Intrinsic *DX* Centers in Ternary Chalcopyrite Semiconductors

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In III-V and II-VI semiconductors, certain nominally electron-donating impurities do not release electrons but instead form deep electron-traps known as "*DX* centers." While in these compounds, such traps occur only after the introduction of foreign impurity atoms, we find from first-principles calculations that in ternary I-III-VI_2 chalcopyrites like $CuInSe_2$ and $CuGaSe_2$, *DX*-like centers can develop without the presence of any extrinsic impurities. These intrinsic *DX* centers are suggested as a cause of the difficulties to maintain high efficiencies in $CuInSe_2$-based thin-film solar-cells when the band gap is increased by addition of Ga.

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Electron-donating impurities are introduced into semiconductors with the expectation that they create *shallow* levels, capable of releasing free electrons. In certain cases, however, the donor atoms form a *deep* "*DX* center" [1,2], i.e., a strongly localized electronic state within the band gap, due to a large lattice relaxation off the lattice site. Such *DX* centers are formed by, e.g., Te or Si in AlGaAs [1,2], O in GaN (under pressure) [3], or Ga in ZnSe [4], and cause trapping of free electrons, thereby pinning the Fermi level below the conduction band minimum (CBM). In these III-V or II-V semiconductors, the elimination of free electrons due to *DX* center formation occurs due to the introduction of *extrinsic* impurities. Here, we predict theoretically that in ternary I-III-VI_2 chalcopyrites semiconductors, such as $CuInSe_2$ and $CuGaSe_2$, free-electron elimination can occur due to *intrinsic DX*-like centers, i.e., without the introduction of any foreign impurity atoms. Thus, multinary semiconductors containing cation species of different valency, such as Cu(I) and Ga(III) in $CuGaSe_2$, generally possess additional channels of self-compensation, Fermi level pinning, and of carrier trapping. In $CuInSe_2$-$CuGaSe_2$ alloys, which presently provide the most efficient absorber materials in polycrystalline thin film solar cells [5], these detrimental effects induced by the intrinsic *DX* centers can limit solar cell efficiencies.

The additional configurational degree of freedom available in ternary I-III-VI_2 chalcopyrites due to the presence of two cation sublattices enables a number of interesting physical effects: (i) Intrinsic *n*-type conductivity in $CuInSe_2$ [6–8] caused by In-on-Cu (In_{Cu}) antisite donors, and intrinsic *p*-type conductivity in $CuInSe_2$ and $CuGaSe_2$ due to Cu-vacancies V_{Cu} [6,7,9], (ii) the occurrence of ordered defect arrays due to stacking of (In_{Cu}-$2V_{Cu}$) [10] defect pairs, which explain the known nonstoichiometric phases and the self-passivation behavior, (iii) the existence of hole-barriers at grain boundaries [11,12], and (iv) the formation of strong metal-metal dimer bonds between the neighbor atoms of anion vacancies [13]. We show here that by capturing two electrons, the ionized *intrinsic* In_{Cu}^{2+} and Ga_{Cu}^{2+} donors in $CuInSe_2$ and $CuGaSe_2$ can transform into a lattice-relaxed, deep *DX*-like state, which is effectively formed as a Frenkel-pair comprising an In or Ga interstitial and a Cu vacancy. By systematically comparing these I-III-VI_2 compounds with their II-VI counterparts ZnSe and ZnO we find that, on an absolute energy scale, Fermi level pinning due to *DX* center formation occurs already at lower Fermi levels in the chalcopyrites compared to the II-VI compounds. As a consequence, the pinning energy occurs inside the band gap of the photovoltaic absorber in ZnO/CdS/Cu(In, Ga)Se_2 solar cell devices [5], thereby setting a limit to the open-circuit voltage. Since we further find that the capability of In_{Cu} and Ga_{Cu} to trap electrons into a deep *DX* state persists even in their complexes with V_{Cu}, which are known to be abundant [5,10], our predicted *DX*-behavior constitutes a previously unrecognized channel for the efficiency limitation that is encountered in $CuIn_{1-x}Ga_xSe_2$ based solar cells when the band gap is increased above $\sim$1.2 eV, i.e., for $x \gtrsim 0.3$.

