Anion vacancies as a source of persistent photoconductivity in II-VI and chalcopyrite semiconductors

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Using first-principles electronic structure calculations we identify the anion vacancies in II-VI and chalcopyrite 
Cu-III-VI2 semiconductors as a class of intrinsic defects that can exhibit metastable behavior. Specifically, 
we predict persistent electron photoconductivity (n-type PPC) caused by the oxygen vacancy V_o in n-ZnO, 
originating from a metastable shallow donor state of V_o. In contrast, we predict persistent hole photoconductivity 
(p-type PPC) caused by the Se vacancy V_se in p-CuInSe2 and p-CuGaSe2. We find that V_se in the 
chalcopyrite materials is amphoteric having two “negative-U”-like transitions, i.e., a double-donor transition 
\( \varepsilon(2+0/0) \) close to the valence band and a double-acceptor transition \( \varepsilon(0/2- -) \) closer to the conduction band. 

I. INTRODUCTION

Impurities and defects in semiconductors create defect-localized states (DLS’s) that are located either in the band 
gap, or resonate within the continuum of the host bands. In general, different host/impurity combinations may be 
divided into two categories: those that create localized gap states, and those that create only resonant states. For example, a DLS 
located within the gap and below the conduction-band minimum (CBM, “\( \alpha \)-type behavior”) is created for most 3d impurities 
in III-V semiconductors, nitrogen, and oxygen in GaP, oxygen in ZnTe, hydrogen in MgO, or oxygen 
vacancies in Al2O3. On the other hand, the DLS is located above the CBM (“\( \beta \)-type behavior”) for nitrogen in GaAs, 
oxigen in ZnS or ZnSe, hydrogen in ZnO, oxygen vacancies in In2O3, as well as for all classic, hydrogenic 
genors in semiconductors. In the “DLS-below-CBM” case, one expects a deep level that has localized wave functions 
and that consequently responds only weakly to external perturbations such as pressure or temperature. Even if such a 
defect level is occupied, it usually does not lead to conductivity due to the localized nature of the state and the ensuing 
high activation energy. Conversely, in the \( \beta \)-type situation where the DLS is resonant with the conduction band, electrons 
in this level will drop to the CBM, and occupy a perturbed-host state (PHS, Ref. 4) rather than the DLS. In this 
case, a delocalized, hydrogeniclike state is created which is conductive and responds more strongly to external 
perturbations, due to its host-band-like character. 

There are unique cases where the same impurity in a solid can assume both type-\( \alpha \) and type-\( \beta \) behavior. This is the case 
for the “DX center”, where a donor atom such as Te in AlGaAs (Ref. 15) or Cl in CdZnTe (Ref. 16) exhibits the 
conducting “DLS-above-CBM” \( \beta \)-type behavior in its normal substitutional configuration, but after a large lattice 
relaxation involving bond breaking, it exhibits the insulating “DLS-below-CBM” \( \alpha \)-type behavior. The hallmark of the 
DX centers is the phenomenon of persistent photoconductivity (PPC), arising from the light induced configuration change from the nonconducting ground state to the metastable conductive state.

In this paper, we discuss the interesting case where intrinsic defects (not impurities) exhibit both \( \alpha \)-type and \( \beta \)-type 
behavior in the same solid, depending on their charge state. Remarkably, this occurs already for one of the simplest point 
defects, namely the anion vacancy in II-VI compounds and in their ternary analogs, i.e., in the I-III-VI2 chalcopyrites.

Through first-principles total-energy calculations, we show that the transition between \( \alpha \)- and \( \beta \)-type configurations 
results in metastable behavior of these defects. Specifically, we predict that the oxygen vacancy V_o leads to persistent 
electron photoconductivity (n-type PPC) in n-ZnO observed 
recently after proton irradiation, whereas the Se vacancy V_se causes persistent hole photoconductivity (p-type PPC) in 
p-CuInSe2 or p-CuGaSe2, constituting the unusual case where a donorlike defect causes p-type PPC. Thus, our results 
shed light on hitherto unknown physical origin of the phenomenon of light-induced metastability in chalcopyrite 
CuInSe2-based photovoltaic devices exhibiting p-type PPC. Here, this light-induced effect can even lead to performance 
enhancement, in stark contrast to “light-induced degradation” of other solar cells, e.g., Staebler-Wronski degradation in a-Si.24

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states (red solid lines in Fig. 1), as a function of the perturbation strength \( \Delta V = e_{\lambda \gamma}^{\text{H}} - e_{\lambda \gamma}^{\text{vac}} \), measured by the difference of atomic orbital energies between the impurity (\( I \)) atom and the host (\( H \)) atom it replaces.\(^{25}\) As one expects, for extremal values of \( \Delta V \) the energy of the DLS state saturates at the value of the host vacancy level. Indeed, when one regards the vacancy itself as the impurity, the energies \( e_{\lambda \gamma}^{\text{vac}} \) of the vacancy states are not altered by interaction with an impurity state \( e_{\lambda \gamma}^{\text{H}} \). As discussed below, the energies of the vacancy states can depend strongly on atomic relaxation, however.

In order to illustrate the range of physical behaviors that is implied with the \( \alpha \) vs \( \beta \) behavior, we now add in Fig. 1 schematically (for the specific case \( \lambda = \text{anion} \) and \( \gamma = a_1 \)) the position of the host band edges (blue horizontal solid lines), and integrate in the figure the examples GaP:O, ZnTe:O, GaAs:N, GaAs:Te, and the neutral anion vacancy \( V_0^0 \) in ZnO, which we discuss in detail below. In all those examples except for the vacancy, the occupied lower energy bonding state represents the impurity atomic-s state, e.g., O-2s, that lies deep below the valence-band maximum (VBM). What determines the physical behavior of the impurity is the energetic position of the DLS created by the antibonding combination of the vacancy and the impurity state. We see in Fig. 1 that the \( \alpha \)-type situation is realized for strongly attractive (i.e., electronegative) impurities with \( e_{\lambda \gamma}^{\text{H}} < e_{\lambda \gamma}^{\text{vac}} \). The host/impurity combinations of Fig. 1 produce the following different physical properties: (i) \( \alpha \)-type behavior for substitution by a donor: For example, GaP:O creates an occupied (closed circle in Fig. 1) deep nonconducting donor state. (ii) \( \alpha \)-type behavior for isoelectronic substitution: ZnTe:O creates an unoccupied (open circle in Fig. 1) acceptor state in the upper part of the gap. (iii) \( \beta \)-type behavior for isoelectronic substitution: For example, GaAs:N creates an unoccupied resonant DLS in the conduction band, but no transition level in the band gap. (iv) \( \beta \)-type behavior for substitution by a donor: GaAs:Te creates an occupied shallow conducting donor state. Here, the donor electron occupies the perturbed-host state (PHS) which is created below the CBM by the long-range, screened Coulomb potential introduced by the donor substitution.

In this paper, we will show that anion vacancies in II-VI and Cu-III-VI\(_2\) compounds can exhibit both type \( \alpha \) and \( \beta \) behavior: The neutral oxygen vacancy \( V_0^0 \) in ZnO shows \( \alpha \)-type behavior, where the doubly occupied DLS is below the CBM in the band gap (Fig. 1). However, the doubly charged state \( V_0^{\pm} \) (not shown in Fig. 1) has an unoccupied \( a_1^0 \) vacancy level above the CBM (\( \beta \)-type behavior with a resonant DLS), and creates a PHS below the CBM. Thus \( V_0^0 \) in ZnO can assume a nonconducting configuration, where both electrons are in the deep DLS (\( \alpha \)-type), and a conducting configuration, where the DLS is empty and the electrons occupy the shallow PHS (\( \beta \)-type).

