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P-V RELATION FOR MERCURIC CALCOGENIDES: AB INITIO METHOD

M. Gautam^{1,2}, ***S. Tenguria***², ***G. Misra***²

¹ Nano Bio Process Division,
Labindia Instruments Pvt. Ltd., India

² Department of Physics, Agra College,
Dr. B.R. Ambedkar University, Agra, India
E-mail: gaurang_misra@rediffmail.com

Mercuric Calcogenides found many applications in electronic and optical devices as semiconducting materials. An equation of state provides useful information about the relationship between pressure (P), volume (V) and temperature (T) that helps to understand the behaviour of materials under the effect of high pressure and high temperature. The present paper sheds light on the electronic structure of Mercuric Calcogenides by simulating its electronic properties through ab initio method. This ab initio method is extended to derive the equation of state for Mercuric Calcogenides. The present equation of state has also been tested for the prediction of End Point. The computed results compare well with Quantum statistical data.

Keywords: MERCURIC CALCOGENIDES, EQUATION OF STATE, AB INITIO METHOD, DFT.

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1. INTRODUCTION

The unique physical properties of Mercuric Calcogenides (MC) as semiconducting materials with promising applications to optical and electronic devices are highlighted everywhere. Similar to other tetrahedral semiconductors, the effect of pressure on the physical properties of MC has been the subject of numerous experimental and theoretical investigations. The vibrational properties of MC under high pressure have been studied in the past using Raman spectroscopy. To achieve a better understanding of the structural and thermodynamical properties of MC it is highly important to develop an atomistic approach leading to the Equation of State (EoS) from ab initio calculations.

In the present work we make use of the ab initio pseudopotential (PP) formalism to generate the EoS from ab initio calculations and compare it with other EoSs, belonging to different classes and categories. We have also analysed our results in the light of Stacey [1, 2] regarding the End Point analysis.

2. GENERATION OF EQUATION OF STATE

An EoS provides useful information about the relationship between pressure (P), volume (V) and temperature (T) that helps to understand the behaviour of materials under the effect of high pressure and high temperature. Up to now a number of workers have endeavoured to search for a simple form of

the EoS, which has a small number of parameters. The parameters are determined by using available low-pressure data such as the equilibrium volume V_o , the isothermal bulk modulus K_o and its pressure derivatives $K'_{o,0}$ and K''_o at zero pressure.

Various attempts have been made in the past to develop empirical and phenomenological forms for the EoS of materials. The EoSs considered can be lumped into three classes: (1) based on the solid mechanics definition of finite strain, (2) based on interatomic potentials and (3) based on assumed relationships between the variables within the EoS. There is yet another way of classifying EoSs. In this method the EoSs can be grouped into three categories: (i) the derivative form, (ii) the volume integral form and (iii) the pressure integral form.

It is interesting to note that the derivative form is much better than the integral forms: the error at large compressions is much exaggerated in the integral forms than in the derivative forms.

The ab initio PP approach to the total crystal energy calculation is presented. Using this approach the expression for the EoS will be derived from the variationally determined valence electron eigen-values and charge densities. The large and geometry-insensitive core contributions are explicitly projected out by using a PP formalism. The DF formalism for the exchange and correlation potential is self consistently employed in the derivation.

Within PP framework, following the conventional DF formalism [3, 4] the total crystal energy (E) is given by:

$$E = \bar{\varepsilon} + \left[\mu_{XC}(\bar{G} = \bar{0}) + \frac{U_{PS}(\bar{G} = \bar{0})}{\Omega_a} \right] Z - \frac{1}{2} \Omega_a \sum_{\bar{G}}' V_H(\bar{G}) \rho(\bar{G}) + \quad (1)$$

$$+ \Omega_a \sum_{\bar{G}}' \left[\varepsilon_{XC}(\bar{G}) - \mu_{XC}(\bar{G}) \right] \rho(\bar{G}) + \gamma_{Ewald}$$

where $\bar{\varepsilon}$ is the mean eigen value averaged over all the occupied states, $V_H(\bar{G})$ is the Hartree potential, $\rho(\bar{G})$ is the (pseudo) charge density, $\varepsilon_{XC}(\bar{G})$ and $\mu_{XC}(\bar{G})$ are the exchange-correlation energy density and potential respectively, Ω_a is the atomic volume, Z is the valency, γ_{Ewald} and $U_{PS}(\bar{G} = \bar{0})$ are respectively the Ewald energy [5] and the PP term generated through the norm-conserving PP scheme of Bachelet, Hamann and (BHS) [6, 7].

