

# FP-LMTO Investigation of the Structural and Electronic Properties of $\text{Cu}_x\text{Ag}_{1-x}\text{I}$ Alloys

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## ABSTRACT

The structural and electronic properties of the ternary  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  alloy have been calculated, using the full-potential linear muffin-tin-orbital (FP-LMTO) method based on density functional theory, within both the local density approximation and the generalized gradient approximation (GGA). The equilibrium lattice constants and the bulk modulus are compared with previous theoretical calculations. The concentration dependence of the electronic band structure and the direct-indirect band gaps is also investigated. Using the approach of Zunger and co-workers the microscopic origins of the gap bowing were also explained.

**Keywords:** (FP-LMTO) Method,  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  Alloy

## 1. Introduction

Silver iodide and copper iodide have received attention as promising materials for applications in technological devices and are used as model systems in both physical and numerical experiments [1]. These compounds which have four valence electrons per atoms, crystallize in a tetrahedral coordinated zinc-blende (ZB) structure [2,3] under ambient conditions. Silver iodide can exist in three crystal polymorphs at atmospheric pressure. Below 420 K silver iodide crystallizes in the hexagonal  $\beta$  phase (wurtzite structure). Copper iodide also has several transformations. The low-temperature cubic  $\gamma$ -CuI phase with the zinc blende structure, transforms to the  $\beta$  phase with a distorted hexagonal structure and a rock salt structure above 673 K ( $\alpha$ -CuI). Another interesting feature of these systems is that the lattice mismatch between CuI and AgI is very small and therefore it is useful to combine them for forming  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  alloys. Indeed, CuI and AgI binary compounds form a continuous series of alloys ( $\text{Cu}_x\text{Ag}_{1-x}\text{I}$ ), where  $0 < x < 1$  denotes the molar fraction of Cu. Both CuI and AgI crystallizes in the cubic zinc blende structure. Hence, one would expect that the different properties of the ternary alloy to be vary smooth-

ly between the end points. Moreover, it was shown experimentally [4] that the  $\alpha$ - $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  based solid solutions in the quasibinary AgI-CuI system exists over a wide temperature range. The ionic transport in  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  was studied by Nölting and co-workers and Kusakabe *et al.* [4,5]. They have observed that the electric conductivity reduced with increasing the copper concentration.

Goldmann [6] reviewed detailed experimental and theoretical information of the valence and conduction band states in CuI, and AgI. He proposed a band structure model which is able to interpret all available experimental information extracted from optical absorption spectroscopy, soft X-ray absorption and emission spectroscopy. Theoretically, many calculations using the molecular dynamics simulations [7,8] have been done to characterize the structural, electronic, and optical properties of these systems.

Thus our main goal of this work is to study the effect of increasing concentration of copper on the structural and electronic properties band structure such as lattice constant, bulk modulus, band gaps and effective masses by using the full potential linear muffin-tin orbitals (FP-LMTO) method. In this work, we have used the “special quasirandom structures” (SQS) approach of

Zunger *et al.* [9] to reproduce the randomness of the alloys for the first few shells around a given site. This approach is reasonably sufficient to describe the alloys with respect to many physical properties that are not affected by the errors introduced using the concept of the periodicity beyond the first few shells.

The organization of the article is as follows. The computational method we have adopted for the calculations is described in Section 2. We present our results in Section 3. Finally, conclusions are given in Section 4.

