

Electronic structure and characteristics of chemical bonds in CuInSe₂, CuGaSe₂ and CuAlSe₂

Tsuyoshi Maeda and Takahiro Wada

Department of Materials Chemistry, Ryukoku University
1-5, Yokotani, Oe-cho, Seta, Otsu, Shiga, 520-2194, Japan
Phone: +81-77-543-7468 E-mail: tmaeda@ad.ryukoku.ac.jp

1. Introduction

Chalcopyrite-type CuInSe₂ (CIS) has a band gap energy (E_g) of 1.04 eV, which is slightly smaller than the ideal value of 1.4 eV as an absorber of solar light. Therefore, such solid solutions as Cu(In,Ga)Se₂ (CIGS) [1], Cu(In,Al)Se₂ (CIAS) [2], and Cu(In,Ga)(Se,S)₂ (CIGSS) [3] were studied for a solar cell absorber. The band gap energy of CIGS in high-performance CIGS solar cells is around 1.1 to 1.2 eV [4]. For a cell with a CIGS absorber with a wider band gap energy of around 1.4 to 1.5 eV, higher efficiency is expected. To obtain higher cell performance, the accurate electronic structures of such chalcopyrite compounds must be clarified. Basic sciences group in National Renewable Energy Laboratory (NREL) has studied the electronic structure of CIS and the related compounds since the 1980's [5]. Recently, we also determined the valence band maximum (VBM) and the conduction band minimum (CBM) of ABX_2 ($A = \text{Cu, Ag}$; $B = \text{In, Ga, Al}$; $X = \text{Se, S}$) by density functional calculations using a generalized gradient approximation (GGA) functional [6]. The VBM of chalcopyrite-type ABX_2 is the antibonding state of (A nd $+X$ n' p), while CBM is the antibonding state of (B n'' + X n' p). However, the previous density functional calculation using a GGA functional underestimated their theoretical band gaps in comparison with their experimental values because the exchange-correlation energy was not exactly calculated.

Recently, the screen-exchange LDA method (sX-LDA) was proposed, and is one of the theories designed to find a better energy functional beyond LDA by modeling the exchange-correlation hole within nonlocal density schemes [7, 8]. Encouraging results were demonstrated for band gaps and structural properties by sX-LDA using the plane-wave pseudopotential method for several semiconductor materials.

In the present study, electronic structural calculations of chalcopyrite-type CuInSe₂ and such related compounds as CuGaSe₂ and CuAlSe₂ were performed with the sX-LDA method to accurately estimate their band gaps.

2. Computational Procedures

We performed first-principles calculations within a density functional theory using a plane-wave pseudopotential method. First, we optimized lattice parameters a and c , and the u -parameter of the Se atom, $u(\text{Se})$, through the minimization of total energy. Structural optimizations and electronic structure calculations were performed using the

primitive cells of the chalcopyrite-type unit cell. The relaxation procedures were truncated when all the residual forces for the relaxed atoms were less than 0.01 eV/Å.

To obtain accurate electronic structure, the band structure, the density of the states, and the band gaps of chalcopyrite-type CuInSe₂, CuGaSe₂, and CuAlSe₂ were calculated with the sX-LDA method. We performed the calculations with the sX-LDA function to obtain more accurate band gaps after performing geometry optimization with the primitive cells using the LDA of the CAPZ (Ceperley Alder, Perdew Zunger) function with cutoff energy of 650 eV.

3. Results and discussion

3.1 Lattice parameters and bond lengths

Table I shows the theoretically determined lattice parameters a , c , c/a , and $u(\text{Se})$ calculated using an LDA functional for comparison with their experimental lattice parameters. The parameter, $u(\text{Se})$, is the x-coordinate of element Se in the chalcopyrite-type unit cell. The calculated lattice parameters of CuInSe₂ had satisfactory agreement with their experimental values (for example, the theoretical lattice parameters a , c and $u(\text{Se})$ for CuInSe₂ were 5.696 Å, 11.455 Å, and 0.212, corresponding to their experimental values of 5.782 Å, 11.620 Å, and 0.235). The calculated c/a ratio of CIS is 2.00, which means theoretical lattice constant c is two times longer than a . Both c/a and $u(\text{Se})$, successfully reproduce their experimental result. The values for CuGaSe₂ and CuAlSe₂ also correspond to their experimental values within an error of $\pm 2\%$. The theoretical lattice parameter of CuInSe₂ ($a=5.696$ Å, $c=11.455$ Å) is longer than those of CuGaSe₂ ($a=5.494$ Å, $c=10.939$ Å) and CuAlSe₂ ($a=5.473$ Å, $c=10.901$ Å). The calculated lattice parameters of these chalcopyrite compounds are successfully reproduced, even though the calculation with the LDA function does not consider the electron's exchange effects on the total energy.

