

## Stabilization of Ternary Compounds via Ordered Arrays of Defect Pairs

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First-principles calculations show that the defect pair  $s2V_{\text{Cu}}^2 + 1 \text{In}_{\text{Cu}}^1$  in  $\text{CuInSe}_2$  has an unusually low formation energy, due both to the relative ease of forming Cu vacancies  $sV_{\text{Cu}}^2$  and to the attractive interactions between  $V_{\text{Cu}}^2$  and  $\text{In}_{\text{Cu}}^1$ . The defect pair is predicted to be electrically inactive. This explains the surprising electrical tolerance of  $\text{CuInSe}_2$  to its huge  $s, 1\%$  concentration of native defects. An attractive interaction among the defect pairs is further predicted to lead to a crystallographic ordering of the pairs, explaining the observed, but hitherto surprising, structures  $\text{CuIn}_5\text{Se}_8$ ,  $\text{CuIn}_3\text{Se}_5$ ,  $\text{Cu}_2\text{In}_4\text{Se}_7$ , etc. [S0031-9007(97)03239-0]

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The field of condensed matter physics of *perfect* crystalline lattices owes its relevance to experiment to the fact that the formation of native defects usually costs significant energy. Thus, perfect crystalline lattices should exist, at least in principle. One may, however, contemplate the possibility of the *spontaneous formation* of defect complexes in crystalline lattices. If  $DH_{fsa}$ ,  $qd$  is the formation energy of a point defect of type *a* (vacancy, antisite, interstitial, ...) in charge state *q*, then, even if  $DH_{fsa}$ ,  $qd = 0$  for a *single* defect, it is possible that the formation energy of a *pair*, a *complex*, or an *array* of interacting defects,

$$DH_{fsa} + 1 \text{bd} - fDH_{fsad} + 1 DH_{fsbdg} + 1 dH_{\text{int}} + 1 dH_{\text{ord}}, \quad (1)$$

could be very small, or even negative. This could happen if the (positive) formation energy of two isolated defects  $fDH_{fsad} + 1 DH_{fsbdg}$  is small, but the attractive interaction energy  $dH_{\text{int}}$  between the components of a defect pair, and/or the pair-pair ordering energy  $dH_{\text{ord}}$  are strongly stabilizing. First-principles calculations have shown, however, that the lowest formation energy of a single, interacting defect pair— $f\text{Ga}_{\text{As}}^{2+} + 1 \text{As}_{\text{Ga}}^{2-}$  in GaAs [1,2], and  $f\text{V}_{\text{Zn}}^{2+} + 1 \text{Zn}_{\text{I}}^{2-}$  in ZnSe [3]—is still as high as 2–3 eV. Thus defect pairs are unlikely to form spontaneously in ordinary binary semiconductors.

We have identified a semiconductor system—the *ternary chalcopyrites* of the  $A^{\text{I}}B^{\text{III}}X_2^{\text{VI}}$  type [4] (e.g.,  $\text{CuInSe}_2$ ), where the formation of ordered arrays [5] of defect pairs can be made exothermic even at low temperatures. Using the local density approximation (LDA), our total energy calculations show the following: (i) The formation of a single *noninteracting* (neutral) defect pair made of two Cu vacancies  $s2V_{\text{Cu}}^0$  plus one In-on-Cu antisite  $s\text{In}_{\text{Cu}}^0$  costs only 4.26 eV. (ii) The strong interaction  $dH_{\text{int}} = 23.45$  eV between  $2V_{\text{Cu}}^0$  and  $\text{In}_{\text{Cu}}^0$  reduces the formation energy to only 0.81 eV, significantly lower than that for the lowest-energy pairs in GaAs or ZnSe. Furthermore, (iii) repeating periodically *m* units of  $s2V_{\text{Cu}}^2 + 1 \text{In}_{\text{Cu}}^1$  for every *n* unit of  $\text{CuInSe}_2$ ,

$$ns\text{CuInSe}_2d + 1 ms\text{In}d \rightarrow \text{Cu}_{sn}23md\text{In}_{sn}1md\text{Se}_{2n} + 1 3ms\text{Cu}d + 1 DH_{fsn}, md, \quad (2)$$