## 2. Method of Calculations

The calculations reported here were carried out using the ab-initio full-potential linear muffin-tin orbital (FP-LMTO) method [10-13] as implemented in the Lmtart code [14]. The exchange and correlation potential was calculated using the local density approximation (LDA) [15] and the generalized approximation (GGA) [16]. This is an improved method compared to previous (LMTO) methods. The FP-LMTO method treats muffin-tin spheres and interstitial regions on the same footing, leading to improvements in the precision of the eigenvalues. At the same time, the FP-LMTO method, in which the space is divided into an interstitial regions (IR) and non overlapping muffin-tin spheres (MTS) surrounding the atomic sites, uses a more complete basis than its predecessors. In the IR regions, the basis functions are represented by Fourier series. Inside the MTS spheres, the basis functions are represented in terms of numerical solutions of the radial Schrödinger equation for the spherical part of the potential multiplied by spherical harmonics. The charge density and the potential are represented inside the MTS by spherical harmonics up to  $l_{\text{max}} = 6$ . The integrals over the Brillouin zone are

performed up to 42 special  $k$ -points for binary compounds and 32 special  $k$ -points for the alloys in the irreducible Brillouin zone (IBZ), using the Blöchl's modified tetrahedron method [17]. The self-consistent calculations are considered to be converged when the total energy of the system is stable within  $10^{-5}$  Ry. In order to avoid the overlap of atomic spheres the MTS radius for each atomic position is taken to be different for each case. Both the plane waves cut-off are varied to ensure the total energy convergence. The values of the sphere radii (MTS), number of plane waves (NPLW), used in our calculation are summarized in **Table 1**.

## 3. Results and Discussions

### 3.1. Structural Properties

As a first step we calculate the structural properties of the compounds CuI, AgI and their alloy in the cubic structure by means of full-potential LMTO method. As for the semiconductor ternary alloys in the type  $\text{B}_x\text{A}_{1-x}\text{C}$ , we have started our FP-LMTO calculation of the structural properties with the zinc-blende structure and let the calculation forces to move the atoms to their equilibrium positions. We have chosen the basic cubic cell as the unit cell. In the unit cell there are four C anions and three A and one B, two A and two B, and one A and three B cations, respectively, for  $x = 0.25, 0.50$  and  $0.75$ . For the considered structures, we perform the structural optimization by calculating the total energies for different volumes around the equilibrium cell volume  $V_0$  for CuI and AgI binary compounds and their alloys. The calculated total energies are fitted to the Murnaghan's equation of state [18] to determine the ground state properties such as the equilibrium lattice constant  $a$ , and the bulk modulus

**Table 1. The plane wave number PW, energy cut-off (in Ry) and the muffin-tin radius (RMT) ( in a.u.) used in calculation for binary AgI and CuI and their alloy in zinc blende (ZB) structure.**

$x$	PW		$E_{\text{cut total}}$ (Ry)			RMT (a.u)	
	LDA	GGA	LDA	GGA		LDA	GGA
0	5064	12050	75.918	123.177	Ag	2.490	2.607
					I	2.808	2.939
0.25	33400	65266	108.971	155.912	Cu	2.449	2.560
					Ag	2.449	2.560
					I	2.762	2.845
0.50	33400	65266	113.796	163.276	Cu	2.350	2.477
					Ag	2.350	2.477
					I	2.750	2.845
0.75	33400	65266	118.805	171.247	Cu	2.300	2.418
					Ag	2.300	2.418
					I	2.691	2.778
1	5064	9984	90.1556	131.503	Cu	2.180	2.267
					I	2.674	2.771

$B$ . The calculated equilibrium parameters ( $a$  and  $B$ ) are given in **Table 2** which also contains results of previous calculations as well as the experimental data. On the whole, our calculated structural parameters are in good agreement with those obtained by first-principles methods within different approximations. The calculated lattice parameters values for the binary compounds are in good agreement with the measured data, which ensure the reliability of the present first-principles computations. The computed lattice parameters slightly underestimates and overestimates the measured data by using LDA and GGA, respectively, which are consistent with the general trend of these approximations. As it can be seen that the calculated lattice parameter for CuI ( $x = 1$ ) is smaller than those of AgI ( $x = 0$ );  $a_0(\text{CuI}) < a_0(\text{AgI})$ . As the anion atom is the same in both compounds, this result can be easily explained by considering the atomic radii of Cu and Ag:  $R(\text{Cu}) = 1.35 \text{ \AA}$ ,  $R(\text{Ag}) = 1.60 \text{ \AA}$ , *i.e.*, the lattice constant increases with increasing atomic size of the cation element. The bulk modulus value for CuI is larger than those of AgI;  $B(\text{CuI}) > B(\text{AgI})$ ; *i.e.*, in inverse sequence to  $a_0$ —in agreement with the well-known relationship between  $B$  and the lattice constants:  $B \propto V_0^{-1}$ , where  $V_0$  is the unit cell volume. Furthermore, the values of the calculated bulk modulus using both approximations decreases from CuI to AgI, suggesting that the compressibility increases from CuI to AgI.

