8236	339.28	361.05
60.8	0.8007	0.8056	0.8014	362.35	391.6
70	0.7812	0.7876	0.7842	384.07	421.5
79.9	0.7619	0.7699	0.7649	406.6	453.67
85.8	0.7511	0.7602	0.756	419.66	472.85

Figure Captions

1. Figure 16.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for metal (Ta). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

2. Figure 16.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for metal (Ta). Figure also shows the comparison of Tait's and Murnaghan's equations of state.

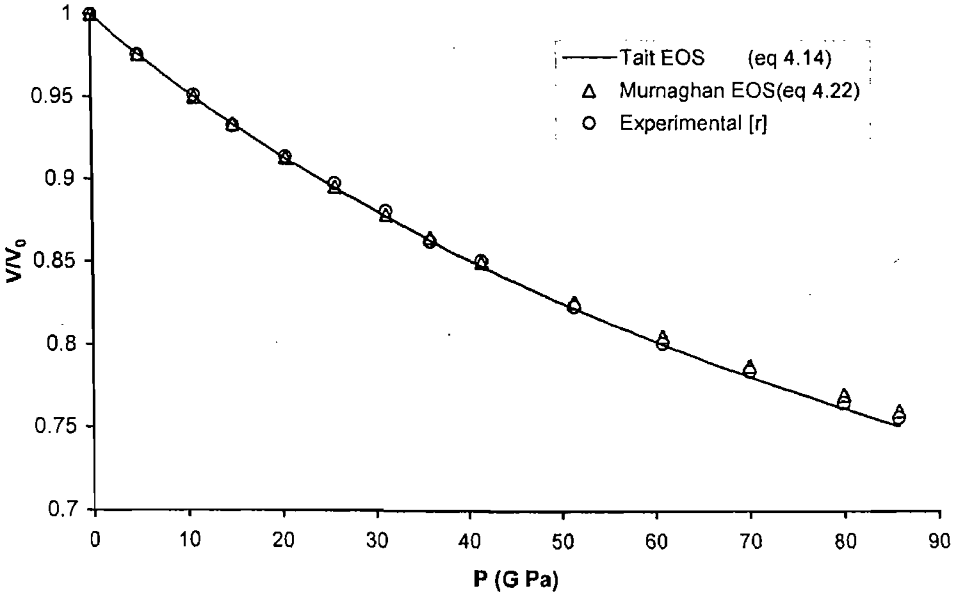


Fig.16.1 Compression behavior of Ta

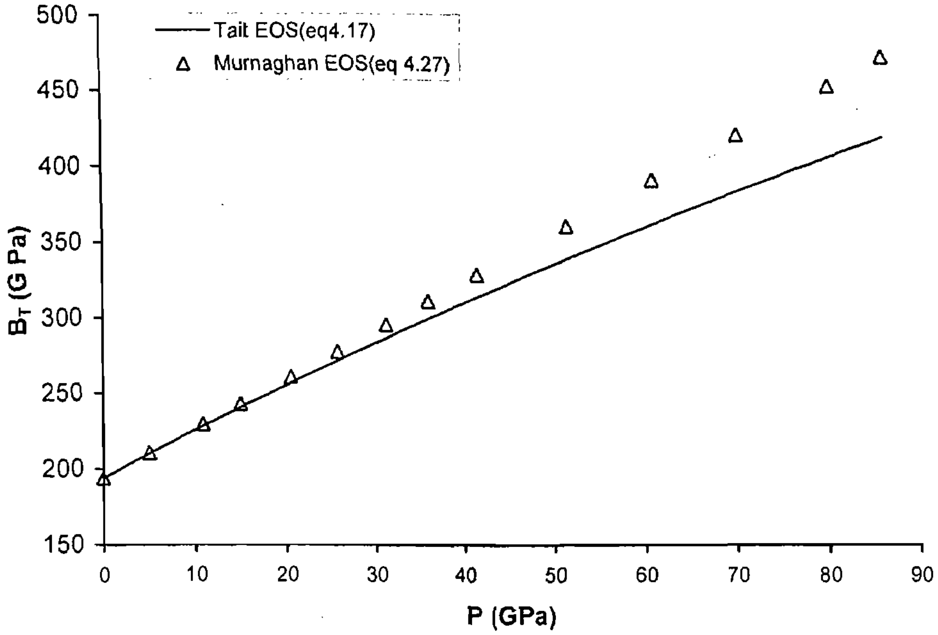


Fig.16.2 variation of bulk modulus at diffrent pressure of Ta

Table 5.27: Compression and bulk modulus behavior of Os under high pressure with corresponding experimental data [s] Kenichi et al., 2004.