Besides its use as a general classification, the distinction between scenario \( \alpha \) and \( \beta \) (Fig. 1) has a technical implication on total-energy supercell calculations: Due to the localized nature of an \( \alpha \)-type defect state, e.g., \( V_0^0 \) in ZnO or in Al\(_2\)O\(_3\), the effects of impurity-impurity interaction and impurity band formation are generally weak and can be rapidly suppressed by increasing the size of the supercell.\(^{26}\) However, due to the delocalized nature of a \( \beta \)-type defect, a highly

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**FIG. 1.** (Color online) Schematic energy-level diagram of a substitutional impurity in a semiconductor. Bonding and antibonding levels (red solid lines) are formed due to the interaction between the energy level \( e_{\lambda \gamma}^{\text{vac}} \) of the pure vacancy and the atomic energy level \( e_{\lambda \gamma}^{\text{H}} \) of the impurity atom (black dotted lines), as a function of the perturbation strength \( \Delta V = e_{\lambda \gamma}^{\text{H}} - e_{\lambda \gamma}^{\text{vac}} \), where \( e_{\lambda \gamma}^{\text{H}} \) is the atomic orbital energy of the replaced host atom (\( \lambda \) denotes the sublattice and \( \gamma \) the symmetry representation). \( \alpha \)- and \( \beta \)-type behavior is distinguished by the relative position of the antibonding state and the host CBM (blue solid line): The defect is \( \alpha \)-type when the DLS is below the CBM; it is \( \beta \)-type when the DLS is above the CBM, and forms a PHS (blue dashed line) just below the CBM.

**II. BASIC PHYSICS OF \( \alpha \)-TYPE AND \( \beta \)-TYPE DEFECT BEHAVIOR**

The distinction between these two types of behaviors can be appreciated from simple two-level models in which the impure system is described via the interaction between an ideal (unrelaxed) vacancy (vac) state \( e_{\lambda \gamma}^{\text{vac}} \) in the pure host crystal and the orbitals \( e_{\lambda \gamma}^{\text{H}} \) of the isolated impurity (I) atom (Fig. 1).\(^{3,25}\) Here, we consider only the dilute limit, where no interaction between impurity states exists. The vacancy of the pure host crystal can occur on either sublattice \( \lambda \) (i.e., \( \lambda = \text{cation} \) or \( \lambda = \text{anion} \)). Different vacancy levels can be constructed from the dangling bond hybrids of the neighboring host atoms, according to the irreducible representations \( \gamma \) of the corresponding \( \lambda \) site symmetry (e.g., \( \gamma = a_1 \) or \( \gamma = t_2 \) in the \( T_d \) point-group symmetry of the zinc-blende structure). We define \( e_{\lambda \gamma}^{\text{vac}} \) in Fig. 1 as the energy of the \( \lambda \)-site vacancy state with symmetry \( \gamma \). Similarly, the isolated impurity atom on site \( \lambda \) has symmetry-adapted orbitals with energy \( e_{\lambda \gamma}^{\text{H}} \). The two unperturbed states \( e_{\lambda \gamma}^{\text{vac}} \) and \( e_{\lambda \gamma}^{\text{H}} \) are shown in Fig. 1 as dotted lines, representing varying impurities in a fixed host system.

Vacancy and impurity states of the same symmetry \( \gamma \) interact and repel each other, creating bonding and antibonding
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dispersive impurity band\textsuperscript{1,9} forms already at rather low concentrations, leading to a Moss-Burstein shift to higher energies if the PHS is occupied. For example, Astala and Bristowe,\textsuperscript{27} as well as Buban and co-workers\textsuperscript{28} calculated $V_{\text{O}}^0$ in SrTiO$_3$ and observed strong changes in total energy and atomic relaxation with increasing cell size (up to 320 atoms). While long-range defect image interaction and long-range relaxation effects were invoked in Refs. 27 and 28, respectively, we note that such behavior could also be explained by the Moss-Burstein-like band-filling effect if $V_{\text{O}}^0$ in SrTiO$_3$ assumes the $\beta$-type scenario: in the limit of large supercells, the two electrons occupy the PHS, while the higher-energy DLS is unoccupied ($a_1^0$ configuration). With decreasing supercell size, the Moss-Burstein effect leads to an upward shift of the Fermi energy, so that the resonant DLS becomes partly occupied. Taking into account that the occupancy of the DLS controls the large lattice relaxations (viz. Ref. 29 and discussion below), both the change in total energy and in atomic relaxation can be explained by this interpretation.

III. METHOD OF CALCULATION

We use first-principles supercell calculations in order to determine the atomic structure, the single-particle defect levels, the defect formation energy $\Delta H$, as well as thermal (equilibrium) and optical (vertical) transition energies $\epsilon$ for the anion vacancy in II-VI and Cu-III-Se$_2$ compounds. Here, the formation energy of the vacancy is defined as

$$\Delta H_{\text{D},q}(E_F,\mu) = (E_{\text{D},q} - E_{\text{H}}) + (\mu_X^{\text{elem}} + \Delta \mu_X) + q(E_V + \Delta E_F),$$

(1)

where $E_{\text{D},q}$ is the total energy of the semiconductor with the defect $D$ (here, the vacancy) in charge state $q$, and $E_{\text{H}}$ is the energy of the pure host. The second term describes the chemical reservoir in equilibrium, where the chemical potential $\mu_X^{\text{elem}} + \Delta \mu_X$ of the removed anion $X$ is given with respect to the elemental phase. For the elemental reference $\mu_X^{\text{elem}}$, we choose the solid phase except for oxygen, where we choose the isolated O$_2$ molecule, i.e., $\mu_O^{\text{elem}}=\frac{1}{2}H_{\text{O}_2}$. The third term in Eq. (1) is the energy of the electron reservoir, i.e., the Fermi energy $E_F=E_V+\Delta E_F$ given with respect to the energy $E_V$ of the VBM. Note that the boundaries of the allowed range of $\mu_X$ are defined by the stability condition of the host material, e.g., $\Delta \mu_Z + \Delta \mu_O = \Delta H(ZnO)$, where $\Delta H$ is the calculated compound formation energy. In case of chalcopyrite, the range of chemical potentials is further restricted by formation of competing phases.\textsuperscript{30}

The thermal transition energy $\epsilon(q/q')$ is the Fermi energy where the lowest-energy charge state changes from $q$ to $q'$ as $\Delta E_F$ rises in the gap, i.e., where $\Delta H(q,q') = \Delta H(q',q)$. From Eq. (1), it follows that

$$\epsilon(q/q') = \frac{E_{\text{D}}(q') - E_{\text{D}}(q)}{q - q'}. $$

(2)

We also calculate the optical (vertical) transition energies, where the following transitions are considered: (i) Excitation of electrons from an occupied defect state to the CBM; the charge state $q$ of the defect changes by +1 during this transition. (ii) Photon emission due to the decay of an electron at the CBM into an unoccupied defect state; the charge state $q$ changes by −1. (iii) Excitation of an electron from the VBM into the unoccupied defect state; the charge state $q$ changes by −1. (iv) Photon emission due to the recombination of an electron in the defect state with a hole at the VBM; the charge state $q$ changes by +1.

