

Full Length Research Paper

First principles study of some thermodynamic properties of Calcium Indium (CaIn) intermetallic compound

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Calculations of some thermodynamic properties of Calcium Indium (CaIn) intermetallic compounds are carried out using the quasi harmonic Debye model. The Debye temperature was studied as a function of both lattice temperature and unit cell volume. The calculations showed that the Debye temperature decreases slowly with elevation of the temperature. It was found that the Debye temperature varies from 130 to 110K when the lattice temperature increases from 10K up to 1600K which indicates a small range of variation with temperature. The dependence of the Debye temperature on the volume revealed that it is generally increased with increasing of the unit cell volume. The temperature dependent bulk modulus of CaIn compound was investigated at zero pressure. It decreases as the temperature increases. This may be attributed to the rapid change of the cell volume as the temperature increases.

Key words: Intermetallic compounds, Debye temperature, bulk modulus, Gruneisen parameter.

INTRODUCTION

Calcium Indium (CaIn) is an intermetallic compound that crystallizes in the CsCl-type structure known as B2 structure (Pearson, 1973). The structural phase, B2, is a superstructure of the cubic BCC (Body centered cubic) lattice. The physics and technological applications of the B2 compounds have attracted lots of interest due to their bound properties (Schafer et al., 1973), low metallic conductivity (Kishio and Brittain, 1979), low paramagnetism and diamagnetism (Yao, 1964).

Christensen (1985) has studied theoretically the structural phase stability of some metallic compounds in B2 structures using the first-principles methods. Other researchers have investigated theoretically the chemical bonding and bond length of these compounds (McNeil et al., 1973; Inglesfield, 1971; Zhu et al., 2009). Experimentally, the lattice structure has been determined by Zintl and Neumayr (1933) using the X-ray diffraction method.

The elastic properties of solid materials are important, because they are related to equations of state, specific heat, thermal expansion and Debye temperature (Chang et al., 2010). Thermodynamic functions of the solid

are commonly described by an appropriate Debye temperature, which is, in general, temperature-dependent (Tosi and Fumi, 1963). The quasi harmonic Debye model presented by Francisco et al. (2001) is used to investigate the thermodynamic properties of a crystal. In this model the phononic effects are considered in the non-equilibrium case.

This work presents a numerical calculation of temperature and volume dependence of Debye temperature and some elastic parameters for CaIn intermetallic compound in B2 phase.

THEORY

In the quasi harmonic Debye model, the non-equilibrium Gibbs function is given by the form (Francisco et al., 2001; Blanco et al., 2004):

$$G(V, p, T) = E(V) + PV + A_{vip}(\Theta(V), T) \quad (1)$$

where $E(V)$ is the total energy, V is the cell volume, PV corresponds to the constant hydrostatic pressure condition and T is

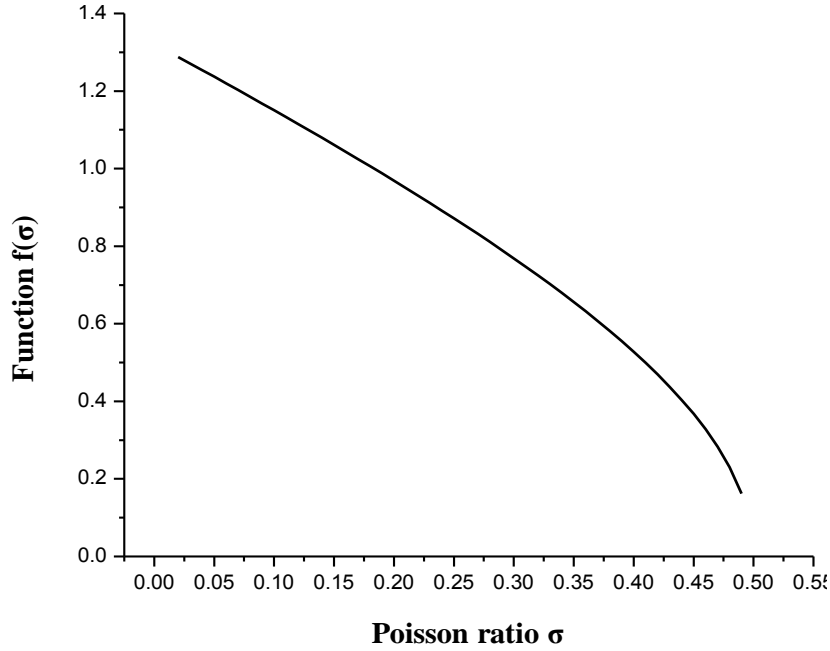


Figure 1. Variation of the function $f(\sigma)$ with Poisson's ratio σ .

