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Ab initio calculations of structural, electronic, and optical properties of $Cu_2HgSnSe_4$

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ABSTRACT

The electronic structure of $Cu_2HgSnSe_4$ in stannite structure is studied by the first-principles calculations. This material is a direct band-gap compound. In addition, the dielectric function, absorption coefficient, reflectivity, and energy-loss function are studied using the density functional theory within the generalized gradient approximation. We discuss the optical transitions between the valence bands and the conduction bands in the spectra of the imaginary part of the dielectric function at length. High and wide optical absorption spectrum is obtained. There are several prominent peaks for $Cu_2HgSnSe_4$ in the reflectivity spectra. And a rapid decrease of reflectance corresponds to the prominent peak in the energy-loss spectrum.

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1. Introduction

Recently, many quaternary compounds I_2–II–IV–VI_4 (I = Cu, Ag; II = Zn, Cd, Hg; IV = Si, Ge, Sn; VI = S, Se) are considered to be appropriate materials for solar cells due to their p-type conductivity and high optical absorption ($>1 \times 10^4 cm^{-1}$) [1–10]. These quaternary semiconductors are synthesized by replacing half of the III atoms in chalcopyrite (CH) I–III–VI_2 (I = Cu, Ag; III = Al, Ga, In; VI = S, Se) with II atoms and the other half with IV atoms. Most of them crystallize in the kesterite (KS) or stannite (ST) structure. Experimentally, samples of Cu_2XSnSe_4 (X = Zn, Cd, Hg) are observed to crystallize in ST structure [space group $I\bar{4}\,2m$] [11].

Although many samples of Cu_2XSnSe_4 (X = Zn, Cd, Hg) are synthesized in all kinds of methods [12–17], the fundamental physical properties are not well understood unfortunately. In addition, increasing atomic number and structural freedom make their physical properties more flexible relative to binary and ternary compounds, which results in more difficult study of these quaternary compounds. Among these three materials, $Cu_2HgSnSe_4$ compound is expected to be the as-grown p-type material in absorption layer of the solar cell (Al/n:ZnO:Al/n-CdS/p-$Cu_2HgSnSe_4$/Na_2S/Mo/SiO_2/SLG). And then, to the best of our knowledge, there is few theoretical reports about any properties of $Cu_2HgSnSe_4$. With such inducement, we will study the structural, electronic, and optical properties of $Cu_2HgSnSe_4$ in stannite phases with the first-principles methods in detail.

2. Method of calculation

The calculations are performed based on the density functional theory (DFT) using ultrasoft pseudopotential and plane-wave pseudopotential method in the CASTEP (CAmbridge Serial Total Energy) package [18,19]. The exchange-correlation energy of the electrons is described in the generalized gradient approximation (GGA) in the scheme of Perdew et al. [20]. During the whole calculation, we only consider the valence electrons, the electronic configurations of constituent elements are Cu($3d^{10}4s^1$), Hg($5d^{10}6s^2$), Sn($5s^25p^2$), and Se($4s^24p^4$), respectively.

The quaternary compound $Cu_2HgSnSe_4$ is optimized for the primitive cells with a specific $8 \times 8 \times 8$ k-point grid according to the Monkhorst-Pack scheme [21]. The tolerance in the self-consistent field (SCF) calculation is 1.0×10^{-6} eV/atom. During the whole calculation, we employ 350 eV as the plane-wave cutoff energy. For the calculations of the electronic and optical properties, $8 \times 8 \times 8$ and $16 \times 16 \times 16$ k-point grids are used for numerical integrations over the Brillouin zone (BZ). The test calculations with higher cutoff energies and denser k-point grids are also performed, and the

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Table 1
Equilibrium lattice constants a, c and u-parameters u_x(Se) and u_z(Se) of stannite-type $Cu_2HgSnSe_4$.

		a(Å)	c(Å)	u_x(Se)	u_z(Se)
$Cu_2HgSnSe_4$	This work	5.83760	11.5008	0.2502	0.1422
	Expt.	5.8288(1)[a], 5.832[b], 5.818[c]	11.4179(2)[a], 11.389[b], 11.48[c]	0.2591(2)[a]	0.13820(9)[a]

[a] Reference [22].
[b] Reference [12].
[c] Reference [11].

overall results remain unchanged. All lattice vectors and atomic positions are fully relaxed by minimizing the quantum-mechanical stresses and forces.

