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Why is Heavily-defected $CuInSe_2$ a Good Opto-electronic Material: Defect Physics in $CuInSe_2$

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Abstract. Our study of the defect physics in $CuInSe_2$ showed that (i) it is much easier to form Cu vacancy than to form cation vacancy in II-VIs. (ii) defect formation energies vary considerably both with the Fermi energy and the chemical potential of the atomic species, and (iii) defect pairs such as $(2V_{Cu} + In_{Cu})$ have low formation energies in Cu-poor samples. These explain that (a) the existence of the ordered defect compounds in $CuInSe_2$ is due to the formation of ordered array of $(2V_{Cu}^{-} + In_{Cu}^{2+})$, (b) the efficient p-type self-doping is due to the exceptionally low formation energy of Cu vacancies and its very shallow energy levels, and (c) the electrically benign character for samples with large defect population is due to an electronic passivation of the deep levels, such as In_{Cu}^{2+}, by its attraction to easily-formed V_{Cu}^{-}. Our calculated defect transition energy levels are in good agreement with the available experimental data.

1. Introduction

$CuInSe_2$ is a prototype member of the family of I-III-VI_2 chalcopyrite semiconductors [1]. Unlike the analogous II-VI binary compounds, $CuInSe_2$ shows three unusual defect-related features: (a) It tolerates thermodynamically a large range of off-stoichiometry. The extreme limit of "off-stoichiometry" manifested in this system is the existence of a series of compounds [2] with integer stoichiometries ($CuIn_5Se_8$, $CuIn_3Se_5$, etc.). (b) It can be doped efficiently to a low-resistivity p or n type merely via introduction of *native* off-stoichiometric defects, without extrinsic impurities [3]. And (c) polycrystalline $CuInSe_2$ is as good an electronic material as its single-crystal counterpart [4], even though it has many non-stoichiometry defects. These unique features makes $CuInSe_2$ a key semiconductor material for thin film solar cell application, having achieved 17% efficiency even in polycrystalline form [5,6].

There were many attempts in the past [7-11] to understand these unusual phenomena. Yet, despite extensive and successful efforts at characterization of the defect *levels* in $CuInSe_2$, very little evidence exists as to the chemical and structural *identification* of the defect *centers* producing those levels. One of the main reasons for the failure to reliably identify these defect centers in $CuInSe_2$ is due to the lack of accurate theoretical energy level predictions. Most of previous studies used the generalization of cavity model of Van Vechten [12]. Although these studies [7-10] provide some insights into the the understanding of defect physics in $CuInSe_2$, they neglected the dependence of the defect formation energies on the chemical potentials and Fermi levels, and considered only point defects. As a result, these models have serious shortcomings. In this work we will use the first-principles self-consistent electronic structure theory to calculate the formation energies and electrical transition levels of point defects *and* defect pairs and arrays in $CuInSe_2$ [13]. Our results will be used to explain the three puzzles discussed above.

2. Method of Calculation

The formation energy $\Delta H_f(\alpha, q)$ of defect α in charge state q depends on the Fern energy ϵ_F^a (where a denotes absolute values) as well as on the atomic chemical potentia μ^a [14]. In $CuInSe_2$,

$$\Delta H_f(\alpha, q) = E(\alpha, q) - E(\mathrm{CuInSe_2}) + n_{Cu}\mu^a_{Cu} + n_{In}\mu^a_{In} + n_{Se}\mu^a_{Se} + q\epsilon^a_F, \quad (1$$

where $E(\alpha, q)$ is the total energy of a supercell containing a defect of type α and charg q, $E(\mathrm{CuInSe_2})$ is the total energy for the same supercell in the absence of the defec the n's are the numbers of Cu, In, Se atoms and q is the the number of electron transferred from the supercell to the reservoir in forming the defect cell. We will nc consider Se-related defects in this study so we take $n_{Se} = 0$. Denoting

$$\Delta E(\alpha, q) = E(\alpha, q) - E(\mathrm{CuInSe_2}) + n_{Cu}\ \mu^{solid}_{Cu} + n_{In}\ \mu^{solid}_{In} + q\ E_V, \quad (2$$