Keeping the VBM as reference, i.e., taking $\Delta E_F=0$ for calculation of $\Delta H$ in Eq. (1), we calculate all optical transition energies from total energy differences. We fix the relaxed atomic positions of the initial state, assuming the Franck-Condon principle. Thus, transitions (i) and (ii) which communicate with electrons (e) at the CBM are calculated as (with $n=+1$ and $n=-1$, respectively)

$$\epsilon_e(q/q+n;ne) = \Delta H(q+n) - \Delta H(q) + nE_e, $$

(3)

where $E_e$ is the (experimental) band-gap energy. Similarly, transitions (iii) and (iv) which communicate with holes (h) at the VBM are calculated as (with $n=+1$ and $n=-1$, respectively)

$$\epsilon_e(q/q-n;nh) = \Delta H(q-n) - \Delta H(q). $$

(4)

Note that only the ground-state energies for the respective charge states enter in Eqs. (3) and (4). Excitation (absorption, $n=+1$) energies are calculated as positive energies from Eqs. (3) and (4), while recombination (emission, $n=-1$) energies are calculated as negative. Such calculated optical transition energies have been used in Ref. 29 to explain the experimentally observed absorption energies in case of the color centers $V_S$ in ZnS and $V_{\text{Se}}$ in ZnSe.

The total energies and atomic forces were calculated in the pseudopotential-momentum space formalism\textsuperscript{31} within the local-density approximation (LDA) of density-functional theory. We use the Ceperley-Alder LDA exchange correlation potential as parametrized by Perdew and Zunger\textsuperscript{32} and projector augmented wave potentials\textsuperscript{33} as implemented in the VASP code.\textsuperscript{34} The energy cutoff in the plane-wave expansion was up to 400 eV. Most results were obtained from supercells with 64 lattice sites for the zinc-blende and chalcopyrite structures, and with 72 sites for the wurtzite ZnO, using experimental lattice constants. Brillouin-zone integrations were performed on a $\Gamma$-centered $3\times3\times3$ mesh ($3\times3\times2$ in ZnO) using the improved tetrahedron method.\textsuperscript{35}

The well-known LDA band-gap error is corrected by acknowledging that the cation-$d$ states in II-VI and chalcopyrites are too shallow on account of their strong, spurious self-interaction.\textsuperscript{32b} Indeed, calculations in the $GW$ approximation which largely correct for the LDA band-gap error, show, e.g., for the II-VI compounds ZnO, ZnS, and ZnSe\textsuperscript{36-38} and for MnO\textsuperscript{39} that the occupied cation-$d$ bands shift downwards relative to LDA. We use here the approximate LDA+U method\textsuperscript{40} to lower the Zn-3d ($U=7$ eV, $J=0$) and Cu-3d ($U=5$ eV, $J=0$) bands so as to yield agreement of the $d$-like density of states with Zn and Cu photoemission data in II-VI and chalcopyrite\textsuperscript{41-44} respectively. This $d$-band lowering weakens the $p$-$d$ repulsion with the anion-$p$ orbitals\textsuperscript{45} and lowers the energy of the VBM. We determine the correction $\Delta E_V$ for the energy of the VBM as the difference of the pure host VBM in LDA+U vs LDA, measured with
respects to the anion-$s$ like $\Gamma_{1g}$ state. Thus $E_V$ in Eq. (1) is corrected by $\Delta E_V=-0.77$, $-0.34-0.28$, and $-0.20$ eV in ZnO, ZnS, ZnSe, and ZnTe, respectively, and by $\Delta E_V= -0.37$ eV in CuGaSe$_2$ and CuInSe$_2$. The amount of correction in the VBM is consistent, e.g., with the GW calculations for ZnO.\textsuperscript{46} Still, the LDA+$U$ band gaps, e.g., $1.53$ eV in ZnO and $\sim0$ eV in CuInSe$_2$, are much smaller than the experimental gaps [3.37 eV in ZnO (Ref. 47) and 1.04 eV in CuInSe$_2$ (Ref. 48)]. The remaining discrepancy is accommodated by shifting CBM upwards (by $\Delta E_C$). In practice, we implement this correction by using the experimental band-gap energy $E_g$ in Eq. (3) and for the allowed range $0 \leq \Delta E_F=\Delta E_C$ of $E_F$ in Eq. (1). We use the LDA+$U$ scheme only to obtain the correction for the host band edges. The formation and transition energies presented in this work are obtained from Eqs. (1)–(4) using supercell total energies that are calculated in LDA. (We find, however, that the transition energies of $V_{\text{anion}}$ calculated from LDA+$U$ supercell energies differ only slightly.)

In the case of $\beta$-type defects that introduce electrons in the PHS, e.g., in the case of shallow donors, a correction $n\Delta E_C$ applies to $\Delta H$ when the PHS is occupied by $n$ electrons. This is because the donor PHS can be assumed to shift along with the host CBM during band-gap correction. Similarly, a correction $-n\Delta E_V$ is applied to shallow acceptors when the acceptor state (valence-band-like PHS) is occupied by $n$ holes. This is because the acceptor PHS can be assumed to shift along with the host VBM during band-gap correction. In the case of $\alpha$-type defects, where the electrons or holes occupy the DLS rather than the host-band-like PHS, the latter two corrections are not applied, because it cannot be assumed that the localized DLS follows the band edges during band-gap correction. This procedure of letting the shallow levels ($\beta$-type PHS) follow the host band edges, but fixing the deep levels ($\alpha$-type DLS) during band-gap correction differs from our previously employed schemes of band-gap correction, e.g., in Refs. 49 and 50. Indeed, the question of the extent of LDA-correction applied to $\alpha$-type levels is a significant source of uncertainty in this and other\textsuperscript{49,50} calculations. In order to assess more quantitatively how deep, $\alpha$-type levels behave upon band-gap correction, GW calculations for such deep defects will be needed.

Several further corrections to the LDA calculated energies were applied, as discussed in more detail in another publication\textsuperscript{51}. First, Moss-Burstein-like band-filling effects (cf. Sec. II) occur when electrons or holes occupy a perturbed-host state forming an impurity band in the supercell calculation. Such band-filling effects have also to be taken into account when, e.g., an unoccupied defect level drops below the VBM in the course of atomic relaxation, thus releasing holes to the valence band (cf. Sec. V). Second, the potential alignment between a charged defect calculation and the perfect host crystal is needed in order to correct for the effect of the compensating background charge. Third, the spurious interaction of periodic image charges is corrected to $O(L^{-5})$\textsuperscript{52}, where $L$ is the linear supercell dimension. The present scheme of treating finite supercell size effects and LDA errors has shown to yield good results for the optical transition energies of the color center in ZnS and ZnSe\textsuperscript{29} when compared with experimentally observed absorption energies.

IV. ANION VACANCIES IN ZnO AND OTHER II-VI

Having introduced in Sec. II the model of $\alpha$- vs $\beta$-type behavior for the general case, where the impurity atomic orbitals interact with the states of the ideal vacancy, we now turn to the levels of the relaxed anion vacancy in ZnO and other II-VI compounds. As we have shown previously\textsuperscript{29}, the energies of the vacancy orbitals (e.g., $a_1$ and $t_2$ in $T_d$ symmetry) depend strongly on atomic relaxation of the cation neighbors. This is because these orbitals are constructed themselves from combinations of the dangling bond hybrids centered at each of the four cation neighbors, the totally symmetric $a_1$ state being bonding like. An inward relaxation increases the overlap between the dangling bond hybrids, thus lowering the energy of the $a_1$ state. Generally, the occupation of this bonding-like state in the neutral charge state $V_0^0$ ($a_1^0$ configuration) leads to atomic relaxation that brings the neighboring cations closer, while in the ionized $V_0^0$ state ($a_1^0$), the cations relax outwards to a near-planar atomic configuration\textsuperscript{29}.