Usually, in the treatment of alloys when the experimental data are scarce, it is assumed that the atoms are located at the ideal lattice sites and the lattice constant varies linearly with composition  $x$  according to the so-called Vegard's law [19].

$$a(A_xB_{1-x}C) = x a_{AC} + (1-x) a_{BC} \quad (1)$$

where  $a_{AC}$  and  $a_{BC}$  are the equilibrium lattice constants of the binary compounds AC and BC respectively,  $a(A_xB_{1-x}C)$  is the alloy lattice constant. However, vio-

lation of Vegard's law has been observed in semiconductor alloys both experimentally [20] and theoretically [21].

Hence, the lattice constant can be written as:

$$a(A_xB_{1-x}C) = x a_{AC} + (1-x) a_{BC} - x(1-x)b \quad (2)$$

where the quadratic term  $b$  is the bowing parameter.

**Figures 1 and 2**, show the variation of the calculated equilibrium lattice constants and the bulk modulus versus concentration  $x$  for  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  alloy. The obtained results for the composition dependence of the calculated equilibrium lattice parameter show an excellent agreement to Vegard's law [19]. In going from AgI to CuI; when the Cu-content increases, the values of the lattice parameters of the  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  alloy decrease. This is due to the fact that the size of the Cu atom is smaller than those of Ag atom. Oppositely, one can see from **Figure 2** that the value of the bulk modulus increases with increasing Cu concentration. The values of the bowing parameters are determined by a polynomial fit. Using the LDA approximation, we obtained upward and downward bowing parameters equal to  $-0.11543 \text{ \AA}$  and  $0.01143 \text{ GPa}$  for the lattice and the bulk modulus, respectively. The GGA approximation gave values of  $-0.11543 \text{ \AA}$  and  $13.95429 \text{ GPa}$  for the bowing lattice parameter and the bulk modulus, respectively. In view of **Table 2**, it is clear that both approximations follow the tendency demonstrated by both experimental measurement and theoretical calculations. To the best of our knowledge, there are no experimental work exploring the structural properties (e.g.; the bulk modulus  $B$  and its pressure derivatives  $B'$ ) and the bowing parameters of the investigated alloys, but our results are relatively close to those of Ref. [22] obtained by using the full potential-linear augmented plane wave (FP-LAPW) method.

### 3.2. Electronic Properties

The energy band gaps of the binary compounds as well

**Table 2.** Calculated lattice parameter  $a$  and bulk modulus  $B$  compared to experimental and other theoretical values of CuI and AgI and their alloys.

$x$	Lattice constant $a$ ( $\text{\AA}$ )				Bulk modulus $B$ (GPa)			
	this work.		expt.	other calc.	this work.		expt.	other calc.
	LDA	GGA			LDA	GGA		
0	6.476	6.779	6.499 <sup>a</sup>	6.650 <sup>c</sup> , 6.61 <sup>d</sup> , 6.872 <sup>e</sup>	34.26	23.82	24 <sup>j</sup>	26.667 <sup>c</sup> , 40 <sup>l</sup>
0.25	6.37	6.646		6.516 <sup>c</sup> , 6.39 <sup>f</sup> , 6.38 <sup>g</sup>	37.93	24.7		27.405 <sup>c</sup> , 20.3 <sup>f</sup> , 26.0 <sup>g</sup>
0.5	6.234	6.505		6.396 <sup>c</sup> , 6.31 <sup>f</sup> , 6.30 <sup>g</sup>	42.2	26.61		30.104 <sup>c</sup> , 23 <sup>f</sup> , 27 <sup>g</sup>
0.75	6.101	6.352		6.256 <sup>c</sup> , 6.19 <sup>f</sup> , 6.18 <sup>g</sup>	45.58	29.55		37.765 <sup>c</sup> , 27 <sup>f</sup> , 28 <sup>g</sup>
1	5.943	6.175	6.054 <sup>b</sup>	6.098 <sup>c</sup> , 6.097 <sup>h</sup> , 6.082 <sup>i</sup>	49.7	36.02	36.6 <sup>b</sup> , 31 <sup>k</sup>	38.872 <sup>c</sup> , 39.447 <sup>h</sup> , 39.7 <sup>i</sup> , 35.2 <sup>m</sup>

