

“High Pressure Structural Phase Transition and Mechanical Properties of Semiconducting Chalcogens.”

A MINOR RESEARCH PROJECT CARRIED OUT UNDER THE FINANCIAL ASSISTANCE OF UNIVERSITY GRANTS COMMISSION, WRO, PUNE.

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Executive Summary of the Project

INTRODUCTION AND ORIGIN OF THE RESEARCH PROBLEM:

The structural and electronic properties of the heavy alkaline earth chalcogenides (AEC's) at high pressures are a subject of considerable theoretical and experimental interest [1]. High pressure, along with ambient-pressure studies on materials, can help with analyzing the nature of interaction among the atoms. These closed shell ionic systems share similar band structures and, in turn, have similar physical properties identified for NaCl structured phases of alkali halides. These compounds crystallized in the NaCl-type (*B1*) structure at ambient conditions-except for BeO and MgTe (crystallized in the wurtzite structure) and the beryllium chalcogenides (crystallized in the zinc-blende structure). The recent flurry in AEC's is because of advances in the generation of ultrahigh static pressures with the diamond anvil cell, the use of synchrotron sources for x-ray diffraction study and technological applications in luminescent devices [2 - 4].

The AEC's form a very important group of semiconductors with large band gap and valence-band width. Pressure is believed to be an attractive thermodynamical variable to reveal the mechanical properties of most of the solids and alloys. Since cohesion of solids is crucial, the interatomic distance changes as a consequence of the application of pressure. A noticeable feature in the electronic band structure of the CaX compounds is that there is no *d* electron in the valence band. The application of pressure on the NaCl structure of the alkaline-earth

chalcogenides undergoes a structural phase transition to CsCl-type (*B2*) structure with eightfold-coordination.

Serious experimental and theoretical efforts has been made to the pressure-induced phase transition, which serves as an important model for structural phase transitions in other fields, such as those observed in geophysics. Luo *et al* [5] has performed an extensive experimental study of the behaviour of CaS, CaSe and CaTe under pressure using energy-dispersive x-ray diffraction. They found that the first two compounds have a phase transition from the *B1* (NaCl) to the *B2* (CsCl) phase at a pressure of 40 and 38 respectively. While to that CaTe first transforms to an intermediate state, which is a mixture of the NaCl and MnP phases at 25 GPa and then, at a pressure slightly greater than 33 GPa, to the *B2* phase. Furthermore, these phase transitions are reversible with small history on loading or unloading pressure. Earlier, Zimmer *et al.* [6] obtained pressure-volume relationships and structural transitions in CaTe using x-ray diffraction. They also mentioned that CaTe transforms to the *B2* structure near 35 GPa, however, with the possible existence of an intermediate unidentified phase at around 32 GPa.

The investigations of structural, mechanical and vibrational properties of semiconducting alloys under pressure are performed by means of empirical lattice models and *ab initio* calculations. The lattice models are often applicable only to a restricted class of solids and have little predictive power. On the other hand, first principles calculations of the cohesive properties are routinely performed on a variety of solids with often a high degree of accuracy. The accuracy of total energies obtained, is in many cases is sufficient to predict which structure, at a given pressure, has the lowest free energy, although most calculations still refer to zero temperature.

A comparison of the free energies of various guessed crystal structures, *ab initio* molecular dynamics methods allow a better determination of the structures and understanding of transformation mechanisms. Yet these computationally techniques do not easily provide insight into dominant physical mechanisms. Conversely, phenomenological lattice models, which take care of various interaction energies for determination of stable structure, cover chemical trends of selected alloys and semiconductors with NaCl structure (*B1*) to CsCl-type (*B2*) structure or zincblende structure (*B3*) to NaCl structure (*B1*).

Khenata *et al.* [7] calculated electronic band structures and the total energies of CaSe and CaTe in NaCl and CsCl-type structures using full-potential linearized augmented plane wave

method (FP-LAPW) within the generalized gradient approximation (GGA). In addition, the transition pressures at which these compounds undergo the structural phase transition from NaCl to CsCl phase are 35.5 and 30.2 GPa for CaSe and CaTe, respectively. They also reported elastic constants at equilibrium in both NaCl and CsCl type structures. Charifi *et al.* [8] also reported similar results using the full potential linearized augmented plane wave method within density functional theory. They used both the local density approximation and the GGA that is based on exchange-correlation energy optimization for calculating the total energy. Earlier, The elastic constants are investigated using pseudopotential [9] and tight binding theory [10]. Moreover, the cohesive properties under pressure of CaX compounds have been calculated by using *ab initio* calculations [11]. To the best of our knowledge there are no experimental works exploring the elastic constants of CaX compounds, and no calculations based on the phenomenological model potential method were performed for any of the CaX compounds.