Eq. (1) can be rewritten as

$$\Delta H_f(\alpha, q) = \Delta E(\alpha, q) + n_{Cu}\ \mu_{Cu} + n_{In}\ \mu_{In} + q\ \epsilon_F, \quad (3$$

where $\epsilon_F = \epsilon^a_F - E_V$, $\mu_{Cu} = \mu^a_{Cu} - \mu^{solid}_{Cu}$ and $\mu_{In} = \mu^a_{In} - \mu^{solid}_{In}$.

There are some thermodynamic limits to (μ, ϵ_F): ϵ_F is bound between the valenc band maximum E_V and the conduction band minimum E_C, and $\{\mu_{Cu}, \mu_{In}\}$ are boun by (i) the values that will cause precipitation of solid elemental Cu, In, and Se, so

$$\mu_{Cu} \leq 0\ ; \quad \mu_{In} \leq 0\ ; \quad \mu_{Se} \leq 0\ , \quad (4$$

(ii) by the values that maintain a stable $CuInSe_2$ compound, so

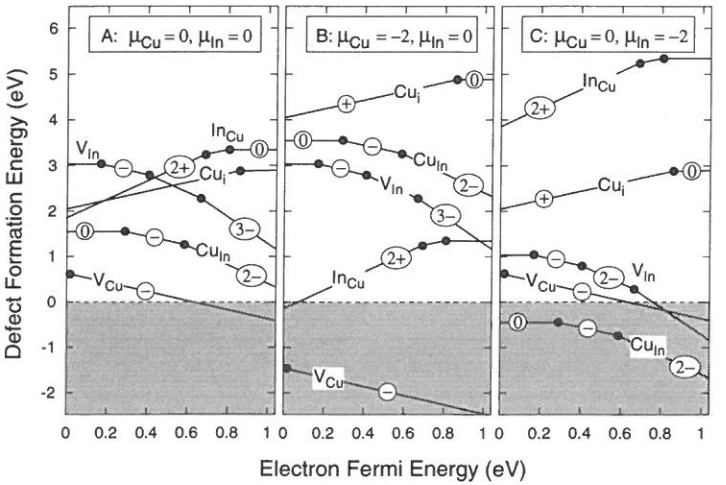

Figure 1. Formation energies of $V_{Cu}, V_{In}, In_{Cu}, Cu_{In}$ and Cu_i, as a function of the electron Fermi energy, ϵ_F at chemical potentials A, B and C (defined in the figure). Charge state q determines the slopes of each line segment. The shaded area highlights negative formation energies. Solid dots denote transition energies.

$$\mu_{Cu} + \mu_{In} + 2\mu_{Se} = \Delta H_f(\mathrm{CuInSe_2}), \tag{5}$$

where $\Delta H_f(\mathrm{CuInSe_2}) = -2.0$ eV is the calculated formation energy of solid $\mathrm{CuInSe_2}$ from the elemental solids, and (iii) by the values that will cause formation of binaries (e.g., $\mathrm{In_2Se_3}$ and $\mathrm{Cu_2Se}$).

The defect transition energy level $\epsilon_\alpha(q/q')$ can be obtained from Eq. (3). It is the Fermi energy in Eq. (3) at which the formation energy $\Delta H_f(\alpha, q)$ of defect α of charge q is equal to that of defect α of another charge q', i.e.,

$$\epsilon_\alpha(q/q') = [\Delta E(\alpha, q) - \Delta E(\alpha, q')]/(q' - q). \tag{6}$$

