Anion displacements and the band-gap anomaly in ternary ABC_2 chalcopyrite semiconductors

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(Received 14 January 1983)

Using a first-principles all-electron band-structure approach, we show that the anomalous ($>50\%$) reduction in the band gaps of the $A^{\mathrm{I}}B^{\mathrm{III}}C_2^{\mathrm{VI}}$ chalcopyrite semiconductors relative to their II-VI isoelectronic analogs results both from a pure structural effect (the anion displacements reflecting the mismatch of classical elemental radii) and from a purely electronic effect (p-d repulsion in the valence band), with a small coupling between the two factors.

The ternary chalcopyrite semiconductors $A^{\mathrm{I}}B^{\mathrm{III}}C_2^{\mathrm{VI}}$ (isoelectronic analogs of the II-VI binaries) and $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ (isoelectronic analogs of the III-V binaries) form a group of nearly 40 different species, spanning a wide range of structural, chemical, and electronic properties.[1-3] Their crystal structure is closely related to that of the zinc-blende binary analogs[1] but with nonideal tetragonal strain parameter $\eta \equiv c/2a \neq 1$ and anion displacement parameter $u = \frac{1}{4} + \alpha/a^2 \neq \frac{1}{4}$ reflecting the unequal cation-anion bond lengths R_{AC} and R_{BC}, where $\alpha \equiv R_{AC}^2 - R_{BC}^2$. We find that the chemical trends in the magnitudes of the 36 observed cubic lattice constants[1-3] a —even for the active d-electron materials $\mathrm{Cu}B^{\mathrm{III}}C_2^{\mathrm{VI}}$ —can be understood quantitatively on the basis of a simple zinc-blende structural model. Specifically, assuming that the cation-anion bond lengths R_{ij} equal the sum of Pauling's tetrahedral radii[4] $d_i + d_j$ (derived solely from data on the binary compounds) and that in analogy with zinc-blende materials the bond angles around the B atom remain tetrahedral,[5] we find that the distribution of all observed a values (Refs. 1–3 and references therein) is closely reproduced (Fig. 1). Remarkably, however, despite this close structural resemblance to zinc-blende semiconductors, the observed optical band gaps of the $A^{\mathrm{I}}B^{\mathrm{III}}C_2^{\mathrm{VI}}$ semiconductors are more than 50% smaller than in their binary analogs[6] (Table I). In fact, it is this anomalous band-gap downshift ΔE_g that makes some of the ternary chalcopyrites (e.g., $\mathrm{CuInSe_2}$) among the strongest known absorbers in the solar spectrum[7] (e.g., linear absorption coefficient at $h\nu = 1.5$ eV of 10^5, 10^4, and $\approx 10^3$ cm^{-1} for $\mathrm{CuInSe_2}$, GaAs, and Si, respectively). This anomaly is largely responsible for the recent emergence of ternary chalcopyrites as new and promising solar cell materials.[8] Shay and Kasper[9] have observed that this band-gap anomaly correlates with the independently observed anomalous reduction in the spin-orbit splitting of the valence-band maximum. They suggested that both anomalies are related to the observed[9] d character in the upper half of the valence band found in the ternaries, but not in the binaries. Available band-structure calculations (e.g., Ref. 10) have ignored the d levels and hence shed no light on the electronic origin of the Shay-Kasper correlation, nor did the calculations show any band-gap anomaly.[10] We have applied the recently developed all-electron first-principles band-structure method[11] to $\mathrm{CuInSe_2}$. We show that the band-gap anomaly has two physically independent sources with comparable contributions—a structural source due to the existence of a nonideal anion displacement $u \neq \frac{1}{4}$ (i.e., bond alternation, $R_{AC} \neq R_{BC}$) which is dictated by the mismatch in the classical atomic radii, and an electronic source due to the p-d level repulsion associated with the noble-atom d orbitals. Having identified a simple structural parameter u that sensitively controls the optical band gap of these materials, we will further show that the distribution of the observed anion displacement parameters u can be