<sup>a</sup>Ref. [29]; <sup>b</sup>Ref. [30]; <sup>c</sup>Ref. [22]; <sup>d</sup>Ref. [31]; <sup>e</sup>Ref. [32]; <sup>f</sup>Ref. [7]; <sup>g</sup>Ref. [33]; <sup>h</sup>Ref. [34]; <sup>i</sup>Ref. [35]; <sup>j</sup>Ref. [36]; <sup>k</sup>Ref. [37]; <sup>l</sup>Ref. [38]; <sup>m</sup>Ref. [39].

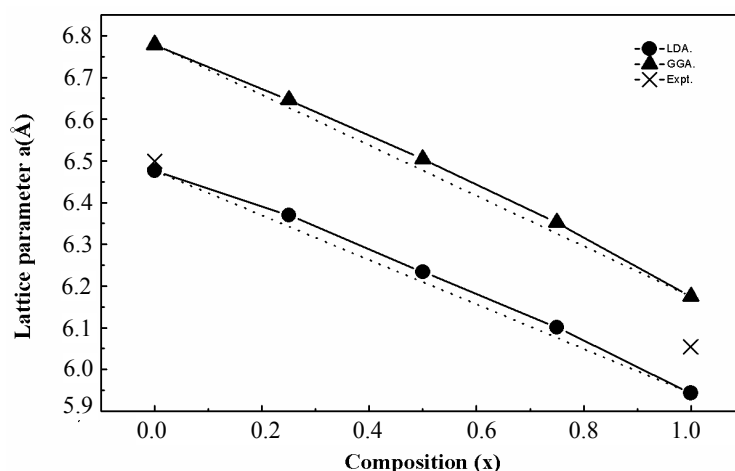


Figure 1. Composition dependence of the calculated lattice constants within LDA (Solid Circle) and GGA (Solid Triangle) of  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  alloy compared with Vegard's prediction (dotted line).

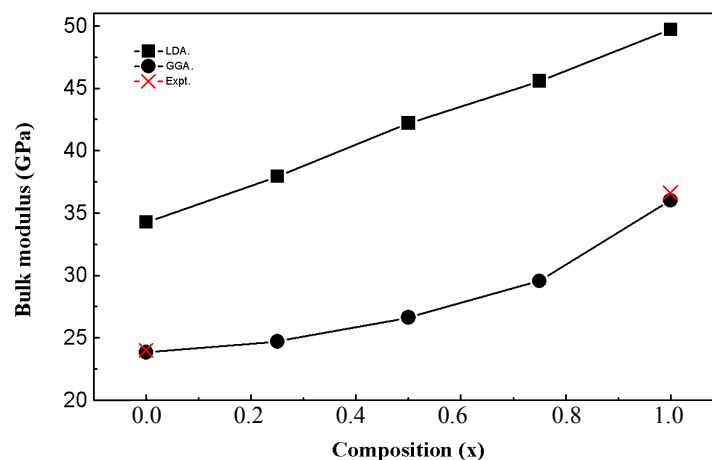


Figure 2. Composition dependence of the calculated bulk modulus within GGA (Solid Circle) and LDA (Solid Square) of  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  alloy.

