Stabilization of Ternary Compounds via Ordered Arrays of Defect Pairs

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(Received 17 January 1997)

First-principles calculations show that the defect pair $(2V_{\mathrm{Cu}}^{-} + \mathrm{In}_{\mathrm{Cu}}^{+})$ in $\mathrm{CuInSe_2}$ 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}^{-} and $\mathrm{In}_{\mathrm{Cu}}^{2+}$. The defect pair is predicted to be electrically inactive. This explains the surprising electrical tolerance of $\mathrm{CuInSe_2}$ 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 $\mathrm{CuIn_5Se_8}$, $\mathrm{CuIn_3Se_5}$, $\mathrm{Cu_2In_4Se_7}$, etc. [S0031-9007(97)03239-0]

PACS numbers: 61.72.Bb, 61.72.Ji, 71.20.Nr

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 $\Delta H_f(\alpha, q)$ is the formation energy of a point defect of type α (vacancy, antisite, interstitial, ...) in charge state q, then, even if $\Delta H_f(\alpha, q) > 0$ for a *single* defect, it is possible that the formation energy of *a pair, a complex, or an array* of interacting defects,

$$\Delta H_f(\alpha + \beta) = [\Delta H_f(\alpha) + \Delta H_f(\beta)] + \delta H_{\mathrm{int}} + \delta H_{\mathrm{ord}}\,, \qquad (1)$$

could be very small, or even negative. This could happen if the (positive) formation energy of two isolated defects $[\Delta H_f(\alpha) + \Delta H_f(\beta)]$ is small, but the attractive interaction energy δH_{int} between the components of a defect pair, and/or the pair-pair ordering energy δH_{ord} are strongly stabilizing. First-principles calculations have shown, however, that the lowest formation energy of a single, interacting defect pair—$[\mathrm{Ga}_{\mathrm{As}}^{2-} + \mathrm{As}_{\mathrm{Ga}}^{2+}]$ in GaAs [1,2], and $[V_{\mathrm{Zn}}^{2-} + \mathrm{Zn}_i^{2+}]$ 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 $A^{\mathrm{I}}B^{\mathrm{III}}X_2^{\mathrm{VI}}$ type [4] (e.g., $\mathrm{CuInSe_2}$), 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 $(2V_{\mathrm{Cu}}^{0})$ plus one In-on-Cu antisite $(\mathrm{In}_{\mathrm{Cu}}^{0})$ costs only 4.26 eV. (ii) The strong interaction $\delta H_{\mathrm{int}} = -3.45$ eV between $2V_{\mathrm{Cu}}^{0}$ and $\mathrm{In}_{\mathrm{Cu}}^{0}$ 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 $(2V_{\mathrm{Cu}}^{-} + \mathrm{In}_{\mathrm{Cu}}^{2+})$ for every n unit of $\mathrm{CuInSe_2}$,

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

where $m = 1, 2, 3, \ldots$, and $n = 3, 4, 5, \ldots$, and where (In) and (Cu) denote In and Cu in their respective equilibrium chemical reservoirs, reduces the energy further by $\delta H_{\mathrm{ord}} \sim -0.8$ eV/pair. Thus, the energy $\Delta H_f(n, m)$ need to form such "*defect pair arrays*" from $\mathrm{CuInSe_2}$ is close to zero and can even be made negative by a proper choice of the reservoir energies. (iv) The charge-compensated defect pair $(2V_{\mathrm{Cu}}^{-} + \mathrm{In}_{\mathrm{Cu}}^{2+})$ 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, $\mathrm{Cu_2Se} + \mathrm{In_2Se_3}$ are known [6] to form a series of compounds such as $\mathrm{CuIn_5Se_8}$, $\mathrm{CuIn_3Se_5}$, $\mathrm{Cu_2In_4Se_7}$, ..., with hitherto unexplained Cu:In:Se ratios. We suggest that the extraordinarily low formation energy of a single pair $(2V_{\mathrm{Cu}}^{-} + \mathrm{In}_{\mathrm{Cu}}^{2+})^0$ and the significant pair-pair ordering energy lead to the formation of "ordered defect arrays" [viz., Eq. (2)], such as $\mathrm{CuIn_5Se_8}$ ($n = 4$, $m = 1$), $\mathrm{CuIn_3Se_5}$ ($n = 5$, $m = 1$), $\mathrm{Cu_2In_4Se_7}$ ($n = 7$, $m = 1$), 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 $\mathrm{CuInSe_2}$ 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}^{-} and $\mathrm{In}_{\mathrm{Cu}}^{2+}$, leading to an effective electric annihilation of these recombination centers.