the absolute temperature. The vibrational contribution A_{vip} can be written as (Blanco et al., 1996):

$$A_{vip}(\Theta, T) = nk_B T \left[\frac{9\Theta}{8T} + 3\ln(1 - e^{-\Theta/T}) - D(\Theta/T) \right] \quad (2)$$

Where n is the number of atoms per formula unit, k_B is the Boltzmann constant and $D(\Theta/T)$ is the Debye integral. For an isotropic solid the Debye temperature Θ_D presented by Blanco et al. (1996) is expressed by:

$$\Theta_D = \frac{\hbar}{k_B} \left[6\pi^2 V^{\frac{1}{3}} n \right]^{\frac{1}{3}} f(\sigma) \sqrt{\frac{B_s}{M}} \quad (3)$$

\hbar is reduced Planck's constant, M is the molecular mass per unit cell, B_s is the adiabatic bulk modulus, σ is Poisson's ratio and $f(\sigma)$ is a function given by:

$$f(\sigma) = \left\{ 3 \left[2 \left(\frac{2(1+\sigma)}{3(1-2\sigma)} \right)^{\frac{3}{2}} + \left(\frac{1+\sigma}{3(1-\sigma)} \right)^{\frac{3}{2}} \right]^{-1} \right\}^{\frac{1}{3}} \quad (4)$$

The non-equilibrium Gibb's function can be minimized with respect to volume:

$$\left(\frac{\partial G(V, P, T)}{\partial V} \right)_{P, T} = 0 \quad (5)$$

By solving equation (5), one can obtain the isothermal bulk modulus

B_T , the heat capacity C_V , and the thermal expansion coefficient α :

$$B_T(P, T) = V \left(\frac{\partial^2 G(V, P, T)}{\partial V^2} \right)_{P, T} \quad (6)$$

$$C_V = 3nk_B \left[4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right] \quad (7)$$

$$\alpha = \frac{\gamma C_V}{B_T V} \quad (8)$$

where γ is the Gruneisen parameter given by:

$$\gamma = - \frac{d \ln \Theta(V)}{d \ln V} \quad (9)$$

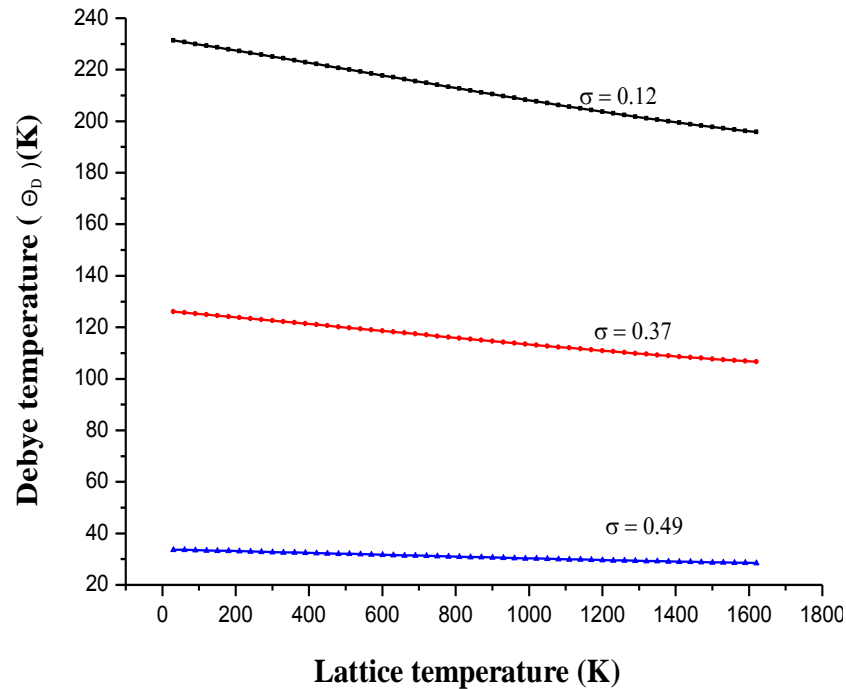
Hence, from the quasi harmonic Debye model one can calculate the thermodynamic functions.