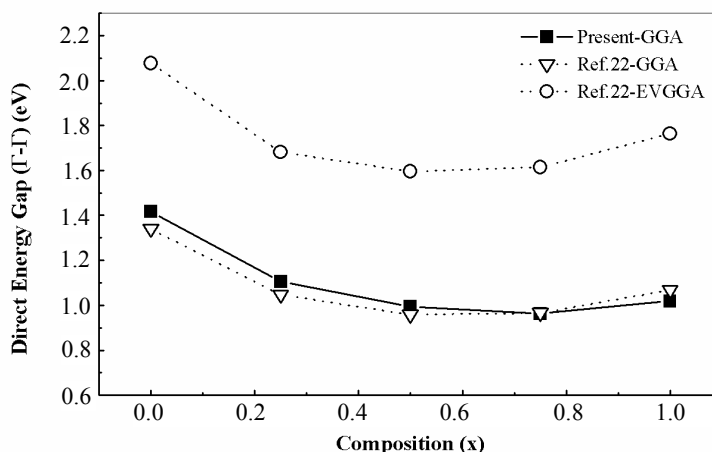
as for their investigated alloy were calculated within the LDA and GGA schemes. In **Table 3** we show the obtained results for the energy band gap of the  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  alloy from our ab initio calculations for different values of the concentration  $x$ . These values correspond to 25, 50, 75 and 100 % CuI and AgI substitution, respectively. The exact value of the band-gap is obviously a crucial point to be addressed because it enters in the applications in technological devices. However, it can be seen from **Table 3** that there is a large discrepancy between the reported experimental and theoretical values. This discrepancy is mainly due to the fact that both the simple form of LDA or GGA do not take into account the quasiparticle self energy correctly [23] which make them not sufficiently flexible to accurately reproduce both exchange and correlation energy and its charge derivative. We worth also mention that in general, it is far to

say that the experimental data are well reproduced by the calculation. On reason for this difference is that in our calculations we have assumed the crystal to be at  $T = 0$  K and thus do not include contributions from lattice vibrations that are present at room temperature measurements. It is important to note that the density functional formalism is limited in its validity (see. Ref [24]) and the band structure derived from it cannot be used directly for comparison with experiment. The variation of the concentration ( $x$ ) versus the value of the direct band gap energy ( $E_g$ ) is with both LDA and GGA approximation is shown in **Figure 3**. It is clearly seen that the direct energy gap show a non linear variation with copper concentration. The obtained energy versus concentration curve is well fitted by the following quadratic phenomenological function.

**Table 3. Calculated direct energy band gap energy ( $\Gamma$ - $\Gamma$ ) of  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  alloys at different Cu concentrations (all values are in eV).**

$x$	$E_g$ (eV)			
	this work.		expt	other calc.
	LDA	GGA		
0	1.171	1.416		1.340 <sup>c</sup> , 2.077 <sup>c</sup> , 1.4 <sup>b</sup> , 0.8 <sup>d</sup>
0.25	1.012	1.106		1.04632 <sup>c</sup> , 1.68286 <sup>c</sup>
0.5	0.979	0.993		0.958 <sup>c</sup> , 1.59617 <sup>c</sup>
0.75	1.020	0.962		0.965 <sup>c</sup> , 1.61436 <sup>c</sup>
1	1.183	1.018	2.95 <sup>a</sup>	1.068 <sup>c</sup> , 1.764 <sup>c</sup> , 1.077 <sup>c</sup> , 1.118 <sup>f</sup> , 3.10 <sup>g</sup>

<sup>a</sup>Ref. [16]; <sup>b</sup>Ref. [40]; <sup>c</sup>Ref. [22]; <sup>d</sup>Ref. [41]; <sup>e</sup>Ref. [34]; <sup>f</sup>Ref. [35]; <sup>g</sup>Ref. [42].