The formation energy $\Delta H_f(\alpha, q)$ of defect α in charge state q depends on the Fermi energy ϵ_F^a (where a denotes absolute values), as well as on the atomic chemical potentials μ^a. In $\mathrm{CuInSe_2}$,

$$\Delta H_f(\alpha, q) = E(\alpha, q) - E(\mathrm{CuInSe_2}) + n_{\mathrm{Cu}}\mu_{\mathrm{Cu}}^a + n_{\mathrm{In}}\mu_{\mathrm{In}}^a + n_{\mathrm{Se}}\mu_{\mathrm{Se}}^a + q\epsilon_F^a\,, \qquad (3)$$

where $E(\alpha, q)$ is the total energy of a supercell containing a defect of type α and charge q, $E(\mathrm{CuInSe_2})$ is the total 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 $n_{\mathrm{Se}} = 0$. Denoting

$$\Delta E(\alpha, q) = E(\alpha, q) - E(\mathrm{CuInSe_2}) + n_{\mathrm{Cu}}\mu_{\mathrm{Cu}}^{\mathrm{solid}} + n_{\mathrm{In}}\mu_{\mathrm{In}}^{\mathrm{solid}} + qE_V\,, \tag{4}$$

$$\Delta H_f(\alpha, q) = \Delta E(\alpha, q) + n_{\mathrm{Cu}}\mu_{\mathrm{Cu}} + n_{\mathrm{In}}\mu_{\mathrm{In}} + q\epsilon_F\,, \tag{5}$$

where $\epsilon_F = \epsilon_F^a - E_V$, $\mu_{\mathrm{Cu}} = \mu_{\mathrm{Cu}}^a - \mu_{\mathrm{Cu}}^{\mathrm{solid}}$, and $\mu_{\mathrm{In}} = \mu_{\mathrm{In}}^a - \mu_{\mathrm{In}}^{\mathrm{solid}}$. Here E_V is defined as $E_V = E_0^{(N)} - E_+^{(N-1)} + \epsilon_{\mathrm{VBM}}$, where $E_0^{(N)} \equiv E(\mathrm{CuInSe_2})$ is the ground state total energy of the N-electron neutral system and $E_+^{(N-1)}$ is the total energy of the CuInSe$_2$ with a hole in the VBM and an electron in the reservoir with an energy ϵ_{VBM} equal to the valence-band maximum (VBM) eigenvalue.

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

$$\mu_{\mathrm{Cu}} \le 0, \qquad \mu_{\mathrm{In}} \le 0, \qquad \mu_{\mathrm{Se}} \le 0\,, \tag{6}$$

(ii) by the values that maintain a stable CuInSe$_2$ compound, so

$$\mu_{\mathrm{Cu}} + \mu_{\mathrm{In}} + 2\mu_{\mathrm{Se}} = \Delta H_f(\mathrm{CuInSe_2})\,, \tag{7}$$

where $\Delta H_f(\mathrm{CuInSe_2}) = -1.97$ eV is the calculated formation energy of solid CuInSe$_2$, and (iii) by the values that will cause formation of binaries, so

