Electronic properties of energy harvesting Cu-chalcogenides: *p-d* hybridization and *d*-electron localization

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Copper-based chalcogenides with the familiar diamond-like structure are superior thin-film light absorbers. Remarkably, several closely related chalcogen-deficient structures have recently been recognized as promising thermoelectric converters with ultra-low thermal conductivities. The combination of various constituent elements provides an ample space for material design. However, first-principles investigations on their electronic properties are complicated by the involvement of the shallow Cu-3*d* semi-core states. Although Cu-3*d* electrons are intrinsically rather localized, they also strongly hybridize with delocalized chalcogen-*p* states. The seemingly incompatible tendencies require delicate theoretical treatments, and the conventional local density approximation (LDA) within density functional theory (DFT) is inadequate. In this work, we carefully analyze the characteristics of the Cu-3*d* states, which form the basis for an in-depth understanding of the electronic properties of Cu-chalcogenides to provide insightful guidance for their energy harvesting applications. We show that the band-edge electronic properties can be reliably predicted by the DFT+*U*+*G*₀*W*₀ or the mBJ+*U* methods. Moreover, the simple mBJ+*U* method works equally well for moderate-gap systems and theoretically challenging narrow-gap systems. Cu-chalcogenides with narrow-gaps usually contain heavy elements, in which relativistic effects are expected to play an important role. We find that the orbital contraction effect tends to reduce the energy of the *s* conduction states in diamond-like structures, and might lead to a structural transformation to chalcogen-deficient structures. Although the spin-orbit coupling effect can be quite strong, its influence on the band structure can also be *suppressed* by strong hybridizations.

Keywords:

Cu-chalcogenides, electronic properties, *p-d* hybridization, *d*-electron localization, DFT+*U*+*G*₀*W*₀ approach, mBJ+*U* approach

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1. INTRODUCTION

Multinary Cu-chalcogenides are composed of Cu^{1+} ions, chalcogen anions (S, Se, Te), and another kind of cations (or more) from group II/III/IV/V (II = Zn, Cd, Hg; III = Al, Ga, In, Tl; IV = Si, Ge, Sn, Pb; V = P, As, Sb, Bi) [1-3]. Among them, $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ and $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ are well recognized as superior solar cell absorbers [4, 5]. Recently, some Cu-chalcogenides are also identified as emerging high-performance thermoelectric converters [6-11]. Very low lattice thermal conductivities were found in Cu_{2-x}Se due to a ‘liquid-like’ behavior of Cu ions [8] and in Cu_3SbSe_3 as a result of a ‘part-crystalline part-liquid’ structure [9]. In addition, it was discovered that the thermoelectric power factor of Cu-chalcopyrites can be significantly improved by enhancing the band degeneracy using a ‘pseudo-cubic’ approach [12]. These novel structures and concepts (or mechanisms) have attracted renewed interest in Cu-chalcogenides for energy harvesting applications.

Each specific application is strongly correlated with their fundamental electronic properties, such as band gap, degeneracy of near-edge bands, and band alignment. Over the past several decades, density functional theory (DFT) has played an important role in the search, design, and optimization of advanced materials. However, previous work showed that a straightforward application of the conventional local density approximation (LDA) and the generalized gradient approximation (GGA) can be problematic for Cu-chalcogenides. An interesting example is the false theoretical identification of various normal narrow-gap semiconductors (e.g., Cu_3SbSe_4 [13] and Cu_2Se [14]) as topological insulators (or metals) [15]. The main difficulty comes from a delicate interplay between the intrinsic localization tendency of the Cu-3d electrons and their bonding tendency with the chalcogen-p states. Therefore, it is crucial to develop reliable, yet practical simple, computational approaches in order to exploit the full potential of Cu-chalcogenides.

In our previous work [13, 14, 16-18], we have shown that the two characteristics of Cu-3d states can be well-captured by introducing an on-site Coulomb U (i.e., within the DFT+ U approach). In addition, the fundamental electronic properties can be reliably predicted by higher-level quasiparticle calculations within the G_0W_0 approximation [19, 20] starting from the DFT+ U mean-field solution (i.e., the DFT+ U + G_0W_0 approach). For narrow-gap systems, however, there is a severe drawback of the single shot G_0W_0 approach since the DFT+ U method still predicts metallic band structures. We also found that the mBJ+ U approach, which combines the modified Becke-Johnson (mBJ) potential [21-23] and the DFT+ U method, works equally well for moderate- and narrow-gap Cu-chalcogenides.