P (G Pa)	V/V_0			B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS(eq 4.22)	Experimental [s]	Tait EOS (eq4.17)	Murnaghan EOS(eq 4.27)
0	1	1	1	395	395
1.2	0.9969	0.9969	0.9966	400.54	400.4
3	0.9925	0.9925	0.9919	408.54	408.5
5.1	0.9875	0.9875	0.9876	417.82	417.95
7.3	0.9823	0.9824	0.9828	427.68	427.85
9.1	0.9783	0.9783	0.9773	435.41	435.95
11	0.9740	0.9741	0.9741	443.87	444.5
13	0.9697	0.9697	0.9695	452.49	453.5
15.1	0.9653	0.9653	0.9651	461.47	462.95
18.1	0.9591	0.9591	0.9591	474.4	476.45
29.3	0.9377	0.9379	0.9384	521.76	526.85
39.3	0.9206	0.921	0.9209	562.76	571.85
48.9	0.9055	0.9062	0.9059	601.46	615.05
58.2	0.8920	0.8931	0.8923	638.16	656.9

Figure Captions

1. Figure 17.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for metal (Os). Figure also shows the comparison of Tait's and Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

2. Figure 17.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for metal (Os). Figure also shows the comparison of Tait's and Murnaghan's equations of state.

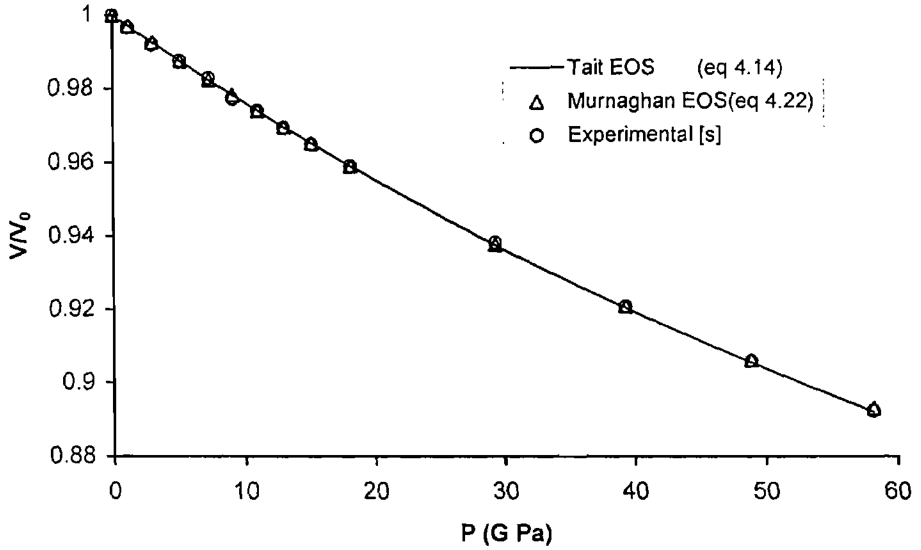


Fig. 17.1 Compression behavior of Os

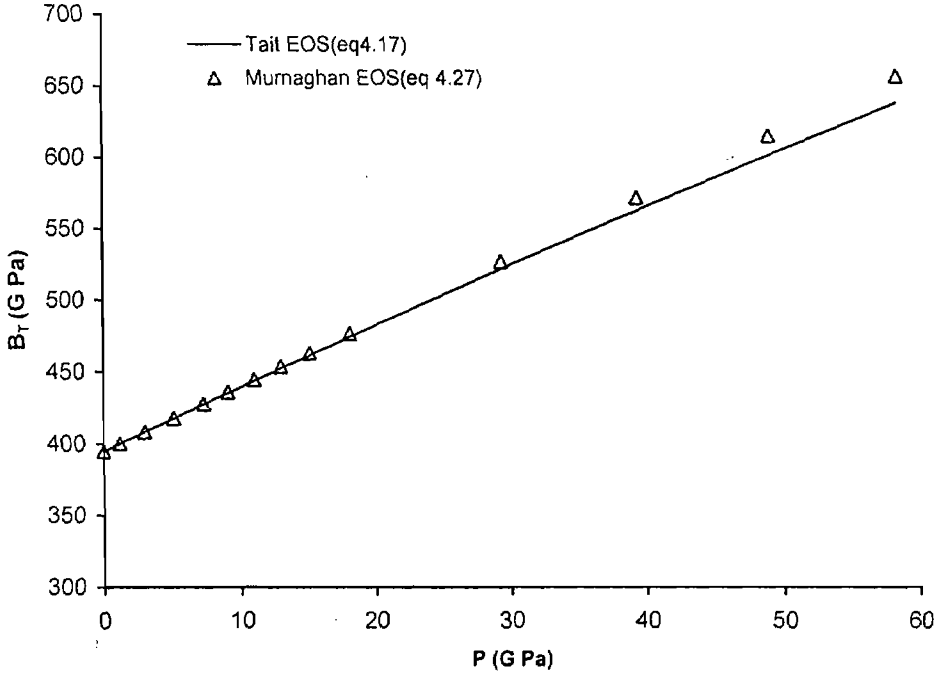


Fig. 17.2 Variation in Bulk modulus with pressure of Os

Table 5.28: Compression behavior of FeSi under high pressure.

P (G Pa)	V/V_0		B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS(eq 4.22)	Tait EOS (eq4.17)	Murnaghan EOS(eq 4.27)
0	1	1	166.42	166.42
5	0.9721	0.9721	187.67	188.42
10	0.9479	0.948	208.09	210.42
15	0.9265	0.9268	228.02	232.42
20	0.9073	0.908	247.27	254.42
25	0.89	0.891	265.98	276.42
30	0.8741	0.8757	284.29	298.42
35	0.8594	0.8616	302.23	320.42
40	0.8459	0.8487	319.73	342.42
45	0.8332	0.8368	336.88	364.42
50	0.8214	0.8257	353.68	386.42

Table 5.29: Thermal expansion and bulk modulus behavior of FeSi under high-temperature with corresponding experimental data [t] Vocadlo et al., 2002.