Methods.—We calculate supercell (64 atoms) total energies in the pseudopotential-momentum-space formalism as implemented in the VASP code [14], and use the local density approximation (LDA) to density functional theory (DFT). The defect formation energy $\Delta H_{D,q}(E_F)$ of a defect *D* in charge state *q* is calculated as a function of E_F according to Ref. [7]. In particular, the underestimated LDA band gap was corrected by a downward shift of E_V (VBM) as determined by the LDA + *U* method [13], and the remaining difference with the experimental gap was accommodated by a shift of E_C (CBM). Image charge corrections are calculated according to Ref. [16].

The Frenkel-pair character of the DX center.— The *DX* center in II-VI semiconductors like ZnSe:Ga is formed by a displacement of the group-III donor Ga_{Zn} along the $[\bar{1}\,\bar{1}\,\bar{1}]$ direction towards the interstitial site that is tetrahedrally coordinated by cations [17]. Thus, the *DX* center resembles a Frenkel-like interstitial-vacancy pair. Since we find here that the intrinsic defects Ga_{Cu} in $CuGaSe_2$ and In_{Cu} in $CuInSe_2$ form a *DX*-like state with an analogous atomic configuration, we now compare systematically the *DX* centers in ZnSe and $CuGaSe_2$. (Note that ZnSe and $CuGaSe_2$ are closely related in that Zn is the "chemical average" of Cu and Ga.) In both cases, the *DX* center is effectively

formed as a Frenkel pair (Fig. 1), i.e., $Ga_{Zn}^{+} + 2e \rightarrow Ga_{DX}^{-} = (Ga_i^{+}\text{-}V_{Zn}^{2-})$ in ZnSe, and $Ga_{Cu}^{2+} + 2e \rightarrow Ga_{DX}^{0} = (Ga_i^{+}\text{-}V_{Cu}^{-})$ in $CuGaSe_2$.

In the case of the singly charged Ga-interstitial Ga_i^{+} in ZnSe [Figs. 1(a) and 1(d)], having T_d point group symmetry, the (Ga4s)–(Se4p) atomic-orbital interaction of Ga_i with the octahedrally coordinated Se anions leads to the formation of two singly degenerate a_1 symmetric levels, i.e., a hyperdeep (HD) bonding state at $\varepsilon_{HD} = E_V - 5.7$ eV [see Fig. 1(a)], and the doubly occupied gap state of the interstitial (IS) at $\varepsilon_{IS} = E_V + 0.6$ eV [Figs. 1(a) and 1(d)], which is the antibonding state. Notice the sphere- and lobelike features around Ga and Se atoms, respectively, of the IS state [Fig. 1(d)], illustrating the atomic Gas–Sep interaction that leads to the ε_{HD}-ε_{IS} level splitting. The Ga-DX center in ZnSe [Figs. 1(b) and 1(e)] is now formed by combining the positively charged Ga_i^{+} (level ε_{IS}) with a doubly-negative Zn vacancy V_{Zn}^{2-}, resulting in the singly-negative Ga_{DX}^{-}, which has a doubly occupied gap level at $\varepsilon_{DX} = E_V + 1.2$ eV. Originating from ε_{IS}, the state ε_{DX} is only modestly perturbed by the nearby presence of V_{Zn} (which lowers the point group symmetry of Ga_i to C_{3v}), and largely retains the orbital-shape and energy of the IS state ε_{IS} [Figs. 1(b) and 1(e)]. In the chalcopyrite $CuGaSe_2$, the intrinsic DX center [Figs. 1(c) and 1(f)] is formed by combining a positively charged Ga_i^{+} with a singly negatively charged Cu vacancy V_{Cu}^{-}, creating the doubly occupied DX level at $\varepsilon_{DX} = E_V + 0.5$ eV [Fig. 1(c)]. Here, the Ga_{DX}^{0} state is *charge-neutral*, in contrast to the generally *negative* charge state of the extrinsic DX centers in II-VI and III-V compounds [2]. When the doubly occupied DX level ε_{DX} [Figs. 1(b) and 1(c)] is emptied either by electron emission or by recombination with free holes, Ga_{DX} transforms into the substitutional donor Ga_{Zn}^{+} or Ga_{Cu}^{2+} (i.e., the Frenkel pairs recombine), whose single-particle levels are resonant inside the conduction band [18]. This deep-to-shallow transformation is the origin of the typical persistent photoconductivity effects in DX systems [1,4,19].