In this work, we revisit the electronic properties of Cu-chalcogenides and also review our previous work. Example systems are selected for illustrating the fundamental issues. We first establish a simple bonding diagram showing the evolution of the key electronic properties from binary to ternary and to quaternary diamond-like systems. The *dual nature* of the Cu-3d states, its influence on the structural and electronic properties, and its theoretical treatments are investigated or reviewed in great detail. In light of the importance of Cu-chalcogenides with moderate- or narrow-gaps for photovoltaic and thermoelectric applications, we expand our discussion on the electronic properties of these materials. We also provide a detailed survey of the band gap prediction using the DFT+ U + G_0W_0 and the mBJ+ U approaches. Finally, we investigate the relativistic effects in Cu-chalcogenides containing heavy main-group elements.

2. COMPUTATIONAL DETAILS

The G_0W_0 approximation is implemented in the Vienna *ab initio* simulation package [24, 25]. The Perdew-Burke-Ernzerhof (PBE) [26] functional is used to calculate ground state wave function for subsequent quasiparticle approximation. Hybrid functional of Heyd-Scuseria-Ernzerhof (HSE) [27, 28] is adopted for structural

relaxation [16]. The mBJ method [21-23] is implemented in the all-electron code WIEN2k [29].

An effective Coulomb U ($U_{eff} = U - J$) of 4 eV for the Cu-3d states is used for all systems studied in this work. This value is obtained for the CuGaS₂ system using an approach combining the Wannier orbitals and the constrained random phase approximation [16, 17, 30]. A critical issue is the transferability of a single U value for various materials with rather scattered band gaps. We believe that the screening effect is similar in all these systems (Section 3.2.1), so that the variation of the U parameter is small. Our understanding is further supported by the satisfactory agreement between theory and experiment for over 90 systems (Section 3.3.3).

The relativistic effects are investigated in the last section. It is necessary to briefly introduce the theoretical approach. A fully relativistic Hamiltonian is written as a non-relativistic component (H^R) with three relativistic terms [31]:

$$H^R = H^{NR} - \frac{p^4}{8c^2} + \frac{\Delta V}{8c^2} \delta(\mathbf{r}) + \frac{1}{2c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{l} \cdot \mathbf{s},$$

where V is Coulomb-like potential, p is electron momentum, c is light speed, $\mathbf{l}$ is orbital angular momentum, and $\mathbf{s}$ is electron spin. The first relativistic term accounts for the mass-velocity shift; this term contributes negatively to the energy and results in orbital contraction. The second term is the Darwin term resulting from the increase in the electron kinetic energy due to the wave function localization. This term is positive and only affects s states. The last one is the spin-orbit coupling (SOC) term.

3. RESULTS AND DISCUSSION

3.1. Structural and chemical bonding characteristics

3.1.1. Introduction to crystal structures

Ternary chalcopyrites are the most intensively investigated Cu-chalcogenides because of their outstanding performance in solar cell applications. Figure 1(a) shows the crystal structure of CuGaS₂, which is obtained through cation mutation from binary ZnS following the octet rule [32], i.e., by replacing two Zn ions with one Cu+Ga pair. Further mutation of two Ga ions with one Zn+Sn pair leads to quaternary Cu₂ZnSnS₄ with either kesterite (KS) or stannite (ST) structure. Both CuGaS₂ and Cu₂ZnSnS₄ are called diamond-like structures because their building blocks are anion-centered (or equivalently cation-centered) tetrahedra, as shown in Fig. 1(b). However, the chemical difference between the Cu and Ga ions introduces: (1) a tetrahedron distortion measured by anion displacement $\mu \equiv 0.25 + (R_{Cu-S}^2 - R_{Ga-S}^2)/a^2$ and (2) a lattice distortion $\eta \equiv c/2a$. As discussed below, the parameter μ strongly affects the band-edge electronic properties such as the band gap. The parameter η , on the other hand, determines the valence band degeneracy [12].

System with heavy main-group elements (e.g., Tl, Sb, Bi) can crystallize into both the diamond-like structure and various chalcogen-deficient (defective) structures. Fig. 1(c) and Fig. 1(d) show the diamond-like Cu₃SbSe₄ and one defective structure Cu₃SbSe₃, respectively. It is seen that the defective structures are more complicated than their diamond-like counterpart. A main feature of all defective structures is the local void spaces near the main-group ions (e.g., Sb in Cu₃SbSe₃), which is induced by the stereochemically active s^2 lone pairs [33, 34]. The void structures are used to understand the novel ‘*part-crystalline part-liquid*’ behavior in Cu₃SbSe₃ [9], which results in ultra-low thermal conductivity.