T (K)	V/V_0			B_T (G Pa)	
	Modified Tait EOS (eq 4.31)	Modified Murnaghan EOS(eq 4.26)	Experimental [t]	Modified Tait EOS (eq4.17)	Modified Murnaghan EOS(eq 4.28)
300	1	1	1	166.42	166.42
400	1.0049	1.0049	1.0052	162.86	162.86
500	1.0099	1.0099	1.0096	159.31	159.31
600	1.01515	1.0151	1.0135	155.7	155.21
700	1.0204	1.0204	1.0179	152.1	152.21
800	1.0259	1.0259	1.0234	148.44	148.66
900	1.0316	1.0316	1.0279	144.74	145.11
1000	1.0375	1.0374	1.0345	141	141.56
1100	1.0435	1.0434	1.0384	137.3	138.00
1200	1.0497	1.0496	1.0439	133.57	134.45

Figure Captions

1. Figure 18.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for iron monosiliside (FeSi). Figure also shows the comparison of Tait's and Murnaghan's equations of state.

2. Figure 18.2 shows the variation of Bulk modulus (B_T) (in GPa) with pressure (P) (in GPa) for iron monosiliside (FeSi). Figure also shows the comparison of Tait's and Murnaghan's equations of state.

3. Figure 18.3 shows the variation of Bulk modulus (B_T) (in GPa) with temperature (T) (in K) for iron monosiliside (FeSi). Figure also shows the comparison of modified Tait's and modified Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

4. Figure 18.4 shows the variation of Bulk modulus (B_T) (in GPa) with temperature (T) (in K) for iron monosiliside (FeSi). Figure also shows the comparison of modified Tait's and modified Murnaghan's equations of state.