The experimental [5, 6] and computational methods [7-11] therefore pose a strong need to study the structural properties of CaX compounds theoretically at high-pressure, which can predict at least the extent of pressure one should generate to observe a structural phase transition and other related properties. In addition, the structural and elastic studies on rare earth chalcogenides [12] and other compounds [13] has further widened the scope of future theoretical and accurate experimental investigations of crystallographic phase transition from *B1* to *B2* in rare earth compounds.

The modeling of lattice models in rare earth compounds is a complicated task and, in many instances, must be guided by experimental evidence of the low degree of freedom in order to obtain a correct minimal model which will capture the observed effect and will make useful predictions. The first principles density functional theory and microscopic tight binding models as well effective Hamiltonian models has been used successfully to address electronic, magnetic and structural ground state properties. On the other hand, empirical lattice models have proven very successful in obtaining qualitative and quantitative understanding with proper parameterization of the input parameters.

Among the phenomenological models, which have been invoked so far, to discuss the mechanical properties of several solids and alloys, charge transfer approach [14], following Hafemeister and Flygare [15] type overlap repulsion extended upto second neighbour ions besides short-range interactions. We refer to the pioneering work of Fumi and Tosi [16], who properly incorporate van der Waals interaction along with multipole (*d-d* and *d-q*) interactions to

reveal the cohesion in several ionic solids. In trying to understand the structural aspects, we admit that the vdW attractions are the corner stone of lattice phenomenological models that is ignored in the first principle microscopic calculations.

Motivated by the experimental studies [5, 6], computational methods [7-11] and the charge transfer effect approach [14] for the successful description of the phase transition and high pressure behavior of binary semiconductors, we thought it is pertinent to employ the two-body interactions that includes vdW attraction, which is not explicitly accounted in band structure calculation in alkaline rare compounds. It is worth noting that vdW interaction appears to be effective in revealing the elastic and structural properties of rare-earth chalcogenides.

OBJECTIVES OF THE STUDY

In the earlier and recent past, there is an extensive theoretical study and understanding of the phase transition and anharmonic properties of solids by means of different forms of cohesion. The major part of the cohesion in these potentials is contributed by long-range Coulomb interactions, which are counterbalanced by the short-range overlap repulsion owing its origin to the Pauli exclusion principle. Born and Mayer take the overlap repulsion with a lattice sum to describe successfully the cohesion in most of the ionic solids. Further Tosi and Fumi, properly incorporated van der Waals (vdW) interaction along with $d-d [r^{-6}]$ and $d-q [r^{-8}]$ interactions to reveal the cohesion in several ionic solids.

The effects of charge transfer following Hafemeister and Flygare type overlap repulsion extended upto second neighbour ions besides short-range interactions create substantial interest. It is worth to mention that the above approach successfully predicts the thermodynamical properties such as phase transition pressure as well associated parameter in rare earth and some II-VI semiconducting compounds. We note that short-range $d-d$ and $d-q$ interactions are the corner stone for all these approaches to discuss the cohesion in ionic solids.

A). The proposed work on rare and alkaline earth compounds is in view of their impact in fundamental physics as well in technology. A survey of literature has revealed that theoretical prediction of the phase-transition in rare earth and alkaline earth II-VI semiconductors have been done by means of the simple model and first-principles pseudopotential calculations. It is worth to mention that these results are quite far from the experimental results. The earlier calculations noticed that rock-salt structure is preferred as the ionicity or charge transfer is increased in materials.