In sum, Cu-chalcogenides have two distinct structures, i.e., the diamond-like structure with deformed tetrahedron building blocks and defective structures with local void spaces. As expected, the structural differences

can lead to a rich diversity of electronic properties. In [Section 3.1.2](#), we review the generic chemical bonding properties of diamond-like structures; the relevant investigation on the defective systems is in [Section 3.4](#).

Fig. 1. (Color online) Crystal structures of (a) diamond-like CuGaS_2 and (b) its tetrahedron building block, (c) diamond-like Cu_3SbSe_4 and (d) defective Cu_3SbSe_3 . The distribution of $\text{Sb-}5s^2$ lone-pair electrons are also shown in the Cu_3SbSe_3 structure.

3.1.2. Chemical bonding of diamond-like structures

The strength of hybridization between two electronic states is determined by their wave function overlap and energy separation. The electronic hybridization in chalcogenides is usually quite strong (stronger than their oxides counterparts) due to the strongly delocalized chalcogen- p orbitals. In Cu-chalcogenides the hybridization can be even stronger because the atomic levels of Cu- $3d$ states (i.e., $\varepsilon_d = -5.1$ eV, see [Table 1](#)) are just slightly higher than the chalcogen- p orbitals (i.e., $\varepsilon_p = -7.0$ eV for S- $3p$ states). The strong p - d hybridization results in a considerable contribution of the Cu- $3d$ states to the near-edge valence bands. As shown in the density of states [see [Fig. 2\(b\)](#)], significant mixing between the Cu- $3d$ and S- $3p$ states is observed from the valence band maximum (VBM) to -6 eV in CuGaS_2 . This is in stark contrast to the weak p - d hybridization in ZnS , in which the Zn- $3d$ orbitals ($\varepsilon_d = -10.2$ eV) are also fully occupied but are much lower in energy than the S- $3p$ states [see [Fig. 2\(a\)](#)]. Another consequence of the strong p - d hybridization in CuGaS_2 is that the VBM is pushed upwardly, resulting in a much smaller band gap ($E_{g,\text{CuGaS}_2} = 2.43$ eV) than that of ZnS ($E_{g,\text{ZnS}} = 3.78$ eV).

TABLE 1. Atomic orbital energies of s , p , d states calculated within the PBE functional. The second column shows the valence electron configuration of each element.

Atoms	States	Atomic orbital levels (eV)		
		ε_s	ε_p	ε_d
Cu	$3d^{10}4s^1$	-4.6		-5.1
Zn	$3d^{10}4s^2$	-6.0		-10.2
Ga	$4s^24p^1$	-9.2	-2.8	
Sn	$5s^25p^2$	-10.8	-4.0	
S	$3s^23p^4$	-17.2	-7.0	

Although the Cu- $3d$ states strongly hybridize with the S- $3p$ states, [Fig. 2\(b\)](#) also suggests that the Cu- $3d$

derived e states are fairly localized. This is easily understood by considering the symmetry properties of d orbitals. The five Cu- $3d$ orbitals split into t_2 and e sub-orbitals due to crystal field effect in the CuS₄ tetrahedron. The t_2 sub-orbitals point to S atoms and strongly hybridize with the S- $3p$ states, resulting in bonding and anti-bonding states. In contrast, the hybridization between the e sub-orbitals and the S- $3p$ is not allowed by symmetry. These chemical bonding features can be clearly seen by analyzing the charge density difference between the self-consistent result (energy-resolved) and the superposition of atomic charges. The electronic charge accumulates along the Cu-S bond in the $-6 \sim -3.5$ eV energy range, showing a typical bonding behavior [see Fig. 3(a)]; charge depletion, on the other hand, is seen in the $-2 \sim 0$ eV range, reflecting the anti-bonding nature of the electronic states [see Fig. 3(b)]; the charge around -2.5 eV only experiences some relaxation near the ions, implying no significant chemical hybridization [see Fig. 3(c)]. The bonding pattern between Cu- $3d$ and S- $3p$ states is further confirmed by the crystal orbital overlap population [COOP, see Fig. 3(d)].

Fig. 2. (Color online) Density of states of (a) ZnS, (b) CuGaS₂, and (c) kesterite Cu₂ZnSnS₄. For CuGaS₂, the Cu- $3d$ states are projected on t_2 and e sub-orbitals; the x-ray photoemission spectroscopy (XPS) data [35] are also shown. The magnitudes of conduction states are amplified for clarity. The VBMs are at zero and shaded areas show the band gaps. The results are obtained from the DFT+ U + G_0W_0 approach.