Alignment of the DX center single-particle energies.—In order to reveal the trend in the single-particle energies ε_{DX} of the DX center state [Figs. 1(b) and 1(c)], on an absolute energy scale, we placed the respective energies in a band-offset diagram, shown in Fig. 2. (The band offsets were obtained by adding the LDA + U corrections for E_V [19] to the LDA-calculated valence band offsets of Ref. [20]). Figure 2 shows that ε_{DX} clearly aligns on an absolute scale among ZnSe, $CuGaSe_2$, and $CuInSe_2$. In ZnO, we find that the energy level of the *unrelaxed* $(Ga_i\text{-}V_{Zn})^{-}$ pair aligns approximately with the energy ε_{DX} in the other materials, being close to the CBM of ZnO. However, this configuration is not stable in ZnO, and transforms spontaneously into the substitutional Ga_{Zn}^{+} donor configuration, emitting two electrons to the CBM. Thus, we find that the Ga DX center does not exist in ZnO, and does not limit n-type doping by Ga donors.

Fermi level pinning energies.—The DX phenomenology occurs when electrons are introduced through doping, formation of a n-p junction, or photoexcitation, leading to a rise of the Fermi level E_F [21] in the gap. We calculate, as a function of E_F, the formation energies of the substitutional ionized donor (e.g., In_{Cu}^{2+}) and the deep DX state (e.g., In_{DX}^{0}) in their relaxed configurations. We define the critical value E_{DX}^{pin} as the Fermi level where the DX state becomes thermodynamically more stable than the substitutional ionized donor, i.e., $\Delta H(In_{DX}^{0}) \leq \Delta H(In_{Cu}^{2+})$ for $E_F \geq E_{DX}^{pin}$. At this point, the trapping of free electrons into the deep DX state leads to pinning of the Fermi level at E_{DX}^{pin}. As shown in Fig. 2, the calculated pinning level $E_{DX}^{pin} = E_C - 0.6$ eV lies inside the gap of ZnSe, indicating that the DX center is the ground state of Ga_{Zn} dopants in n-type ZnSe, in accord with experiment [4]. Also in $CuGaSe_2$, $E_{DX}^{pin} = E_C - 0.8$ eV lies well inside the gap, indicating that the Ga_{Cu} double donors are deep and do not produce free electrons. Only in $CuInSe_2$, which has a relatively small band gap ($E_g = 1.0$ eV), $E_{DX}^{pin} = E_C - 0.1$ eV is sufficiently close to the CBM to allow for free-electron densities in the 10^{16} cm^{-3} range [6,8], before the electron trapping into the deep DX level occurs. Comparing the pinning levels E_{DX}^{pin} in ZnSe, $CuGaSe_2$, and $CuInSe_2$ on an absolute energy scale (Fig. 2), we see that E_{DX}^{pin} lies considerably lower in energy in the chalcopyrites compared to ZnSe. This observation is surprising at first, because the