$$\begin{aligned} 2\mu_{\mathrm{In}} + 3\mu_{\mathrm{Se}} &\le \Delta H_f(\mathrm{In_2Se_3})\,, \\ 2\mu_{\mathrm{Cu}} + \mu_{\mathrm{Se}} &\le \Delta H_f(\mathrm{Cu_2Se})\,, \end{aligned} \tag{8}$$

where our calculated $\Delta H_f(\text{tetragonal In}_2\text{Se}_3) = -2.07$ eV [8] and $\Delta H_f(\mathrm{Cu_2Se}) = -0.31$ eV, respectively. Figure 1 gives the calculated "stability triangle" in the two-dimensional $(\mu_{\mathrm{Cu}}, \mu_{\mathrm{In}})$ plane as defined by Eqs. (6) and (7). The vertices are A (the Cu-rich and In-rich limit), B (the Cu-poor and In-rich limit), and C (the Cu-rich and In-poor limit). Equation (8) defines the regions where In$_2$Se$_3$ and Cu$_2$Se are stable.

We calculated $\Delta H_f(\alpha, q)$ for $\alpha = V_{\mathrm{Cu}}, V_{\mathrm{In}}, \mathrm{In_{Cu}}, \mathrm{Cu_{In}}$, and interstitial Cu (Cu$_i$) using a 32-atom supercell and a uniform jellium background where $q \neq 0$. The total energies are calculated using the LDA as implemented by the general potential linearized augmented plane wave (LAPW) method [9]. We used Ceperley-Alder exchange correlation potential [10] as parametrized by Perdew and Zunger [11]. The core states are treated relativistically, while the valence states are treated nonrelativistically. The LDA error on the band gap is corrected by adding a constant potential to the conduction states so that the band gap of CuInSe$_2$ matches the experimental value of 1.04 eV [7]. The atomic positions were fully relaxed for the $q = 0$ charge state, but no further relaxation was attempted for $q \neq 0$. We estimated that the error in our calculated defect formation energies is ±0.2 eV per defect.

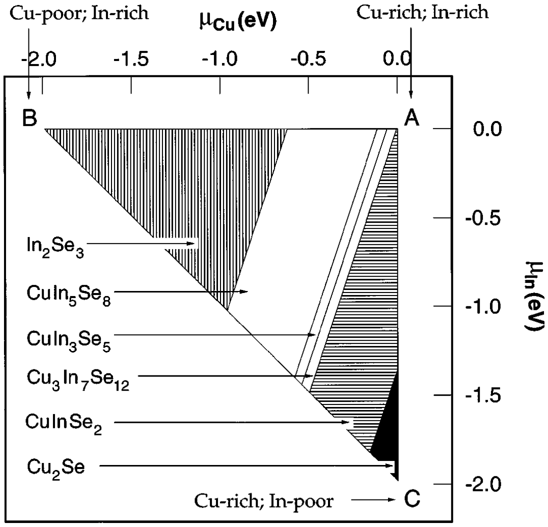

FIG. 1. The calculated stability triangle of the Cu-In-Se systems [Eqs. (6) and (7)] in the $\{\mu_{\mathrm{Cu}}, \mu_{\mathrm{In}}\}$ plane. The vertices correspond to (A) Cu-rich, In-rich; (B) Cu-poor, In-rich; and (C) Cu-rich, In-poor, respectively.

Figure 2 shows the defect formation energy $\Delta H_f(\alpha, q)$ for single defects as a function of the electron Fermi energy ϵ_F at the chemical potential values A, B, and C denoted in Fig. 1. The solid dots 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 $E_\alpha(q/q')$. Figure 2 shows the following:

(i) The formation energies of single neutral defects in CuInSe$_2$ are extraordinarily low, e.g., $\Delta H_f(V_{\mathrm{Cu}}^0) = -1.2$ eV (at B) and $\Delta H_f(\mathrm{Cu_{In}^0}) = -0.3$ eV (at C). In