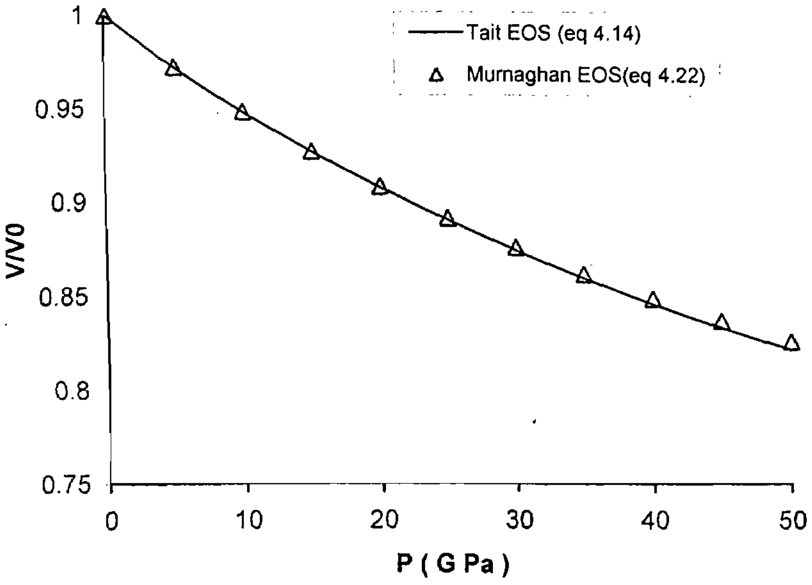


Fig. 18.1 Compression behavior of FeSi

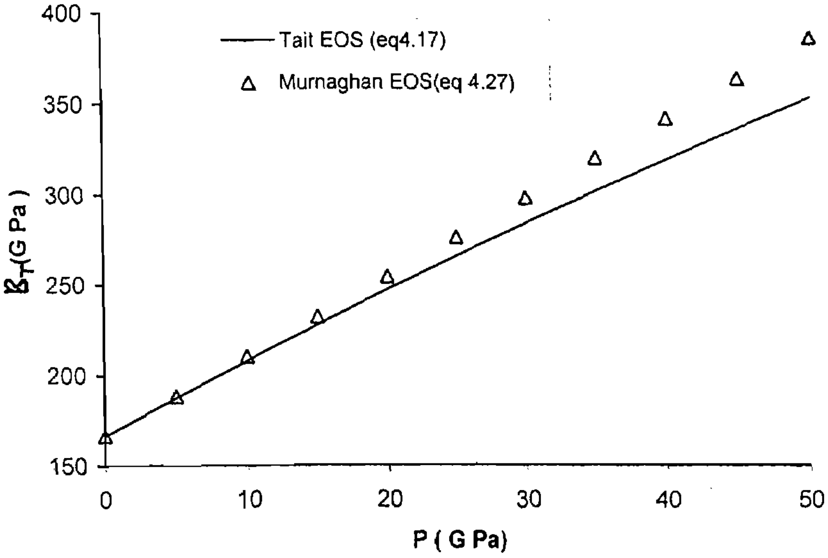


Fig. 18.2 Bulk modulus of FeSi at different pressure

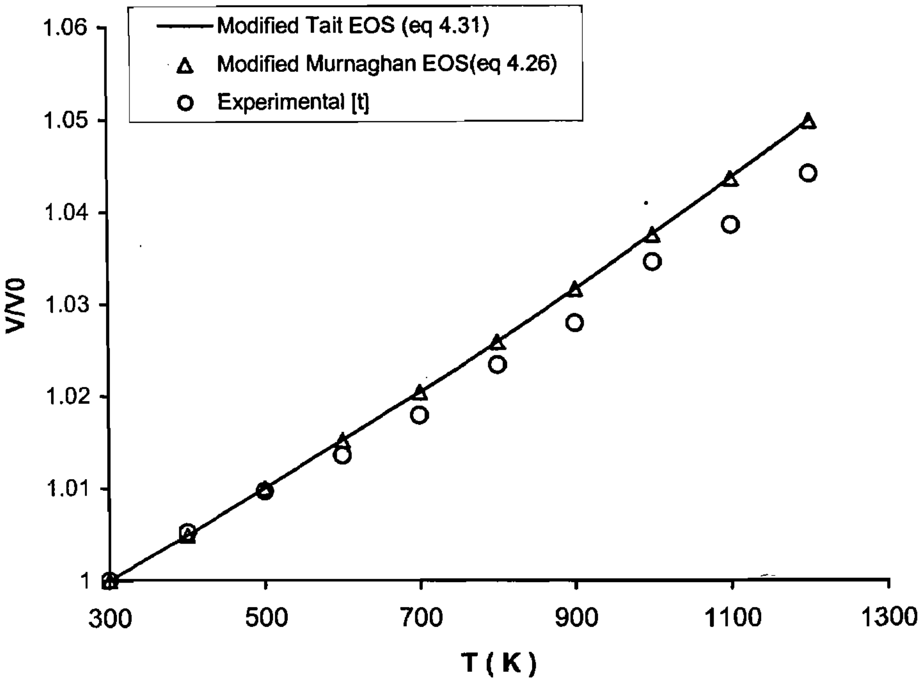


Fig 18.3 Thermal expension behavior of FeSi

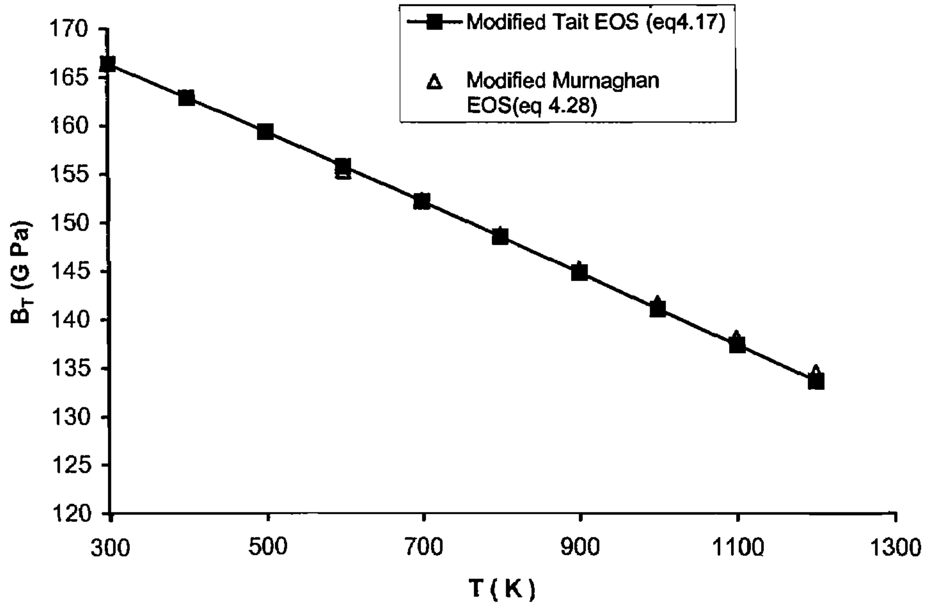


Fig. 18.4 Bulk modulus of FeSi at different temperature

Table 5.30: Compression and bulk modulus behavior of TiO_2 under high pressure.

P (G Pa)	V/V_0		B_T (G Pa)	
	Tait EOS (eq 4.14)	Murnaghan EOS(eq 4.22)	Tait EOS (eq4.17)	Murnaghan EOS(eq 4.27)
0	1	1	210	210
10	0.9594	0.9595	275.41	277
20	0.9285	0.9289	338.14	344
30	0.9036	0.9046	398.62	411
40	0.8827	0.8844	457.39	478
50	0.8647	0.8673	514.67	545
60	0.8489	0.8524	570.64	612
70	0.8348	0.8393	625.52	679
80	0.8221	0.8276	679.28	746
90	0.8105	0.817	732.27	813
100	0.7999	0.8074	784.15	880

Table 5.31: Thermal expansion and bulk modulus behavior of TiO_2 under high temperature with corresponding experimental data [u] Saxena et al., 1993.

