Extended Abstract

Optical properties of cadmium and mercury defective chalcopyrites by many-body perturbation theory: Investigation of excitonic effects

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Abstract

In this study, the electronic and optical properties of the compounds $HgAl_2S_4$, $HgGa_2S_4$, and $CdAl_2S_4$ were investigated by solving the equation of motion of the two-particle Green's function and the Bethe-Salpeter equation (BSE). This was achieved using the augmented plane wave (APW) basis sets and the full potential method, and the results were compared with those obtained by the random phase approximation (RPA). All three compounds are semiconductors with direct band gaps at the center of the Brillouin zone, with GW values of 3.412, 2.644, and 3.79 eV, respectively. The optical responses of these materials differ for polarizations parallel and perpendicular to the direction of light radiation, and consequently, the materials are anisotropic. In the dielectric functions of the three compounds, the presence of strong excitonic features in the band gap region and beyond results in the modification of the one-particle responses of the materials.

Keywords: Defective chalcopyrites, Optical properties, Bethe-Salpeter equation (BSE), Excitonic effects.

1. INTRODUCTION

The ternary compounds known as chalcopyrites, due to their interesting physical and chemical properties, have been the subject of many scientific studies. As a subclass of these materials, defective chalcopyrites with the chemical formula AB_2C_4, where A, B, and C are, respectively, a transition metal, an aluminum, gallium or indium atom, and a chalcogen, have attracted the attention of scientists for their industrial applications. Structural and electronic properties of many of defective chalcopyrites have been studied [1,2]. Recently, in a theoretical study, we studied the energy loss near edge structure (ELNES) spectra of sulfur atom in $HgAl_2S_4$, $HgGa_2S_4$, and $HgIn_2S_4$ chalcopyrites [3], including the interaction of a high-energy electron beam with the materials. In some theoretical studies, electronic and optical properties of mercury-based chalcopyrites have been studied in the density functional theory (DFT) [4]. Although the relative weakness of DFT in obtaining the excited states properties of materials has been known, to our knowledge, there isn't any study based on the many-body perturbation theory (MBPT) for this purpose. Since the knowledge of material characteristics, especially their optical properties including the effects of the coupling between the transmitted electron and the left hole by the electron transition (excitonic effects), is mandatory for their use in electronic and optoelectronic industries, the present study deals with optical properties of $CdAl_2S_4$ and HgX_2S_4 (X=Al, Ga) defective chalcopyrites by solving the Bethe-Salpeter equation (BSE), the equation of motion of the two-particle Green's function [5].

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2. MATERIALS AND METHODS

2.1. Computational parameters

The present work utilized the WIEN2k computational package for calculating the ground state properties, including the structural properties, the densities of states, and the band structures. It also used the exciting code for the excited state properties of defective chalcopyrites, including their optical properties. The linearized augmented plane wave (LAPW) method was used for solving the Kohn-Sham equations, and the generalized gradient approx**imation (GGA)** was used for **calculating** the **exchange-correlation functional**. The **k-mesh** in the **Brillouin zone** with the dimensions of **14x14x14**, **consisting of 375 k-points**, led to the **convergence of the results**.

2.2. Excitonic effects

The eigenvalue equation below includes the two-particle excitations due to the coupling of the transmitted electron and the left hole:

$$\sum H^{eff}_{vck,v'c'k'} = E^i A^i \qquad (1)$$

where E^i and EA^i are the exciting energy and the electron-hole coupling coefficient in the valence (v) and conduction (c) states. The effective kernel includes the energy difference between the quasi-particles, the attractive coulombic interaction between the electron and the hole, and the exchange interaction. Finally, the imaginary part of the dielectric function which is the main quantity for getting the optical response of the materials, is obtained by its relation with the two-particle correlation function.

3. RESULTS AND DISCUSSION

3.1 Structural and electronic properties

The defective chalcopyrites are crystallized in a zinc sulfide crystal structure with a space group of $I4^-$ (No. 82). Substituting aluminum with gallium results in increasing the lattice dimensions and atomic bond lengths. Fig. 1 shows that the $CdAl_2S_4$, $HgAl_2S_4$, and $HgGa_2S_4$ compounds are direct band gap semiconductors at Γ point, with the GGA (GW) band gaps of 2.77 (3.79), 2.19 (3.412), and 1.57 (2.644) eV, respectively.

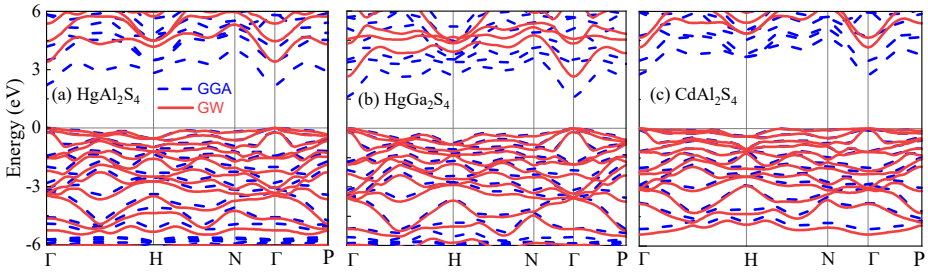


Fig. 1. The electronic band structures of (a) $HgAl_2S_4$, (b) $HgGa_2S_4$, and (c) $CdAl_2S_4$ in GGA (dashed lines), and GW (solid lines).