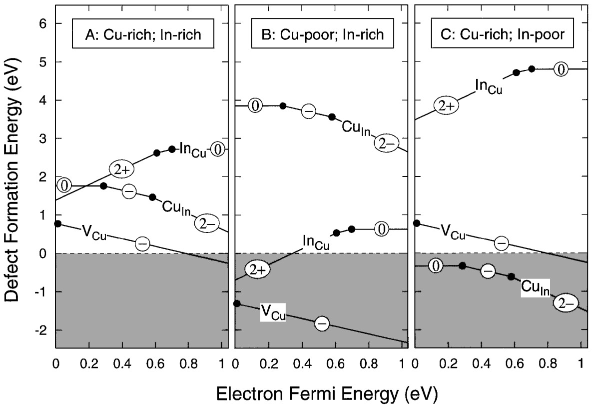

FIG. 2. Formation energies [Eq. (5)] of V_{Cu}, In$_{\mathrm{Cu}}$, and Cu$_{\mathrm{In}}$ as a function of the electron Fermi energy ϵ_F at chemical potentials A, B, and C as shown in Fig. 1. Charge state q determines the slope of each line segment. The shaded area highlights negative formation energies.

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 $\mathrm{CuInSe_2}$. 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 ϵ_F and μ. 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 $(2V_{\mathrm{Cu}}^0 + \mathrm{In}_{\mathrm{Cu}}^0)$ of -1.74 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 δH_{int} between the component of an isolated pair [Eq. (1)] is calculated as the difference $\Delta H_f(\alpha + \beta) - \Delta H_f(\alpha) - \Delta H_f(\beta)$ (using the 32-atom supercell [13]). Total energy minimization shows that (Table I) δH_{int} is -4 to -1 eV. We have analyzed the physical origins of δH_{int} by breaking it into recognizable terms. For $(2V_{\mathrm{Cu}}^- + \mathrm{In}_{\mathrm{Cu}}^{2+})$, for example, we find $\delta H_{\mathrm{int}} = -3.45$ eV with three contributions: (i) the transfer of two electrons from the high-energy donor level to low-energy acceptor level releases ~ -1.0 eV (see Fig. 2) and produces *charged* defect components, (ii) a strong electrostatic attraction between the ensuing charged defects releases ~ -1.5 eV, and (iii) atomic relaxations upon pairing releases -0.9 eV. The equilibrium geometry of the pair is shown in Fig. 3, where two Cu vacancies are fcc nearest neighbors to the $\mathrm{In_{Cu}}$ 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 $\mathrm{In_{Cu}}$ with Cu vacancies reduces the strain energy.

TABLE I. The calculated formation energies $\Delta H_{\mathrm{non}} = \Delta H_f(\alpha) + \Delta H_f(\beta)$ (in eV) of noninteracting *neutral* defects, the intrapair interaction energies δH_{int}, and the pair-pair ordering energies $\delta H_{\mathrm{ord}}(n, m = 1)$ at chemical potentials *A*, *B*, and *C* as shown in Fig. 1.

	$2V_{\mathrm{Cu}}^0 + \mathrm{In}_{\mathrm{Cu}}^0$	$\mathrm{Cu}_{\mathrm{In}}^0 + 2\mathrm{Cu}_i^0$	$V_{\mathrm{Cu}}^0 + \mathrm{Cu}_i^0$	$\mathrm{In}_{\mathrm{Cu}}^0 + \mathrm{Cu}_{\mathrm{In}}^0$
ΔH_{non}	4.26(*A*)	6.07(*A*)	2.93(*A*)	4.47(*A*)
	−1.74(*B*)	12.07(*B*)	2.93(*B*)	4.47(*B*)
	6.26(*C*)	4.07(*C*)	2.93(*C*)	4.47(*C*)
δH_{int}	−3.45	−2.61	−1.13	−3.67
δH_{ord}	~ -0.8	⋯	⋯	⋯

