

ADVANCED THEORETICALLY ENGINEERING OF NOVEL PHOTOVOLTAIC INTERMEDIATE BAND MATERIALS BASED ON METAL DOPED CHALCOGENIDES

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ABSTRACT: In the present work properties of derived chalcogenide compounds are obtained quantum mechanically using beyond Density Functional Theory (DFT) calculations and several candidates are proposed to be novel photovoltaic materials for the design of intermediate band solar cells with enhanced efficiencies. Substituting appropriately some Ga atoms with transition metals can give a compound with a narrow, partially-filled electronic band located inside the host semiconductor forbidden energy band-gap. Optical properties according to the experimental band-gap of the host semiconductor are obtained for both $\text{TiCu}_4\text{Ga}_3\text{S}_8$ and $\text{CrCu}_4\text{Ga}_3\text{S}_8$. The band originated from the 3d states of the transition metal plays a determining role in the absorption of low energy photons. The effect of the strong correlation present in the 3d-Ti electrons of $\text{TiCu}_4\text{Ga}_3\text{S}_8$ is also studied by first principles. As a result a value of 0.6 eV for U is found. This value turns out to be lower than that of other Ti based compounds. From a subsequent GGA+U calculation the effect of the correlation is reasoned to be not dangerous for the formation of an isolated intermediate band.

Keywords: Intermediate Band, Chalcopyrite, Quantum Calculation

1 INTRODUCTION

In the quest of novel high performance solar cells which could improve the thermodynamic efficiency limit of conventional photovoltaic solar cells (40.7%) obtained by Shockley and Queisser [1] a number of proposals have been introduced. Among them, a novel concept of a solar cell based on an intermediate band photovoltaic material proposed by Luque and Martí [2] could reach an efficiency up to 63.2% [3].

In this cell the enhancement of the photo-current would be provided from the additional absorption of low energy photons, apart from the absorption of high energy photons which generates conduction electrons coming directly from the valence band. These additional carriers would be obtained due to the action of a narrow intermediate electronic band located inside the semiconductor band-gap which play as both destination of electrons excited from the valence band and origin of electrons towards the conduction band.

The intermediate band must be completely isolated from the semiconductor bands in order to prevent non-radiative recombinations and must be partially filled to enable electrons to arrive at it from the valence band and to go from it to the conduction band.

A possible method to find an intermediate band material consists on modifying the atomic structure of a host semiconductor by means of the introduction of a transition metal [4]. Our purpose is that the 3d electronic shell of the transition metal atoms could generate an intermediate band with the appropriate characteristics.

Previous works have predicted that the replacement of Ga atoms with Ti in III-V semiconductors, such as GaAs [4] or GaP [5], can provide an intermediate band photovoltaic material.

In the present work chalcogenide derived compounds are modelled in order to find a novel intermediate band material. The advantage of this family of compounds is that they are well known in the field of photovoltaic technology and therefore the production of an intermediate band solar cell based on these compounds would be easier to achieve than with other kind of materials.

Due to its band gap (2.4 eV) which results to be appropriate to the requirements to hold an appropriate intermediate band within it, CuGaS_2 chalcopyrite has been chosen to be the host semiconductor in our intermediate band candidate. In it we have modelled a related compound by means of partially substituting Ti for Ga. In particular the compound depicted has $\text{MCu}_4\text{Ga}_3\text{S}_8$ structure, M being Ti or Cr.

In previous studies a general characterization of the properties of $\text{MCu}_4\text{Ga}_3\text{S}_8$ compounds was done [6,7]. In this occasion the study arrives to a deeper level of intuition of the properties of these materials focusing mainly on two aspects. In the first part, a more realistic method for obtaining the optoelectronic properties improving the quality of the results, specially the features concerning to the band-gap of the host semiconductor, is applied. In the second part, a refined analysis of the strong Coulomb interactions present in the localized 3d orbitals of the substituting transition metals by means of *ab initio* GGA+U calculations is carried out.

2 STRUCTURE

CuGaS_2 chalcopyrite structure crystallizes in the body centered tetragonal space group I-42d. The unit cell is composed of 16 atoms ($\text{Cu}_4\text{Ga}_4\text{S}_8$) in which every element is located in a site coordinated tetrahedrally to four first neighbours.

The intermediate band material candidates are modelled from the parent CuGaS_2 by means of the replacement of one Ga atom of the $\text{Cu}_4\text{Ga}_4\text{S}_8$ primitive cell by one transition element M (specifically Ti or Cr) and resulting a $\text{MCu}_4\text{Ga}_3\text{S}_8$ compound (see [6,7]). In this structure the nearest neighbouring Ti atoms are separated by 12.4 Å.