Fig. 3. (Color online) Chemical bonding pattern in CuGaS₂. (a – c) Charge density difference between the self-consistent result and the superposition of atomic charges along a Cu-S bond for selected bands (see text). Charge accumulation and depletion regions are colored blue and red, respectively. (d) Crystal orbital overlap population analysis for Cu- $3d$ S- $3p$ and Ga- $4s$ S- $3p$ states [36]. Positive and negative values manifest the bonding and anti-bonding hybridizations, respectively.

The chemical bonding in quaternary $\text{Cu}_2\text{ZnSnS}_4$ [see Fig. 2(c)] is similar to that in CuGaS_2 . However, the CBM is mainly composed of the Sn-5s (and also some S-3p character) in $\text{Cu}_2\text{ZnSnS}_4$, to be compared with the Ga-4s states in CuGaS_2 . It is noticed that (1) the conduction band minimum (CBM) is dominated by anti-bonding states, e.g., Ga-4s S-3p anti-bonding states in CuGaS_2 [see Fig. 3(d)], and (2) the Sn-5s atomic orbital ($\epsilon_s = -10.8$ eV, see Table 1) is much lower in energy than the Ga-4s orbital ($\epsilon_s = -9.2$ eV). Therefore, the CBM level in $\text{Cu}_2\text{ZnSnS}_4$ is lower than that of CuGaS_2 , leading to a further band gap reduction in $\text{Cu}_2\text{ZnSnS}_4$ ($E_{g,\text{CuGaS}_2} = 2.43$ eV and $E_{g,\text{Cu}_2\text{ZnSnS}_4} = 1.50$ eV) [37]. In other words, the major influence of the main-group elements (e.g., Ga and Sn) is on the CBM states. Such effect is more evident for heavier elements such as Sb, Pb, and Bi. In these cases relativistic effects can cause significant changes to the electronic properties, as will be discussed in Section 3.4.

Based on the above discussions, the electronic structures of three representative diamond-like chalcogenides are summarized into easy-to-understand band diagrams as shown in Fig. 4. We summarize the main features. (1) ZnS is a simple *sp* semiconductor with weak S-3p Zn-3d hybridization. (2) In CuGaS_2 , whereas Cu-3d electrons with the *e* symmetry are localized and do not couple with other states, electrons in the t_2 sub-orbitals strongly hybridize with S-3p states. The strong *p-d* hybridization is responsible for the considerable band gap reduction in CuGaS_2 [1-3, 38]. (3) The difference between $\text{Cu}_2\text{ZnSnS}_4$ and CuGaS_2 is mainly found in the conduction states, with the deeper Sn-5s states lead to a further band gap reduction [37]. (4) The VBM of Cu-chalcogenide is dominated by *p-d* anti-bonding states, in contrast to the bonding states in ZnS.

Fig. 4. (Color online) Schematic bonding diagrams for (a) ZnS, (b) CuGaS_2 , and (c) $\text{Cu}_2\text{ZnSnS}_4$

3.2. Interplay between bonding and localization tendencies of Cu-3d states

3.2.1. The dual nature of Cu-3d states

The 3d states in transition metals are strongly localized, which tends to prevent them from involving in a

strong chemical hybridization with other states. However, it is also seen in Fig. 2 that the Cu-3d states strongly mixed with the S-3p states in CuGaS₂, suggesting a strong *p-d* hybridization. This view is further supported by projecting the band wave functions onto atomic states [see Fig. 5(a)]. Consistent with the schematic bonding diagram discussed earlier, the near-edge valence bands (from the VBM to -1.5 eV) are composed of the S-3p Cu-3d- t_2 anti-bonding states. The bonding states are located around -3.5 eV, and the flat bands around -2 eV are the non-bonding states with *e* symmetry. In this regard, the Cu-3d states in Cu-chalcogenides have a *dual nature*, i.e., intrinsic localization and strong chemical hybridization with chalcogen-*p* states.

Moreover, the interplay between these two tendencies can have a significant impact on the fundamental electronic properties. To better illustrate this point, we theoretically tune (enhance) the Cu-3d localization by applying a strong on-site Coulomb *U* (The calculated *U* value is around 4 eV and a value of 8 eV is used here for illustrative purpose). A direct consequence of applying a large *U* is that all the Cu-3d states, both in the isolated flat bands and in the hybridized bands, are pushed downward substantially [see Fig. 5(b)]. Moreover, the effect is more noticeable for the isolated *e* states than the t_2 states, because the latter are *pinned* by hybridization. Another consequence is that the overall band structure is modified substantially with the application of a large *U*. The VBM position is lowered by about 1 eV, and thus the bands in the $0 \sim -6$ eV range are strongly compressed. In addition, the energy gap between the bonding and anti-bonding states disappears.