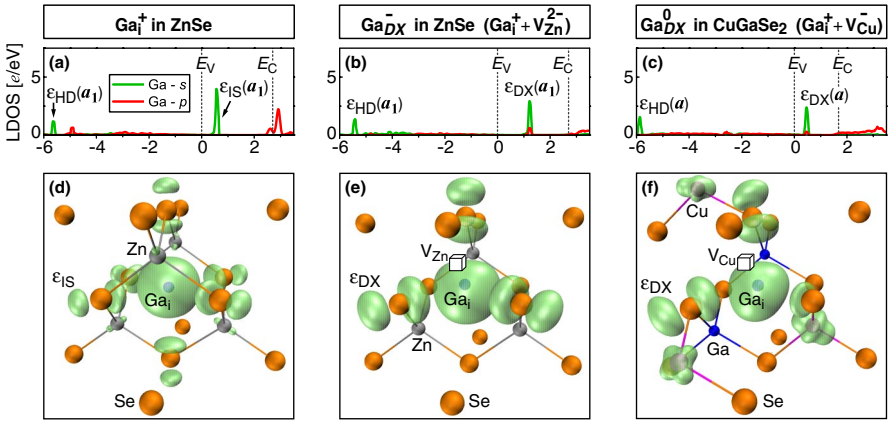

FIG. 1 (color online). The Ga-site local density of states (LDOS) with respect to E_V (in eV) for the Ga-interstitial in ZnSe, showing the hyper-deep state ε_{HD} and the gap level ε_{IS} of Ga_i^{+}, and for the DX centers Ga_{DX}^{-} in ZnSe and Ga_{DX}^{0} in $CuGaSe_2$, showing the deep ε_{DX} gap level. (d)–(f) The isosurface (green) of the wave function square for the ε_{IS} and ε_{DX} levels, depicting the respective electron orbits. The Frenkel-pair character of the DX centers is apparent in the atomic structure of $Ga_{DX}^{-} = (Ga_i^{+} - V_{Zn}^{2-})$ in ZnSe (e), and in that of $Ga_{DX}^{0} = (Ga_i^{+} - V_{Cu}^{-})$ in $CuGaSe_2$ (f).

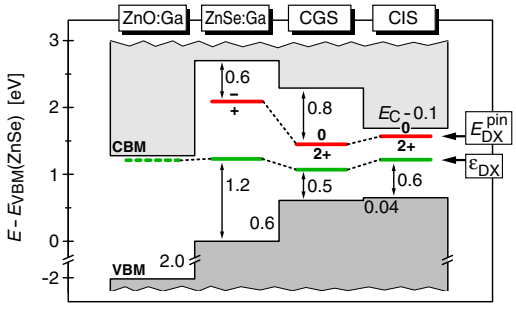

FIG. 2 (color online). The single-particle energies ε_{DX} (cf. Fig. 1) and the Fermi level pinning energies E_{DX}^{pin} caused by the DX state of Ga_{Zn} in ZnSe, of Ga_{Cu} in $CuGaSe_2$, and of In_{Cu} in $CuInSe_2$, on a common energy scale. For ZnO:Ga, where the DX center unstable, the single-particle energy of the unrelaxed $(Ga_i\text{-}V_{Zn})$ pair is shown.

DX center *single-particle* energies ε_{DX} are well aligned (Fig. 2). Considering, however, the Frenkel-pair character of the DX center, we find that this difference results from the much lower formation energy of the cation-vacancy partner of the Frenkel pair in the chalcopyrites: For example, we find $\Delta H(V_{Zn}^{2-}) = 4.3$ eV in ZnSe (under metal-rich conditions and for $E_F = E_V$), compared to only $\Delta H(V_{Cu}^{-}) = 0.6$ eV and $H(V_{Cu}^{-}) = 0.9$ eV in $CuGaSe_2$ and $CuInSe_2$, respectively.

While the spontaneous formation of V_{Cu} acceptors has been identified before as a cause of Fermi level pinning at $E_{VCu}^{\text{pin}} = E_V + 0.9$ eV in $CuInSe_2$ and at $E_V + 0.6$ eV $CuGaSe_2$ [6,7], the DX center can pin the Fermi level, simply by a change of the atomic configuration without the formation of new lattice defects. Thus, electron trapping into deep DX states can occur at room temperature, e.g., when free electrons are produced by photo-excitation during solar cell operation, whereas the spontaneous formation of charged Cu-vacancies generally occurs during crystal growth at higher temperatures.