Furthermore, during the determination of the Hubbard term, a $2 \times 2 \times 1$ supercell (with formula $\text{Ti}_4\text{Cu}_{16}\text{Ga}_{12}\text{S}_8$) was modelled in order to take into account the response from several correlated Ti sites apart from the local one, which it is always considered. As a result, both two nearest (at 12.4 Å) and one second nearest (at 14.3 Å) neighbouring Ti atoms were included in the calculation.

3 METHODOLOGY

All the calculations were performed following the Density Functional Theory (DFT) [8,9] with a plane wave basis set and taking the Generalized Gradient approximation (GGA) parametrized by Perdew and Wang (PW91 [10]) for the exchange-correlation potential allowing also spin polarization. All the calculations were carried out after having relaxed the crystal structure up to a 0.01 eV/Å threshold.

However, different computational details were taken to obtain the two advanced features analysed below.

3.1 Optoelectronic properties

In order to obtain the optoelectronic properties, the calculations were carried out using the VASP [11] program in which core electrons were pseudized through projector augmented wave (PAW) potentials [12].

For the determination of the optical properties we have used the relation between the microscopic properties of the material, obtained in the ground state calculation, and the macroscopic dielectric function, within the Random Phase Approximation (RPA). For a more detailed explanation see refs. [13,14]. For these calculations we found converged optical properties by sampling the Brillouin Zone with a 12x12x12 Monkhorst-Pack grid [15].

3.2 Effect of strong electronic correlation

In order to see the effect of strong Coulomb interaction of 3d transition metal levels over the density of states GGA+U calculations were carried out. This method includes in the hamiltonian an extra Hartree-Fock like component for the localized orbital states of the system [16]. In this way partial occupancies of these orbitals are discouraged with a strength given by a Hubbard term U which accounts for the on-site Coulomb correlations.

In previously presented GGA+U studies the values of the on-site correlation term U (as the exchange coupling constant J) were chosen according to other works in which the transition metal had a similar valence and environment [7].

In the present calculations the value of a rotational invariant effective U (corresponding to $U-J$) [17] is calculated following a first principles linear response method introduced by M. Cococcioni and S. de Gironcoli [18]. In their work the meaning of U is related to a spurious curvature found in the function that represents the GGA total energy versus the number of electrons of the system.

The linear response function χ_{ij} is then obtained from constrained DFT calculations in which the electronic occupancy n_i of the correlated site i is varied through the application in the site j of a small additional potential shift α_j :

$$\chi_{ij} = \frac{\partial n_i}{\partial \alpha_j}$$

The value of U is therefore:

$$U = (\chi_0^{-1} - \chi^{-1})_{ii}$$

The “zero” subindex above refers to the response produced by a bare perturbation, that is, without allowing redistribution of the charge density, while its absence means that the response was taken after achieving the self-consistency among all the valence electronic structure.

The strongly correlated occupancies mentioned above are calculated from projections of the Kohn-Sham states over localized Wannier type functions [19] which in turn were obtained from previously converged GGA calculations.

All of the features referring to the U determination and the GGA+U calculations were calculated using the Quantum-Espresso package [20] and ultrasoft type pseudopotentials [21].

4 RESULTS

4.1 Optoelectronic properties

The results of optical absorption coefficients for the different chalcopyrite compounds are shown in Fig. 1. In all the cases a scissor operator which applies a rigid shift to the unoccupied electronic levels was applied. In this way the absorption spectrum obtained using the scissor operator agrees with that reported experimentally from ref. [22].

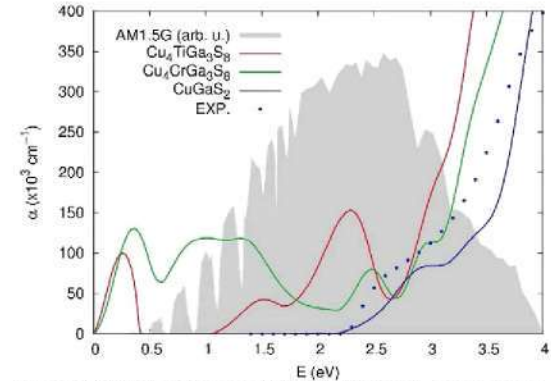


Figure 1: Absorption coefficient of doped compounds compared to that of CuGaS_2 parent semiconductor. In dots experimental results from ref. [22] are included. In the shady background the solar spectrum AM1.5G is represented.

It can be seen that the partial substitution of Ga by a transition metal causes an enhancement of the absorption in the relevant energy range of the solar spectrum, according to our expectations.