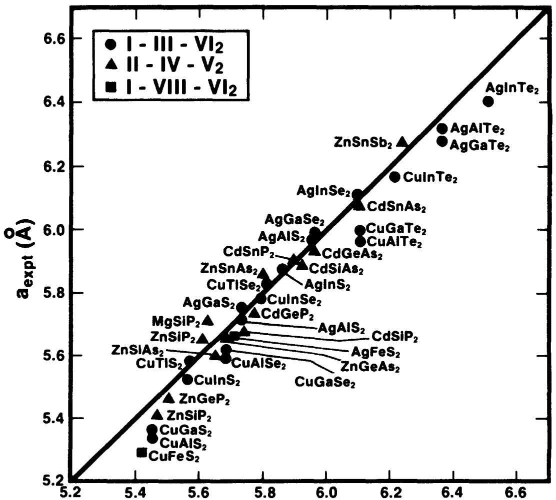

FIG. 1. Correlation between the observed (Refs. 1–3) and calculated (using the conservation of tetrahedral bond model) cubic lattice constants of ternary chalcopyrites.

TABLE I. Observed lowest band gaps of the Cu-based ternary chalcopyrites (Ref. 1) and the amount ΔE_g by which they are lowered from the values of the binary analogs (Ref. 6).

Ternary	Band gap (eV)	Binary	Band-gap anomaly ΔE_g (eV)
$CuAlS_2$	3.49	$Mg_{0.5}Zn_{0.5}S$	2.4
$CuGaS_2$	2.43	ZnS	1.4
$CuInS_2$	1.53	$Zn_{0.5}Cd_{0.5}S$	1.6
$CuAlSe_2$	2.71	$Mg_{0.5}Zn_{0.5}Se$	1.4
$CuGaSe_2$	1.68	ZnSe	1.0
$CuInSe_2$	1.04	$Zn_{0.5}Cd_{0.5}Se$	1.3
$CuGaTe_2$	1.24	ZnTe	1.3
$CuInTe_2$	1.06	$Zn_{0.5}Cd_{0.5}Te$	1.1

predicted solely from Pauling's tetrahedral radii[4] or from the quantum-mechanical orbital radii[12] that scale linearly with them,[12] by assuming the conservation (and hence transferability) of elemental atomic radii in compounds. This establishes a unique relationship between the structural and optical properties of ternary chalcopyrite semiconductors.

We use the newly developed first-principles and self-consistent mixed-basis potential-variation (MBPV) band-structure method[11] recently used within the density functional formalism to obtain the first theoretical analysis of the observed valence-band x-ray photoemission spectra[13] of $CuInSe_2$. Unlike pseudopotential methods,[10] the all-electron MBPV approach can treat self-consistently all core and valence orbitals on equal footing, and does not bias the calculation by using the crystal potential of the binary analogs to describe the properties of ternary semiconductors.[10] Furthermore, it offers a means for accurately assessing the influence of selected atomic subshells on the global electronic structure of the compound by solving for the self-consistent electronic bands in the field of selectively frozen atomic orbitals. To elucidate quantitatively the microscopic origin of the Shay-Kasper correlation, we have solved the self-consistent band structure of $CuInSe_2$ in the field of frozen Cu $3d$ orbitals. We use a mixed basis consisting of 130 numerical "compressed atom" orbitals[11] plus 380 plane waves; self-consistency is attained to a tolerance level of 1 mRy. Comparison with the dynamic all-electron results of Ref. 11 shows that upon freezing, the noble-atom $3d$ bands separate from the main valence band and are lowered by 8.7 eV. This virtually eliminates the p-d hybridization, leading to a reduce repulsiveness between the (upper) p-like and the (lower) d-like Γ_{15}-derived valence-band states as the energy denominator in the interaction matrix element

$$\langle \Gamma_{15}(p) | V | \Gamma_{15}(d) \rangle / [\epsilon_{\Gamma_{15}(p)} - \epsilon_{\Gamma_{15}(d)}]$$

increases. This leads to a lowering of the valence-band maximum and to an increase of 0.7 eV in the band gap, both for the experimental and anion-distorted configuration ($u = 0.224$), and for the ideal zinc-blende configuration ($u = \frac{1}{4}$). Hence, p-d hybridization[9] accounts for about half of the band-gap anomaly.

