Current Applied Physics 15 (2015) 1417–1420

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Structural, electronic, and optical properties of bulk Cu_2Se

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ARTICLE INFO

Article history:
Received 22 June 2015
Received in revised form
30 July 2015
Accepted 8 August 2015
Available online 12 August 2015

Keywords:
Solar cell
Cuprous chalcogenide
Photovoltaic material
van der Waals interaction
GW–Bethe–Salpeter equation approach
Density functional theory

ABSTRACT

By using first-principles calculations within the density functional theory and the many-body perturbation theory, we investigate the structural, electronic, and optical properties of bulk Cu_2Se with a recently discovered low-temperature layered configuration. We demonstrate that the effects of the van der Waals forces significantly modify the interlayer binding and distance in the layered Cu_2Se, while the band gap is invariant. Our density functional theory and post-processing *GW* calculations reveal that for the layered structure, *GW* correction remedies the serious band-gap underestimation of the density functional theory from 0.12 eV to 0.99 eV. By solving the Bethe–Salpeter equation, we find that the optical gap of the layered Cu_2Se is 0.86 eV, which is in close agreement with previous experimental observations. In addition, we show that the high-temperature fluorite structure has no band gap, even after *GW* correction, explaining that the band gap controversy among the theories stems from different structural models. This work may serve as an important guide in designing and evaluating photovoltaic devices using Cu_2Se-based materials.

1. Introduction

Copper chalcogenide compounds have attracted much attention over the last few decades because of their potential applications in photovoltaic and thermoelectric devices [1,2]. As a prototype cuprous chalcogenide, Cu_2Se has been widely used in solar cells [3,4], opto-electronic devices [5,6], and thermoelectric generators [7]. In particular, Cu_2Se is an important constituent material in $Cu(In,Ga)Se_2$ (CIGS) solar cells, which is one of the most promising technologies in the renewable energy industry. Despite the simple chemical formula of Cu_2Se and its significance in a wide range of device applications, the atomic structure of the low-temperature Cu_2Se phase was unknown until recently, which hampered theoretical investigations of the physical properties of Cu_2Se. Indeed, a few first-principles studies [8,9] of Cu_2Se were based on the high-temperature phase instead, likely resulting in a serious discrepancy between the theory and the experiment, as discussed below. For the low-temperature Cu_2Se phase, Gulay et al. proposed a complex monoclinic structure using X-ray diffraction measurements [10]. Nguyen et al. predicted a simpler layered Cu_2Se structure through a genetic algorithm study [11], and a similar layered configuration was observed experimentally [7] nearly at the same time. It was found that the new layered configuration is energetically the most stable among the proposed structural models [11].

As transition metal chalcogenides have been emerging as strong candidates for applications in future nano-scale devices [12], their layered nature is also attracting much interest. In fact, their layered structures are weakly bound by attractive van der Waals (vdW) forces, enabling the facile isolation of the layered building blocks and consequent application of their exotic two-dimensional properties in various fields of materials science [12]. The newly proposed [11] structural model of Cu_2Se also possesses layered building blocks that consist of six strongly bonded atomic layers, as shown in Fig. 1(a). Therefore, it is highly desirable to understand the effects of vdW forces on the structure and energetics of Cu_2Se for realizing better control of the layered building blocks.

The measured band gaps of Cu_2Se in optical experiments [13–15] are in the range of 1.0–1.3 eV. In contrast, metallic or semimetallic electronic structures of Cu_2Se were reported in the previous first-principles studies [8,9] for the high-temperature fluorite structural model. It is notable that the new low-temperature layered Cu_2Se structure shows a substantial band gap of 0.74 eV within the meta-generalized gradient approximation [11]. However, it is unclear whether the stark discrepancy among the theories originates from the different structural models, because the previous studies were conducted using various computational

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http://dx.doi.org/10.1016/j.cap.2015.08.006
1567-1739/

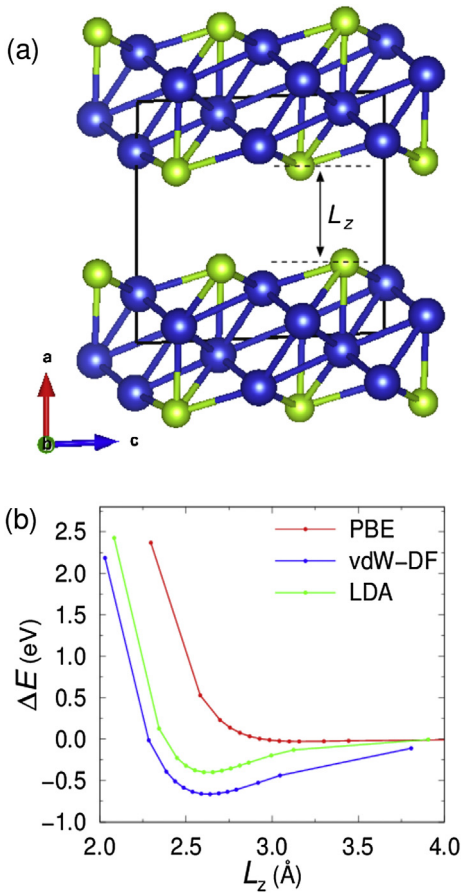

Fig. 1. (a) Optimized atomic geometry of the low-temperature layered Cu_2Se. The unit cell is indicated by the solid lines. In (a), the interlayer separation L_z is indicated by the arrow. The blue and green balls represent the Cu and Se atoms, respectively. (b) The relative energy ΔE as a function of L_z within the PBE, vdW-DF, and LDA schemes. The zero energy references are set to the total energies of the isolated Cu_2Se building-block layer for each scheme. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

methods with different accuracies, ranging from the local density approximation (LDA) [16] to the hybrid functionals [9]. Therefore, further theoretical efforts are needed to address such discrepancies.