With the intention of seeing where this enhancement comes from it is useful to analyse the separated transitions that can contribute to the absorption coefficient. The electronic structure of the compounds studied here consists of a valence band (VB) fully occupied, a conduction band (CB) empty and a narrow intermediate band (IB) partially filled. As a result there are three kinds of inter-band transitions that can be produced by photo-absorption, that is, from the VB to the CB, from the VB to the IB and from the IB to the CB. Additionally, intra-band transitions within the IB also can happen. All these contributions are shown in Fig. 2 and Fig. 3 for $\text{TiCu}_4\text{Ga}_3\text{S}_8$ and $\text{CrCu}_4\text{Ga}_3\text{S}_8$, respectively.

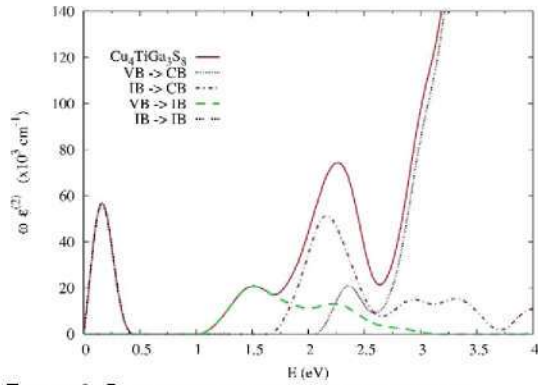


Figure 2: Partial contributions to the absorption coefficient of the $\text{TiCu}_4\text{Ga}_3\text{S}_8$ compound.

In the case of $\text{TiCu}_4\text{Ga}_3\text{S}_8$ it can be seen that transitions from VB to CB are the dominant contribution for energies higher than 2.6 eV. At energies about 2.2 eV the main contribution comes from transitions involving IB and CB, whereas transitions from VB to IB are important only in the proximity of 1.5 eV. The peak present at few tenths of electronvolt is caused by the transitions involving only IB states.

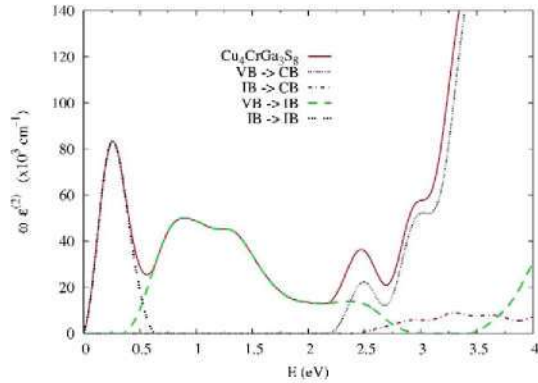


Figure 3: Partial contributions to the absorption coefficient of the $\text{CrCu}_4\text{Ga}_3\text{S}_8$ compound.

The picture found for $\text{CrCu}_4\text{Ga}_3\text{S}_8$ is rather different to that described above. The transition from the VB to the CB is again the most important in the range of high energies. However transitions from VB to IB are now much more significant than those from IB to CB, especially in the interesting range of the solar spectrum. The reason why this is observed is because the IB is much closer to VB than to CB. Another appreciable difference is that the intra-band peak of the IB is enlarged, probably because of the fact that the IB of the Cr doped compound is a triplet while that of $\text{TiCu}_4\text{Ga}_3\text{S}_8$ is a doublet.

4.2 Effect of strong electronic correlation

In order to determine the linear response matrices χ and χ_0 , which are needed to obtain Hubbard term U , calculations of the correlated occupancies of each site i upon applying a concrete potential shift in the site j were carried out. The results obtained are shown in Fig. 4. It can be seen that the effect of the linear response of the second nearest neighbouring Ti atom is almost identical to that of the first nearest ones. This means that the role played by the different neighbours does not depend to a large extent of the interatomic distance. This is indicative

of a reasonably converged value of U . However, it must be taken into account that the distances from the perturbed atom are rather similar (12.4 and 14.3 Å, respectively).

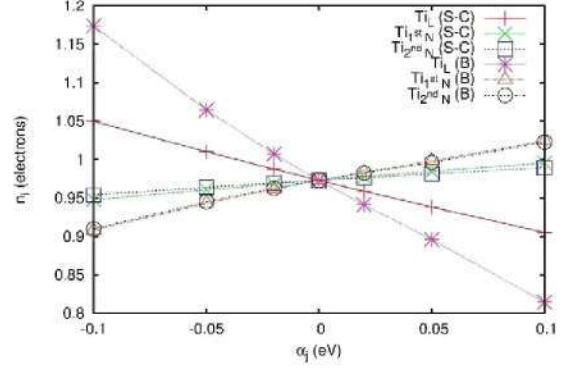


Figure 4: Occupancies of the localized levels of the different Ti_j atoms of $\text{Ti}_4\text{Cu}_{16}\text{Ga}_{12}\text{S}_{32}$ compound with respect to α_j potential shifts both allowing the relaxation towards the self-consistency (S-C) and not (B), for constructing χ and χ_0 , respectively. The Ti_L label corresponds to the response in the same atom in which α_j is applied, $Ti_{1st N}$ is referred to the two first neighbouring Ti atoms and $Ti_{2nd N}$ corresponds to the only second neighbouring Ti atom.