where  $m = 1, 2, 3, \dots$ , and  $n = 3, 4, 5, \dots$ , and where (In) and (Cu) denote In and Cu in their respective equilibrium chemical reservoirs, reduces the energy further by  $dH_{\text{ord}} = 20.8$  eVpair. Thus, the energy  $DH_{fsn}, md$  need to form such “*defect pair arrays*” from  $\text{CuInSe}_2$  is close to zero and can even be made negative by a proper choice of the reservoir energies. (iv) The charge-compensated defect pair  $s2V_{\text{Cu}}^2 + 1 \text{In}_{\text{Cu}}^1$  is found to have no electric energy levels in the band gap. Our findings can potentially explain two long-standing puzzles in the chalcopyrite material system [6,7]: First,  $\text{Cu}_2\text{Se} + 1 \text{In}_2\text{Se}_3$  are known [6] to form a series of compounds such as  $\text{CuIn}_5\text{Se}_8$ ,  $\text{CuIn}_3\text{Se}_5$ ,  $\text{Cu}_2\text{In}_4\text{Se}_7$ , ..., with hitherto unexplained Cu:In:Se ratios. We suggest that the extraordinarily low formation energy of a single pair  $s2V_{\text{Cu}}^2 + 1 \text{In}_{\text{Cu}}^1$  and the significant pair-pair ordering energy lead to the formation of “ordered defect arrays” [viz., Eq. (2)], such as  $\text{CuIn}_5\text{Se}_8$  ( $n = 4, m = 1$ ),  $\text{CuIn}_3\text{Se}_5$  ( $n = 5, m = 1$ ),  $\text{Cu}_2\text{In}_4\text{Se}_7$  ( $n = 7, m = 1$ ), etc. Second, while, in ordinary semiconductors, polycrystallinity leads to a high concentration of electrically active defects that have a detrimental effect on the performance of optoelectronic devices, polycrystalline  $\text{CuInSe}_2$  is as good an electronic material as its single-crystal counterpart [7], even though it has a huge amount of structural defects. We explain this by the attractive interaction between  $V_{\text{Cu}}^2$  and  $\text{In}_{\text{Cu}}^1$ , leading to an effective electric annihilation of these recombination centers.

The formation energy  $DH_{fsa}, qd$  of defect *a* in charge state *q* depends on the Fermi energy  $e_F^a$  (where *a* denotes absolute values), as well as on the atomic chemical potentials  $m^a$ . In  $\text{CuInSe}_2$ ,

$$DH_{fsa}, qd = E_{sa}, qd - 2 E_{s\text{CuInSe}_2d} + 1 n_{\text{Cu}}m_{\text{Cu}}^a$$

energy for the same supercell in the absence of the defect, the  $n$ 's are the numbers of Cu, In, and Se atoms, and  $q$  is the number of electrons, transferred from the defect-free supercell to the reservoirs in forming the defect cell. We will not consider Se-related defects in this study so we take  $n_{\text{Se}} = 0$ . Denoting

$$D E_{s a, q d} - E_{s a, q d} \mathcal{Z} E_{s \text{CuInSe}_2 d} + n_{\text{Cu}} m_{\text{Cu}}^{\text{solid}} + n_{\text{In}} m_{\text{In}}^{\text{solid}} + q E_V, \quad (4)$$

$$D H_{f s a, q d} - D E_{s a, q d} + n_{\text{Cu}} m_{\text{Cu}} + n_{\text{In}} m_{\text{In}} + q e_F, \quad (5)$$

where  $e_F = e_F^a \mathcal{Z} E_V$ ,  $m_{\text{Cu}} = m_{\text{Cu}}^a \mathcal{Z} m_{\text{Cu}}^{\text{solid}}$ , and  $m_{\text{In}} = m_{\text{In}}^a \mathcal{Z} m_{\text{In}}^{\text{solid}}$ . Here  $E_V$  is defined as  $E_V = E_0^{sN d} \mathcal{Z} E_1^{sN \mathcal{Z} 1 d} + e_{\text{VBM}}$ , where  $E_0^{sN d}$ ;  $E_{s \text{CuInSe}_2 d}$  is the ground state total energy of the  $N$ -electron neutral system and  $E_1^{sN \mathcal{Z} 1 d}$  is the total energy of the  $\text{CuInSe}_2$  with a hole in the VBM and an electron in the reservoir with an energy  $e_{\text{VBM}}$  equal to the valence-band maximum (VBM) eigenvalue.