**Figure 3. Calculated direct energy band gap ( $\Gamma$ - $\Gamma$ ) of  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  alloys as a function of Cu concentration using GGA approximation (solid square-solid line) compared with Ref. 22, using GGA (Open Triangle-dotted line) and EVGGA (Open Circle-dotted line).**

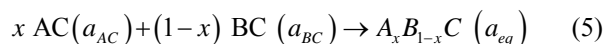
$$E_g(x) = xE_{AC} + (1-x)E_{BC} - bx(1-x) \quad (3)$$

where  $E_{AC}$  and  $E_{BC}$  corresponds to the gap of the CuI and AgI for the  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  alloy.

The obtained results are shown in **Figure 3** and are summarized as follows:

$$\text{Cu}_x\text{Ag}_{1-x}\text{I} \rightarrow \begin{cases} E_{\Gamma-\Gamma} = 1.67 - 0.81x + 0.82x^2 & (LDA) \\ E_{\Gamma-\Gamma} = 1.40 - 1.31x - 0.93x^2 & (GGA) \end{cases} \quad (4)$$

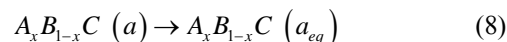
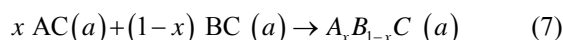
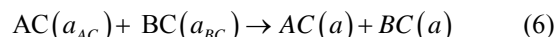
In order to better understand the physical origins of bowing parameters in  $\text{A}_x\text{B}_{1-x}\text{C}$  alloys, we follow the procedure of Bernard and Zunger [25], and decompose the total bowing parameter  $b$  into physically distinct contributions. The overall bowing coefficient at a given average composition  $x$  measures the change in the band gap according to the formal reaction



where  $a_{AC}$  and  $a_{BC}$  are the equilibrium lattice constants of the binary compounds and  $a_{eq}$  is the equilibrium

lattice constant of the alloy with the average composition  $x$ .

The Equation (5) is decomposed into three steps:



The first step measures the volume deformation (VD) effect on the bowing. The corresponding contributions  $b_{VD}$  to the bowing parameter represents the relative response of the band structure of the binary compounds AC and BC to hydrostatic pressure, which here arises from the change of their individual equilibrium lattice constants to the alloy value  $a = a(x)$ . The second contribution, the charge exchange (CE) contribution  $b_{CE}$ , reflects the charge transfer effect which is due to the different (averaged) bonding behavior at the lattice constant  $a$ . The final step measure changes due to the structural relaxation (SR) in passing from the unrelaxed to the relaxed alloy by  $b_{SR}$ . Consequently, the total bowing parameter is de-

defined as

$$b = b_{\text{VD}} + b_{\text{CE}} + b_{\text{SR}}. \quad (9)$$

The general representation of the composition-dependent band gap of the alloys in terms of binary compounds gaps of the,  $E_{\text{AC}}(a_{\text{AC}})$  and  $E_{\text{BC}}(a_{\text{BC}})$ , and the total band gap bowing parameter  $b$  is defined as:

$$E_g(x) = xE_{\text{AC}}(a_{\text{AC}}) + (1-x)E_{\text{BC}}(a_{\text{BC}}) - bx(1-x) \quad (10)$$

This allows a division of the total gap bowing  $b$  into three contributions according the following expressions:

$$b_{\text{VD}} = \frac{E_{\text{AC}}(a_{\text{AC}}) - E_{\text{AC}}(a)}{1-x} + \frac{E_{\text{BC}}(a_{\text{BC}}) - E_{\text{BC}}(a)}{x} \quad (11)$$

$$b_{\text{CE}} = \frac{E_{\text{AC}}(a)}{1-x} + \frac{E_{\text{BC}}(a)}{x} - \frac{E_{\text{ABC}}(a)}{x(1-x)} \quad (12)$$

