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K. C. Bhamu

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Temperature and Pressure Dependent Thermodynamic Behavior of 2H-CuInO₂

K.C. Bhamu^{1,2}

¹*Department of Physics, Goa University, Taleigao Plateau, Goa 403 206, India*

²*Physical and Materials Chemistry Division, CSIR_National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune-411008, India*

Corresponding author Email: kcbhamu85@gmail.com

Abstract. Density functional theory and quasi-harmonic Debye model has been used to study the thermodynamic properties of 2H-CuInO₂. At the optimized structural parameters, pressure (0 to 80 GPa) dependent variation in the various thermodynamic properties, i.e. unit cell volume (V), bulk modulus (B), specific heat (C_v), Debye temperature (Θ_D), Grüneisen parameter (γ) and thermal expansion coefficient (α) are calculated for various temperature values. The results predict that the pressure has significant effect on unit cell volume and bulk modulus while the temperature shows negligible effect on both parameters. With increasing temperature thermal expansion coefficient increase while with increasing pressure it decreases. The specific heat remains close to zero for ambient pressure and temperature values and it increases with increasing temperature. It is observed that the pressure has high impact on Debye temperature and Grüneisen parameter instead of temperature. Debye temperature and Grüneisen parameter both remains almost constant for the temperature range (0-300K) while Grüneisen parameter decrease with increasing pressure at constant temperature and Debye temperature increases rapidly with increasing pressure. An increase in Debye temperature with respect to pressure shows that the thermal vibration frequency changes rapidly

INTRODUCTION

“Transparent electronic devices (TEDs),” are the central component of novel flat panel systems and solar cells. The wide band gap (~3.0 eV) of transparent conducting oxides (TCOs) are fascinating for TEDs. TCOs are frequently considered in numerous optoelectronic applications viz. flat panel displays, photovoltaic, touch panels, stacked solar cells, transparent electrodes, etc. [1-7]. CuInO₂, a well-known TCO due to its unique and potential characteristics capable of bipolarity [8, 9] has generated much research interest in the past [9]. The unit cell of CuInO₂ retains 10₂ layer stacking which is responsible for two different types of layered structures for CuInO₂ i.e. *R-3m* (3R-) or *P6₃/mmc* (2H-) space group [10-12]. Both the layered phases differ only in layered stacking having different number of atoms. The reported 3R- structure is more favorable but the difference between the calculated ground state energy of 3R- and 2H- phases is in the order of few meV/atom. We obtained this difference equal to 0.00048 eV which is in tune with the values reported by [13]. A detailed analysis on crystal structure of delafossites has been reported in [14]. As far as we know, a few experimental and theoretical [15-17] studies are available for both prototypes while for 2H-CuInO₂, only few reports on electronic and optical properties are available [17]. As far as we know, no report is available on thermodynamic properties of 2H-CuInO₂. In this work, we report the pressure dependent variation on various thermodynamical properties i.e. unit cell volume, bulk modulus, specific heat, Debye temperature, Grüneisen parameter and thermal expansion coefficient for different temperatures.

METHODOLOGY

The structural properties were carried out using density functional theory (DFT) based computer code, Wien2K [18] within Perdew-Burke-Ernzerhof (PBE) functionals [19]. The structural optimization is carried out with a

11x11x2 mesh size in the irreducible part of the Brillouin zone (IBZ). The convergence criterion for total energy, charge and force on the atoms in the unit cell was set to be 10^{-5} Ry, 10^{-4} and 1.0 mRy/a.u. In Present computations, $R_{mt} \times K_{max}$ (G_{max}) was taken to be 8.0 (14 a.u. $^{-1}$) where, R_{mt} is the radius of muffin-tin sphere, K_{max} is the maximal value of the reciprocal lattice vector used in the plane wave expansion and G_{max} is the plane-wave expansion cutoff. Quasi-harmonic Debye model (QHDM) [20, 21] has been used to calculate thermodynamic properties of 2H-CuInO₂. The QHDM uses the non-equilibrium Gibbs function $G^*(V; P, T)$ which includes energy of the system, hydrostatic pressure, Debye temperature and vibration term of phonon density of states. More details about Gibbs function can be found in Refs. [20, 21].