Fig. 5. (Color online) Band structure of CuGaS₂ calculated using (a) the PBE and (b) the PBE+*U* approaches. Projection of the band wave functions onto the Cu-3d- t_2 and *e* sub-orbitals, and the S-3p orbitals are shown as vertical bars. The CBM energy from the PBE+*U* calculation is aligned with the PBE result.

3.2.2. Effects on the structural and electronic properties

Besides its effects on the band structure, the interplay between the two characteristics of the Cu-3d states also has a strong influence on the structural properties [16]. We calculate the anion displacement parameter μ of CuGaS₂ using the HSE hybrid functional, in which the localization tendency can be theoretically tuned by changing the Fock-exchange ratios. The calculated μ is 0.2471 using the PBE functional; this value is improved to 0.2539 using the HSE functional with 25% Fock-exchange. Moreover, μ increases linearly with respect to the fraction of the Fock-exchange included. Recall that the parameter μ measures the difference between the Cu-S and the Ga-S bond lengths. A larger Fock-exchange fraction contributes to an enhanced localization of Cu-3d orbitals and thus a suppressed *p-d* hybridization, resulting in longer Cu-S bonds and improved μ values.

Interestingly, the calculated band gap depends sensitively on the parameter μ [39], as shown in Fig. 6(b). The calculated $dE_g/d\mu$ is as large as 34 eV. This is easily understood because the μ parameter is directly correlated with band-edge states, i.e., the VBM with the Cu-3d S-3p anti-bonding states and the CBM with the Ga-4s S-3p anti-bonding states. Therefore, a longer Cu-S bond results in a weaker Cu-3d S-3p hybridization and thus a lowered VBM. In the meantime, a shorter Ga-S bond results in a stronger Ga-4s S-3p hybridization and thus a higher CBM level (see Fig. 4) [16]. Unfortunately, a reliable theoretical prediction of the parameter μ is still challenging. In addition, experimental results are also quite scattered, with reported results ranging from 0.242 to 0.259 for CuGaS₂ [16]. This uncertainty in the μ would lead to an uncertainty of 0.58 eV in the calculated band gap.

Fig. 6. (Color online) (a) Anion displacements calculated from the HSE functional with different Fock-exchange ratios. (b) Band gaps calculated from the HSE for different structures.

Summarizing this section, the Cu-3d states have two seemingly incompatible characteristics (or *dual nature*), i.e., the intrinsic localization and covalent bonding tendencies. These two characteristics are strongly coupled and their balance and subtle interplay ultimately determine the electronic properties of these materials. An adequate theoretical treatment of the Cu-3d states is essential for a better understanding of the electronic and structural properties of these materials.

3.3. Energy harvesting applications and electronic properties

With the above understanding of the properties of Cu-3d states, we further investigate the band-edge electronic properties of Cu-chalcogenides, such as the band gap, band ordering, and band degeneracy, aiming to provide insightful guidance for exploring their potential for energy harvesting applications such as high-efficient photon absorbers in solar cells or advanced thermoelectric energy conversion materials. We also aim to develop a reliable yet computational simple and affordable approach, which has practical significance for theoretical material investigations.

3.3.1. Moderate-gap materials for photovoltaics: the DFT+ U + G_0W_0 approach

Band gap is one of the most important criteria for selecting photovoltaic absorbers. We calculate the gaps of four representative materials, i.e., CuGaS₂, CuGaSe₂, CuInS₂, and CuInSe₂, using the state-of-the-art GW approach. Surprisingly, compared with experiments, the band gaps of the first three materials are still underestimated by 0.6 ~ 0.8 eV within the G_0W_0 approach (i.e., the PBE+ G_0W_0 in Table 2).