The BHS scheme is used because it has optimum transferability in comparison to ultra-soft PP and can be extended to describe the electronic and structural properties of magnetic systems [8] also. The prime on the summation in Eq. (1) denotes that the $\bar{G} = \bar{0}$ term is excluded from the summation.

The pressure $P(\eta)$ as a function of the compression $\eta = V/V_o$ can then be calculated using the following relation:

$$P(\eta) = -\frac{\partial E}{\partial V} = \frac{K_o}{20} \left[\alpha \{ 6\eta^{-2} - 15\eta^{-5/3} + 10\eta^{-4/3} - \eta^{-1/3} \} + \right. \\ \left. + \beta \{ 3\eta^{-2} - 5\eta^{-4/3} + 2\eta^{-1/3} \} + \gamma \{ \eta^{-2} - \eta^{-1/3} \} \right] \quad (2)$$

with:

$$\alpha = 6 + 9K_o K_o'' + (3K_o' - 4)(3K_o' - 7), \beta = 2(3K_o' - 7), \gamma = 12.$$

K_o , K_o' and K_o'' are respectively the isothermal bulk modulus, its first and second pressure derivatives.

3. RESULTS AND DISCUSSION

From first-principles calculations the EoS is generated using the ab initio PP framework. Also through the ab initio approach, no experimental data are used in the generation of EoS other than atomic variables. Due to these the present model for EoS is superior to the existing ones and is also applicable in case of binary compounds.

The compression curves for MC are plotted in Fig. 1 and 2. In same figures the compression curves for MC from other EoSs belonging to different classes and categories are also plotted. For comparison we have taken the well-known Birch-Murnaghan [9, 10], Thomsen [11], Bardeen [12], Vinet et al. [13], Dodson [14], Brennan-Stacey [15] and Kumari-Dass [16] EoSs. These plots reveal that up to 15-20 GPa all compression curves coincide which is true for low pressure in accordance with Anderson [17]. Beyond this and up to 50 GPa the curves diverge more or less and this divergence increases significantly at higher pressures. The reason for this

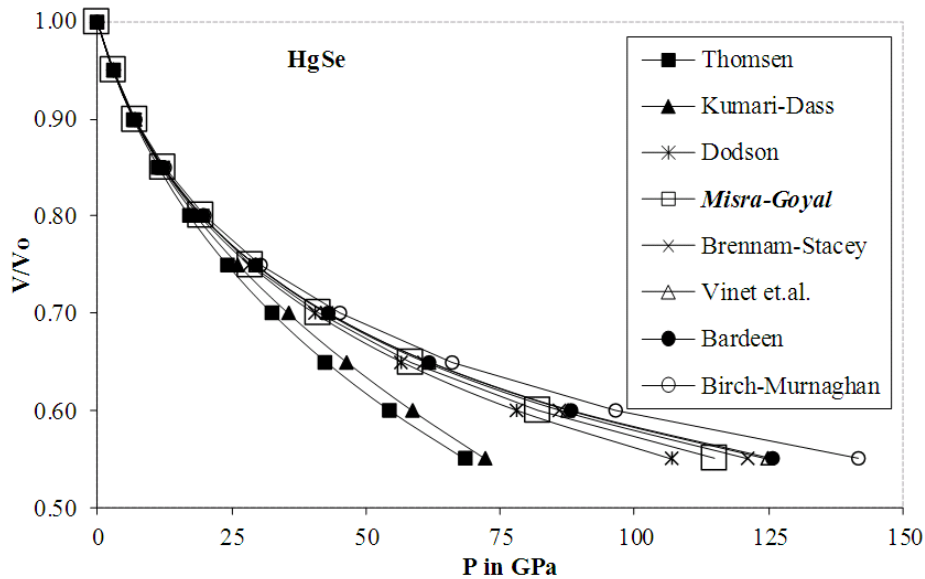


Fig. 1 – Isothermal compression curves from various EoSs belonging to different classes and categories and the present EoS for HgSe