3. Result and discussion

3.1. Structural parameters

First-principles total-energy calculations show that the energy stability presents a obvious dependence on the cation size difference and the ionicity of $Cu_2HgSnSe_4$. As more attention is being paid to the application of this compound, it becomes necessary to have a complete and clear understanding of structural parameters and their influence on the electronic and other physical properties. So we firstly use the initial crystallographic parameters [22] analyzed by X-ray diffraction (XRD) as a beginning for geometry optimization. The calculated equilibrium lattice constants (a and c) and u-parameters (u_x(Se) and u_z(Se)) for $Cu_2HgSnSe_4$ are compared with the available data in Table 1. The parameter, u_x(Se), is the x-coordinate of Se, and u_z(Se) is the z-coordinate of Se in the unit cell. Both of them are the parameters of x/a and z/a, respectively. In Table 1, our calculated lattice parameters a and c are in agreement with the previous experimental results [11,12,22]. And the other two theoretical u-parameters have also satisfactory agreement with their experimental values [22]. It can be seen that the optimized structure is reasonable. Therefore the following calculations about the electronic and optical properties for this compound are very credible.

3.2. Electronic structure

We calculate the energy band structure of $Cu_2HgSnSe_4$ and present it in Fig. 1, and the insert shows a close-up figure of the band structure for the band edges. It can be seen that this crystal is a direct gap semiconductor ($\Gamma - \Gamma$). And the theoretical band gap is almost near to 0 eV. According to the report of S.A. Mkrtchyan et al., the thermal gap energy of $Cu_2HgSnSe_4$ is equal to 0.17 eV [23]. Obviously, our calculated band gap of $Cu_2HgSnSe_4$ is much smaller than that of the experimental value and the difference between them is 0.17 eV. Such an underestimation of the calculated band gaps is an intrinsic feature of the ab initio method and is related to the DFT limitations, namely not taking into account the discontinuity in the exchange-correlation potential [24]. To overcome such a discrepancy, the so called scissors operator (SO) [25] is introduced by means of a simple rigid shift of the unoccupied conduction bands (CBs) with respect to the valence bands (VBs). It effectively describes the difference between the theoretical and experimental band gap values. It is simply set the scissors operator to the difference between the two values. In our case the value of the scissors operator is 0.17 eV. We use this value to modify the electronic structure and the optical properties. After calculating with this SO, the corrected energy band structure is plotted in Fig. 1 with

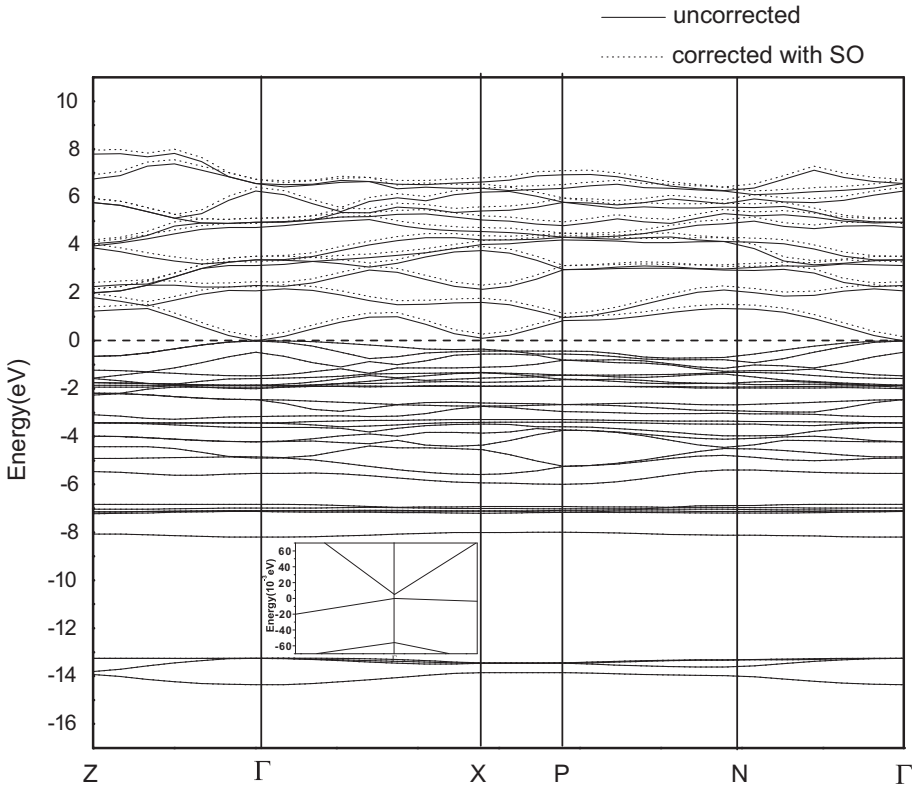

Fig. 1. The uncorrected (solid curve) and corrected with SO (dotted curve) band structures of $Cu_2HgSnSe_4$. The insert shows a close-up figure of the band structure for the band edges.

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