Following the method explained in the third section U was obtained from the variations reported above and the value found is 0.6 eV. This value is smaller than those used in most of the references in which the Ti is treated in a GGA+ U approach [16], although it must be kept on mind that the compounds studied here have a less ionic character and this points to a lesser degree of correlation.

Once having obtained the value of U , a subsequent GGA+ U calculation was carried out (see Fig. 5). The application of the Hubbard parameter splits the intermediate band levels into two manifolds, one completely filled and another totally empty. Initially this result is not compatible with the required fulfillments of an efficient intermediate band.

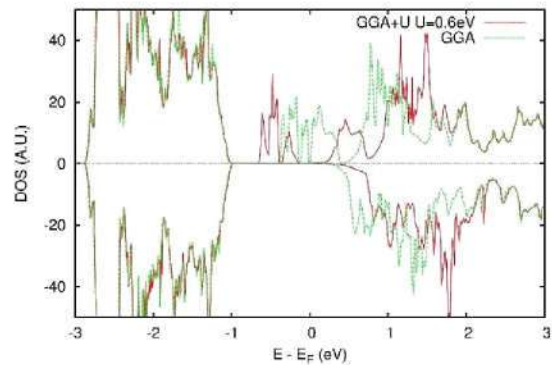


Figure 5: Total density of states of $\text{Ti}_4\text{Cu}_{16}\text{Ga}_{12}\text{S}_{32}$ compound for both the GGA+ U and GGA calculations. Fermi level is set to zero.

However, two things must be taken into consideration before reaching preconceived conclusions. First, that the GGA+ U method was originally introduced to reproduce the electronic structure of Mott insulators

and therefore the energy spectrum near the Fermi energy is usually neglected, reason why strongly correlated metals are not correctly described (their total energy is overestimated). Once having verified that the magnitude of U (0.6 eV) is not larger than the bandwidth of the intermediate band (about 1 eV) it is assumed that there will be electronic states covering the range between the Hubbard bands. A more complex study including Dynamic Mean Field Theory could reproduce this feature more accurately.

The second fact that must be considered is that although the empty manifold intersects the conduction band of the host semiconductor it is important to realize about that the conduction band must be 2.4 eV above the valence band and that the upper limit of the most energetic manifold is less than 2 eV above from the valence band. Therefore it is expected that in a refined approximation it would be found no overlap between the intermediate levels and the host conduction band.

5 SUMMARY

In conclusion, advanced quantum calculations have been carried out in order to obtain highly accurate properties of chalcopyrite derived compounds.

On the one hand optical absorptions in which a scissor operator has been included to reproduce the experimental band-gap of CuGaS_2 have been calculated and analyzed. The absorption coefficient of both $\text{TiCu}_4\text{Ga}_3\text{S}_8$ and $\text{CrCu}_4\text{Ga}_3\text{S}_8$ compounds is appreciably enhanced with regards to that of host semiconductor CuGaS_2 , especially in the range of low energies.

The role of the intermediate band in the different components of the absorption is shown to be important. Electronic transitions from the valence band to the intermediate band are the principal contributors to increase the absorption for photon energies lower than that of the band-gap. This observation is considerably more evident in the case of the $\text{CrCu}_4\text{Ga}_3\text{S}_8$ compound due to the fact that the intermediate band is closer to the valence band in it than in the Ti substituted chalcopyrite.

The peak observed at few tenths of electronvolt corresponds to intra-band transitions within the intermediate band and are not expected to contribute to the enhancement of the efficiency of an intermediate band solar cell due to non-radiative recombinations that also would take place there.

Furthermore an *ab initio* study of the on-site Coulomb correlation of the 3d electrons of Ti has been carried out. The value of the effective Hubbard term U has turned out to be 0.6 eV, which is less than other strongly correlated compounds including Ti. This is explained by the covalent character of the Ti bonding compared with those ionic in oxides or sulphides.

A subsequent GGA+ U calculation in which $U=0.6$ eV has been carried out. The density of states shows a splitting of the intermediate band into two separated manifolds and the immersion of the upper manifold into the conduction band.

Even though both manifolds seem to be completely separated it must be taken into account that GGA+ U scheme is not designed to work properly with strongly correlated metals and that a more accurate description of the correlation would include an electronic density with energetic spectrum in the vicinity of the Fermi level which would link energetically both manifolds.

Besides, although there is an overlap between the upper manifold and the conduction band belonging to the host semiconductor, it is expected that considering the experimental band-gap of CuGaS_2 this overlap will not be produced because the upper limit of the manifold it is located less than 2 eV above the valence band edge and hence clearly below the conduction band.

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