Stability, geometry, and electronic structure of an alternative I-III-VI$_2$ material, CuScS$_2$: A hybrid density functional theory analysis

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Cu based I-III-VI$_2$ materials have received much attention due to their utility in solar cell applications. The vast majority these studies have focused on materials with group IIIA cations as the trivalent metal. In this study we utilize the screened hybrid exchange functional, HSE06, to investigate the stability of CuScS$_2$ in the crystal structures of all the other I-III-VI$_2$ materials, and find that it preferentially forms in its own unique structure. We analyze the electronic structure and optical properties of CuScS$_2$ and in light of this discuss its semiconducting ability. © *2010 American Institute of Physics*. [doi:10.1063/1.3491179]

Ternary semiconducting compounds with the general structure type I-III-VI$_2$ (where I=Cu; III=Al, Ga, In, and VI=S, Se, or Te) have long been investigated due to their potential applications in optoelectronics, nonlinear optics, and as absorbers in solar cells.[1] These I-III-VI$_2$ materials crystallize in the chalcopyrite structure,[2] Fig. 1(e), possess direct band gaps and display predominantly *p*-type conductivity.[3]

While the majority of this research has centered on the group 13 (Group IIIA; Al, Ga, In) containing I-III-VI$_2$ materials, very little attention has been focused on the group 3 (Group IIIB; Sc, Y, La) materials. In the literature CuScS$_2$,[4] CuYS$_2$,[5] and CuLaS$_2$ (Ref. 6) have all been reported, however, only CuScS$_2$ has had its semiconducting properties investigated.[4]

CuScS$_2$ (CSS) has been reported to crystallize with a noncentrosymmetric *P*3*m*1 space group, in which the structure can be thought of as a hexagonally close packed array of S atoms, with Cu and Sc occupying tetrahedral and octahedral holes respectively.[4] The two S atoms in the unit cell, Fig. 1(b), are easily distinguishable with one S tetrahedrally coordinated to one Cu and three Sc, and one S octahedrally coordinated to three Cu and three Sc. The structure can be considered as being intermediate between the wurtzite and NiAs structures.

CSS was found to be a semiconductor, possessing a direct band gap of 2.3 eV and an indirect band gap of 1.8 eV from optical absorption analysis.[4] The electrical resistivity of *undoped* CSS was $\sim 2 \times 10^3$ Ω cm, however, doping of CSS with Zn to make it *n*-type, with the Zn *assumed* to dope on the tetrahedral Cu site, resulted in a resistivity of $\sim 10^{-3}$ Ω cm.[4] Attempts to dope CSS with Ca (on the Sc site) and P (on the S sites) to make it *p*-type were not successful.[4]

CSS, therefore, appears to be a good *n*-type semiconductor when doped, but thus far *p*-type conductivity has not been realized. This is quite surprising, as CSS would be expected to have a valence band maximum (VBM) made up of Cu 3*d* states mixing with S 3*p* states, which generally results in materials with good *p*-type semiconducting ability, e.g., Cu$_2$S,[7] group 13 I-III-VI$_2$ materials,[8] and layered oxychalcogenide materials.[9]

In this paper we utilize state of the art screened hybrid density functional theory (DFT) to investigate the stability of CSS in all of the previously reported I-III-VI$_2$ structures. We show: (i) that CSS preferentially crystallizes in its own unique structure, (ii) the closest polytype in energy is the CuYS$_2$ structure, with the chalcopyrite, CuAu like and CuCrS$_2$ type structures being significantly less stable, (iii) CSS is predicted to possess an indirect band gap of 1.99 eV and a direct band gap of 2.72 eV and (iv) the VBM of CSS is dominated by Cu 3*d* and S 3*p* states, which are quite dis-
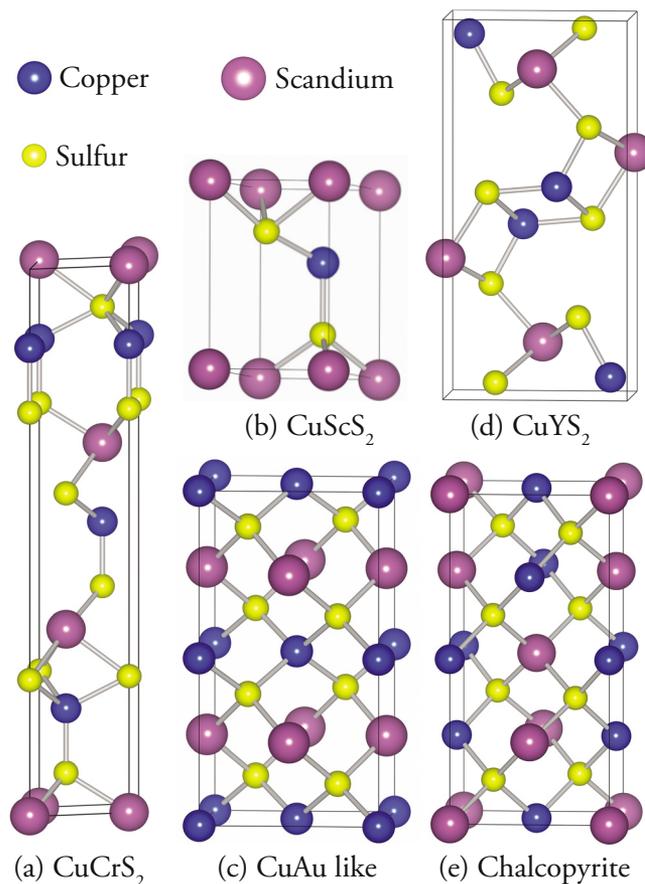