T (K)	V/V_0			B_T (G Pa)		
	Modified Tait EOS (eq 4.31	Modified Murnaghan EOS(eq4.26)	Experimental [u]	Tait EOS (eq4.17)	Murnaghan EOS(eq 4.28)	Experimental [u]
300	1	1	1	210.0	210.0	210.0
400	1.0022	1.00226	1.002	206.93	206.83	
600	1.0069	1.0069	1.006	200.50	200.5	200.0
800	1.0117	1.0117	1.011	194.15	194.17	190.5
1000	1.0167	1.0167	1.017	187.74	187.83	182.0
1200	1.0220	1.0220	1.021	181.17	181.5	173.7
1400	1.0274	1.0274	1.026	174.71	175.17	162.9
1500	1.0302	1.0302	1.032	171.45	171.6	158.4
1600	1.0331	1.0333	1.034	167.91	167.4	153.7
1800	1.0390	1.0390	1.041	161.59	160.0	145.7

Figure Captions

1. Figure 19.1 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for rutile (TiO_2). Figure also shows the comparison of Tait's and Murnaghan's equations of state.

2. Figure 19.2 shows the variation of Volume compression (V/V_0) with pressure (P) (in GPa) for rutile (TiO_2). Figure also shows the comparison of Tait's and Murnaghan's equations of state.

3. Figure 19.3 shows the variation of Bulk modulus (B_T) (in GPa) with temperature (T) (in K) for rutile (TiO_2). Figure also shows the comparison of modified Tait's and modified Murnaghan's equations of state with experimental data. The square bracket with experimental values shows the reference given in table.

4. Figure 19.4 shows the variation of Bulk modulus (B_T) (in GPa) with temperature (T) (in K) for rutile (TiO_2). Figure also shows the comparison of modified Tait's and modified Murnaghan's equations of state.