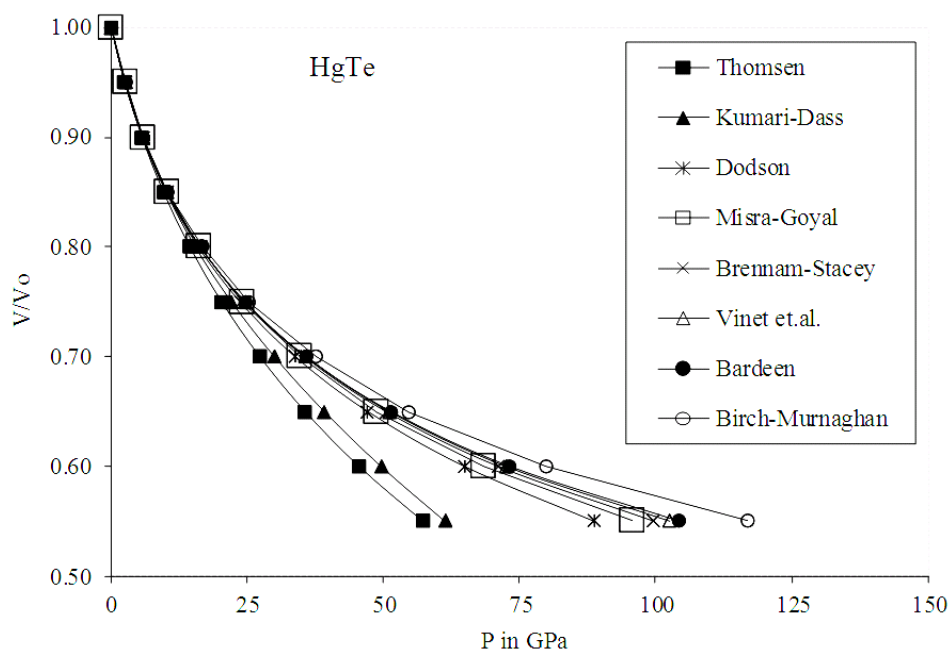


Fig. 2 – Isothermal compression curves from various EoSs belonging to different classes and categories and the present EoS for HgTe

behaviour is that for the EoSs based on Lagrangian strain, the Taylor series expansion in pressure fails because of the limited radius of convergence, whereas the EoSs based on Eulerian strain are in good agreement with the EoSs based on interatomic potentials.

According to Stacey [1, 2] the plot of K' versus P/K has a fixed End Point corresponding to the infinite pressure extrapolation. This concept of fixed End Point provides an effective and critical test for an EoS. The calculations based on Quantum Statistical Model (QSM) [18] reveal that $K'_{\infty} = 5/3 \approx 1.7$ in the limit $P \rightarrow \infty$. Thus a correct EoS should approach this End Point in the limit of extremely high compressions. Recognition of K'_{∞} offers the possibility of a powerful constraint on high pressure EoSs. The most important reason to know K'_{∞} is that it provides a close control on the curvature of the plot of K' versus P/K and therefore on the thermodynamic parameters that can be inferred from such a plot. We have thus plotted the dimensionless isothermal curves K' versus P/K for MC in Fig. 3. The plots of Fig. 3 suggest that the End Point is 1.99, which is very close to the QSM result. Thus the present EoS also fulfills the concept of fixed End Point as suggested by Stacey [1, 2].

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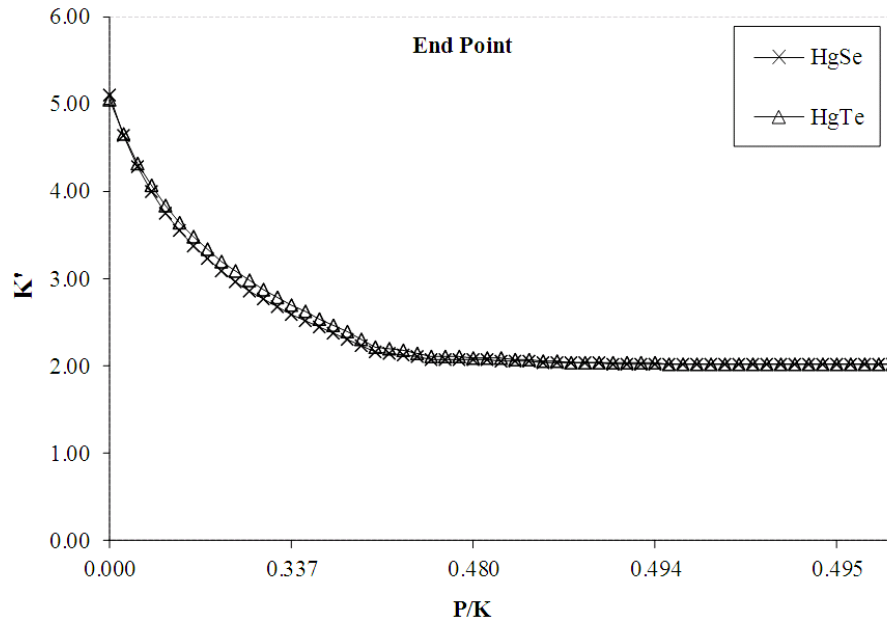


Fig. 3 – Dimensionless isothermal curves K' versus P/K for HgSe and HgTe using the present EoS

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