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THERMODYNAMICS PROPERTIES OF COPPER HALIDE ALLOY ($CUBR_{0.5}CL_{0.5}$)

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Abstract: *Ab initio density functional theory (DFT) has been used to investigate the thermal properties of the* $CuBr_{0.5}Cl_{0.5}$ *alloys over a wide range of temperature. Using the quasiharmonic approximation (QHA) for the some physical quantities of interest such as heat capacity at constant volume and entropy are calculated and discussed. The theoretical results show good agreement with the available experimental data for CuBr and CuCl. The present results show that symmetric and asymmetric structure of CuBr0.5Cl0.5 have a good agreement with the calculatingly value for heat capacity.*

Keywords: DFT, PWSCF, Thermodynamics properties, $CuBr_{0.5}Cl_{0.5}$.

1. Introduction

During the last three decades, the CuX (X = Br, Cl and I) have been a subject of many theoretical and experimental studies. The CuX compounds are big direct gap semiconductors, which crystallise at ambient condition in the cubic NaCl structure, and posses 10 valence electrons instead of eight for common zinc-blend and wurtzite III-V and II-VI compounds. The copper halides are prototype materials for nonlinear optical experiments (Konigsberg and Schrunner, 1989).They found renewed interest because of the possibility of producing microcrystals (Frohlich et al., 1971). As promising candidates for photosensitive and semiconducting materials, copper halides attract much attention and several theoretical and experimental results have been reported (Blacha et al., 1986; Hsueh and Maclean, 1995). The copper halides CuBr and CuCl crystallize under ambient conditions in the zinc-blende structure. A closer look at the structural properties of I-VII semiconductor alloys made possible by more measurements (Endo et al., 1993) reveals, however, that these alloys form a complete solid solution. In 1998 the band structures of CuCl1-xBrx (Heireche et al., 1998), CuCl1-xIx (Bouhafs et al.,1998) and CuBr1-xIx (Bouhafs et al.,1998) alloys are used tight-binding (TB) theory within the virtual crystal approximation (VCA) studied. The miscibility of copper halides is studied by using a three-body potential (Sekkal et al., 1999). The electronic structure and disorder effects in copper halides alloys are studied by using the full potential linearized augmented plane wave (FLAPW) method (El Haj Hassan and Zaoui, 2001). It is showed that X-ray diffraction patterns of CuBr1-xIx crystals indicated a cubic zinc-blende structure and is showed that the lattice parameter changed linearly without changes in the crystal structure (Bouhafs et al., 1998).

In this paper we present a first principles study of the ground state and thermodynamic properties of $CuBr_xCl_{1-x}$ compounds by employing plane wave pseudo-potential method and density-functional theory. The paper is organized as follows. In Section 2, we briefly review the computational method used. In Section 3, the result of our calculations are presented and discussed. Finally, a summary of the work will be given in Section 4.

2. Methods

The present theoretical calculations are performed using the PWSCF software package (Baroni et al., 2001). During first-principles calculations, the exchange-correlation functional is treated with GGA Perdew–Wang 91 (Perdew and Wang, 1992; Perdew et al., 1992), in which the expansion of the augmentation charges is required. The core-valence electron interaction is described via ultrasoft pseudopotential (Vanderbilt, 1990). For the eight atom supercell considered here (Fig. 1), many possible