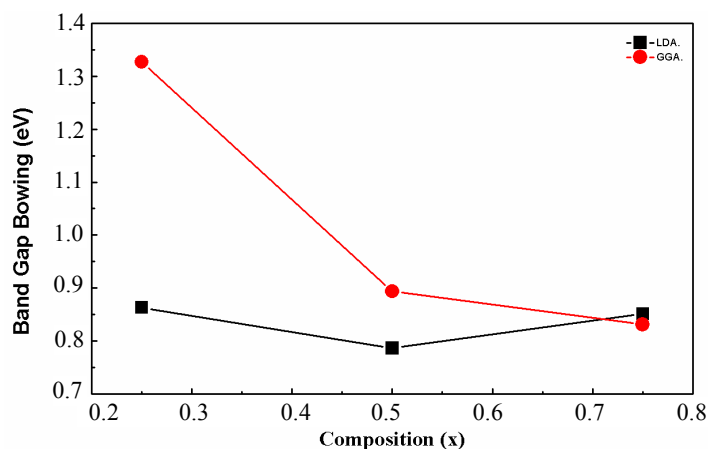
$$b_{\text{SR}} = \frac{E_{\text{ABC}}(a) - E_{\text{ABC}}(a_{\text{eq}})}{x(1-x)} \quad (13)$$

All these energy gaps occurring in expressions (11)-(13) have been calculated for the indicated atomic structures and lattice constants. **Table 4** shows our results for the optical band gap bowing  $b$ , as calculated for three different molar fractions ( $x = 0.25, 0.5$  and  $0.75$ ). The calculated GGA-band gap bowing parameter exhibits strong composition dependence. This is different from LDA calculations, which show a weakly composition dependent bowing parameter. Indeed, **Figure 4**, shows the variation of the band gap bowing versus concentration. The bowing remains linear and varies slowly in going from  $x = 0.0$  to  $x = 1.0$ . The calculated gap bowing coefficient for random  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  alloy ranges from

**Table 4.** Decomposition of optical bowing into volume deformation (VD), charge exchange (CE) and structural relaxation (SR) contributions (all values in eV).

		this work.		other calc.	
		LDA	GGA		
$x$					
0.25	$b_{\text{VD}}$	0.5896	0.5435		
	$b_{\text{CE}}$	0.7138	0.7338		
	$b_{\text{SR}}$	-0.439	0.0498		
	$b$	0.8629	1.3273		
0.5	$b_{\text{VD}}$	0.5964	0.5963	0.55252 <sup>a</sup>	0.5719 <sup>a</sup>
	$b_{\text{CE}}$	0.1270	0.2490	0.9184 <sup>a</sup>	1.21098 <sup>a</sup>
	$b_{\text{SR}}$	0.0629	0.0585	0.06772 <sup>a</sup>	0.08624 <sup>a</sup>
	$b$	0.7863	0.8939	1.53864 <sup>a</sup>	1.86912 <sup>a</sup>
0.75	$b_{\text{VD}}$	0.6408	0.6029		
	$b_{\text{CE}}$	0.0789	0.1033		
	$b_{\text{SR}}$	0.1315	0.1250		
	$b$	0.8512	0.8313		

<sup>a</sup>Ref. [22]



**Figure 4.** Calculated band gap bowing parameter as a function of Cu concentration with LDA (Solid Square) and GGA (Solid Circle).

0.8629 eV ( $x = 0.25$ ) to 0.8512 ( $x = 0.75$ ). Our result for  $x = 0.5$  is in excellent agreement with those obtained by using EVGGA-FPLAPW method [22]. We can also note that the volume-deformation term  $b_{VD}$  of  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  is large. The importance of  $b_{VD}$  can be correlated with the mismatch of the lattice constants of the corresponding binary compounds. As consequence, the main contribution to the gap bowing is raised from the volume deformation effect. The only exception is for  $x = 0.25$  in which the charge transfer contribution  $b_{CE}$  has been found greater than  $b_{VD}$ . This contribution is due to the different electronegativities of the Ag and Cu or I atoms. Indeed,  $b_{CE}$  scales with the electronegativity mismatch. The contribution of structural relaxation is negligible; the band gap bowing is due essentially to the charge exchange effect. We conclude that our calculations show that both structural (volume deformation) and chemical effects appear to control the optical gap bowing of  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  alloy.