The *GW* approach has been regarded as one of the most accurate techniques for describing the band structures of semiconductors [17–20]. However, the *GW* method alone is often insufficient for describing the excitonic electron–hole interactions, which are critical to the optical properties of semiconductors. The best way to describe such excitonic interactions is to solve the Bethe–Salpeter equation (BSE) based on the *GW* results [17–20].

In this work, by using first-principles calculations within the density functional theory (DFT) and the *GW*–BSE, we investigate the structural, electronic, and optical properties of Cu_2Se. To include the effects of vdW forces, the van der Waals-density functional (vdW-DF) [21,22] scheme is employed. We found that the inclusion of the vdW forces considerably modifies the interlayer binding and distance in the layered Cu_2Se. Our *GW*–BSE calculations further reveal that the layered Cu_2Se possesses a quasi-particle band gap of 0.99 eV and an optical gap of 0.86 eV, remedying the seriously underestimated band gap (0.12 eV) in the present DFT calculations; the calculated optical gap is in close agreement with those (1.0–1.3 eV) obtained by optical measurements [13–15]. The corresponding exciton binding energy is 0.13 eV. In addition, we demonstrate that the high-temperature fluorite structure has no band gap, even after the *GW* approximation, explaining that the band gap controversy among the theories stems from the different structural models. These findings shed more light on the physical properties of Cu_2Se-based photovoltaic materials.

2. Computational details

The first-principles DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [23]. We used the projector-augmented wave (PAW) [24] pseudo-potentials. To examine the effects of vdW forces, we compared the results from two different exchange-correlation functionals: the Perdew–Burke–Ernzerhof (PBE) [25] and the vdW-DF. The cutoff energy used for the plane-wave basis set is 400 eV. Monkhorst-Pack's scheme [26] was used for *k*-point sampling; a $6 \times 9 \times 6$ k-point mesh was employed. All atoms were allowed to relax fully until the forces on each atom were less than 0.02 eV/Å. For comparison, we also calculated the high-temperature fluorite structure. The optimized lattice constant of the fluorite structure is 5.857 Å in the vdW-DF calculations. The *GW*–BSE calculations started from the preceding DFT results within the HSE06 hybrid functional [27,28]. We performed single-shot G_0W_0 calculations. The energy cutoff for the response functions was set to be 266.7 eV. The following BSE calculations were performed using the 26 highest valence bands and 26 lowest conduction bands. We obtained essentially the same quasi-particle band gap and optical gap from the convergence tests using the energy cutoff of 200 eV for the response functions and a $4 \times 7 \times 4$ *k*-point mesh, indicating that our *GW*–BSE calculations provide well-converged energy gaps.

3. Results and discussion

We revisit the new layered structure of Cu_2Se that was proposed by the previous genetic algorithm study combined with the LDA scheme [11] by using a more elaborate vdW-DF method, which was successful for describing interlayer interactions in other layered systems, such as graphite and hexagonal boron nitride [29]. To investigate the effects of vdW forces on the layered Cu_2Se structure, we compare the results obtained from the PBE and vdW-DF schemes. The optimized atomic structure from the PBE calculation is shown in Fig. 1(a). The structure has a monoclinic (space group $P2_1/c$) unit cell with a = 6.889 Å, b = 4.313 Å, c = 6.857 Å, $\alpha = 90.00°$, $\beta = 87.34°$, and $\gamma = 90.00°$. The Wyckoff positions of Cu1, Cu2, and Se are (0.0622, −0.4183, 0.1704), (−0.2002, −0.0772, −0.0070), and (0.2873, −0.0621, 0.3420), respectively. The lattice parameters for the vdW-DF are a = 6.754 Å, b = 4.332 Å, c = 6.908 Å, $\alpha = 90.00°$, $\beta = 87.45°$, and $\gamma = 90.00°$; the Wyckoff positions are (0.0626, −0.4170, 0.1707), (−0.2051, −0.0786, −0.0068), and (0.2954, −0.0628, 0.3409) for Cu1, Cu2, and Se, respectively. Fig. 1(b) shows the relative energy of the layered Cu_2Se configurations versus the interlayer separation between the six-atomic-layer building blocks [denoted as L_z in Fig. 1(a) and (b)]. For comparison, the results obtained using the LDA scheme are also shown in Fig. 1(b). The lowest energy interlayer separations are 3.16 Å, 2.54 Å, and 2.60 Å for the PBE, vdW-DF, and LDA calculations, respectively; the values of the LDA and vdW-DF calculations are close to each other, which is similar to the cases of graphite and hexagonal boron nitride [29]. By comparing the PBE and vdW-DF results, we found that the effects of the vdW forces enhance the interlayer binding of the layered building blocks, as reflected by the calculated binding energy of 0.16 eV per formula unit, whereas the PBE potential energy profile is repulsive. The binding energy is slightly larger than those (0.07–0.12 eV) of other transition metal chalcogenides [30].