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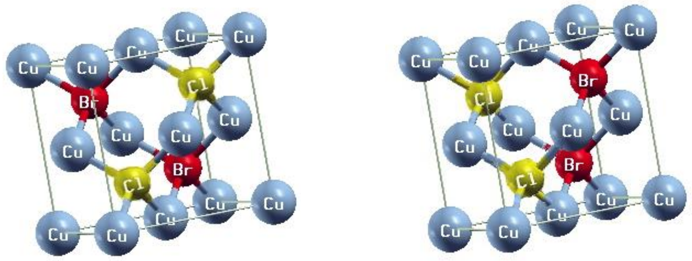
atomic arrangements may exist for the alloy. The unit cell contains four Cu atoms, two atoms of Cl and two atoms of Br, where the tetrahedral nearest neighbor environment of each Cl or Br atom is 4 Cu atoms in the symmetrical type that showed in Fig. 1a and the Asymmetric type that showed in Fig. 1b. The basis set is truncated to a kinetic energy cutoff of 36 Ry for Symmetrical type of alloy and a kinetic energy cutoff of 37 Ry for Asymmetric type. The Brillouin-zone integrations are performed using a 5×5×5 grid mesh of Monkhorst-Pack scheme for both. With QHA, a fourth-order finite strain equation of state (EOS) (Silveira et al., 2006; Karki and Wentzcovitch, 2000;Wu and Wentzcovitch, 2008; Sun and Umemoto, 2008; Li et al., 2012) is used to obtain the Helmholtz free energy F(T,V) at various temperatures. From the Helmholtz free energy, several physical quantities of interest are obtained, which are as a function of temperature.



a) *b)*

Fig. 1: Schematic picture of the possible atomic arrangements of Cu in the CuBr0.5Cl0.5 cubic supercell. (a) shows the symmetrical and (b) shows the Asymmetric type.

3. Results and Discussion

3.1. Structural properties

$CuBr_{0.5}Cl_{0.5}$ has two CsCl-type simple cubic structures with space group of F43m (Dwight, 1959). As shown in Fig. 1, its unit cell has three kinds of atom with lattice constant a = 5.62 A° for asymmetrical type and a = 5.61 A° for symmetrical type. We first determine the ground-state structural parameters of symmetrical and asymmetrical of $CuBr_{0.5}Cl_{0.5}$.The ground state properties are obtained by minimization of the total energy with respect to the unit cell volume V, which is directly related to the lattice constant. Our results of $CuBr_{0.5}Cl_{0.5}$ crystals indicated a cubic zinc-blende structure and showed that the lattice parameter changed linearly with Br: Cl concentration ratio without changes in the crystal structure.

3.2. Thermodynamic properties

The thermodynamic properties of $CuBr_{0.5}Cl_{0.5}$ can be determined in detail by the entire phonon spectrum. The quasi-harmonic approximation can describe such properties quite satisfactorily. In the present work, the more explicit forms of the phonon contribution to the entropy S, and constant-volume specific heat Cv, at temperature T, in the harmonic approximation per unit cell are given (Lee and Gonze, 1995) as follows:

$$C_V = 3nNk_\beta \int_0^{\omega_{max}} \left(\frac{\hbar\omega}{2k_BT}\right)^2 \operatorname{csch}^2\left(\frac{\hbar\omega}{2k_BT}\right) g(\omega)d\omega \qquad (1)$$

$$S = 3nNk_\beta \int_0^{\omega_{max}} \left[\frac{\hbar\omega}{2k_BT}\coth\frac{\hbar\omega}{2k_BT} - \ln\left\{2\sinh\frac{\hbar\omega}{2k_BT}\right\}\right] g(\omega)\,d\omega \qquad (2)$$

Where k_β is the Boltzmann´s constant, h is the Planck´s constant, n is the number of atoms per unit cell, N is the number of unit cells, ω is the phonon frequencies, ωmax is the largest phonon frequency, and g(ω) is the normalized phonon density of states.