RESULTS AND DISCUSSION

To investigate pressure and temperature effect on thermodynamic properties of 2H-CuInO₂, the QHDM method was used. The structural parameters used in QHDM was geometry optimized by fitting energy vs. volume (E-V) curve into Birch Murnaghan's equation of state (BMEOS). We considered the valid pressure (0 to 80 GPa) range where the quasi-harmonic model remains fully valid at different temperature values in the temperature range of 0 to 300 K. The pressure and temperature dependent thermodynamic properties, namely unit cell volume (V), bulk modulus (B), specific heat (C_v), Debye temperature (Θ_D), Grüneisen parameter (γ) and thermal expansion coefficient (α) are presented in Figs. 1-3.

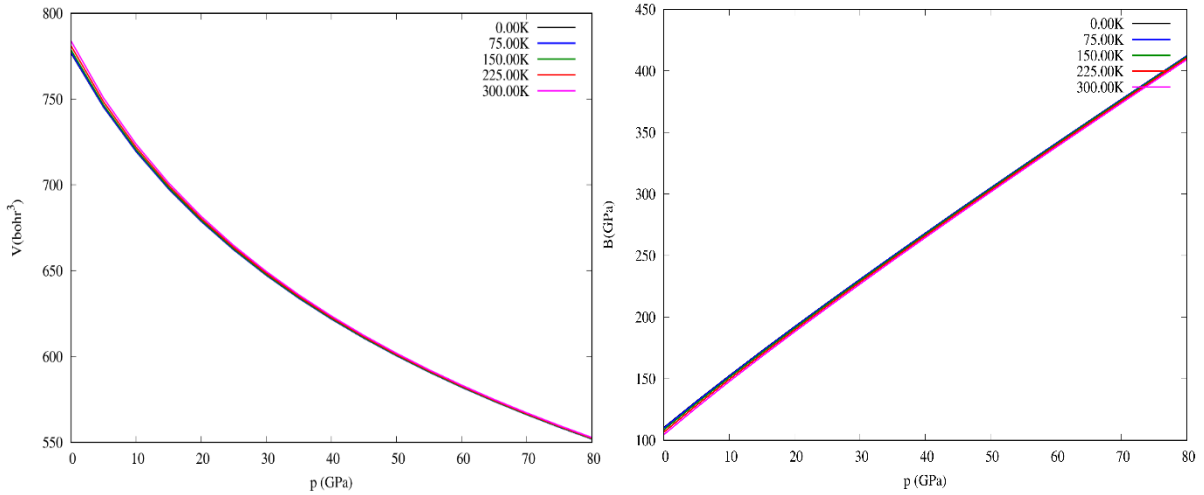


FIGURE 1. The dependence of the volume, V , (left side) and of the Bulk modulus, B , (right side) with pressure for different temperature.

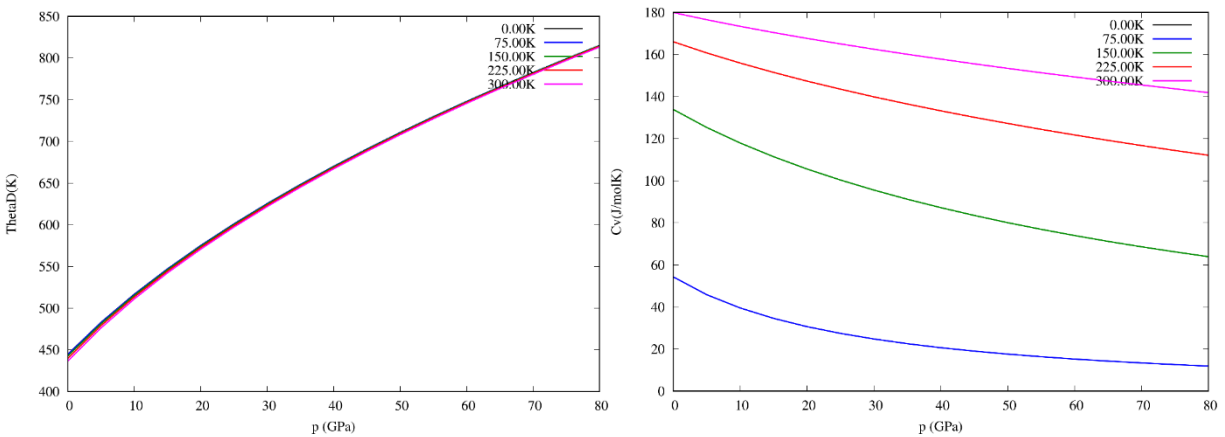


FIGURE 2. The dependence of the Debye temperature, Θ_D , (left side) and of the specific heat, C_v , (right side) with pressure for different temperature.