TABLE 2. Band gaps (in eV) of selected Cu-chalcogenides calculated using various approaches

Systems	PBE	PBE+ U	PBE+ G_0W_0	PBE+ U + G_0W_0	mBJ	mBJ+ U	Experiment
CuGaS ₂	0.84	1.25	1.68	2.41	1.74	2.29	2.43
CuGaSe ₂	0.21	0.53	1.11	1.60	1.05	1.57	1.68
CuInS ₂	0	0.40	0.77	1.41	0.71	1.27	1.53
CuInSe ₂	-0.29	0.08	/	0.95	0.46	0.97	1.04
Cu ₂ Se	-1.29	-0.71	/	/	-0.29	0.50	1.1 ~ 1.23
Cu ₂ SnSe ₃	-0.58	-0.35	/	/	-0.11	0.34	0.6 ~ 0.96

As we have discussed earlier, accurate predictions of the electronic properties of these materials rely on a satisfactory treatment of the Cu-3d states. Unfortunately, the 3d states are usually under-bound within the conventional LDA/GGA. A well-known example [40] is the ZnO, in which the inaccurate account for the Zn-3d energy level leads to an overestimation of the p - d hybridization. A better theoretical description of the p - d hybridization can be achieved by pushing down the Zn-3d states using the DFT+ U approach [40, 41]. Similar effects are observed in Fig. 5 for CuGaS₂. However, it should be pointed out that the underestimation of the Cu-3d energy level leads to an underestimation of the p - d hybridization because Cu-3d orbitals are shallower than S-3p orbitals (see Table 1). Despite of the differences, much improved gaps for CuGaS₂, CuGaSe₂, and CuInS₂ are obtained for the perturbative G_0W_0 correction based on the DFT+ U solution (i.e., the PBE+ U + G_0W_0 approach, see Table 2) [16, 18].

Fig. 7. (Color online) Band structure of CuInSe₂ calculated using the (a) PBE, (b) PBE+ U , and (c) PBE+ U + G_0W_0 approaches, reproduced from Ref. [13]. Projection of the wave functions onto In-4s orbitals is shown as circles. The quasiparticle band structure is interpolated using maximally localized Wannier functions.

The reason for applying a Coulomb U is that it will lead to a better description of the Cu-3d states, resulting in a better starting solution for further many-body perturbation treatments. For example, in the case of CuInSe₂ [see Fig. 7], the wave function is wrongly predicted to be metallic ($E_g = -0.29$ eV) within the PBE; the semiconducting

band ordering is restored within the PBE+ U approximation; finally, both the band structure and the band gap are more accurately predicted within the PBE+ U + G_0W_0 approach. Fig. 8 also shows the quasiparticle corrections to Kohn-Sham levels for CuGaS₂ (CuGaS₂ is studied here because there are relevant XPS data [35] for comparison). It is seen that the PBE+ U + G_0W_0 approach opens up band gap by pushing the VBM downward and the CBM upward, respectively. In addition, the localized Cu-3d states are effectively pushed downwardly [see C, D, E, and VBM points in Fig. 8(b)] as expected. As a result, both the band gap and band widths are well reproduced compared with experimental results. In contrast, the PBE+ G_0W_0 approach fails to reproduce the band gap, and it also incorrectly pushes the localized states upwardly [see D and E points in Fig. 8(a)].

Fig. 8. (Color online) Quasiparticle corrections to Kohn-Sham states in CuGaS₂ using (a) the PBE+ G_0W_0 and (b) the PBE+ U + G_0W_0 approaches. The density of states from quasiparticle calculations and XPS data [35] are also shown.

3.3.2. Narrow-gap materials for thermoelectrics: the mBJ+ U approach

Cu-chalcogenides with even smaller gap, such as Cu₂Se [8] and Cu₂SnSe₃ [6, 42], can be useful for thermoelectric applications. In these cases, the G_0W_0 approach is problematic because the starting mean-field solution is metallic within the PBE or the PBE+ U approach [see Fig. 9(a – b)]. We notice that the recently proposed mBJ potential is quite reliable for band gap prediction for simple semiconductors [21–23]. This motivates us to apply the mBJ potential to narrow-gap Cu-chalcogenides. Unfortunately, the band gap of Cu₂SnSe₃ is still negative within the mBJ [see Fig. 9(c)]. According to above discussions, it is natural to ascribe the remaining uncertainty to the inadequate treatment of Cu-3d localization effect. We therefore augment the mBJ potentials with an on-site Coulomb U , which is called the mBJ+ U method [13], in our calculations. Interestingly, correct band ordering is restored within the mBJ+ U approach for Cu₂SnSe₃ [see Fig. 9(d) and Table 2], with a calculated band gap of 0.34 eV. We mention that this approach is conceptually simple and also computationally affordable, which allows the study of large systems.

It is also interesting to investigate the improvement of the calculated results from the mBJ approach. Fig. 10 shows the differences of exchange-correlation potential v_{XC} and charge density ρ between the mBJ and PBE calculations for CuGaS₂. Compared with the PBE functional, the mBJ v_{XC} is more positive (repulsive) around Cu and Ga, but more negative (attractive) around Se, due to the involvement of the kinetic density [21–23]. There is a charge depletion of about 0.27 electron around the Cu site and a charge enhancement of about 0.14 electron around the S site, indicating a charge transfer from Cu to S; the integrated charge around Ga site remains nearly unchanged, implying that the charge redistribution around Ga is caused by contraction. As a result, both the Cu-S covalent bonding and the Ga-S ionic bonding are strengthened within the mBJ functional [43], and the calculated gap is increased from 0.87 eV with PBE to 1.74 eV with mBJ.