We calculated $\Delta H_f(\alpha, q)$ for point defect $\alpha = V_{Cu}, V_{In}, In_{Cu}, Cu_{In}, Cu_i$ and selected defect pairs. We place defect α at the center of a 32-atom tetragonal supercell with lattice vectors $(1,1,0)a$, $(-1,1,0)a$, and $(0,0,2\eta)a$, where $a = 5.768$ Å and $\eta = c/a = 1.008$ are the calculated lattice constants for $\mathrm{CuInSe_2}$. The total energies and band structures are calculated using the local density functional formalism [15] as implemented by the general potential linearized augmented plane wave (LAPW) method [16]. The LDA error on the band gap is corrected by adding a constant potential to the conduction states so the band gap of $\mathrm{CuInSe_2}$ matches the experimental value of 1.04 eV. We estimated that the uncertainty in our calculation of defect formation energy is ± 0.2 eV per point defect. The uncertainty in point defect transition energy levels is estimated to be ± 0.05 eV, and approximately ± 0.1 eV for defect pairs. The uncertainty here comes mainly from the difficulty in determining the valence and conduction band edges in the defect-containing 32-atom supercell.

3. Defect Formation Energies

Table I lists the point defect formation energies $\Delta H_f(\alpha, q)$ in terms of $\Delta E(\alpha, q), n_{Cu}, n_{In}$ and q, as in Eq. (3). The Fermi energy dependence of the defect formation energy at three limiting atomic chemical potentials (A, B, and C) are plotted in Fig. 1. We see from Fig. 1 and Table I that: (i) The relative stability of various defects depends critically on the chemical potentials: $\Delta H_f(V_{Cu})$ can vary by as much as 2 eV from point A to B, and $\Delta H_f(Cu_{In})$ can vary by as much as 4 eV from point B to C. (ii) The formation energies also have a significant dependence on the Fermi energy. In general, acceptor states such as V_{Cu}^- form more easily in n-type material while donor states such as In_{Cu}^{2+} form more easily in p-type material. (iii) Some of the formation energies of single neutral defects in $\mathrm{CuInSe_2}$ are extraordinary low, e.g., $\Delta H_f(V_{Cu}^0) = -1.4$ eV (at B) and $\Delta H_f(Cu_{In}^0) = -0.5$ eV (at C). In particular, the formation energy of the neutral Cu vacancy in $\mathrm{CuInSe_2}$ is significantly lower than that of neutral cation vacancy in II-VIs [17]. This is because (i) the Cu-Se bond is less covalent than the II-VI bond so it is easier to break, and (ii) Cu is monovalent while cations in II-VI are divalent, so less electrostatic energy is needed to form a Cu vacancy.

Figure 1 further reveals the coexistence of several low energy *point* defects of opposite charges at the same ϵ_F and μ [e.g., $(2V_{Cu}^- + In_{Cu}^{2+})$]. Indeed, the formation energy of neutral defect pair can be lowered considerably through interaction. The interaction includes (a) charge compensation, (b) subsequent Coulomb attraction and (c) atomic relaxations. We have analyzed the defects interaction energy δH_{int} for $(2V_{Cu}^- + In_{Cu}^{2+})$ defect pair. We find that in this case $\delta H_{int} = -4.2$ eV of which (a) the transfer of two electrons from the high-energy In_{Cu} donor level to low-energy V_{Cu} acceptor level (i.e., charge compensation) releases ~ -1.4 eV (see Fig. 1), (b) a strong electrostatic attraction between the ensuing charged defects In_{Cu}^{2+} and $2V_{Cu}^-$ releases ~ -2.5 eV, and (c) atomic relaxations upon pairing releases -0.3 eV.

Table I. Defect formation energies $\Delta E(\alpha, q)$ in Eq. (3) and defect transition levels $\epsilon_\alpha(q/q')$ of Eq. (6). The n_{Cu} and n_{In} are the numbers of Cu and In atoms and q is the number of excess electrons, transferred from the defect-free crystal to the reservoirs to form one defect.