- B). We aim to unlock some of the hidden theoretical aspects of the rare/ alkaline earth and magnetic chalcogen materials by formulating an effective interaction among nearest ions. The applicability of charge transfer effect for the successful description of the high-pressure behavior of binary semiconductors, motivated us to make a comprehensive study of several potential terms on cohesive, thermophysical, harmonic and anharmonic elastic properties of rare earth chalcogen and some partially ionic chalcogen (II-VI). The key idea we have in mind is to include the vdW interaction effect, which is not explicitly accounted for in first-principles pseudopotential.
- C).The model is used to investigate the phase transition, structural stability and pressure dependence of elastic constants. Besides, phase transition and pressure dependence of SOEC and TOEC, we will also analyze various physical properties, such as force constant (f), Debye temperature (θ_D), thermal expansion coefficient (α_v), volumetric compressibility (β) and ductility and brittleness. Looking to these properties of mentioned test materials it is pertinent to develop a unified approach which interpret the behaviour and it has a scope of its extension to other class of alloys and compounds which is of immense use to scientific, technological and industrial applications.
- D). The above approach will also allow us in tracing the developments of the basic concepts and postulates involved in various models so that a critical assessment of their usefulness may be possible. This critical comparison is aimed to establish the apparent correlations between phenomenological and microscopic models and among themselves also. Furthermore, the above mentioned studies will enable us to judge the many-fold capabilities and wide-ranging applicability of these models and the role-offered by the many-body interactions in the lattice statics and dynamics of several binary and magnetic semiconducting chalcogens.

METHODOLOGY:

- A) An effective interionic potential will be developed, which will incorporates the long-range Coulomb, with and without many body interactions, van der Waals (vdW) interaction, and the short-range overlap repulsive interaction up to second-neighbor ions within the Hafemeister and Flygare approach.
- B) Usually, the lattice modeling of a solid-state structural transformation with hydrostatic pressures has only been described in thermodynamic limit. While estimating the free

parameters those involved in effective interionic potential, we will first deduce the van der Waals coefficients from the variational method. It is the purpose of these investigations to understand the importance of the effective interionic potential.

- C) Considering pressure and temperature as the external variables (hydrostatic conditions), the free energy of a particular crystal structure at a particular temperature and pressure will be obtained by minimizing G with respect to V .
- D) In order to make the proposed work more revealing we will explore the applicability of three-body-force shell model to describe the harmonic and anharmonic properties of these compounds. The study of the elastic constants (second and third order) and their pressure derivatives at 0 K is quite important for understanding the nature of the interionic forces in them.

As emphasized earlier, the formulation of the effective interaction potential will give the understanding of mechanism and nature of interactions. The proposed approach will give a clear understanding and with necessary modification, the approach is extended for others class of compounds with ZnS ($B3$) to NaCl ($B1$) and/ or NaCl ($B1$) to CsCl ($B2$) structural phase transformation.

ACHIEVEMENTS FROM THE PROJECT:-

A). In order to predict the stability of crystal structures and mechanical (elastic) properties at finite pressures and temperatures, the Gibb's free energy should be considered; the structure with lowest free energy is the most stable. Yet it is difficult to minimize the Gibb's free energy for randomly generated structures even with advanced computational techniques. Although the computational methods for the determination of cohesive, structural and vibrational properties under pressure are now successfully being performed by means of ab initio calculations but the nature of interatomic forces is not well understood about these materials and lattice dynamical models are important in interpreting and cover the chemical trends in the structural stabilities. The realistic description of structural and mechanical properties of AEC's compounds need to take in to account various interactive forces when the lattice is strained and a balance of them to attend the stable structure depending upon the ionic or covalent nature.

We therefore calculated the pressure-induced elastic properties of AECs as SrX (IIA-VIA) semiconducting compounds with stable rocksalt structures following the lattice models. To

further simplify our lattice model calculations, the temperature has been set to zero. Here, the entropy of the crystal is therefore ignored, keeping in mind that the contribution of temperature to free energy is small for the experimental data is considered.

An effective interionic interaction potential is formulated in analyzing the structural (NaCl→CsCl) as well as elastic properties in CaX compounds. Deduced values of material parameters allow us to predict phase transition pressure and associated volume collapse consistent with the known results. The results of the lattice model calculations yields the phase transition pressures ($P_t = 40, 38, 34$ GPa) for AECs (CaS, CaSe and CaTe). For these three compounds excellent agreement is found with available data. The models ability to predict realistic cohesive energy, associated volume collapses, the bulk modulus, its derivative with pressure, the relative stability of crystal structures, and transition pressures exemplified in terms of the screening of the effective Coulomb potential through modified ionic charge. The main result of the paper is the vast volume discontinuity in pressure volume phase diagram identifies the structural phase transition from NaCl to CsCl structure[1].