A. Oxygen vacancies cause $n$-type PPC in ZnO

Figure 2(a) shows the LDA calculated angular-momentum decomposed vacancy-site local density of states (DOS) of the relaxed neutral ($V_0^0$) and charged ($V_0^+$) oxygen vacancy in ZnO, and the DOS of the host semiconductor. We see that the relaxed neutral vacancy $V_0^0$ in ZnO [Fig. 2(a), middle panel] has an occupied $a_1$ symmetric ($s$-like) state in the band gap. [Note that the correction $\Delta E$ described in Sec. III shifts this level to somewhat higher energies with respect to the VBM than indicated in Fig. 2(a)]. Thus $V_0^0$ assumes the $\alpha$-type DLS-below-CBM behavior, outlined in the Introduction and in Fig. 1. The energy of this state is deepened by the inward relaxation of the nearest-neighbor Zn atoms towards the vacancy site, leading to a local symmetry with one Zn atom at 1.78 Å from the vacancy, and three Zn atoms at 1.83 Å from the vacancy. The resulting average Zn-Zn distance is $d_{\text{Zn-Zn}}=3.0$ Å, compared to $d_{\text{Zn-Zn}}=3.23$ Å in the unperturbed ZnO lattice.

When forming the ionized $2^+$ state $V_0^{2+}$, in which the DLS is unoccupied, the Zn neighbors relax instead outwards, leading to a configuration with a much larger $d_{\text{Zn-Zn}}=4.0$ Å. As a result of the outward relaxation, the $a_1$ state is shifted to higher energies, becoming a broad unoccupied resonance in the conduction band at $\sim E_C+0.4$ eV [Fig. 2(a), bottom panel]. Thus, the ionized $V_0^{2+}$ creates a PHS below the DLS, constituting $\beta$-type behavior.

Figure 3(a) summarizes schematically the calculated energy levels discussed above. Upon photoexcitation, the electrons in the occupied DLS of $V_0^0$ [Fig. 3(a), left-hand side] are promoted into the conduction band, creating the ionized state $V_0^{2+}$ [Fig. 3(a), right-hand side]. This process is described by the semiquantitative\textsuperscript{53} configuration coordinate diagram, shown in Fig. 3(b): First, both electrons occupy the deep and nonconducting $\alpha$-type state $V_0^0$. The average Zn-Zn distance, serving as the reaction coordinate, is small in this configuration ($d_{\text{Zn-Zn}}=3.0$ Å). Optical excitation of the $V_0^0$ ground state to the $V_0^{2+}+e$ excited state occurs at the energy $\varepsilon_o(0+/+e)=+2.83$ eV. This transition creates $V_0^{2+}$ having a
singly occupied DLS within the band gap, i.e., being \( \alpha \)-type. The equilibrium Zn-Zn distance of \( V_{\text{O}}^0 \) is estimated as \( d_{\text{Zn-Zn}} \approx 3.2 \) Å [Fig. 3(b)]. Due to the single occupancy of the DLS, the \( V_{\text{O}}^+ \) state is active in electron paramagnetic resonance (EPR), and is indeed observed in EPR experiments under illumination. A second excitation \( V_{\text{O}}^+ \rightarrow V_{\text{Se}}^{2+} + e \) occurs at \( E_s / +2 + e = +2.4 \) eV, producing the \( V_{\text{Se}}^{2+} \) state with \( d_{\text{Zn-Se}} = 4.0 \) Å [Fig. 3(b)]. Following this large outward relaxation, the DLS moves upward, becoming resonant inside the conduction band [Fig. 3(a), right-hand side]. Consequently, the photoexcited electrons occupy the lower energy PHS rather than the DLS, i.e., the \( V_{\text{O}}^0 \) vacancy assumes \( \beta \)-type behavior [Fig. 3(a), right-hand side]. The electrons in the PHS are now only shallowly bound through the screened Coulomb potential.

Figure 4(a) shows as a function of the Fermi energy \( E_F \) the formation energies of the light-induced metastable configuration of \( V_{\text{O}}^0 \) and \( V_{\text{O}}^+ \) (dashed lines), relative to the corresponding formation energies in the respective equilibrium stable configuration (solid lines). The transition energies in the metastable \( \beta \)-type configuration [open circles in Fig. 4(a)] are close to the CBM, so that this configuration is conductive. These shallow binding energies of the electrons in the PHS are also schematically indicated in Fig. 3. The reaction path including both excitations in Fig. 3(b) leads to the light-induced transition

\[
V_{\text{O}}^0 \rightarrow V_{\text{Se}}^{2+} + 2e, \tag{5}
\]

which results in metastable configuration change from non-conducting \( \alpha \)-to conducting \( \beta \)-behavior, constituting persistent electron photoconductivity (\( n \)-type PPC).

The unoccupied DLS of \( V_{\text{O}}^0 \) drops below the (experimental) CBM at a Zn-Zn distance of \( d_{\text{Zn-Zn}} \approx 3.7 \) Å. Since the atomic relaxation from the large Zn-Zn distance (\( \beta \)-type) to the small Zn-Zn distance (\( \alpha \)-type) is controlled by the occupancy of the DLS, the light-induced \( \beta \)-type configuration with an empty DLS (\( a^0 \)) is (meta)stable against the depopulation of electrons from the PHS into the deep ground state with an energy barrier \( \Delta E \approx 0.2 \) eV [Fig. 3(b)]. In order to return into the \( \alpha \)-type deep ground state \( V_{\text{O}}^0 \) with small \( d_{\text{Zn-Se}} \), the metastable state must be thermally activated across \( \Delta E \) and, simultaneously, an electron must be captured by the DLS from the conduction band. The requirement of these two conditions to be met at the same time leads to a slower decay of the PPC than expected from an activation across \( \Delta E \approx 0.2 \) eV alone.

\section*{B. Transition and formation energies of \( V_{\text{O}} \) in ZnO: Comparison with experiment}

We compare our calculated optical transition energies of the oxygen vacancy with recent experimental findings obtained by optically detected magnetic resonance (ODMR) (Refs. 58 and 59) and photoluminescence excitation (PLE) spectroscopy studies. The green emission of ZnO around 2.45 eV was identified by ODMR as arising from a \( S=1 \) spin triplet state attributed to \( V_{\text{O}}^0 \). In addition, the PLE experiments in Ref. 60 have shown that the \( S=1 \) state can be produced by sub-band-gap light of 3.1 eV. The latter energy is only little higher than our calculated optical transition energy \( E_s (0/+ + e) = +2.83 \) eV corresponding to the \( V_{\text{O}}^0 \rightarrow V_{\text{Se}}^{2+} + e \) transition. Thus, we interpret both the experimental results in the following way: First, the neutral \( V_{\text{O}}^0 \) is excited to \( V_{\text{O}}^+ \), where the electron is released to the conduction band [the
Due to its positive charge, $V_0^+$ creates a hydrogenic-like PHS below the CBM, which can be populated by a conduction-band electron. The spin of the electron in the PHS can align either parallel $S=1$ or antiparallel $S=0$ with the spin of the electron in the deep $\alpha_1$ state (DLS) of $V_0^+$. While the short-lived singlet $S=0$ state does not give rise to any ODMR signal, the triplet $S=1$ state is active in ODMR and has a rather long lifetime, because the radiative recombination of the electron from the PHS into the DLS involves a spin flip. This recombination causes the green emission at 2.45 eV, corresponding to the theoretical $\varepsilon_0(+/0;+e)\approx-2.1$ eV transition in Fig. 3(b).