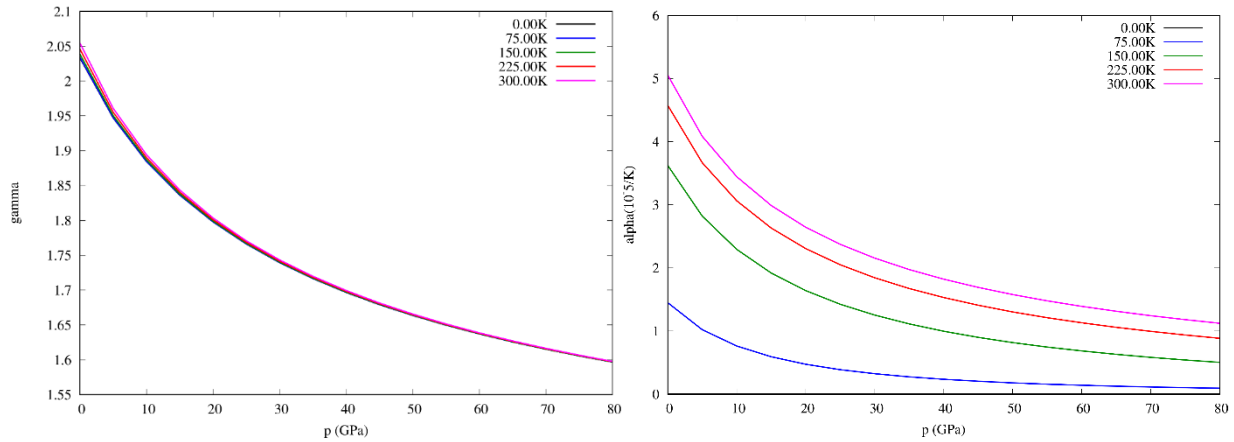


FIGURE 3. The dependence of the Grüneisen parameter (γ) (left side) and of thermal expansion coefficient (α) (right side) with pressure for different temperature.

Fig. 1 (left panel) presents the effect of pressure at fix temperature values on the unit cell volume. We see that the volume of 2H-CuInO₂ show slight increases with increasing temperature at low pressure side while at higher pressure temperature has negligible effect on volume. The unit cell volume increases with temperature at zero pressure is due to the expansion of its dimensions with temperature while the volume decreases with pressure due to compression. The variation of the bulk modulus with pressure at different temperature is shown in right panel of the Fig. 1. We see that the effect of pressure and temperature on bulk modulus is just opposite to that of the effect on volume. We notice that the volume and bulk modulus are weakly temperature dependent while pressure has significant effect on the volume and bulk modulus.

The pressure and temperature dependent Debye temperature (Θ_D) is presented in Fig. 2 (left side). In the vicinity of zero pressure, Θ_D vary slowly while at higher pressure it remains almost constant. With increasing pressure, Θ_D varies rapidly. A rapid variation in Θ_D with pressure predicts that the thermal vibration frequency of the atoms changes rapidly with increasing pressure while vibrational frequency changes slowly with increasing temperature. At the ambient temperature and zero pressure, the Θ_D value is found to be nearly equal to 447 K. The specific heat of a material indicates material's heat retention or loss ability. The specific heat, Fig. 2 (right side), remains zero below 25 K and above 25 K it gradually decreases with respect to pressure while it increases slowly with respect to temperature. We observe that the effect of temperature is significant while specific heat is not influenced much by pressure. It means that at low temperature, less degree of freedom are available for depositing the energy while with increasing temperature degrees of freedom become more for depositing energy. Fig. 3 (left side) depicts the variation in Grüneisen parameter with respect to pressure and temperature. At zero pressure, Grüneisen parameter increases with increasing temperature while at higher pressure the variation in Grüneisen parameter with temperature is negligible. The pressure shows the significant effect on Grüneisen parameter and Grüneisen parameter decreases with increasing pressure. The variation in thermal expansion coefficient with respect to pressure for various temperature values is presented in Fig. 3 (right side). Thermal expansion coefficient remains almost zero below 20K and then gradually increases with increasing pressure while at low temperature the pressure does not show any effect on thermal expansion coefficient while at higher temperature, thermal expansion coefficient decreases with increasing pressure.

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