DX behavior of antisite-vacancy defect pairs.—When the Fermi level E_F lies within ~1 eV from the VBM, as is the case in naturally p-type $CuInSe_2$ and $CuGaSe_2$ bulk or thin-film semiconductors [6], the mutual passivation between In_{Cu}^{2+} or Ga_{Cu}^{2+} donors and V_{Cu}^{-} acceptors leads to electrically inactive, *charge-neutral* complexes, e.g., $(In_{Cu}^{2+}\text{-}2V_{Cu}^{-})^0$ [10]. We find here that when E_F rises higher in the gap, the capture of electrons into the deep DX level of In_{Cu} or Ga_{Cu} leads the formation of *negatively charged* complexes, e.g., $(In_{Cu}\text{-}2V_{Cu})^0 + 2e \rightarrow (In_{DX}\text{-}2V_{Cu})^{2-}$. Since, compared to the isolated donors, the respective pinning levels of such complexes (Table I) are shifted only slightly towards higher energies, the $(In_{Cu}\text{-}2V_{Cu})$ defect pairs will affect solar cells in essentially the same way as isolated In_{Cu}. This finding is significant, since the formation of large quantities of isolated In_{Cu} and isolated V_{Cu} during crystal growth occurs very close to a 1:2 ratio [6], so that most In_{Cu} will eventually exist as $(In_{Cu}\text{-}2V_{Cu})$ pairs, whereas the amount of uncompensated isolated In_{Cu} donors stays below 10^{18} cm^{-3} [6].

TABLE I. The Fermi level pinning energies E_{DX}^{pin} (in eV) due to the transition of the substitutional M_{Cu} (M = In, Ga) donors into the deep DX state, given for the isolated M_{Cu} donors and their defect pairs with V_{Cu}. In parenthesis, the calculated values without the image charge correction of Ref. [16] are given. Note that transition energies above the band gap of pure $CuInSe_2$ ($E_g = 1.04$ eV) will occur inside the gap in the wider-gap $Cu(In, Ga)Se_2$ alloys typically used in solar cells.

Transition	$CuInSe_2$	$CuGaSe_2$
M_{Cu}^{2+}/M_{DX}^{0}	$E_V + 0.92(1.07)$	0.84(1.04)
$(M_{Cu}\text{-}V_{Cu})^{+}/(M_{DX}\text{-}V_{Cu})^{-}$	$E_V + 1.11(1.11)$	1.02(1.02)
$(M_{Cu}\text{-}2V_{Cu})^{0}/(M_{DX}\text{-}2V_{Cu})^{2-}$	$E_V + 1.30(1.15)$	1.36(1.16)

Configuration coordinate diagram of the intrinsic DX center.—In order to compare below the properties of the intrinsic DX center to experiment, we calculated the configuration coordinate diagram for the In_{Cu} donor in $CuInSe_2$ (Fig. 3): The neutral substitutional donor In_{Cu}^{0} (Fig. 3, left), has its single-particle level resonant inside the conduction band [18], and releases the electrons into a shallow, conduction-band-like perturbed-host state (PHS) just below the CBM, which produces free electrons, i.e., $In_{Cu}^{0} \rightarrow In_{Cu}^{2+} + 2e$. In the deep DX configuration In_{DX}^{0} (Fig. 3, right), which is the ground state for $E_F > E_{DX}^{\text{pin}}$ (Table I), two electrons occupy the deep, defect-localized state (DLS) ε_{DX} in the gap (see Ref. [19] for a discussion of different defect behaviors creating either a PHS or a DLS in the gap). The transition from the deep DX state into the shallow substitutional configuration can proceed in three ways (see Fig. 3): (i) Through optical recombination with free holes $In_{DX}^{0} + h \rightarrow In_{DX}^{+}$, and subsequent lattice relaxation of In_{DX}^{+} to the substitutional configuration. The optical transition is calculated from total-energies [19] at $E_{\text{PL}} = 0.25$ eV (since, Koopman's theorem does not apply in DFT, E_{PL} differs from the single-particle energy difference

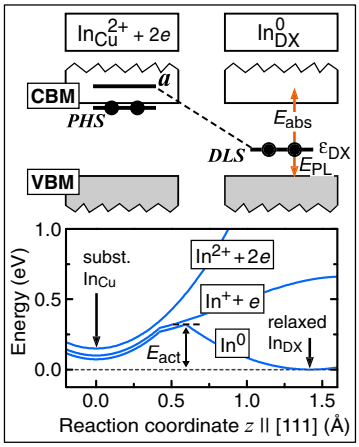

FIG. 3 (color online). Schematic defect level diagram and the calculated configuration coordinate diagram for the In_{Cu} donor in $CuInSe_2$. Note that increasing the band gap through Ga alloying increases the energy of the substitutional In_{Cu} configuration and the barrier height E_{act}.