The observation of a $S=1$ state in the recent experiments using moderately $n$-type samples contrasts with the observation of a $S=1/2$ state in the classic EPR experiments, where the samples were compensated either by additional Li.
doping\textsuperscript{55} or by high-energy electron irradiation,\textsuperscript{54,62} which creates a variety of intrinsic defects. This behavior is readily understood in our model where the $\alpha$-type $V_O^0$ forms the triplet state by binding a conduction-band electron in $n$-ZnO, but not in the compensated samples, where photoexcited electrons can recombine with acceptor states, or relax from the conduction band into other donor states.

Very recently, after completion of our calculations and submission of our paper, ODMR experiments in high-energy electron irradiated ZnO were reported.\textsuperscript{63} Before the electron irradiation, the $S=1$ triplet was detected, similar to what was observed in Refs. \textsuperscript{58 and 59}. This required excitation above the energy threshold of 3.1 eV required for the $V_O^0 \rightarrow V_O^0+e\text{ transition}$. After the electron irradiation, only the $S=1/2$ state was observed. This state was also produced by excitation far below the 3.1 eV absorption level, indicating that in the defect-rich irradiated samples, where electrons and holes can be created by sub-bandgap illumination, there exist other channels for the excitation of the paramagnetic $V_O^0$ state, such as, e.g., $V_O^0+h\rightarrow V_O^0$. In fact, already the classic $F$-center experiments\textsuperscript{62} showed, in addition to the 3.1 eV level, a broad absorption band in the EPR excitation spectrum with an onset around 1.6 eV and a maximum around 2.3 eV. In Ref. \textsuperscript{63}, the authors showed that the ODMR of the $S=1/2$ state of $V_O^0$ results from a spin-dependent electron capture process, where an electron is transferred from a shallow donor into the $a_1^\prime$ level of $V_O^0\text{, thus forming }V_O^0(\alpha_1^\prime)$. They suggest two models that cannot be distinguished by their experiment: In the first, direct model, the photoluminescence used to detect the ODMR originates from the radiative electron capture itself. Taking into account the Stokes shift, this model places the $\epsilon(+/0)$ level at $-E_V+0.9$ eV. In the second, indirect model, the luminescence results from a subsequent hole capture of $V_O^0$. In this model, the $\epsilon(+/0)$ would be at $-E_V+2.5$ eV. Our numerical result $\epsilon(+/0)=0.94$ eV is in very good agreement with the direct model (cf. Fig. 4 and discussion of thermal transition energies below), but inconsistent with the indirect model.

Whether $V_O^0$ is present in ZnO in relevant concentrations, depends on the thermodynamic boundary conditions during crystal growth, i.e., on the chemical potentials $\Delta\mu$, and on the position of the Fermi energy $\Delta E_F$ in the gap, which depends on doping. For the limit of maximally oxygen-poor conditions under which $\Delta H(V_O^0)$ is lowest, i.e., $\Delta\mu_O = \Delta H(V_O^0)(\text{ZnO})=-3.53$ eV, Fig. 4(a) shows as a function of $\Delta E_F$ the formation and transition energies for the different charge states in their equilibrium configuration (solid lines and closed circles).\textsuperscript{64} We see that $\Delta H(V_O^0)=0$ at $E_F=E_V+1$ eV, which means that $V_O^0$ forms spontaneously and acts as a hole killer when $E_F$ approaches the VBM. The formation energy of $V_O^0$, being the equilibrium stable state in $n$-ZnO, is $\Delta H(V_O^0)=1.14$ eV under oxygen-poor conditions, which yields an equilibrium concentration of, e.g., $c(V_O^0) = 10^{17}$ cm$^{-3}$ at $T=1000$ K. The rather high formation energy $\Delta H(V_O^0)=4.67$ eV under oxygen-rich growth conditions ($\Delta\mu_O=0$) indicates that significant concentrations of $V_O^0$ would not occur under these conditions, except if $E_F$ would be close to the VBM (i.e., in $p$-type ZnO), in which case $\Delta H$ of $V_O^0$ is lowered by forming the ionized $V_O^{2+}$ state [cf. Fig. 4(a)].

As a consequence of the large lattice relaxations in the neutral and in the fully ionized (2+) state, the calculated transition energies of Fig. 4(a) show a net attractive electron-electron interaction, i.e., a negative effective Hubbard-$U$ of $U_{\text{eff}}=-1.32$ eV, being typical for anion vacancies in II-VI semiconductors.\textsuperscript{65} Figure 4(a) shows the thermal transition energies between the equilibrium configurations of the respective charge states (closed circles).\textsuperscript{58} Due to the negative-$U$ behavior, the first ionization energy $\epsilon(+/0)=E_V+0.94$ eV is deeper (farther from the CBM) than the second ionization energy $\epsilon(2+/+)=E_V+2.26$ eV, leading to a calculated $\epsilon(2+/0)$ transition at $E_F=E_V+1.60$ eV from the 2+ state directly into the neutral state. Owing to this deep transition level, the equilibrium stable $\alpha$-type configuration of $V_O^0$ is not expected to provide for $n$-type doping. While Zn$_i$ and hydrogen have recently been identified as a source of $n$-type conductivity in ZnO,\textsuperscript{60,61} an additional contribution could, however, arise from PPC of $V_O$ under illumination, due to the shallow transition energies of the $\beta$-type metastable configuration [open circles in Fig. 4(a)]. Note that the back transition from the conducting ($\beta$-type) to the nonconducting ($\alpha$-type) configuration requires thermal activation across $\Delta E$ [Fig. 3(b)] and simultaneous capture of an electron. Thus, the lifetime of our predicted metastable shallow donor state of $V_O$, and hence its concentration during constant illumination, should increase with decreasing temperature and electron concentration. Our results further suggest that the recently observed\textsuperscript{58} persistent increase of capacitance after illumination of proton-irradiated ZnO results from PPC of oxygen vacancies created by the irradiation.

Comparing our results on $V_O$ with other first-principles calculations, we note that only the energies of the ground-state configurations [solid lines in Fig. 4(a)] have been calculated so far, and that there exists quite a spread in the values of the calculated formation and transition energies in literature. For example, $\Delta H(V_O^0)$ in the oxygen-rich regime is calculated as $\sim 3$ eV,\textsuperscript{67} 4.0 eV,\textsuperscript{68} and 5.5 eV.\textsuperscript{49} The $\epsilon(2+/0)$ transition energy was found within 0.5 eV from the VBM in Refs. 68 and 67, but high in the gap around $\sim E_V+2.7$ eV in Refs. 49 and 69. Such discrepancies arise mainly due to different methodologies to correct the LDA band-gap error, but may to some extent\textsuperscript{70} also stem from different choices of the host lattice constants, which can be taken from experiment (present work), or be determined in LDA (smaller than experiment),\textsuperscript{58} or in the generalized gradient approximation (GGA, larger than experiment).\textsuperscript{67} Regarding the accuracy of our present results, which are well within the range of literature data, the good agreement of the calculated optical transition energies with experimental data within our method (Ref. 29 and present work) gives us confidence that the calculated formation energies are accurate within a few tenths of an eV.