(b) Ordering: Defect pairs whose components are charged may order in the lowest electrostatic Madelung energy configuration. Indeed, we found that the directly calculated LAPW ordering energies scale with the Madelung ordering energies of the same charged defect pair arrays. We thus searched for the lowest-energy array made of $(2V_{\mathrm{Cu}}^- + \mathrm{In}_{\mathrm{Cu}}^{2+})$ units by considering a large number of ordered configurations, using a simple point-ion model. The lowest energy configuration found forms a tetragonal superstructure with lattice vectors along the $[110]$, $[1\bar{1}2]$, and $[\bar{1}12]$ directions, respectively, resulting in a $\mathrm{Cu} - V_{\mathrm{Cu}} - \mathrm{In_{Cu}} - V_{\mathrm{Cu}}$ $[110]$ superlattice (which can also be viewed as $[001]$ stacking of the vacancy planes). The pair-pair ordering energy $\delta H_{\mathrm{ord}}(n, m = 1)$ (Table I) for the most stable structure was then calculated by subtracting from the LAPW energy of the defect array the energy of the isolated $(2V_{\mathrm{Cu}}^- + \mathrm{In}_{\mathrm{Cu}}^{2+})$ pair. $\delta H_{\mathrm{ord}}(n, m = 1)$ depends on n with an average value of -0.8 eV.

We can see from Table I that the sum of interaction and ordering energies $\delta H_{\mathrm{int}} + \delta H_{\mathrm{ord}}$ of Eq. (1) for the defect pair array $(2V_{\mathrm{Cu}}^- + \mathrm{In}_{\mathrm{Cu}}^{2+})$ is about -4.25 eV, which cancels most of the (positive) formation energy of the isolated, neutral pair: $2\Delta H_f(V_{\mathrm{Cu}}^0) + \Delta H_f(\mathrm{In}_{\mathrm{Cu}}^0) = 4.26$ eV at *A*. Table II shows the formation energies $\Delta H_f(n, m = 1)$ for a few ordered arrays of $(2V_{\mathrm{Cu}}^- + \mathrm{In}_{\mathrm{Cu}}^{2+})$ for the chemical potentials *A*, *B*, and *C*, respectively. We see that a *spontaneous* formation of stable defect arrays is predicted. The arrows in Fig. 1 point to the chemical potential domains where these ordered defect arrays will be thermodynamically stable.

The results of Table II and Fig. 1 can be used to understand the peculiar Cu-In-Se structures known [6] to exist. They can be divided into two classes: those that are on the $\mathrm{Cu_2Se}$-$\mathrm{In_2Se_3}$ tie line [i.e., the compound that can be written as $(\mathrm{Cu_2Se})_x(\mathrm{In_2Se_3})_{1-x}$ with $0 \le x \le 1$] and those that are not. We predict the stability of all observed tie-line compounds as resulting from the repetition of m units

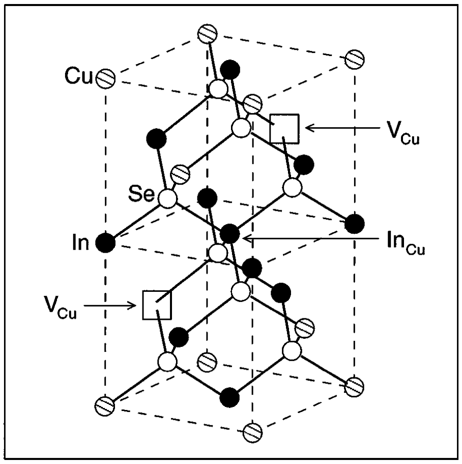

FIG. 3. The calculated structural model for the $(2V_{\mathrm{Cu}}^- + \mathrm{In}_{\mathrm{Cu}}^{2+})$ defect pair.