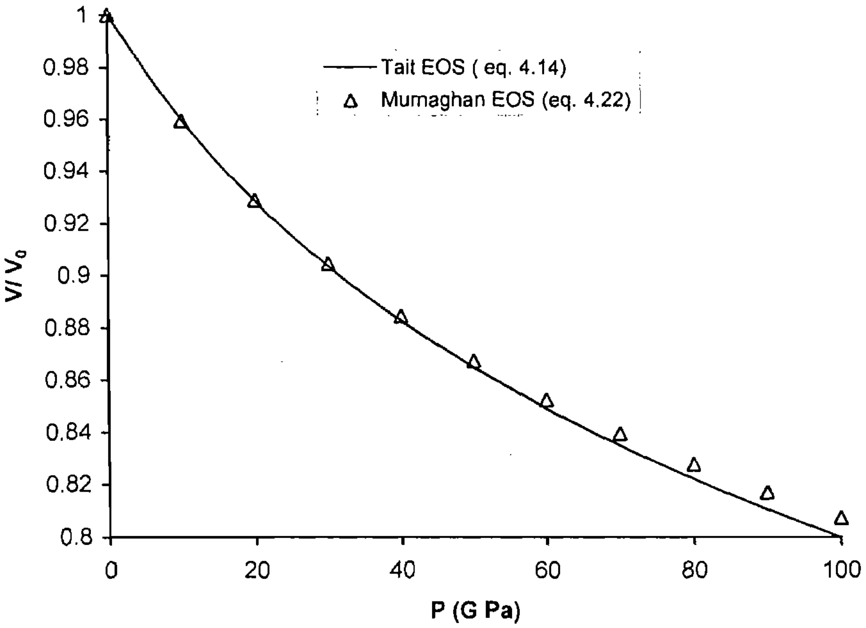


Fig. 19.1 Compression behavior of TiO_2

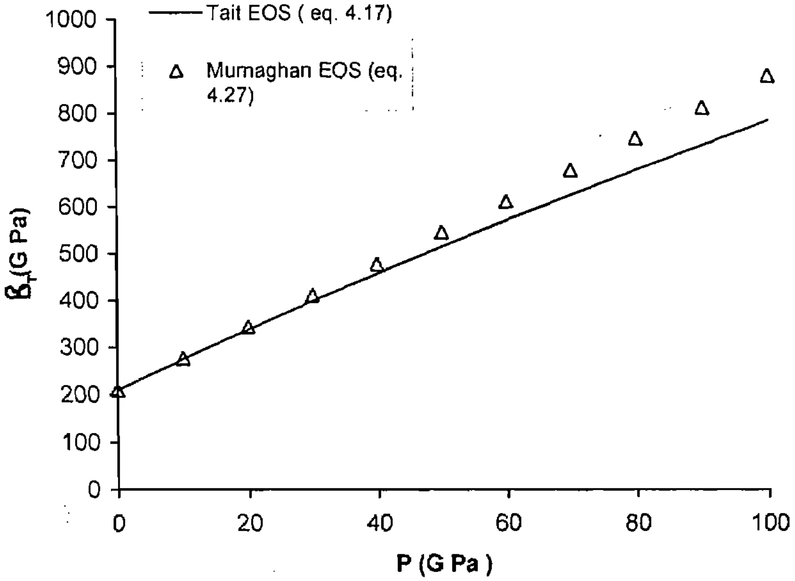


Fig. 19.2 Variation in bulk modulus with pressure

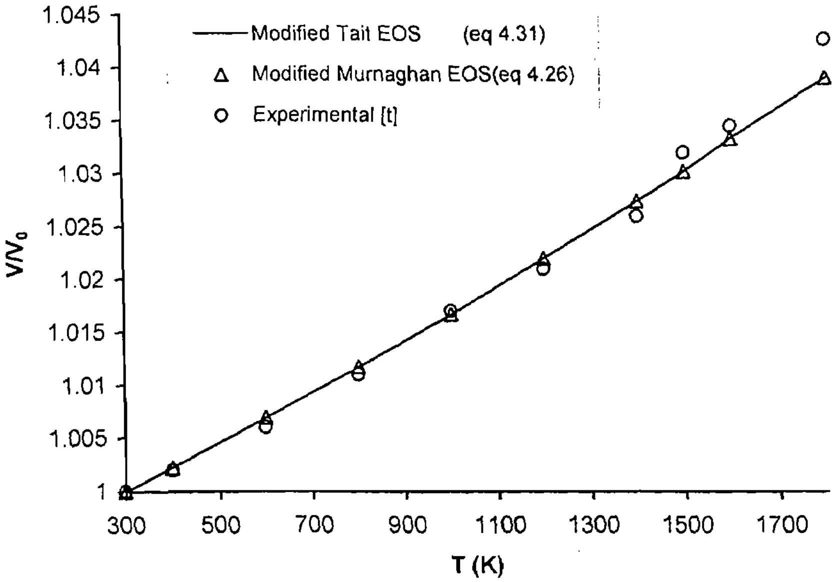


Fig. 19.3 Thermal expansion behavior of TiO_2

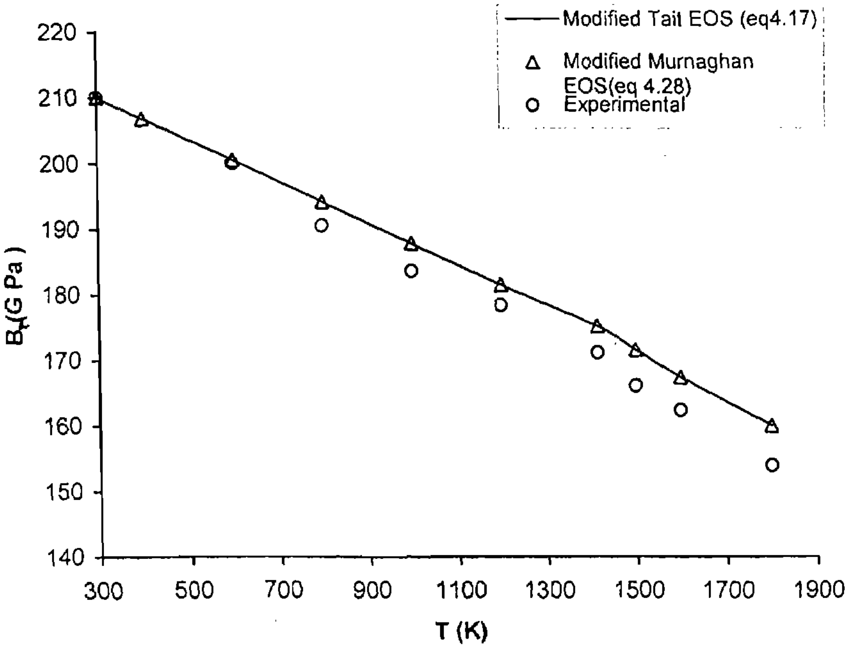


Fig. 19.4 Variation in bulk modulus with temperature.

Summary

"Summary of results provide
further leads to prosperity"

CHAPTER 6 SUMMARY

In the present thesis we have studied the thermophysical properties of different class of solids such as inert gas solids (Ne, Ar, Kr, Xe), semiconductors (Ge, Si, $FeSi_2$, SnS, SiC, MoN, MoN_2, AlN, GaN) and some metals (Mo, W, Ta, Os). Apart from these classes of solids we have also employed the EOS in FeSi and TiO_2 crystals which are found into earth's core and planetary system respectively. We have made effort to cover all main classes of solid from very weakly bonded inert gas solid to extremely hard solid in order to test the applicability and validity of different EOSs.

The previous workers explained only some traditional solids (Ionic solids, NaCl, CsCl etc, Metals, Al, Cu Na etc Minerals, MgO, CaO) by different ways but we have studied those solids, which are very important from the point of view of modern technological i. e. semiconductors and TiO_2 and FeSi crystals which are very important from earth and planetary science point of view. We have presented a straightforward and simple theoretical method to analyse the thermophysical properties within the framework of equations of state as suggested by previous workers and then by making of use of modified equations of state.

Two types of equations of state (i) Isothermal equation of state; (ii) isobaric equation of state are used to analyse the thermophysical properties of these crystals. To calculate the properties under high pressure we have used the Tait's isothermal EOS to explain the compression in solids. A good agreement with the available experimental values is found. However Tait's equation does not explain these results under high temperature. We have, therefore, modified the both Tait's and Murnaghn's equation of state by considering the concept of phonon pressure (thermal pressure) in order to make it isobaric so as to use in high temperature range. After modifying it we have employed the modified Tait's and Murnaghan's equation of state to determine the thermal expansion and bulk modulus of variety of solids (inert gas solids, semiconductors and metals including FeSi and TiO_2 under high temperature.

It is also noted that for inert gas solids which exist at very low temperature, the Singh-Gupta equation of state explains the thermophysical properties successfully. Most of the previous equations of state have been failed to explain the thermophysical properties at low temperature i. e. below the Debye temperature but Singh-Gupta's equation of state predict the results satisfactorily even in low temperature range. These equations may also be applied in other crystal systems where temperature dependence of Gurneisen parameter is not available at present.