C. Anion vacancies in ZnO vs other II-VI compounds

We next discuss the possibility of metastable behavior and occurrence of PPC in other II-VI compounds. For ZnO, ZnS, ZnSe, and ZnTe, Fig. 5 shows both the calculated single-particle $\alpha_1$ energy levels and the $\epsilon(2+/0)$ transition energies.
of $V_X$ ($X=O$, $S$, $Se$, and $Te$). The band edges are aligned according to the calculated\textsuperscript{71,72} band offsets, taking also into account the present correction $\Delta E_V$ for the VBM (see Sec. III). According to our reaction path for the light-induced transition from $\alpha$ to $\beta$ behavior (Fig. 3), two conditions have to be satisfied for the occurrence of PPC: (i) The neutral charge state $V^0_X$ must be the initial equilibrium stable state. This means that PPC can occur only when the Fermi level is above the $e(2+/0)$ transition level. Since the calculated $e(2+/0)$ level (blue line in Fig. 5) is located around mid-gap in all II-VI compounds, PPC can occur in $n$-type, but not in $p$-type material. (ii) $V^0_X$ must assume the conducting $\beta$-type behavior, i.e., the unoccupied $a^0_1$ has to be above the CBM (otherwise, the photoexcited electrons relax into the DLS and the vacancy returns into the nonconducting $\alpha$-type $V^0_X$ state without activation). Comparing the single-particle energies of the unoccupied $a^0_1$ state of $V^0_X$ (red line in Fig. 5), we see that the $\beta$-type DLS-above-PHS scenario is realized only in ZnO. This reflects the unusually low conduction band (high electron affinity) of ZnO. Thus, among the Zn-based II-VI compounds, persistent photoconductivity is expected only in ZnO, provided that the Fermi level lies in the upper part of the gap above the $e(2+/0)$ level, e.g., in $n$-ZnO. We note that a previous study in CdTe (Ref. 73) has shown that also the doubly charged $V^0_{Te}$ has the DLS above the CBM, so that the Te vacancy in CdTe is likely to exhibit similar metastability as $V^0_O$ in ZnO.

It is interesting to compare the chemical trends in the anion vacancy electronic states along the ZnO-$\rightarrow$ZnS $\rightarrow$ZnSe$\rightarrow$ZnTe series while taking into account the valence-band offset.\textsuperscript{71,72} For $V^0_X$, we find that the occupied $a^0_1$ state comes closer to the VBM along this sequence, but shifts effectively to higher energies from ZnO to ZnTe (Fig. 5). Had the Zn dangling bonds been constructed only from Zn atomic orbitals, one would expect an alignment of the Zn-Zn metal bond on an absolute scale. Analysis of the wave functions shows, however, that the dangling bonds are constructed from Zn-3$s$/$p$ and from anion-$p$ orbitals of those anions that are also neighbors to the nearest-neighbor Zn atoms. Because the atomic anion-$p$ orbital energy increases from O to Te, this admixture of O-$p$, S-$p$, Se-$p$, or Te-$p$ contributions into the Zn-centered dangling bond causes an increase of the DLS energy on an absolute scale.

In ZnO, we find that $V^0_O$ has locally a near-tetrahedral ($T_d$) symmetry, with one Zn atom relaxing inwards by a slightly larger amount than the other three equivalent Zn neighbors. In the other II-VI compounds with larger size anions, we find an unexpected symmetry-lowering relaxation mode with orthorhombic $C_{2v}$ symmetry,\textsuperscript{25} where two cation neighbors relax inwards and two relax outwards. The calculated metal-metal distances around the anion vacancy are given in Table I for the different symmetries. The total-energy difference $E[C_{2v}]-E[T_d]$ between the fully relaxed and the constrained $T_d$ symmetric structure is calculated to be $-0.11$, $-0.32$, and $-0.57$ eV for ZnS, ZnSe, and ZnTe, respectively,\textsuperscript{74} showing that the lower $C_{2v}$ is stabilized by a larger anion. This can be understood as a competition between the energy gain resulting from the lowering of the DLS level following by the inward relaxation, and the energy loss due to elastic deformation of $N$ bonds. We see in Table I that in case of ZnO, already the near-$T_d$ configuration with $N=4$ leads to a rather close Zn-Zn distance of 3.0 Å, while in the larger-anion compound ZnTe, the inward relaxation is limited by the elastic energy loss for $N=4$, leading to a rather large $d_{Zn-Zn}$.

### Table I. Calculated distances between the metal neighbors to the anion vacancy in II-VI and I-III-VI \(_2\) semiconductors.

<table>
<thead>
<tr>
<th></th>
<th>ZnO</th>
<th>ZnS</th>
<th>ZnSe</th>
<th>ZnTe</th>
<th>CuGaSe(_2)</th>
<th>CulnSe(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V^0_{\text{anion}})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T_d)</td>
<td>~3.0</td>
<td>3.48</td>
<td>3.63</td>
<td>3.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_{2v}) (in)</td>
<td>2.59</td>
<td>2.52</td>
<td>2.48</td>
<td>2.83 (Ga-Ga)</td>
<td>3.04 (In-In)</td>
<td></td>
</tr>
<tr>
<td>(C_{2v}) (out)</td>
<td>4.52</td>
<td>4.86</td>
<td>5.29</td>
<td>4.91 (Cu-Cu)</td>
<td>5.15 (Cu-Cu)</td>
<td></td>
</tr>
<tr>
<td>(V^0_{\text{anion}})</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T_d)</td>
<td>~4.0</td>
<td>4.83</td>
<td>5.06</td>
<td>5.40</td>
<td>5.29 (Ga-Ga)</td>
<td>5.45 (In-In)</td>
</tr>
<tr>
<td>(C_{2v}) (out)</td>
<td>4.96</td>
<td>5.21</td>
<td>5.21</td>
<td>3.93</td>
<td>4.10</td>
<td></td>
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<tr>
<td>Host</td>
<td>3.23</td>
<td>3.83</td>
<td>4.01</td>
<td>4.30</td>
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charged/H20849 CuInSe\textsubscript{2} and CuGaSe\textsubscript{2} lies much lower in energy than the \( V \) relaxed middle panel.

ture of dinitrated by two Cu atoms and two In atoms. The local structures show that the lowest energy configuration for the anion vacancy in the chalcopyrite materials is always assumed when the dimer is formed by the group-III atoms (Ga, In) while the Cu atoms relax outward (Table I). As we found in the II-VI semiconductors each anion has four identical cation neighbors, in chalcopyrites, e.g., CuInSe\textsubscript{2}, the anion is coordinated by two Cu atoms and two In atoms. The local structure of \( V^0_{\text{Se}} \) in CuInSe\textsubscript{2} and CuGaSe\textsubscript{2} has two cations moving inwards and two moving outwards. The total-energy calculations show that the lowest energy configuration for the anion vacancy in the chalcopyrite materials is always assumed when the dimer is formed by the group-III atoms (Ga, In) while the Cu atoms relax outward (Table I). As we found in the II-VI compounds, the wave function of the occupied DLS of \( V^0_{\text{Se}} \) is made of \( s \) and \( p \) contributions at the cation site (Ga, In). Since the energies of the atomic cation \( s \) and \( p \) orbitals become deeper along the sequence Cu→Zn→Ga/In, this explains the very deep energies of the anion vacancy DLS in chalcopyrites (Ga-Ga dimers with deep energies) relative to II-VI compounds (Zn-Zn dimers with shallower energies). We also see why Ga-Ga and In-In dimer formation is favorable over Ga-Cu, In-Cu, or Cu-Cu combinations.