RESULTS AND DISCUSSION

Calculations of some thermodynamic properties are carried out by using the first principle methods depending on the quasi harmonic Debye model. One of the important thermodynamic functions is the Debye temperature. Since the Debye temperature is dependent on the Poisson's ratio, the function $f(\sigma)$ is examined for solid materials. Figure 1 shows the variation of the

Table 1. The parameters of B2 phase of CaIn used in the calculations.

Parameter	Value
Lattice constant (a)	3.8775 Å
Number of atoms per formula unit (n)	4
Molecular mass per unit cell (M)	154.896 a.m.u
Poisson's ratio (σ)	0.37

**Figure 2.** Change of Debye temperature with lattice temperature.

function with Poisson's ratio. The graph indicates that the function $f(\sigma)$ decreases as the Poisson's ratio increases. In the case of CaIn compound with B2 phase structure the Poisson's ratio is taken as 0.37 (Ozayman et al., 2011) and then the function $f(\sigma)$ is estimated at 0.6073.

The Debye temperature of CaIn material was calculated as a function of temperature in a range up to 1700K. The parameters of CaIn B2 structure used in the calculation are shown in Table 1 (Ozayman et al., 2011).

Figure 2 demonstrates the Debye temperature versus the lattice temperature of CaIn compared with the calculated Debye temperature of other two materials of Poisson's ratio 0.12 and 0.49. We have chosen these materials since CaIn has a value of σ between the two materials.

The Debye temperature decreases slowly with elevation of the temperature. In the case of CaIn compound the Debye temperature changes from 130K at very low temperature to about 110K at 1600K which indicates a small range of variation with temperature.

The dependence of the Debye temperature on the cell volume is depicted in Figure 3 at three cases of Poisson's ratio. The Debye temperature generally increases with the volume. In order to estimate the Gruneisen parameter γ we plot $\ln\theta_D$ versus $\ln V$, the slope of the yielded straight line equals minus of the Gruneisen parameter. From Figure 4, one can estimate the value of γ at -0.16667.

The temperature dependent bulk modulus of CaIn compound was studied in a temperature range up to 1700K at zero pressure. Figure 5 demonstrates the behavior of B with T . The Bulk modulus decreases as the temperature increases. This may be due to the rapid change of the cell volume as the temperature increases. Estimation of the bulk modulus at room temperature records the value of 26.146 GPa.

Conclusions

Calculations of some thermodynamic properties of CaIn

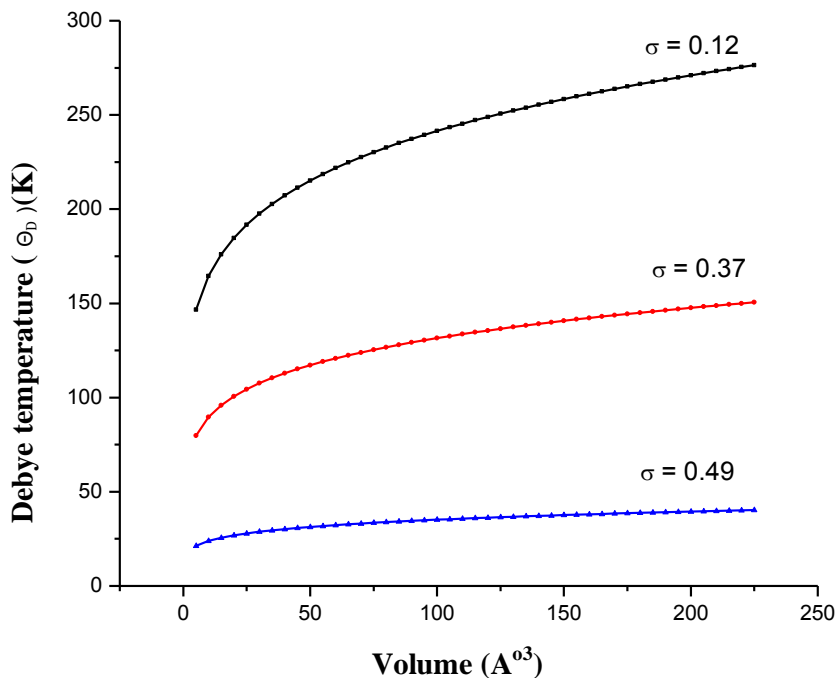


Figure 3. The Debye temperature as a function of Volume.