The valence energy bands of $CdAl_2S_4$ are primarily composed of the p states of sulfur. In contrast, the valence bands of the mercury-based compounds ($HgAl_2S_4$ and $HgGa_2S_4$) are made up of both the p states of sulfur and the d states of mercury. The conduction energy bands for all three compounds are mainly composed of the s states of the transition metal (Cadmium or Mercury) and the p states of the sulfur atom. At energies beyond 5 eV, the conduction bands are formed by the p states of the aluminum/gallium and the p states of the transition metals.

3.2 Optical properties

Fig. 2 compares the imaginary parts of the dielectric functions of the studied compounds with (BSE+GW) and without (RPA) excitonic effects. Due to the tetragonal symmetry, these functions have the two independent xx and zz components, and as these two components have different spectral dispersion, these compounds are anisotropic. Since the effect of the electron-hole coupling mostly appears at the energy band gap region, the

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spectra are compared at the first 8 eV. In comparison with the RPA, the dielectric constants obtained from the BSE increase, and they decrease (increase) from Al to Ga (Cd to Hg). From $CdAl_2S_4$ to $HgAl_2S_4$, the optical gap in both approximations decreases, and then it increases to $HgGa_2S_4$. This behavior can be attributed to the presence of the gallium atom and the change in the electronic states in the valence and conduction bands (Ga p→S p), and therefore in the electron transitions.

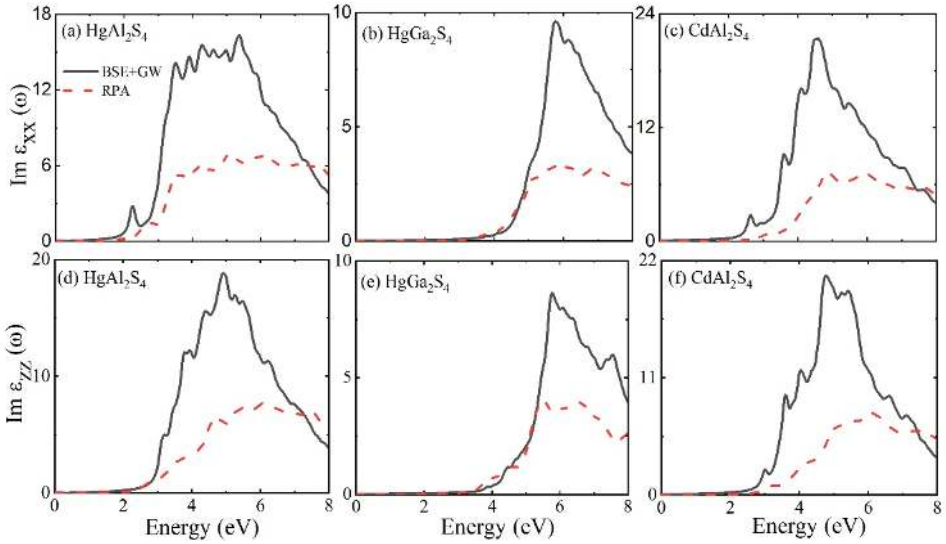


Fig. 2. The *xx* (up) components of the imaginary parts of the dielectric functions of (a) $HgAl_2S_4$, (b) $HgGa_2S_4$, and (c) $CdAl_2S_4$, compared with their *zz* (down) components from (d) to (f), in BSE+GW (solid lines) and RPA (dashed lines).

The presence of spectral features in the band gap regions indicates the strong electron-hole coupling in the materials. The first peaks in Im ϵxx(ω) of $HgAl_2S_4$ ($CdAl_2S_4$) at 2.258, 3.15, and 3.312 eV (2.64 and 3.59 eV) are the excitonic features with strong oscillator strengths at the center of the first Brillouin zone (Γ), resulting from the electron transition of the Hg d (Cd d) states to a hybridization of Hg s (Cd s) and Al p states. Due to a larger band gap, the excitonic effects in $CdAl_2S_4$ are stronger than those in $HgAl_2S_4$. For $HgGa_2S_4$, the excitonic structure in the xx (zz) components of the Im ϵ(ω) is a feature with a weak (strong) oscillator strength beyond the electronic band gap at the energy position of 3.71 (3.592) eV, resulting from the electron transition of a hybridization of Ga s and Hg d states below the Fermi level to the unoccupied Ga p and S p states. The spectral excitonic features in the loss functions (L(ω)) of the studied materials can be attributed to those in the dielectric functions, as shown by the equation $L(\omega)=-\mathrm{Im}(1/\epsilon(\omega))$. Therefore, the excitonic peaks in L(ω) can be assigned to the similar excitonic peaks in Im ϵ(ω) that result from the interband electron transitions.

4. CONCLUSION

In optical properties of defective chalcopyrites of mercury and cadmium, the coupling of transmitted electron and the left hole by the electron transition, and the formation of the bound electron-hole couple, exciton quasiparticle, lead to the redistribution of the oscillator strengths in the dielectric and loss functions of the materials and the appearance of the excitonic structures in the band gap regions.

5. REFERENCES

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