In the present work of thesis we have thus formulated new modified forms of Tait's and Murnaghan's equations of state for isobaric study of solids as cited. The advantage of the modified EOS is that our modified forms of EOS require less number of parameter unlike the previous EOS. The original isothermal forms of EOS have been modified by including the phonon pressure term and made it isobaric to explain the thermophysical properties of all type of crystal structure solids. It is also found that the modified Tait's EOS and Modified Murnaghan's EOS may be treated as the universal equations to predict the thermophysical properties of solids in the high temperature range.

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"When you achieve the goal,
Let's remember the former's role"

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*Original not seen

List of Publications

1. **Kamal Devlal** and **B. R. K. Gupta***; "Pressure dependence of bulk modulus and cell volume of SiC and Ge crystals"; Indian J. of Phys. (In Press) (2004).
2. **Kamal Devlal** and **B. R. K. Gupta** "Analysis of thermal expansion in FeSi and TiO_2 as prototype crystals" Communicated to High Temp. - High Press. (U. K.) (2005).
3. **Kamal Devlal and B. R. K. Gupta;** "Thermal expansion behavior of FeSi cubic crystalline material"; Paper Published in D. A. E. National Symposium on Solid State Physics (2004).
4. **Kamal Devlal**, M. Kumar and **B. R. K. Gupta**; "High-pressure equation of state of germanium"; Published in D. A. E. National Symposium on Solid State Physics (2004).
5. **Kamal Devlal**, K. Y. Singh and **B. R. K. Gupta*** "Equation of state for thermal expansion behavior of rutile TiO_2 crystalline material"; Oral Presentation in National Conference on Advances in Solid State Physics at Patiala (2005).
6. Meenakshi Joshi, **Kamal Devlal** and **B. R. K. Gupta*** "Analysis of temperature dependence of adiabatic elastic moduli for Iron bearing Olivines"; Indian J. of Phys. (Communicated) (2004).

Equation of State for Thermal Expansion Behavior of Rutile TiO_2 Crystalline Material

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ABASTRACT

The equation of state model is a fundamental equation to analyse the thermodynamic properties of basic and applied condense matter physics researches. The Murnaghan first order equation for compression and bulk modulus are basic equations of state in litreture. In present study, we modified these equations by introducing the concept of thermal pressure. The modified new equations are temperature dependent, however, the original equations were pressure dependent. The modified new equations are applied to study the thermal expansion behavior of rutile TiO_2 of example. The results obtained by using this equation gives beautiful agreement with experimental results.

KEY WORDS: Equation of State; rutile TiO_2; compression; thermal expansion.

1. INTRODUCTION

In recent years several isobaric equations of state (EOS) have been proposed. However, tl main drawbacks in these EOS are that they involve many input parameters and do n predict the accurate results. The reason for this may be attributed to ignore the therm pressure developed at high pressure in these equations of state. Motivated with this we ha included the term of phonon pressure (thermal pressure) arising due to the expansion solids at high temperature. In the present study we have thus modified the Murnagh equation of state in view of thermal pressure concept. The modified new equations a applied to study the rutile TiO_2. Rutile has an interesting property of being a crystallograph analog of stishovite SiO_2, which is important high-pressure quartz phase in earth's low mantle. On including the term of thermal pressure the modified Murnaghan EOS predict t results on thermal expansion, which are found in excellent agreement with available exper mental data.

2. METHOD OF ANALYSIS

The Murnaghan EOS [5,6] is expressed as

$$\frac{V}{V_0} = \left(1 + \frac{B_0'}{B_0} P\right)^{-1/B_0'} \tag{1}$$

This is pressure dependent EOS at a constant temperature. Now if thermal pressure is taken in account then the effective pressure is reduced as compared to applied pressure due to thermal pressure [7,8].

The thermal pressure P_{Th} is expressed as [7,8]

$$P_{Th} = \int_{T_0}^{T} \alpha_0 B_0 dT \tag{2}$$

where á$_0$ is thermal expansion coefficient and B_0 is bulk modulus at the zero reference pressure. By using eq. 2, the eq. (1) is modified as

$$\frac{V}{V_0} = \left(1 + \frac{B_0'}{B_0}(P - P_{Th})\right)^{-1/B_0'} \tag{3}$$

On integrating eq. (2) and putting the value of thermal pressure in eq.3 this equation can be expressed as

$$\frac{V}{V_0} = \left(1 + \frac{B_0'}{B_0}(P - \alpha_0 B_0 (T - T_0))\right)^{-1/B_0'} \tag{4}$$

It may be considered that, if the reference pressure is zero then the eq. (4) can be expressed as

$$\frac{V}{V_0} = (1 - B_0' \alpha_0 (T - T_0))^{-1/B_0'} \tag{5}$$

Similarly on inclusion of the concept of thermal pressure on the Murnaghan's first order equation [5-6] for bulk modulus can be modified as follows

$$B_T = B_0 + B_0' P \tag{6}$$

Again taking the account the effect of thermal pressure the above equation is written as

$$B_T = B_0 + B_0'(P - P_{Th})$$

on further simplification, we get

$$B_T = B_0(1 - B_0' \alpha (T - T_0)) \tag{7}$$

The eq. (5) and eq. (7) are final modified Murnaghan EOS, which are temperature dependent expression for expansion and bulk.