FIG. 1. (Color online) Crystal structures of I-III-VI$_2$ materials tested for CSS in this study: (a) CuCrS$_2$, (b) CuScS$_2$, (c) CuAu like, (d) CuYS$_2$ (PNMA), and (e) chalcopyrite. Blue (dark grey), purple (medium grey), and yellow (light grey) spheres denote Cu, Sc, and S atoms respectively.

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TABLE I. HSE06 calculated lattice parameters and energy difference per formula unit compared to the lowest energy structure for $CuScS_2$ in the CSS, CH, CA, CCS, and PNMA structures. The experimental results from Ref. 4 given in parentheses.

	a (Å)	b (Å)	c (Å)	ΔE (eV/f.u.)
CSS	3.75 (3.73)	3.75 (3.73)	6.03 (6.09)	0.00
PNMA	12.80	3.80	6.10	0.07
CCS	3.65	3.65	18.70	0.25
CA	5.64	5.64	10.68	0.58
CH	5.45	5.45	11.44	0.60

perse in the band structure at the VBM, indicating that CSS *should* be readily made *p*-type.

All DFT calculations were performed using the VASP code,[10] with the projector augmented wave[11] approach, used to describe the interactions between the core (Cu:[Ar], Sc:[Ne], and S:[Ne]) and the valence electrons. The calculations were performed using the screened hybrid functional as proposed by Heyd, Scuseria, and Ernzerhof[12] (HSE06) in which a percentage of the exact nonlocal Fock exchange ($\alpha=25\%$) is added to the Perdew, Burke, and Ernzerhoff[13] functional with a screening of $\omega=0.11$ bohr^{-1} applied to partition the Coulomb potential into long range and short range terms. HSE consistently produces structural data and band gap descriptions that are more accurate than LDA/GGA and meta-GGA data.[9,14–20] A cutoff of 400 eV was used, with calculations deemed to have converged when the forces on all the atoms were less than 0.01 eV Å^{-1}. The optical transition matrix elements and the optical absorption spectrum were calculated within the transversal approximation.[21] Within this methodology, the adsorption spectra is summed over all direct VB to CB transitions and therefore ignores indirect and intraband adsorptions.[22]

We tested the stability of CSS in six different crystal structures: $CuScS_2$ (CSS), chalcopyrite (CH), CuAu like (CA), $CuCrS_2$ (CCS), and two proposed $CuYS_2$ structures [PNMA (Ref. 23) and $P2_12_12_1$ (Ref. 5)]. The equilibrium structures and stabilities are listed in Table I. Our calculated lattice parameters for CSS are within 1% of experiment. The CSS structure was found to have the lowest energy, with the PNMA structure closest in energy. The $P2_12_12_1$ structure relaxed to the PNMA structure, indicating that CSS favors the higher symmetry structure. The CH and CA structures were found to be considerably higher in energy, possibly due to the fact that Sc prefers octahedral symmetry, and group 13 atoms show a preference for the tetrahedral coordination found in the CH structure. The CCS structure was also higher in energy, but this is not surprising, as the S atoms in the $CuCrS_2$ structure are cubic close packed, with the structure thought to be stabilized due to the *d*-electron stabilization between Cr and Cu.[24] In CSS, the Sc and Cu atoms experience no metal–metal bonding.

Analysis of the partial electronic densities of states (PEDOS), Fig. 2(a), reveals that, as expected, the upper VB of CSS is dominated by Cu 3*d* and S 3*p* states, with the main Cu 3*d* peak occurring at ∼−3 eV. This type of mixing is characteristic of other Cu–S containing materials such as CIGS and layered oxychalcogenides. The Sc 3*d* states are present in the VB from just under the VBM to ∼−7 eV, but are very small and will not play a significant role in any
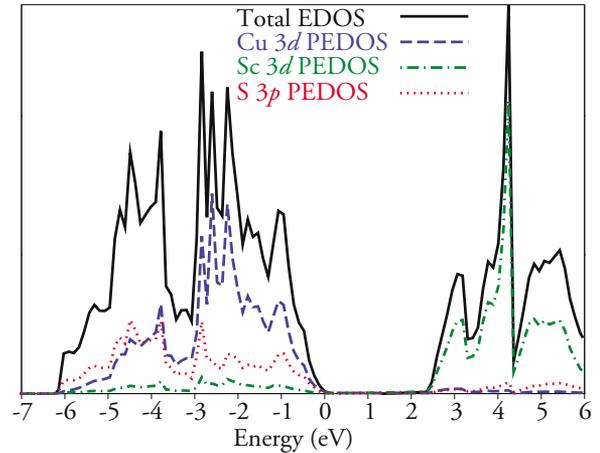