There are some thermodynamic limits to  $\text{sm}, e_F$ :  $e_F$

particular, the formation energy of the neutral Cu vacancy is significantly lower than the vacancy formation energies for cations in II-VI's. There are two reasons ("ionic" and "covalent") for this. First, Cu is monovalent, while cations in II-VI's are divalent, so the point-ion (Madelung) contribution to the removal energy of the cation is larger in II-VI's. Second, the covalent Cu-Se bond is easier to break than that of Zn-Se because the Cu  $4p$  energy is higher than the Zn  $4p$  energy (thus the Cu-Se bond is less covalent). Furthermore, the formation of  $sp^3$  hybrids costs more energy in CuInSe<sub>2</sub>. This is so because the high-lying Cu  $3d$  orbital (relative to the Zn  $3d$  orbital) repels the Se  $4p$  orbital to higher energy [12], thus raising the Se  $4s \rightarrow 4p$  promotion energy.

(ii) Several low-energy point defects of opposite charges exist at the same  $e_F$  and  $m$ . This allows the formation of charge-compensated defect pairs of low energies, listed in Table I. Notable in Table I is the low formation energy neutral pair  $s2V_{Cu}^0 \ 1 \ In_{Cu}^0$  of 21.74 eV at point B.

The formation energy of the noninteracting defect pairs can be lowered considerably through *interaction* and *ordering*:

(a) Interaction: The interaction energy  $dH_{int}$  between the component of an isolated pair [Eq. (1)] is calculated as the difference  $DH_{f,sa} \ 1 \ bd \ 2 \ DH_{f,sad} \ 2 \ DH_{f,sbd}$  (using the 32-atom supercell [13]). Total energy minimization shows that (Table I)  $dH_{int}$  is 24 to 21 eV. We have analyzed the physical origins of  $dH_{int}$  by breaking it into recognizable terms. For  $s2V_{Cu}^2 \ 1 \ In_{Cu}^2$ , for example, we find  $dH_{int} = 23.45$  eV with three contributions: (i) the transfer of two electrons from the high-energy donor level to low-energy acceptor level releases , 21.0 eV (see Fig. 2) and produces *charged* defect components, (ii) a strong electrostatic attraction between the ensuing charged defects releases , 21.5 eV, and (iii) atomic relaxations upon pairing releases 20.9 eV. The equilibrium geometry of the pair is shown in Fig. 3, where two Cu vacancies are fcc nearest neighbors to the  $In_{Cu}$  antisite. This arrangement maximizes the point-ion interactions. Furthermore, it lowers the strain: The atomic radius of In is about 23% larger than that of Cu, therefore the pairing of  $In_{Cu}$  with Cu vacancies reduces the strain energy.

TABLE I. The calculated formation energies  $DH_{non} - DH_{f,sa} \ 1 \ DH_{f,sbd}$  (in eV) of noninteracting *neutral* defects, the intrapair interaction energies  $dH_{int}$ , and the pair-pair ordering energies  $dH_{ord}^{sn, m} - 1d$  at chemical potentials A, B, and C as shown in Fig. 1.

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$$2V_{Cu}^0 \ 1 \ In_{Cu}^0 \ Cu_{In}^0 \ 1 \ 2Cu_i^0$$

TABLE II. Calculated formation energies  $DH_{f,sn,m-1d} - DH_{\text{non}sm} - dH_{\text{int}} - dH_{\text{ord}sn,m-1d}$  [Eq. (2)] (in eV) of the ordered arrays of  $n$  units of  $s2V_{\text{Cu}}^2 - 1 \text{In}_{\text{Cu}}^1d$  for every  $m$  unit of  $\text{CuInSe}_2$ .  $dH_{\text{ord}sn,m-1d}$  are 20.76, 20.78, and 20.79 eV for  $n = 4, 5$ , and 6, respectively, while  $dH_{\text{int}}$  and  $DH_{\text{non}sm}$  are taken from the first column of Table I.

	$n$	$m - A$	$m - B$	$m - C$
$\text{CuIn}_5\text{Se}_8$	4	0.05	25.95	2.05
$\text{CuIn}_3\text{Se}_5$	5	0.03	25.97	2.03
$\text{Cu}_3\text{In}_7\text{Se}_{12}$	6	0.02	25.98	2.02

of  $s2V_{\text{Cu}}^2 - 1 \text{In}_{\text{Cu}}^1d$  for every  $n$  unit of  $\text{CuInSe}$