When forming the ionized 2+ state \( V^+_{\text{Se}} \), in which the DLS is unoccupied, both the neighboring Cu and group-III atoms relax outwards (Table I). As a result of the outward relaxation, the DLS of \( V^+_{\text{Se}} \), i.e., the \( d^0 \) single-particle level (cf. Figs. 2 and 5), is shifted to higher energies becoming an unoccupied resonance in the conduction band, similar to the situation in ZnO. Thus, we observe a change from \( \alpha \)-\( (V^0_{\text{Se}}) \) to \( \beta \)-\( (V^+_{\text{Se}}) \) behavior like in ZnO, but with the important distinction that the DLS of the neutral vacancy in the chalcopyrite materials is located not only below the CBM, but even below the VBM. These results are summarized in Fig. 6(a). In the \( V^+_{\text{Se}} \) state where the DLS is singly occupied \( (a^1) \), the inward relaxation of the group-III atoms leads to the same structure as for \( V^0_{\text{Se}} \) with the DLS deep below the VBM. This is seen in Fig. 6 showing schematically the calculated energy levels for \( V_{\text{Se}} \) in CuInSe\textsubscript{2} [Fig. 6(a)] and the corresponding configuration coordinate diagram [Fig. 6(b)]. During relaxation, the \( a^1 \) state of \( V^0_{\text{Se}} \) becomes doubly occupied and releases one hole to the VBM, i.e., \( V^0_{\text{Se}} \) is unstable against \( V^+_\text{Se} \rightarrow V^0_{\text{Se}} + h \). A similar behavior of \( V^0_{\text{Se}} \) was observed in CuGaSe\textsubscript{2}.

Figure 2(b) shows that \( V^0_{\text{Se}} \) introduces also an empty gap state \( (b^0) \). The \( p \)-like character in the angular momentum decomposition with respect to the vacancy site [Fig. 2(b), middle panel] indicates that this level originates from an antibonding combination of the In-centered dangling bond orbitals. When this state is occupied, \( V^0_{\text{Se}} \) assumes the

FIG. 6. (Color online) (a) Schematic energy diagram for \( V^0_{\text{Se}} \) in CuInSe\textsubscript{2}, causing \( p \)-type PPC. (b) Configuration coordinate diagram, where the calculated defect formation energies \( \Delta H \) (squares) refer to Se-rich conditions \( (\Delta \mu_{\text{Se}}=0) \) and to \( \Delta E_F=0 \) (the relative energies of the branches do not depend on \( \Delta E_F \)). Note that the LDA calculated formation energies for \( V^0_{\text{Se}} \) and \( V^+_{\text{Se}} \) are underestimated when \( d_{\text{In-In}} \) exceeds 3.9 Å (dotted lines, cf. Ref. 53). In these cases, the solid lines show a qualitative continuation of the \( \Delta H \). In the metastable \( \alpha \)-type state, two free holes are released to the valence band, leading to \( p \)-type PPC.

FIG. 2. (a) Local DOS of the CuInSe\textsubscript{2} free holes. (b) Schematic energy diagram for \( V^0_{\text{Se}} \) in CuInSe\textsubscript{2}, causing \( p \)-type PPC.
tively charged states $V_{\text{Se}}^-$ and $V_{\text{Se}}^{2-}$. While the singly charged $V_{\text{Se}}^-$ and $V_{\text{Se}}^+$ are undisturbed due to negative-\textit{U} behavior, the doubly charged $V_{\text{Se}}^{2-}$ gives rise to a very deep acceptor state of $V_{\text{Se}}$ which is actually close to the CBM, i.e., $\varepsilon(0/2-)=E_V+0.97\ eV=E_C-0.07\ eV$. In CuGaSe$_2$, which has a larger band gap ($E_g=1.7\ eV$), the deep acceptor level is located around mid-gap, i.e., $\varepsilon(0/2-)=E_V+1.10\ eV$. Such negative, “inverted” charge states of anion vacancies have also been reported for some zinc-blende II-VI semiconductors.\textsuperscript{75} Note, however, that the metastable effects discussed in Sec. IV and below rely only on the properties of the neutral and doubly positive states, not on the inverted negative states.

The formation energies of the stable charge states of $V_{\text{Se}}$ in CuInSe$_2$, i.e., $V_{\text{Se}}^{2+}$, $V_{\text{Se}}^0$, and $V_{\text{Se}}^{2-}$, are shown in Fig. 4(b) as a function of $\Delta E_F$, indicating also the respective transition energies $\varepsilon(2+/0)=E_V+0.02\ eV$ and $\varepsilon(0/2-) = E_V+0.97\ eV$. We see that only at very low values of $\Delta E_F$ (below 0.02 eV) the system is in the $V_{\text{Se}}^{2+}$ state, transforming directly into $V_{\text{Se}}^0$ (negative-\textit{U} behavior), while at $E_F$ near the CBM, $V_{\text{Se}}^{2-}$ transforms directly into $V_{\text{Se}}^{2-}$ (also a negative-\textit{U} transition). Thus, for most of the range of $\Delta E_F$ (and actually also for realistic values of $\Delta E_F$) $V_{\text{Se}}^0$ is the ground state. The absence of any shallow donor states (contrasting with the expectation\textsuperscript{76,77} that formation of Se vacancies is responsible for the n-type conductivity observed after Se-poor growth\textsuperscript{78}) and the absence of any deep transitions within the experimentally accessible range of $\Delta E_F$ indicates that the isolated Se vacancy would hardly affect the electronic properties of CuInSe$_2$. As discussed below, however, we find that the complex formation of $V_{\text{Se}}$ with the abundant acceptor $V_{\text{Cu}}$ plays an important role, and gives rise to gap states and to PPC.

A. Defect physics of p-type PPC caused by $V_{\text{Se}}$

The fact that the vacancy DLS can shift to energies below the VBM in Cu-III-VI$_2$ compounds leads to the possibility of persistent hole photovoltaic energy (p-type PPC). While we find that the PPC actually observed in experiments is caused by the vacancy complex with $V_{\text{Cu}}$, the basic physics of this metastability follows already from the behavior of the isolated $V_{\text{Se}}$, which we discuss first: As shown in Fig. 6 the reaction pathway leading to p-type PPC in CuInSe$_2$ starts from the ionized, $\beta$-type $V_{\text{Se}}^{2+}$ (DLS-above-PHS) state. Note that the initial ionized charge state $V_{\text{Se}}^{2+}$ here is different from the initial neutral $V_{\text{Se}}^0$ state required in ZnO. Illumination\textsuperscript{19-23} or electron injection\textsuperscript{79} of such CuInSe$_2$ samples create occupation of the shallow PHS [Fig. 6(a) right-hand side]. The corresponding optical transition $V_{\text{Se}}^{2+}\rightarrow V_{\text{Se}}^{2+}+h$, shown in the diagram of Fig. 6(b), requires an energy $\varepsilon_p(2+/+;h)$ which practically equals the band-gap energy.\textsuperscript{80} Immediately after the optical excitation, the electron in the $V_{\text{Se}}^{2+}$ state occupies the shallow PHS rather than the DLS (viz. Fig. 6), so that the $\beta$-type configuration with the large In-In distance $d_{\text{In-In}}=5.45\ \text{Å}$ is stabilized. However, the DLS can capture the electron from the PHS with a small activation energy $\Delta E_1$ [Fig. 6(b)], because the DLS energy shifts to energies below the CBM for In-In distances smaller than $\sim 4.8\ \text{Å}$. After this thermally activated transition from situation $\beta$ to situation $\alpha$ (DLS-below-CBM), atomic relaxation leads, without further activation, to the formation of the In-In dimer [$d_{\text{In-In}}=3.0\ \text{Å}$, cf. Fig. 6(b), left-hand side]. During this relaxation, which is driven by the occupation of the DLS, the DLS shifts to energies below the VBM (for $d_{\text{In-In}}<3.9\ \text{Å}$), and becomes doubly occupied, i.e., $V_{\text{Se}}^0$ is formed. Thus the optical excitation initiates the overall reaction