FIG. 2. (Color online) HSE06 PEDOS for CSS, calculated using the tetrahedron method. Black (full line), blue (dash), green (dot-dash), and red (dotted) lines denote Total DOS, Cu 3*d* PEDOS, Sc 3*d* PEDOS, and S 3*p* PEDOS, respectively.

p-type conductivity. Sc 3*d* states dominate the CB with some minor mixing with Cu *d* and S *p* states.

The HSE06 calculated band structure is shown in Fig. 3. The VBM occurs at the Γ point, with the conduction band minimum (CBM) occurring at the L point. The calculated fundamental indirect band gap is 1.99 eV, with the fundamental direct band gap occurring at Γ and measuring 2.72 eV. It is clear from the band structure that there is *significant* curvature of the VB of CSS, and that the CBM is not as disperse at the VBM. This simple visual analysis is normally indicative of a better *p*-type rather than *n*-type material.

In order to quantify this dispersion, we have calculated the effective masses of the band edges. The effective mass (m^*) is calculated using the following:

$$\frac{1}{m^*(E)} = \frac{1}{\hbar^2 k}\frac{dE}{dk},\tag{1}$$

where $E(k)$ is the band edge energy as a function of wave vector k, obtained directly from the HSE06 calculation.[25] In this way the diagonal elements of the effective mass tensor can be calculated for a certain k-point. The lowest effective mass of the VBM is along the Γ-A line and measures $0.93m_O$, with the lowest effective mass of the CB in the L-M direction, measuring $1.03m_O$, indicating that hole mobility *should* be higher than electron mobility in CSS.
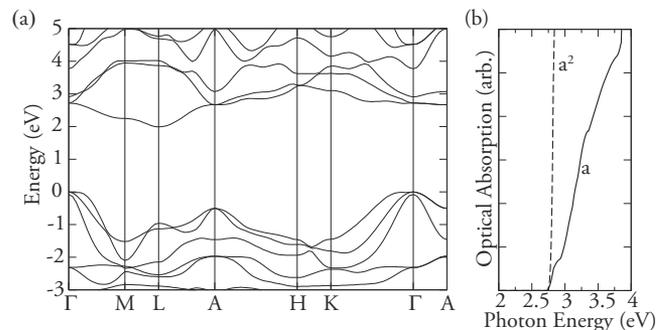

FIG. 3. (a) HSE06 calculated band structure for CSS. The VBM is set to 0 eV. (b) Calculated optical absorption spectrum of CSS summed over all possible direct valence to conduction band transitions.

The HSE06 calculated optical absorption spectra for CSS is shown in Fig. 3(b). Using the Tauc relation ($E_g \propto \alpha^2$), we find that the optical band gaps of CSS is 2.72 eV. This onset of absorption corresponds with the direct band gap at the Γ point from the band structure, and calculation of the dipole transition matrix elements between the VB and CB states confirms that the direct *optical* band gap does indeed occur at the Γ point. This is an overestimation compared to the sole experimentally reported direct optical gap of 2.3 eV.[4]

Our calculations indicate that the electronic structure of CSS bears many important resemblances to that of the chalcopyrites. Most important of these is the strong mixing between Cu $3d$ states and S $3p$ states at the VBM. This mixing, coupled with the visible dispersion at the top of the VB from the band structure, is indicative of a *p*-type material. It is therefore quite puzzling that Dismukes *et al.* were unable to successfully dope CSS *p*-type, but were able to lower the resistivity of CSS by ~ 6 orders of magnitude by *n*-type doping with Zn.[4] As the *n*-type ability of doped CSS is not in doubt, and our HSE06 calculated electronic structure *strongly* indicates a natively *p*-type material, it would seem very prudent to re-evaluate the semi-conducting ability of this possibly *bi-polar* I-III-VI$_2$ material, both theoretically and experimentally.

In conclusion, we have used state of the art *ab initio* calculations to analyze the electronic structure of CuScS$_2$, a material that had successfully been doped *n*-type, but had not previously been doped *p*-type.[4] Our results reveal that the material possesses all the characteristics of a *p*-type semiconducting material. Further exploration of the defect physics and semi-conducting behavior of this possibly bi-polar semiconductor is thus warranted.

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