An immediate consequence of our lattice model calculations is the validity of Born criterion. The second order elastic constants C_{11} and C_{12} increase with increase in pressure up to phase transition pressure that supports high-pressure structural stability of CaX compounds. Further, C_{44} decreases linearly with the increase of pressure and does not tend to zero at the phase transition pressures in B1 phase and is in accordance with the first order character of the transition. We should emphasize that our conclusions have been established only within the framework of Shell model with overlap repulsion up to second nearest neighbor interactions. In order to carry out a more complete comparison on the high-pressure phase transition studies between theory and available experiment, it is therefore necessary to include the effects brought about by the many body interactions. Nevertheless, it has been found that this simple model as compared to complicated band structure calculations may account for a considerable part of the available experimental and theoretical results for the high-pressure studies.

B). Abstract: High Pressure structural phase transition and elastic properties of UX (X = S, Se, Te) Compounds.

An effective interionic interaction potential (EIOIP) approach is employed for description of phase transition and equation of state of Uranium monochalcogenides (UX; X = S, Se and Te) are presented. An effective interionic interaction potential is constructed consisting of the long-

range Coulomb and the Hafemeister and Flygare type short-range overlap repulsion extended upto the second neighbor ions and the van der Waals (vdW) interaction. Particular attention is devoted to evaluate the vdW coefficients following the Slater-Kirkwood variational method, as both the ions are polarizable. Our calculated results have revealed reasonably good agreement with the available experimental data on the phase transition pressures ($P_t = 81, 21, 13$ GPa) and the elastic properties of UX ($X = S, Se$ and Te). The equation of state curves (plotted between $V(P)/V(0)$ and pressure) for both the NaCl-type (B1) and CsCl-type (B2) structures obtained by us are in fairly good agreement with the experimental results. The calculated values of the volume collapses [$\Delta V(P)/V(0)$] are also closer to their observed data. The variations of the second and third order elastic constants with pressure have followed a systematic trend, which are almost identical to those exhibited by the measured and observed data in other compounds of NaCl-type structure family [2].

C). Abstract: Ab Initio study of Structural And High Pressure Properties Of LaX ($X = S, Se, Te$), Pressure induced structural aspects of NaCl-type (B1) to CsCl-type (B2) structure in lanthanum monochalcogenides LaX [$X = S, Se, Te$] compounds are presented. An effective interionic interaction potential (EIOP) with long range Coulomb, van der Waals (vdW) interaction and the short-range repulsive interaction upto second-neighbor ions within the Hafemeister and Flygare approach with modified ionic charge is developed. Particular attention is devoted to evaluate the vdW coefficients following the Slater-Kirkwood variational method, as both the ions are polarizable. Our result on vast volume discontinuity in pressure volume phase diagram identifies the structural phase transition from B1 to B2 structure. The estimated value of the phase transition pressure (P_t) is consistent as compared to the reported data. The variations of elastic constants and their combinations with pressure follow a systematic trend identical to that observed in others compounds of NaCl type structure family and the Born and relative stability criteria is valid in lanthanum monochalcogenides LaX [$X = S, Se, Te$] compounds [3].

CONTRIBUTION TO THE SOCIETY:-

1. Society will get the work done based on this topic and may be helpful in technical aspects either the one way or other.
2. Same study may be used by researchers to develop some newer compounds of future use which will serve the society in their development.

NO. OF PUBLICATIONS OUT OF THE PROJECT:-

- [1] Dinesh Varshney, V. Rathore, **R. Kinge**, R.K. Singh, Journal of Alloys and Compounds 484 (2009) 239–245.
- [2] Ravi Kinge, National Symposium on Recent Advances in Physics, 15 February, 2011, Organized by Govt. Holkar Science College, Indore.
- [3] Ravi Kinge, Dinesh Varshney, National Conference on Materials and Devices for Future Technology, 7 March, 2011, Organized by School of Physical Sciences, North Maharashtra University, Jalgaon.

CONCLUSIONS:

An immediate consequence of our lattice model calculations is the validity of Born criterion. The second order elastic constants C_{11} and C_{12} increase with increase in pressure up to phase transition pressure that supports high-pressure structural stability of CaX compounds. Further, C_{44} decreases linearly with the increase of pressure and does not tend to zero at the phase transition pressures in $B1$ phase and is in accordance with the first order character of the transition. We should emphasize that our conclusions have been established only within the framework of Shell model with overlap repulsion up to second nearest neighbour interactions. In order to carry out a more complete comparison on the high-pressure phase transition studies between theory and available experiment, it is therefore necessary to include the effects brought about by the many body interactions. Nevertheless, it has been found that this simple model as compared to complicated band structure calculations may account for a considerable part of the available experimental and theoretical results for the high-pressure studies.

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PRINCIPAL INVESTIGATOR

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