Defect α	$\Delta E(\alpha, q)$ (eV)	n_{Cu}	n_{In}	q
V_{Cu}^{0}	0.60	+1	0	0
V_{Cu}^{-}	0.63			-1
Defect transition level: (-/0) = E_V + 0.03 eV				
V_{In}^{0}	3.04			0
V_{In}^{-}	3.21	0	+1	-1
V_{In}^{2-}	3.62			-2
V_{In}^{3-}	4.29			-3
Defect transition levels: (-/0) = E_V + 0.17 eV; (2-/-) = E_V + 0.41 eV; (3-/2-) = E_V +0.67 eV				
Cu_{In}^{0}	1.54			0
Cu_{In}^{-}	1.83	-1	+1	-1
Cu_{In}^{2-}	2.41			-2
Defect transition levels: (-/0) = E_V + 0.29 eV; (2-/-) = E_V + 0.58 eV				
In_{Cu}^{2+}	1.85			+2
In_{Cu}^{+}	2.55	+1	-1	+1
In_{Cu}^{0}	3.34			0
Defect transition levels: (0/+) = E_C - 0.25 eV; (+/2+) = E_C - 0.34 eV				
Cu_{i}^{+}	2.04	-1	0	+1
Cu_{i}^{0}	2.88			0
Defect transition level: (0/+) = E_C - 0.20 eV				

Defect pairs whose components are charged may further lower their formation energy at low temperature through ordering. The ordered arrays of the $(2V_{Cu}^{-} + In_{Cu}^{2+})$ defect pairs can be written as

$$n(\mathrm{CuInSe_2}) + m(\mathrm{In}) \rightarrow \mathrm{Cu}_{(n-3m)}\mathrm{In}_{(n+m)}\mathrm{Se}_{2n} + 3m(\mathrm{Cu}) - \Delta H_f(n, m), \qquad (7)$$

where m = 1, 2, 3, $\cdots$ and n = 3, 4, 5, $\cdots$, and where (In) and (Cu) denote In and Cu in their respective equilibrium chemical reservoirs. We find that the pair-pair ordering energy $\delta H_{ord}(n, m) = \Delta H_f(n, m) - H_f(2V_{Cu}^{-} + In_{Cu}^{2+})$ for the defect array $(2V_{Cu}^{-} + In_{Cu}^{2+})$ depends weakly on n. For m=1, it has an average value of ~ -0.4 eV.

The analysis above shows that the sum of interaction and ordering energies $\delta H_{int} + \delta H_{ord}$ for the defect pair array $(2V_{Cu}^{-} + In_{Cu}^{2+})$ is about -4.6 eV, which cancels most of the (positive) formation energy of the isolated non-interacting pair: $2\Delta H_f(V_{Cu}^0) + \Delta H_f(In_{Cu}^0) = 4.5$ eV at point A in Fig. 1. The total formation energy of the defect array could be as low as -6.1 eV at point B. Thus, spontaneous formation of stable ordered defect compounds ($CuIn_5Se_8$, $CuIn_3Se_5$, etc.) is predicted in this system.

4. Defect Transition Energy Levels

The solid dots in Fig. 1 denote points where the slope of $\Delta H_f(\alpha, q)$ vs q changes. The corresponding value of ϵ_F is the defect transition energy $\epsilon_\alpha(q/q')$ defined in Eq. (6) and is listed in Table I. We see from Fig. 1 and Table I that the Cu vacancy has a shallow acceptor level $E(0/-) = E_V + 0.03$ eV, the In vacancy has a somewhat deeper level at $E(0/-) = E_V + 0.17$ eV. All other defect levels are relatively deep including the two In vacancy acceptor levels at 0.41 and 0.67 eV above E_V, respectively. The Cu_{In} antisite also has two deep acceptor levels at 0.29 and 0.58 eV above E_V. The deep donors in $CuInSe_2$ are the In_{Cu} antisite with two levels 0.25 and 0.34 eV below E_C, and the Cu interstitial with one level at 0.20 eV below E_C, respectively.