Table I Theoretical and experimental lattice parameters and bond lengths of CuBSe₂, ($B=\text{In, Ga, Al}$)

		a (Å)	c (Å)	$u(\text{Se})$	Cu-Se (Å)	M-Se (Å)
CuInSe ₂	Theor.	5.696	11.455	0.212	2.354	2.601
	Exp.	5.782	11.620	0.235	2.459	2.559
CuGaSe ₂	Theor.	5.494	10.939	0.241	2.343	2.408
	Exp.	5.614	11.022	0.250	2.416	2.416
CuAlSe ₂	Theor.	5.473	10.900	0.246	2.352	2.380
	Exp.	5.606	10.901	0.267	2.462	2.351

3.2 Electronic structures

Figure 1 shows the partial density of states (PDOS) of CuInSe₂(a), CuGaSe₂(b), and CuAlSe₂(c) calculated by screen-exchange LDA (sX-LDA) method. The valence band maximum of CuInSe₂ is set to 0 eV. The theoretical band gaps of CuInSe₂, CuGaSe₂, and CuAlSe₂ obtained from conventional calculation using GGA and LDA functionals were 0.04, 0.14, and 1.11 eV, respectively, which were also considerably underestimated in comparison with their experimental values of 1.04, 1.68, and 2.67 eV. The conventional exchange-correlation function underestimates their band gaps by about 1.0-1.5 eV in comparison with their experimental band gaps. Therefore, reproducing the experimental band gaps is difficult, and we cannot discuss the absolute values of the band gaps calculated with conventional density functional theory using GGA-PBE or LDA-CAPZ functions, which do not include the exact calculations of the exchange-correlation energy. The sX-LDA calculation successfully reproduced the band gaps of CuInSe₂ and related compounds (CuInSe₂: 0.96 eV, CuGaSe₂: 1.36 eV, CuAlSe₂: 2.22 eV).

In the present sX-LDA calculation, the valence band maximum of CuInSe₂ mainly consists of an occupied antibonding of Cu 3d and Se 4p, while the conduction band minimum consists of an unoccupied antibonding of In 5s and Se 4p as well as previous calculations with GGA functionals. Recently, we reported the schematic molecular orbital diagram of tetrahedral CuSe₄⁷⁻ and tetrahedral InSe₄⁵⁻ clusters [9]. For CIS, the bottom of the valence band (at -16 ~ -14 eV) consists of In 4d (*e*, *t*₂) and Se 4s (*a*₁) orbitals and the peak at -6 eV consists of In 5s and Se 4p (*a*₁) orbitals. The peaks at -5 ~ -3 eV consist of bonding (*a*₁, *e*, *t*₂) and nonbonding (*t*₁) orbitals of Cu 3d and Se 4p. The upper valence band (at -2 ~ -0 eV) consists of the antibonding orbitals of Cu 3d and Se 4p (*e*^{*}, *t*₂^{*}). The bottom of the conduction band (at 1~ 2 eV) consists of the antibonding of In 5s and Se 4p (*a*₁^{*}). The Cu-Se bond has a nonbonding character because electrons occupy both bonding and antibonding orbitals of Cu 4d and Se 4p. On the other hand, the In-Se bond has an ionic character because most of the In 5s and 5p (*a*₁^{*}, *t*₂^{*}) orbitals are unoccupied.

The VBM of CuBSe₂ (*B*= In, Ga, Al) is also an antibonding of Cu 3d and Se 4p (*t*₂^{*}), while CBM is an antibonding *B* ns and Se 4p (*a*₁^{*}). Thus, the VBM of chalcopyrite-type CuBSe₂ (*B*= In, Ga, Al) consists of Cu 3d and Se 4p, while CBM consists of *B* ns and Se 4p in both the previous GGA and the present sX-LDA calculations. The energy level of the VBM of CuGaSe₂ was a little higher than CuInSe₂ because the bond length of Cu-Se in CGS (2.343Å) is shorter than that in CIS (2.354Å). On the other hand, the energy level of the VBM of CuAlSe₂ was lower than CuGaSe₂ because the bond length of Cu-Se in CAS (2.352Å) is longer than that in CGS (2.343Å). On the other hand, the CBMs of CuGaSe₂ and CuAlSe₂ are greatly higher than that of CuInSe₂. The antibonding *B* ns and Se 4p in the conduction bands is shifted to higher energy with increasing band gaps of CuBSe₂.

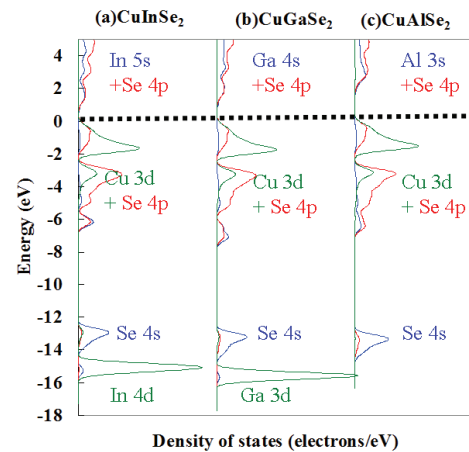


Fig. 1. Partial density of states (PDOS) of CuInSe₂, CuGaSe₂ and CuAlSe₂ calculated by screen-exchange LDA method.

4. Conclusions

The sX-LDA calculation successfully reproduced the band gaps of CuInSe₂ and related compounds (CuInSe₂: 0.96 eV, CuGaSe₂: 1.36 eV, CuAlSe₂: 2.22 eV). The energy levels of the CBMs of CuGaSe₂ and CuAlSe₂ were greatly higher than that of CuInSe₂. The antibonding *B* ns and Se 4p in the conduction bands shifted to higher energy with increasing band gaps of CuBSe₂.

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