$$V_{\text{Se}}^{2+}\rightarrow V_{\text{Se}}^0+2h$$

(6)

after which two electrons are trapped in the deep DLS [Fig. 6(a), left-hand side], and two free holes are released to the valence band, leading to p-type PPC. The energy of the metastable ($V_{\text{Se}}^0+2h$) state is shown in Fig. 4(b) as dashed line. Note that, in contrast to the case in ZnO, the released carriers are not bound by $V_{\text{Se}}^0$ in the metastable configuration, and no new transition energies emerge as they do in ZnO [open circles in Fig. 4(a)]. However, the initial presence of $V_{\text{Se}}^0$ requires the presence of acceptors that compensate the $V_{\text{Se}}$ double donor, and the released holes can be bound by these acceptors.

Comparing CuInSe$_2$ and CuGaSe$_2$, we see in Fig. 5 that the energy of the unoccupied $\varphi$ level of $V_{\text{Se}}^{2+}$ is much closer to the conduction band edge in CuGaSe$_2$. Thus we expect that electrons brought into the PHS after illumination or electron injection can be captured by the DLS practically without activation in CuGaSe$_2$ ($\Delta E_1=0$). The presence of a barrier $\Delta E_1$ in CuInSe$_2$ implies that the $V_{\text{Se}}^{2+}$ state could be stable against capture of electrons at low temperature. Consequently, it might be possible to freeze-out the light-induced effect in CuInSe$_2$, but not in CuGaSe$_2$. However, once $V_{\text{Se}}^0$ has captured an electron, the transition into the trapped ($V_{\text{Se}}^0+2h$) state and the occurrence of p-type PPC should be very similar in CuInSe$_2$ and CuGaSe$_2$. In either material, the PPC is lost again when the metastable ($V_{\text{Se}}^0+2h$) state is thermally activated across the barrier $\Delta E_2$ [Fig. 6(b)] towards the $V_{\text{Se}}^2$ state. Note that this process requires simultaneous capture of two holes from the valence band, so that it can be quite slow despite the moderate calculated barrier height $\Delta E_2=0.35\ \text{Å}$ for CuInSe$_2$.

B. Formation of ($V_{\text{Se}}$-$V_{\text{Cu}}$) vacancy complexes

Our model for the metastability of $V_{\text{Se}}$ can account for the experimentally observed p-type PPC in Cu(In,Ga)Se$_2$. However, it requires that $V_{\text{Se}}^{2+}$ be the equilibrium ground state, implying that the Fermi level has to be unrealistically close to the VBM, i.e., below the $\varepsilon(2+/0)=E_V+0.02\ eV$ transition level. Also, detailed studies\textsuperscript{22,79} revealed that for every two electrons captured by the metastable defect, one hole trap is created. (In different words, one deep acceptor state is created for every two holes released to the valence band.) Such behavior cannot be explained by the isolated Se vacancy, but by a vacancy complex formed with $V_{\text{Se}}$ and $V_{\text{Cu}}$, the latter being an abundant acceptor in CuInSe$_2$ and CuGaSe$_2$ due to its rather low formation energy.\textsuperscript{81-83} We find a quite large binding energy of the vacancy complex of up to $\sim 0.8\ eV$ in p-type CuInSe$_2$ indicating that such complex formation plays an important role. According to the above discussion, the isolated $V_{\text{Se}}$ is excited into the metastable state via the tran-
the vacancy complex rather than from the isolated Se vacancy. A more detailed account of the properties of the vacancy complex will be given elsewhere.

VI. CONCLUSION

Using first-principles electronic structure calculations, we identified the anion vacancies in II-VI and chalcopyrite Cu-III-VI$_2$ semiconductors as a class of intrinsic defects that can exhibit metastable behavior. The metastability arises from the crossover of the energy of the defect localized state with respect to the host band edges when the charge state is changed. Specifically, we find that the oxygen vacancy causes persistent electron photoconductivity (n-type PPC) in n-ZnO. Whereas in thermal equilibrium, $V_{\text{O}}$ is deep and does not provide for n-type doping, we predict that there exists a shallow metastable state of $V_{\text{O}}$ which could contribute to n-type conductivity under illumination. For the chalcopyrite semiconductors CuInSe$_2$ and CuGaSe$_2$, we find that $V_{\text{Se}}$ causes persistent hole photoconductivity (p-type PPC) in p-type material, constituting the unusual case where a donor produces p-type PPC. The vacancy complex ($V_{\text{Se}}$-$V_{\text{Cu}}$) produces p-type PPC similar to the isolated Se vacancy, but, at the same time, can account for the experimental observation of a deep hole trap that appears in the metastable state. Thus, our theoretical results for the anion vacancies provide a model for the hitherto poorly understood mechanism that causes light-induced metastability in CuInSe$_2$ based photocathodic materials.

ACKNOWLEDGMENT

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G. Kresse and D. Joubert, Phys. Rev. B 54, 13321 (1996). We denote here by "equilibrium stable configuration" the lower of the two energy minima of the V_{Zn}^0 and V_{Zn}^* branches in Fig. 3(b) which have two local minima each. However, in a different sense, V_{Zn}^0 is not equilibrium stable due to the exothermic 2V_{Zn}^0 \rightarrow V_{Zn}^0 + V_{O}^{2+} disproportion (negative-U behavior).

The calculation of the shallow binding energies of the electrons in the extended PHS is complicated by the technical issues outlined in Sec. II. Instead, we infer from effective mass theory that both transition levels are within 0.2 eV from the CBM.


The energy of the V_{O}^{*+e} branch in Fig. 3(b) does not include the hydrogenic binding energy between the electron in the PHS and V_{O}^{*} and the energy gain due to spin alignment. These effects may reduce the emission energy somewhat.


Due to the problem described in Ref. 53, V_{O}^{0} incorrectly relaxes in LDA to the \beta-type "DLS-above-PHS" configuration with large Zn-Zn distance. Therefore we use here \Delta E[V_{O}^{0}] corresponding to the estimated d_{Zn-Zn}=3.2 Å in Fig. 3(b).


For example, we find that \Delta E[V_{Se}^{0}] in ZnSe for \Delta E_{Se}=0 (Se-rich) is lowered by ~0.28 eV when we use the LDA lattice constants instead of the experimental ones.
The choice of the host lattice constant affects somewhat the calculated energy differences: Using the (smaller) LDA lattice constant instead of the experimental one, we find \( E[C_{2v}] - E[T_d] = +0.02, -0.09, \) and \(-0.38\) eV for ZnS, ZnSe, and ZnTe, respectively. However, using the GGA for the exchange-correlation potential and the respective (larger) GGA equilibrium lattice constant yields again a larger energy gain due to symmetry lowering and metal-metal dimer formation, e.g., 
\[ E[C_{2v}] - E[T_d] = -0.26 \text{ eV} \] for \( V_\text{Se} \) in ZnSe.