Examination of the experimental data [1–3] already suggests that p-d hybridization is insufficient to fully explain the band-gap anomaly. For instance, whereas $CuInSe_2$ and $CuGaSe_2$ have nearly identical d characters,[1] the former compound has a band gap that is 40% smaller (Table I). We suggest that the structural anomaly of ternary chalcopyrites reflected in bond alternation and hence in a displaced arrangement of anions (e.g., $u = 0.250$ for $CuGaSe_2$ but 0.224 in $CuInSe_2$) is directly related to the band-gap anomaly. To understand how the structural anomaly is dictated by the properties of the atoms, we hypothesize that the independent crystal parameters u, η, and a will attain such values that the two anion-cation bond lengths $R_{AC}(u,\eta,a)$ and $R_{BC}(u,\eta,a)$ will equal the respective sums of Pauling's elemental tetrahedral radii $d_A + d_C$ and $d_B + d_C$ and that the bond angle around the B atom will be tetrahedral, implying $\eta = [\frac{1}{4} + 8(\frac{1}{2} - u)^2]^{1/2}$. This simple rule of conservation of tetrahedral bonds (CTB) in different compounds, underlying Bragg's classical notion of transferability of elemental radii in molecules and crystals,[14] provides direct predictions for a (Fig. 1), u (Fig. 2; notice the large scatter of the experimental data), and η with no adjustable parameters and, in contrast with previous work,[5] without the use of data from the ternaries. Its success enables one to predict a, u, and η for compounds for which they are not known[15] and to systematize the known structural parameters in terms of simple and known classical elemental radii. In turn, the classical radii are linearly related to the quantum-mechanical orbital radii[12] reflecting the shell structure of the atoms. This

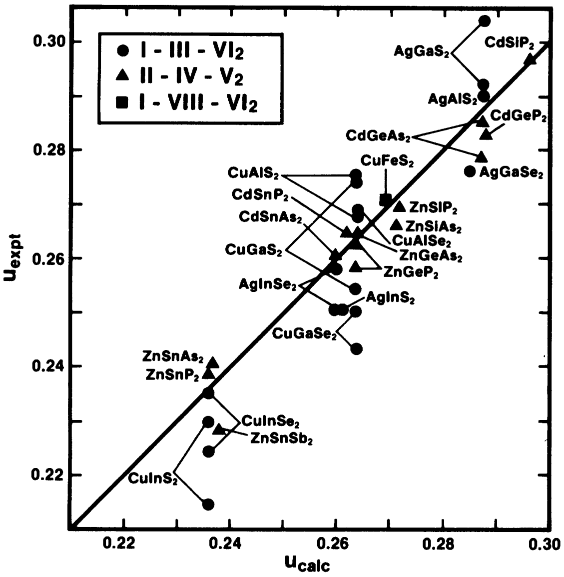

FIG. 2. Correlation between the observed (Refs. 1–3) and calculated (using the CTB model) anion displacement parameters for the ternary chalcopyrites. The uncertain data for the telurides is omitted. Multiple arrows denote various experimental determinations.

method is also consistent with the behavior of chalcopyrite lattice constants with alloying; for example, in the system $CuInS_{2(1-x)}Se_{2x}$, if we take

$$d_{\text{anion}} = x d_{\text{Se}} + (1-x) d_{\text{S}}$$

then the variations in $a_{\text{calc}}(x)$ obtained by the CTB method are within $\lesssim 0.1\%$ of the observed (Vegard-type) variations.[16]