TABLE II. Calculated formation energies $\Delta H_f(n, m = 1) = \Delta H_{\mathrm{non}}(\mu) + \delta H_{\mathrm{int}} + \delta H_{\mathrm{ord}}(n, m = 1)$ [Eq. (2)] (in eV) of the ordered arrays of n units of $(2V_{\mathrm{Cu}}^{-} + \mathrm{In}_{\mathrm{Cu}}^{2+})$ for every m unit of $\mathrm{CuInSe_2}$. $\delta H_{\mathrm{ord}}(n, m = 1)$ are -0.76, -0.78, and -0.79 eV for $n = 4$, 5, and 6, respectively, while δH_{int} and $\Delta H_{\mathrm{non}}(\mu)$ are taken from the first column of Table I.

	n	$\mu = A$	$\mu = B$	$\mu = C$
$\mathrm{CuIn_5Se_8}$	4	0.05	-5.95	2.05
$\mathrm{CuIn_3Se_5}$	5	0.03	-5.97	2.03
$\mathrm{Cu_3In_7Se_{12}}$	6	0.02	-5.98	2.02

of $(2V_{\mathrm{Cu}}^{-} + \mathrm{In}_{\mathrm{Cu}}^{2+})$ for every n unit of $\mathrm{CuInSe_2}$. These are $\mathrm{CuIn_5Se_8}$ ($n = 4$, $m = 1$), $\mathrm{CuIn_3Se_5}$ ($n = 5$, $m = 1$), $\mathrm{Cu_2In_4Se_7}$ ($n = 7$, $m = 1$), $\mathrm{Cu_3In_5Se_9}$ ($n = 9$, $m = 1$), and $\mathrm{Cu_7In_{19}Se_{32}}$ ($n = 16$, $m = 3$). Electron diffraction data on $\mathrm{CuIn_3Se_5}$ [14] suggest [001] stacking of the vacancies, in agreement with our calculations. There are three off-the-tie-line compounds that are observed [6] but not accounted for by the above argument: $\mathrm{CuIn_7Se_{12}}$, $\mathrm{Cu_4In_9Se_{16}}$, and $\mathrm{Cu_3In_6Se_{11}}$. In light of the low formation energy of neutral Cu vacancy (Fig. 2), we can rationalize the stabilities of these three compounds as emerging from the creation of 2, 1, and 1 Cu vacancies per molecule in the (tie-line) compounds $\mathrm{Cu_3In_7Se_{12}}$ ($n = 6$, $m = 1$), $\mathrm{Cu_5In_9Se_{16}}$ ($n = 8, m = 1$), and $\mathrm{Cu_4In_6Se_{11}}$ ($n = 11, m = 1$), respectively.

To understand why $\mathrm{CuInSe_2}$ exhibits a surprising electric tolerance to its $>1\%$ structural point defects, we calculated the electronic structure of an isolated, interacting $(2V_{\mathrm{Cu}}^{-} + \mathrm{In}_{\mathrm{Cu}}^{2+})$ pair. All the deep defect levels of V_{Cu} and $\mathrm{In_{Cu}}$ (which act as the recombination centers) are removed from the band gap due to pairing. We also find that, when the defect array orders, the (LDA-corrected) band gaps of the "ordered defect compounds" $\mathrm{CuIn_5Se_8}$, $\mathrm{CuIn_3Se_5}$, and $\mathrm{Cu_3In_7Se_{12}}$ are 1.38, 1.29, and 1.23 eV, respectively, all larger than the 1.04 eV band gap of $\mathrm{CuInSe_2}$. This explains the surprising electrical tolerance of nonstoichiometric $\mathrm{CuInSe_2}$ to its structural defects [7].

In summary, the key factors that stabilize spontaneous defect-pair formation and ordering in $\mathrm{CuInSe_2}$ are (i) the ability to form charge-compensating defects solely on the cation sublattices (thus, the need for two heterovalent cations), (ii) the low metal vacancy formation energy (thus, the need for low-valent cations with possibly active d orbitals), and (iii) the large interdefect electrostatic interactions (thus, the need for partially ionic systems).

This work was supported by the U.S. Department of Energy, DOE-EERE under Contract No. DE-AC36-83CH10093.

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