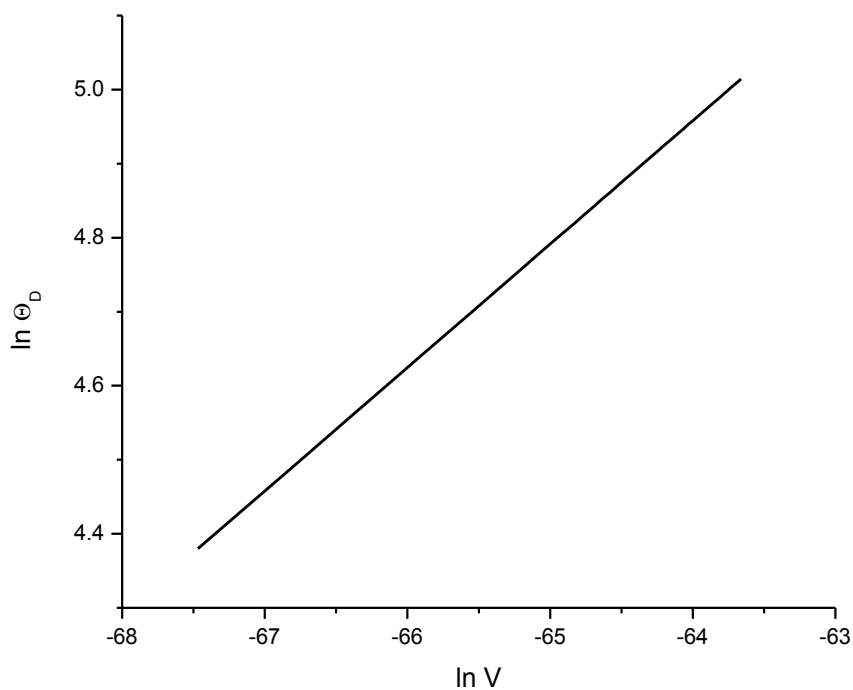


Figure 4. $\ln \Theta_D$ versus $\ln V$ for CaIn compound.

intermetallic compounds are carried out using the first principle methods depending on the quasi harmonic Debye model. The Debye temperature (Θ_D) is calculated as a function of temperature in a range up to 1700K. The Debye temperature decreases slowly with elevation of

the temperature. It changes from 130K at very low temperature to about 110K at 1600K indicating a small range of variation with temperature. The dependence of Θ_D on the unit cell volume is investigated. The Debye temperature generally increases with the volume. The

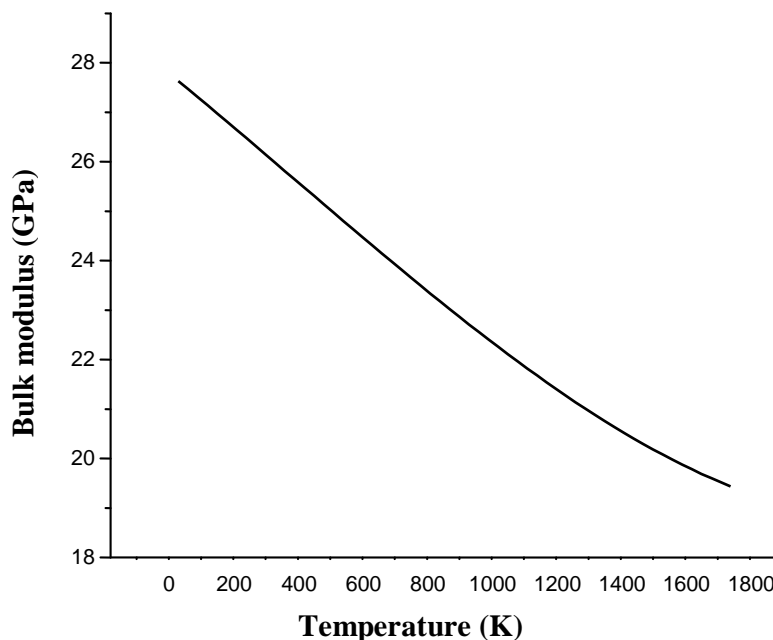


Figure 5. Variation of the Bulk modulus with temperature.

Gruneisen parameter is estimated at the value of -0.16667. The Bulk modulus at zero pressure decreases as the temperature increases. This may be attributed to the rapid change of the cell volume with the temperature. From the plot of the Bulk modulus versus temperature as shown in Figure 5, the value of the Bulk modulus at room temperature can be estimated as 26.146 GPa.

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