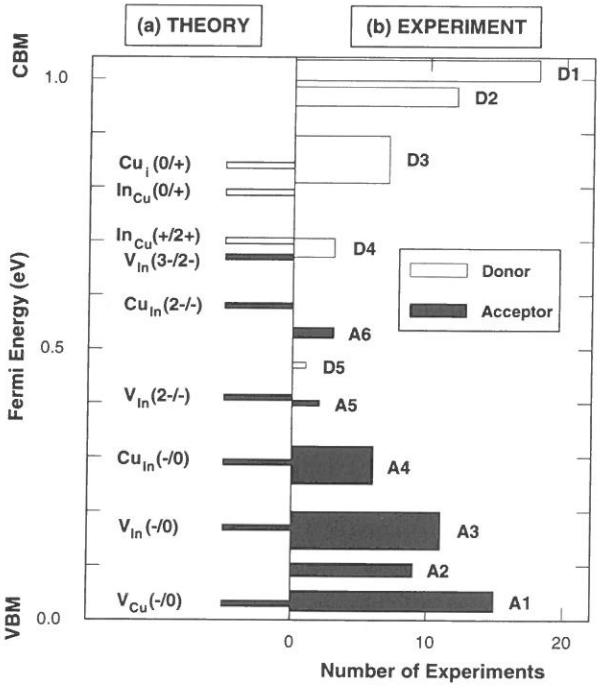

Figure 2. Defect transition energy levels from (a) the current theory and (b) experiments. The filled histograms indicate acceptor levels while the open ones indicate donor levels. In (b), the horizontal axis indicates the number of experiments that have been performed and the widths of the histograms indicate the spread of the experimental data. References to experimental observations are collected in Ref. [13].

For isolated interacting $(2V_{Cu}^{-} + In_{Cu}^{2+})$ pair, we find that the pairing pushes up tl deep In_{Cu} levels to positions much closer to the conduction band minimum. So the In_{C} levels in the pair are no longer harmful electron traps. This, combined with the fa of very low formation energy for this pair, explains the surprising electric tolerance $CuInSe_2$ to large amount of structural defects. We also calculated the (+/0) transitic energy for $(In_{Cu} + V_{Cu})$ and find that it has a donor level located at $E_C - 0.20$ eV.

In Fig. 2, our predicted defect transition levels (Fig. 2a) are compared with expe mental data (Fig. 2b) from various experimental techniques [3-11,13]. The scattering the experimental data is represented in Fig. 2b by the width of the histogram, where the height of the histogram indicates the number of experiments reporting that defe level. Comparing Fig. 2a and 2b, we see that: (i) Our calculated defect levels are good accord with experiment, especially those of low ionizations, i.e., (-/0) or (0/+ Thus, the calculated V_{Cu}(-/0) acceptor level corresponds to the observed A1 level; tl V_{In}(-/0) level corresponds to the A3 level; the Cu_{In}(-/0) level corresponds to the A level and the V_{In}(2-/-) level corresponds to the A5 level. The Cu_{In}(2-/-) level, with the uncertainty of the calculation, could be the A6 level. For donors, both the Cu_i(0/- and In_{Cu}(0/+) levels may be responsible for the measured D3 level which has a broa range of $\sim$ 90 meV. The In_{Cu}(+/2+) level corresponds to the D4 level. (ii) There are number of misassignments of the defect levels in existing literature, including the assig ment of (a) the Al level to V_{In} [7]; (b) the A1 level to Cu_{In} [9]; (c) the D3 level to I [9]; and (d) the D1 level to both In_{Cu} [8,9] and Cu_i [8]. (iii) The shallow donor leve D1 and D2 are not identified from our calculations. However, it has been speculate that V_{Se} (which was not calculated here) is responsible for the D1 level. The D2 lev on the other hand, may be caused by the (0/+) transition of the $(In_{Cu} + V_{Cu})$ pair by V_{Se}(+/2+). On the other hand, the unresolved A2 level could be the (0/-) transitic of the $(Cu_{In} + Cu_i)$ pair. The uncertainty ($\sim \pm 0.1$ eV) in the current calculation f defect pair energy levels makes it difficult to make a definitive assignment here. (iv) Tl calculated V_{In}(3-/2-) level is yet to be measured experimentally. This level is feature by its deep position inside the band gap and a high charge state.