By mapping the all-electron band structure as a function of the structural parameters, we next investigate how atomic radii, encoded in u, η, and a (Figs. 1 and 2) control the electronic properties.[17] We find that whereas variations in the tetragonal strain parameter η merely lead to small ($\approx 10^{-2}$ eV) changes in the crystal-field splitting and the band gaps, the anion displacement parameter sensitively controls all of the band gaps in the system (Fig. 3). Even a small increase in u from its equilibrium value of 0.224 ($R_{\text{Cu-Se}} = 2.42$ Å, $R_{\text{In-Se}} = 2.60$ Å) to its ideal zinc-blende value $u = 0.25$ ($R_{\text{Cu-Se}} = R_{\text{In-Se}} = 2.51$ Å) leads to a substantial ionic polarization of the bonds (more charge on Se and less on Cu) and consequently to a dramatic increase in the band gaps (0.5 eV for $CuInSe_2$) with a rate $\partial E_g/\partial u$ ranging from 17.5 eV (the $\Gamma\Gamma^*$ gap) to 25.6 eV (the TT^* gap). We have verified that this conclusion is not affected by the choice of the exchange-correlation potential[17] by performing a similar calculation for $CuAlS_2$, using Ceperley's correlation[18] (this material shows a large $\Gamma\Gamma^*$ band gap even with this correlation). We find $\partial E_g/\partial u = 17.4$ eV, confirming the controlling influence of u on the band gaps of $A^{\text{I}}B^{\text{III}}C_2^{\text{VI}}$ compounds.

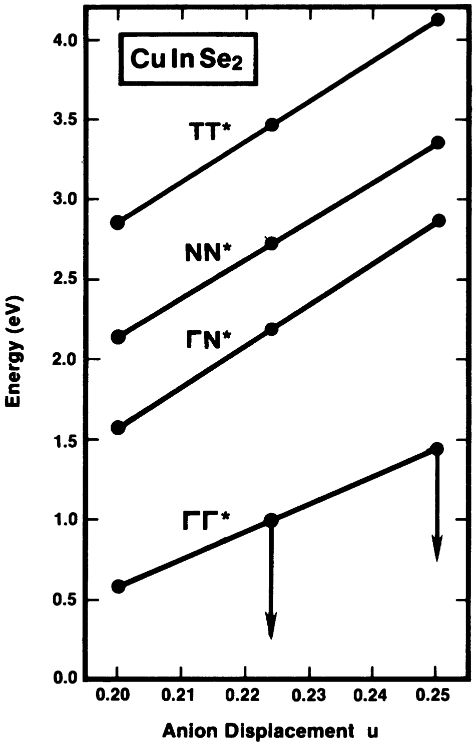

FIG. 3. Dependence of the direct ($\Gamma\Gamma^*$) and indirect band gaps of $CuInSe_2$ on the anion displacement parameter u. The equilibrium value is $u = 0.224$ whereas $u = 0.25$ is the ideal (equal bond) zinc-blende value. The vertical arrows denote the lowering in the direct gap due to unfreezing the Cu $3d$ orbitals.

We conclude that the band-gap anomaly in ternary chalcopyrites is produced both by a purely electronic factor—the repulsive p-d interactions in the valence band associated with the A-atom d orbitals, and by a pure structural factor—the anion distortions, reflecting the classical atomic size mismatch in the A-C and B-C bonds. By commuting the operations of freezing the d orbitals and displacing the anions we find that the coupling between these two factors is small (< 0.1 eV). This analysis clarifies the hitherto unexplained difference in band gaps between chalcopyrites with equal d character[9] but different sizes of the B atom (e.g., $CuInSe_2$ vs $CuGaSe_2$), or materials with equal anion displacements but different d character (e.g., $CuAlSe_2$ and $ZnSiP_2$, both with $u = 0.269$). Indeed, recent experiments on $CuInSe_2$-$CuInS_2$ alloys[19] have indicated that despite a substantial difference in the d character of the valence bands in these two materials,[9] the alloy band gap follows a precise linear variation with composition. In contrast, similar experiments on $CuInSe_2$-$CuGaSe_2$ alloys[20] show considerable positive bowing (the gap of the alloy is lower than the composition weighted average of the gaps of the constituent semiconductors), despite a nearly identical d character in the two systems.[9] This is consistent with the controlling role of the anion displacements: We calculate the same equilibrium u for CuInSe_2 and CuInS_2 ($u = 0.236$), but a larger u value for CuGaSe_2 (0.264), leading to

$$E_g(\text{CuGaSe}_2) - E_g(\text{CuInSe}_2) \approx \Delta u \frac{\partial E_g}{\partial u} = 0.5 \text{ eV}$$

and positive bowing, in good agreement with experiment. Our separation of the band-gap anomaly into structural and chemical factors may hence provide insight and guidelines for designing and constructing ternary chalcopyrites with tailored optical properties, as needed in device applications.[8]

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