The variation of entropy with temperature for $CuBr_{0.5}Cl_{0.5}$ is given in Fig. 3. Entropy is a measure for the disorder of the micro-particle in thermodynamic system. The change of entropy can determine whether a thermodynamic process is a reversible process. The lattice contribution to the C_v is calculated and shown in Fig. 2. In the low-temperature limit, the specific heat exhibits the expected T^3 power-law behavior and approaches at high temperatures the Dulong- Petit limit of $C_v = 3nNk_B = 74.830$ J/mol K. Due to the lack of experimental or other theoretical values existing on the thermodynamics for comparison with our results, we have calculated the thermodynamic properties for a number of materials such as CuBr and CuCl to further test of our computational methodology. Theory and experiment show satisfactory agreement within the limitation of the PWSCF program and the harmonic approximation. Here, we just list the calculated results S and C_p for CuBr and Cucl in Tab. 1 together with the corresponding experimental data (Cox et al., 1989; Pedley, 1994; Gurvich, 1994). CuBr has a cubic symmetry structure and two kinds of atoms with lattice parameters of a = 6.695A°, the Cu atom occupies the (0, 0, 0) site and Br atoms occupy the (1/4, 1/4, 1/4) site. The calculated lattice parameters are 6.706A°. Compared with the experimental results, the maximal deviation is only 0.16%, a normal agreement by GGA standards. The good agreement for CuBr can predict that the calculated thermodynamic properties of $CuBr_{0.5}Cl_{0.5}$ can also be at the same level of accuracy. Our calculated results can be seen as a prediction for the future investigations.

Tab. 1: The calculated thermodynamic functions for CuBr and CuCl compared with experimental results.

	S(J/molK)		Cp(J/molK)		ΔH(kJ/mol)	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
CuBr	95.7	96.1	54.1	54.7	-104.1	-104.6
CuCl	85.8	86.2	48.1	48.5	-136.9	-137.2

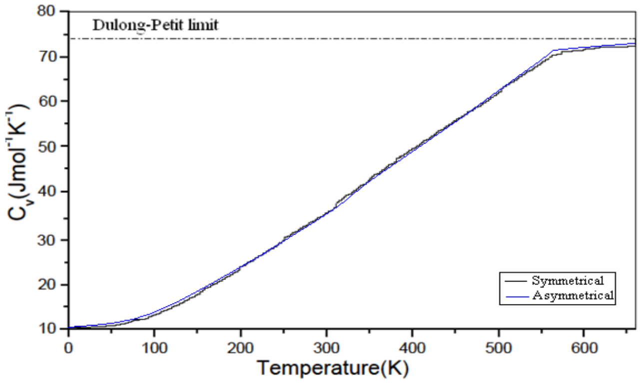


Fig. 2: Calculated temperature dependence of heat capacity of $CuBr_{0.5}Cl_{0.5}$ at constant volume (C_V) for symetrical and asymmetrical type.

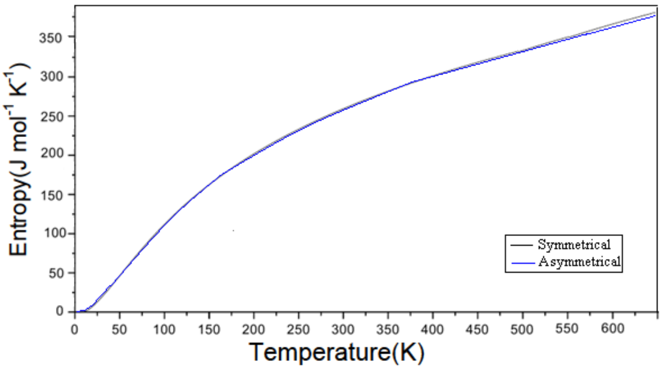


Fig. 3: Variation of entropy S with temperature T for symetrical and asymmetrical type.

4. Conclusions

In summary, the calculation of thermodynamic properties of $CuBr_{0.5}Cl_{0.5}$ using DFT and pseudo-potential methods are performed. The heat capasity is found to be in good agreement with the calculatingly value (dulong petit value) with the error less than 0.19%. Finally, we predicate the important thermodynamics properties including the entropy and constant-volume specific heat within the quasi harmonic approximation (QHA). Our thermodynamic calculations of $CuBr_{0.5}Cl_{0.5}$ compound is showed similar in symmetrical and asymetrical type and will certainly be very useful for the interpretation of future experiments.

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