### 3.3. Calculated Effective Masses

Knowledge of the electron and hole effective mass values is indispensable for the understanding of transport phenomena, exciton effects and electro-hole in semiconductors. Excitonic properties are of great interest for binary CuI, AgI and their alloys, therefore, it is worthwhile to estimate the electron and hole effective mass values for these materials. Experimentally, the effective masses are usually determined by cyclotron resonance, electro reflectance measurements or from analysis of transport data or transport measurements [43]. Theoretically, the effective masses can be estimated from the energy band curvatures. Generally, the effective mass is a tensor with nine components, however for the much idealized simple case, where the  $E$ - $k$  diagram can be fitted by a parabola  $E = \hbar^2 k^2 / 2m^*$ , the effective mass becomes a scalar at high symmetry point in Brillouin zone. We have computed the electron effective mass at the conduction band minima (CBM) and the hole effective mass at the valence

band maxima (VBM) for CuI, AgI and their ternary alloys. The electron and the hole effective masses are obtained from the curvature of the energy band near the  $\Gamma$ -point at the conduction band minimum (CBM) and valence band maximum (VBM), respectively. The calculated electron and hole effective masses values for the parent binary compounds CuI and AgI and their alloy are given in **Table 5**. Results from earlier theoretical works are also quoted for comparison. The calculated electron effective masses are in good agreement with those obtained by using the full potential linear augmented plane wave (FP-LAPW) method whin EVGGA approximation [22] which is known to improve the values of the band gaps rather than LDA and GGA [26-28]. This agreement disappears in the case of hole effective masses. This disagreement could be expected because the computation of the effective mass is very sensitive to the topology of band structure. The highest curvature of the electronic band yields the smallest effective mass of the charge carriers and the highest conductivity. Therefore, the effective masses that depend strongly on the form of energy band match the expected accuracy. From **Table 5** data, we can outline that holes are much heavier than electrons, for all concentrations in  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  alloy, so carrier transport in this alloy should be dominated by electrons. We notice that no experimental data are available for effective masses of this alloy; all results are obtained via theoretical methods. Future experimental work will testify all calculated results.

### 4. Conclusions

In summary, by means of the (FP-LMTO) method, we have calculated the structural and the electronic properties of zinc-blende CuI, AgI, and their related  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  alloy. We have found that except the lattice parameter, the variation of structural parameters versus copper concentration not obeys Vegard's law. Our results of the electronic band structure show a non linear variation of the fundamental band gaps versus copper concentration.

**Table 5.** The electron and hole effective masses for  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$  ternary alloy as function of Cu concentrations using LDA and GGA. All values are in units of a free-electron mass  $m_0$ .

$x$	$m_e^*$				$m_{hh}^*$				$m_{lh}^*$	
	this work.		other calc.		this work.		other calc.		this work.	other calc.
	LDA	GGA			LDA	GGA			LDA	GGA
0	0.271	0.270	0.226 <sup>a</sup>	0.272 <sup>a</sup>	0.949	0.960			1.818	1.804
0.25	0.226	0.329	0.197 <sup>a</sup>	0.261 <sup>a</sup>	0.500	0.634			0.524	0.642
0.50	0.3006	0.306	0.191 <sup>a</sup>	0.256 <sup>a</sup>	0.439	0.577			0.466	0.591
0.75	0.238	0.285	0.188 <sup>a</sup>	0.251 <sup>a</sup>	0.453	0.5339			0.465	0.541
1	0.229	0.220	0.186 <sup>a</sup>	0.249 <sup>a</sup>	0.573	0.601			0.804	0.768

<sup>a</sup>Ref. [22].

We have characterized the deviation from the linear behavior by calculating the optical bowing parameter. The effective masses of the systems studied in this work were calculated and are found comparable to those obtained by FPLAPW method.

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