Fig. 9. (Color online) Band structure of narrow-gap Cu_2SnSe_3 calculated within the (a) PBE, (b) PBE+ U , (c) mBJ, and (d) mBJ+ U approaches. Projection of the wave functions onto the Sn-5s orbitals is shown as circles.

Fig. 10. Differences of (a) exchange-correlation potential, i.e., $\Delta v_{xc}(\mathbf{r}) = v_{xc}^{\text{mBJ}}(\mathbf{r}) - v_{xc}^{\text{PBE}}(\mathbf{r})$, and (b) valence charge density, i.e., $\Delta\rho(\mathbf{r}) = \rho^{\text{mBJ}}(\mathbf{r}) - \rho^{\text{PBE}}(\mathbf{r})$, for CuGaS_2 between the mBJ and PBE calculations

3.3.3. A survey on the band gap prediction

Using the above discussed approaches, we carry out a survey of band gap prediction over 90 Cu-chalcogenides and compare them with available experiments [see Fig.11 and Supplementary material]. We point out that there is substantial uncertainty in the measured gaps due to several extrinsic factors such as sample quality. For example, $\text{Cu}_2\text{ZnSnSe}_4$ samples mixed with a ZnSe secondary phase will have much greater gaps ($E_g \sim 1.5$ eV) than high quality samples ($E_g \sim 1.0$ eV) [44, 45]. For anti-fluorite Cu_2Se , the measured gap of 1.2 eV [46, 47] is strongly affected by the crystal phases and Cu-vacancies. The calculated band gap of Cu_2Se is 0.50 eV using the mBJ+ U approach [14]. The gap of the defective CuSbS_2 strongly depends on temperature: it is 1.89, 1.67, 1.40, 1.13, and 0.91 eV measured at 25, 100, 150, 170, 200 °C, respectively [48]. Nevertheless, several clear trends for the band

gap variation with chemical composition and crystal structure can be clearly seen for our theoretical results. Most importantly, the band gaps from the PBE+ U + G_0W_0 and mBJ+ U calculations agree with reliable experiments to within ± 0.2 eV.

Fig. 11. (Color online) Band gaps of Cu-chalcogenides calculated using various approaches. Available experimental results are shown with error bars. The cyan lines are guides to eyes.

3.4. Relativistic effects in Cu-chalcogenides

Cu-chalcogenides with negative band gaps are interesting because the normal band ordering (i.e., valence chalcogen- p and conduction cation- s) is inverted, indicating that they may be topological insulators. Although a negative gap is usually caused by the theoretical errors in the calculation of narrow-gap systems, band inversion is indeed predicted for CuTiSe_2 , Cu_3SbTe_4 , and Cu_3AsTe_4 within the more reliable mBJ+ U approach (see Fig. 11). A negative band gap for CuTiSe_2 is not unexpected considering the trend of the Cu-III-Se $_2$ gaps, which decrease from CuAlSe_2 ($E_g = 2.68$ [49]), to CuGaSe_2 ($E_g = 1.68$ [50]), and to CuInSe_2 ($E_g = 1.04$ eV [51]). This trend is ascribed to the relativistic effects as we have discussed briefly earlier (Section 3.1.2). We now examine the relativistic effects in more detail by focusing on the Cu-V-VI series because Cu_3SbSe_3 is recently recognized as an interesting thermoelectric material [9].

3.4.1. Relativistic orbital contraction in systems with heavy elements

Fig. 12(a – c) show the band structure of the diamond-like Cu_3SbSe_4 with different levels of approximation to the relativistic effects. Here we summarize the results. (1) Result shown in Fig. 12(a) is obtained from the non-relativistic approximation, in which both the mass-velocity and Darwin terms are removed in the calculation. In this case, the calculated direct gap is 0.80 eV, much greater than the experimental value of 0.10 ~ 0.31 eV. (2) The *standard* scalar-relativistic calculation includes both the mass-velocity and Darwin terms; the result is shown in Fig. 12(b). The most important change is a decrease of band gap to 0.24 eV, which agrees better with experiments. The band gap reduction is a result of a significantly downward shift of the lowest conduction band, which is composed of the Sb-5 s (and the Se-4 p) states. Hence the relativistic orbital contraction effect from the mass-velocity term is responsible for the small band gap (recall that the Darwin term contributes positively to the energy). (3) The SOC effect is also considered in the fully-relativistic calculation, as shown in Fig. 12(c). The main

consequence of the SOC is the removal of the band degeneracy of the VBM, with relatively small influence on the band gap (a reduction of 0.09 eV).