3. RESULTS AND DISCUSSION

The bulk modulus B_0, B_0' and α_0 at reference temperature 300K and zero pressure are taken as 210GPa, 6.7 and 22.5x10^{-6} K^{-1} respectively [9,10]. These values are taken as input parameters and calculate the thermal expansion by using eq. 5 . The result presented in figu 1. The results are compared with available experimental values [10,11], which show excellent agreement with experimental values. This approach is further applied to expla the thermal expansion and bulk modulus of other materials at different temperature rang

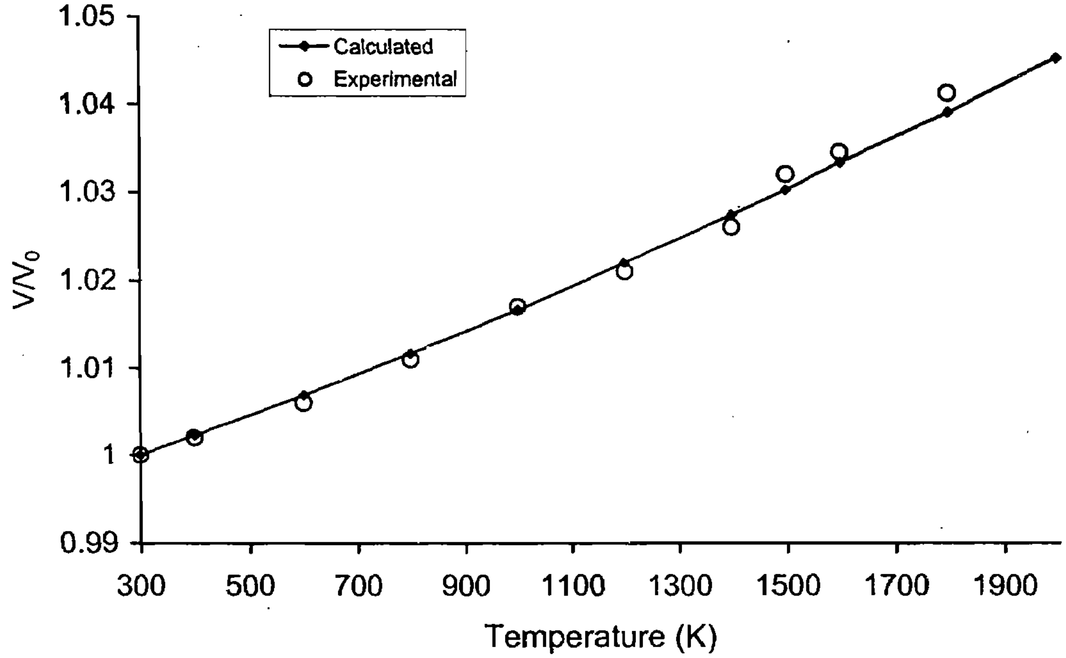

Fig.1 Thermal Expansion behavior of TiO_2

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Thermal expansion behavior of FeSi cubic crystalline material

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Abstract

The thermal expansion behavior of FeSi has been investigated by using EOS model. No doubt a lot of EOS model are available in the literature. Most of these are complicated with many parameters and some time input parameters are not available. Murnaghan's EOS is one of the basic and most favorite Eos. In present study this EOS has been modified and it has been shown that its results obtained by using this EOS have good agreement with experimental results.

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High pressure equation of state of germanium

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Abstract

Three different theories based on different physical origins are used to predict the high-pressure equation of state (EOS) of germanium crystal. It is found that the results based on the Suzuki formation are low as compared with the experimental data. Shanker formation improves the results obtained by Suzuki theory. Moreover, the agreement is not good. These results are further improved by the theory of equation of state proposed by Kumar.

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VITA

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Thesis Title:“Study of thermophysical properties of differen class of solids under high pressure and hig temperature ”

ABSTRACT

The studies of thermophysical properties based on equation of state are widely important not only in physics but also in chemistry and geophysics. In the present research work, a comparative study has been made for different class of solids (inert gas solids, semiconductors and some metals) by using different EOSs under high pressure and high temperature. Apart from these solids we have also employed these EOS in FeSi and TiO_2, which are important from earth and planetary science point of view. Our work does not only predict the thermophysical properties of different solids but also test the applicability of different EOS. We have predicted the isothermal and isobaric properties of solids.

The isothermal compression and bulk modulus are calculated by the original Tait EOS and original Murnaghan EOS. It is found that the results achieved from Tait’s equation of state are in better agreement with the available experimental data as compared to those obtained from Murnaghan EOS. The isobaric thermal expansion and bulk modulus are calculated by modified Tait and Modified Murnaghan EOS, which give a fairly good agreement with the available experimental data. However, the Singh-Gupta EOS gives better agreement with the available experimental data for inert gas solids. We have therefore, modified the both Tait’s and Murnaghan equations of state by including the concept of phonon pressure (thermal pressure) in order to explain the thermophysical properties satisfactorily in the range of high temperature upto their melting temperature. It is also emphasized in the text of thesis that the modified isobaric Tait’s EOS and modified Murnaghan’s EOS may be treated as the universal equations of state.

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