

Stabilization of Ternary Compounds via Ordered Arrays of Defect Pairs

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First-principles calculations show that the defect pair ($2V_{\text{Cu}}^2 \ 1 \ \text{In}_{\text{Cu}}^1$) in CuInSe_2 has an unusually low formation energy, due both to the relative ease of forming Cu vacancies (V_{Cu}) and to the attractive interactions between V_{Cu}^2 and In_{Cu}^1 . The defect pair is predicted to be electrically inactive. This explains the surprising electrical tolerance of CuInSe_2 to its huge ($\sim 1\%$) 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 CuIn_3Se_8 , CuIn_3Se_5 , $\text{Cu}_2\text{In}_4\text{Se}_7$, etc. [S0031-9007(97)03239-0]

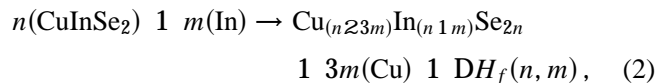
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The field of condensed matter physics of *perfect* crystalline lattices owes its relevance to experiment to the fact that the formation of native defects usually costs significant energy. Thus, perfect crystalline lattices should exist, at least in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

$$DH_f(\mathbf{a} \ 1 \ \mathbf{b}) - [DH_f(\mathbf{a}) \ 1 \ DH_f(\mathbf{b})] + dH_{\text{int}} \ 1 \ dH_{\text{ord}}, \quad (1)$$

could be very small, or even negative. This could happen if the (positive) formation energy of two isolated defects [$DH_f(\mathbf{a}) \ 1 \ DH_f(\mathbf{b})$] is small, but the attractive interaction energy dH_{int} between the components of a defect pair, and/or the pair-pair ordering energy dH_{ord} are strongly stabilizing. First-principles calculations have shown, however, that the lowest formation energy of a single, interacting defect pair— $[\text{Ga}_{\text{As}}^{22} \ 1 \ \text{As}_{\text{Ga}}^{21}]$ in GaAs [1,2], and $[V_{\text{Zn}}^{22} \ 1 \ \text{Zn}_{\text{I}}^{21}]$ 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., 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 ($2V_{\text{Cu}}^0$) plus one In-on-Cu antisite (In_{Cu}^0) costs only 4.26 eV. (ii) The strong interaction $dH_{\text{int}} = 23.45$ eV between $2V_{\text{Cu}}^0$ and In_{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 ($2V_{\text{Cu}}^2 \ 1 \ \text{In}_{\text{Cu}}^1$) for every n unit of CuInSe_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 $dH_{\text{ord}} \sim 20.8$ eV/pair. Thus, the energy $DH_f(n, m)$ need to form such “*defect pair arrays*” from 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 ($2V_{\text{Cu}}^2 \ 1 \ \text{In}_{\text{Cu}}^1$) 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 CuIn_3Se_8 , CuIn_3Se_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 ($2V_{\text{Cu}}^2 \ 1 \ \text{In}_{\text{Cu}}^1$)⁰ and the significant pair-pair ordering energy lead to the formation of “ordered defect arrays” [viz., Eq. (2)], such as CuIn_3Se_8 ($n = 4, m = 1$), CuIn_3Se_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 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_{Cu}^2 and In_{Cu}^1 , leading to an effective electric annihilation of these recombination centers.

The formation energy $DH_f(\mathbf{a}, q)$ of defect \mathbf{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 CuInSe_2 ,

$$DH_f(\mathbf{a}, q) = E(\mathbf{a}, q) - E(\text{CuInSe}_2) - n_{\text{Cu}}m_{\text{Cu}}^a$$

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

$$DE(\mathbf{a}, q) = E(\mathbf{a}, q) - E(\text{CuInSe}_2) - n_{\text{Cu}}m_{\text{Cu}}^{\text{solid}} - n_{\text{In}}m_{\text{In}}^{\text{solid}} - qE_V, \quad (4)$$

$$DH_f(\mathbf{a}, q) = DE(\mathbf{a}, q) - n_{\text{Cu}}m_{\text{Cu}} - n_{\text{In}}m_{\text{In}} - qe_F, \quad (5)$$

where $e_F = e_F^a - E_V$, $m_{\text{Cu}} = m_{\text{Cu}}^a - m_{\text{Cu}}^{\text{solid}}$, and $m_{\text{In}} = m_{\text{In}}^a - m_{\text{In}}^{\text{solid}}$. Here E_V is defined as $E_V = E_0^{(N)} - E_1^{(N\pm 1)} - e_{\text{VBM}}$, where $E_0^{(N)} \equiv E(\text{CuInSe}_2)$ is the ground state total energy of the N -electron neutral system and $E_1^{(N\pm 1)}$ is the total energy of the CuInSe_2 with a hole in the VBM and an electron in the reservoir with an energy e_{VBM} equal to the valence-band maximum (VBM) eigenvalue.

There are some thermodynamic limits to (\mathbf{m}, 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 CuInSe₂. 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 ($2V_{Cu}^0$ 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 $DH_f(a$ 1 $b) \approx DH_f(a) \approx DH_f(b)$ (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 ($2V_{Cu}^0$ 1 In_{Cu}^0), 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 $DH_{non} - DH_f(a) - DH_f(b)$ (in eV) of noninteracting *neutral* defects, the intrapair interaction energies dH_{int} , and the pair-pair ordering energies $dH_{ord}(n, m - 1)$ at chemical potentials A , B , and C as shown in Fig. 1.

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

TABLE II. Calculated formation energies $DH_f(n, m - 1) - DH_{\text{non}}(m) - dH_{\text{int}} - dH_{\text{ord}}(n, m - 1)$ [Eq. (2)] (in eV) of the ordered arrays of n units of $(2V_{\text{Cu}}^2 - 1 \text{ In}_{\text{Cu}}^1)$ for every m unit of CuInSe_2 . $dH_{\text{ord}}(n, m - 1)$ are 20.76, 20.78, and 20.79 eV for $n = 4, 5$, and 6, respectively, while dH_{int} and $DH_{\text{non}}(m)$ are taken from the first column of Table I.

	n	$m - A$	$m - B$	$m - C$
CuIn_5Se_8	4	0.05	25.95	2.05
CuIn_3Se_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 $(2V_{\text{Cu}}^2 - 1 \text{ In}_{\text{Cu}}^1)$ for every n unit of CuInSe