Fig. 12. (Color online) Band structures and density of states of the diamond-like Cu_3SbSe_4 calculated with different levels of approximation to the relativistic effects (see text): (a) non-relativistic, (b) scalar-relativistic, and (c) fully-relativistic. (d) Scalar-relativistic approximation for the defective Cu_3SbSe_3 .

Therefore, we conclude that the small band gap of diamond-like Cu_3SbSe_4 is mainly due to the strong relativistic orbital contraction effect. In fact, this effect is so strong that the Sb-5s^2 electrons are energetically unfavorable to be ionized; instead, they tend to become lone-pair electrons [see Fig. 1(d)] in valence bands. Moreover, the change in electronic properties can prompt successive changes to the crystal structures, i.e., the stereochemically active lone-pair may also lead to defective structures. For example, the Cu-Sb-Se systems can also crystalize into Cu_3SbSe_3 [see Fig. 1(d)] and CuSbSe_2 . Furthermore, defective structures are the only stable structures for materials with heavier Bi element.

3.4.2. Spin-orbit coupling effect in defective structures

The electronic properties of defective Cu_3SbSe_3 are quite different from those of the diamond-like Cu_3SbSe_4 [see Fig. 12(b) and (d)]. In Cu_3SbSe_3 , the (occupied) anti-bonding Sb-5s states are also valence states; the lowest conduction band is mainly composed of Sb-5p states (with some Se-4p character), which have higher energies than the Sb-5s states. As a result, the band gap of Cu_3SbSe_3 is much greater than that of Cu_3SbSe_4 . Although the SOC effect is expected to be strong in Cu_3SbSe_3 because its CBM is derived from the Sb-5p states, the effect actually causes only a small change to the CBM energy ($\Delta E_{\text{CBM}} \sim 0.10$ eV for Cu_3SbSe_3). The *suppressed* SOC effect is due to a strong hybridization with the Se-4p states. Therefore, it is expected that the strongest SOC effect will be

found in CuBiTe_2 (see Fig. 13), which contains much heavier elements Bi and Te. The band gap is reduced from 0.76 eV within the scalar-relativistic calculation to 0.35 eV within the fully-relativistic calculation, resulting in a reduction of 0.41 eV.

Fig. 13. (Color online) Band structure of CuBiTe_2 : (a) within the scalar-relativistic calculation and (b) within the fully-relativistic calculation

We summarize the relativistic effects on the electronic properties of these materials. The orbital contraction of the $\text{Sb-}5s^2$ electrons leads to a low CBM position and thus a small band gap for the diamond-like Cu_3SbSe_4 . In some cases the $\text{Sb-}5s^2$ electrons are energetically unfavorable to be ionized, resulting in lone-pair electrons and defective structures. The SOC can have significant effect on the band structures for defective systems. The effect, however, maybe *suppressed* because of strong chemical hybridization. As a result, defective structures usually have larger band gaps than their diamond-like counterparts.

4. CONCLUSIONS

Cu-chalcogenides are a large group of materials used in photovoltaics and thermoelectrics. We review some of the fundamental aspects of the electronic properties of these materials and the theoretical challenges. A reliable theory must be able to capture both aspects of the $\text{Cu-}3d$ electrons, i.e., tendencies of intrinsic localization and strong covalent bonding. The fundamental electronic properties of Cu-chalcogenides can be reliably predicted by the $\text{DFT}+U+G_0W_0$ and $\text{mBJ}+U$ approaches. Moreover, the simple $\text{mBJ}+U$ method works equally well for both moderate- and narrow-gap systems, and the computational efficiency makes this approach more suitable for practical applications to large systems. Finally, the relativistic effects contribute significantly to the band gap reduction in diamond-like structures, sometimes even lead to a structure transition to chalcogen-deficient structures.

ACKNOWLEDGMENTS

This work is supported by the National Basic Research Program of China (2013CB632501), National Natural Science Foundation of China (11234012, 11204333 and 11328401), and Key Research Program of Chinese Academy of Sciences (KGZD-EW-T06). PZ is also supported by the US National Science Foundation (DMR-0946404 and DMR-1506669) and SUNY Networks of Excellence.

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