$\varepsilon_{DX} - E_V$ in Fig. 2). Because of the small energy E_{PL}, the DX center will appear essentially as a nonradiative recombination center in most experiments. (ii) Through the optical absorption $In^0_{DX} \rightarrow In^+_{DX} + e$, and subsequent relaxation ($E_{abs} = 0.81$ eV). (iii) Through the activation of a structural energy barrier activation plus simultaneous electron emission to the CBM ($E_{act} = 0.32$ eV).

Effect of the DX center in solar cells.— Electrical characterization of ZnO/CdS/Cu(In, Ga)Se_2 n/p-heterojunction solar cells [22] has shown the trapping of photo-generated electrons upon illumination under reverse bias at low temperature (120 K). While the trap level must be close to the CBM, because it is initially empty at the high Fermi level above $E_C - 0.2$ eV ($\sim E_V + 1.0$ eV) close to the n/p-junction, the trapped electrons are not emitted up to 300 K, which implies an activation energy of at least 0.6 eV [22]. This apparently paradoxical behavior can be explained by our calculated DX transition energies (Table I) and configuration coordinate diagram: At a Fermi level above $E_V + 1.0$ eV, i.e., $E_F > E^{pin}_{DX}$ (Table I), the DX state is initially empty (Fig. 3, left). Photoexcitation of free electrons leads then to the filling of the trap, i.e., the electrons are captured into the deep DX state (Fig. 3, right). In the presence of free holes, the DX state is immediately emptied again due to recombination [cf. transition (i) above], explaining why the application of reverse bias, reducing the hole-concentration, was necessary in Ref. [22] to stabilize the trapped state. In the absence of free holes, the emptying of the electron traps occurs through activation of the barrier E_{act} (Fig. 3) and electron-emission [cf. transition (iii) above]. Using our transition-rate model [15] for activated transitions involving carrier-capture or emission, we find that electron-emission would occur at $\sim$160 K for the barrier $E_{act} = 0.32$ eV in $CuInSe_2$. Because of the larger band gap of the Cu(In, Ga)Se_2 alloys used in the experiment of Ref. [22], however, the barrier is larger there, and the metastable DX state persists up to 300 K.

While our predicted intrinsic DX behavior should be rather benign for smaller-gap $CuIn_{1-x}Ga_xSe_2$ absorbers ($x \leq 0.3$; $E_g \lesssim 1.2$ eV), the calculated E^{pin}_{DX} pinning energies (Fig. 2 and Table I) show that these defect complexes could be responsible for the limitation of the open-circuit voltage V_{OC} below 1 eV [5] (V_{OC} equals the difference in E_F between the two sides of the n-p-heterojunction under illumination). This is, because photoexcited electrons are trapped into the DX state and recombine with photoexcited holes when E_F [21] approaches E^{pin}_{DX}. Note, that the V_{Se}-V_{Cu} divacancy complex could be a second, independent source of V_{OC} limitation [15]. Thus, the control of intrinsic defects in Cu(In, Ga)Se_2 is essential for any attempt to improve solar cell efficiency through larger absorber band gaps (higher Ga content) in a single-junction cell, or through utilization of a wide-gap top cell (e.g., pure $CuGaSe_2$) in a tandem device design.

Conclusion.—In contrast to conventional III-V or II-VI systems, free-electron eliminating DX-like centers can develop in I-III-VI_2 ternary semiconductors even in the absence of extrinsic impurities. Close to a n/p heterojunction, these centers cause Fermi level pinning and trapping of photoexcited electrons, thereby limiting the efficiency of Cu(In, Ga)Se_2 photovoltaic absorbers.

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