5. Summary

We have studied theoretically the defect physics in $CuInSe_2$ using a first-principles bar structure method. We show that (i) it is much easier to form Cu vacancy in $CuInSe_2$ tha to form cation vacancy in II-VIs. (ii) The defect formation energies depends strongly c the Fermi level and on the chemical potential of the atomic species, and (iii) defect pai such as $(2V_{Cu}^{-} + In_{Cu}^{2+})$ are abundant and can alter the electric activity in the sampl These results explained (a) the existence of the off-stoichiometric ordered compounds a repeat of one unit of the highly stable $(2V_{Cu}^{-} + In_{Cu}^{2+})$ for every n units of $CuInSe$ This gives, for example, the observed n=4 phase $CuIn_5Se_8$; the observed n=5 pha $CuIn_3Se_5$, etc. (b) The very efficient p-type self-doping ability of $CuInSe_2$ is in part consequence of abundant Cu vacancies due to its exceptionally low formation energ And (c) the electrically benign character of the large defect population in $CuInSe_2$ is d to an electronic passivation of the unwanted deep levels, such as In_{Cu}^{2+}, by its attracti to the easily-formed $2V_{Cu}^{-}$.

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References

[1] Shay, J L and Wernick, J H, 1975, *Ternary Chalcopyrite Semiconductors*, Pergamon, Oxford.

[2] Villars, P and Calvert, L D, 1991, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, ASM International, Materials Park, and references therein.

[3] Coutts, T J, Kazmerski, L L and Wagner, S (eds), 1986, *Copper Indium Diselenide for Photovoltaic Applications*, Elsevier, Amsterdam.

[4] Rockett, A and Birkmire, E W, 1991, J. Appl. Phys. **70**, R81.

[5] Hedstrom, J, Olsen, H J, Bodegard, M, Kylner, A, Stolt, L, Hariskos, D, Ruckh, M and Schock, H W, 1993, *Proc. 23rd IEEE PV Specialists Conf.*, IEEE, New York, p.364.

[6] Gabor, A M, Tuttle, J R, Albin, D S, Contreras, M A, Noufi, R and Hermann, A M, 1994, Appl. Phys. Lett. **65**, 198.

[7] Neumann, H, Nowak, E and Kuhn, G, 1981, Res. Technol. **16**, 1369; Neumann, H, 1983, Res. Technol. **18**, 483; Neumann, H, 1983, Res. Technol. **18**, 901.

[8] Abou-Elfotouh, F, Moutinho, H, Bakry, A, Coutts, T J and Kazmerski, L L, 1991, Solar Cells **30**, 151.

[9] Rincon C and Wasim, S M, 1987, *Ternary and Multinary Compounds*, Materials Research Society, Pittsburgh, p. 443.

[10] Rincon, C and Bellabarba, C, 1986, Phys. Rev. B **33**, 7160; Wasim, S M, 1986, Solar Cells **16**, 289.

[11] Cahen, D and Noufi, R, 1992, J. Phys. Chem. Solids **53**, 991.

[12] Van Vechten, J A, 1980, *Handbook of semiconductors*, vol. **3**, North-Holland, Amsterdam, p. 1.

[13] Zhang, S B, Wei, S H and Zunger, A, 1997, Phys. Rev. Lett. *78*, 4059; *ibid*, 1998, Phys. Rev. B, to be published, and references therein.

[14] Zhang, S B and Northrup, J E, 1991, Phys. Rev. Lett. **67**, 2339.

[15] Perdew, J P and Zunger, A, 1981, Phys. Rev. B **23**, 5048.

[16] Wei, S H and Krakauer, H, 1985, Phys. Rev. Lett. **55**, 1200, and references therein.

[17] Laks, D. B., et al., 1992, Phys. Rev. B **45**, 10965; Van De Walle, C, private communication.