Electronic and Optical Properties of ZnIn$_2$Te$_4$

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Abstract. Band structure and optical properties of defect- Chalcopyrite type semiconductor ZnIn$_2$Te$_4$ have been studied by TB-LMTO first principle technique. The optical absorption calculation suggest that ZnIn$_2$Te$_4$ is a direct-gap semiconductor having a band gap of 1.40 eV., which confirms the experimentally measured value. The calculated complex dielectric-function $\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$ reveal distinct structures at energies of the critical points in the Brillouin zone.

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1. Introduction

The ternary semiconducting compounds $A^{II}B^{III}C^{IV}$ have been widely investigated because of their potential applications in electro-optic, optoelectronic, and non-linear optical devices [1]. Most of these compounds have the defect chalcopyrite or stanite structure [2, 3]. In an $A^{II}B^{III}C^{IV}$ defect chalcopyrite compound, A, B, and C atoms and the vacancy E, are distributed as follows [3]: A site at $(a/2,0,c/4)$, B at $(0,0,c/2)$ and $(0,a/2,c/4)$, C at $(\alpha,\beta,\gamma)$, $(\alpha,\beta,\gamma)$, $(\beta,\alpha,\gamma)$ and $(\beta,\alpha,\gamma)$ and E at $(0,0,0)$. Its lattice parameters are given by $\alpha = \beta = a/4$, $\gamma = c/8$ and $c = 2a$, as shown in the figure 1.

In this communication we shall investigate the electronic structure and optical properties of the defect chalcopyrite ZnIn$_2$Te$_4$ from a first principles approach. The chosen system is not only important for its application in technology, but is also important for the study of the effect of defect or impurity on various properties of materials. There is also growing interest in the study of defect and nano structures [12, 13]. One of the experimental method for the preparation of nano-structures is to fill in the structural voids in a “host” compound with atoms of a given substance. These structures could either be local void clusters or even tubulary voids. The characteristics dimensions. The host compound helps to form a matrix in which these nano structures stabilize. In a subsequent communication, we shall extend the present work to include nano structures in host materials.

Recently Ozaki et al [4, 5] have carried out a detailed experimental and theoretical study of optical properties of amorphous and crystalline ZnIn$_2$Te$_4$. There are few other experimental measurement [6]-[10] on the compound also but there has been no first principles calculation for the electronic structure and optical properties of this material.

The band structure calculations by empirical parameterized tight-binding methods has been carried out for ZnIn$_2$Te$_4$ by Meloni et al [11] and Ozaki et al [5]. These calculations required fitted parameters. The actual crystal structures also seem to have been simplified. Meloni et al have assumed a pseudocubic structure (space group $V_d$), rather than the actual chalcopyrite type structure. Ozaki et al have taken a defect chalcopyrite structure. However, the space group $S^2_4$, which they assumed, does not reflect the correct symmetry of this structure. This is the usual chalcopyrite structure but with vacancies at the sites as shown in the figure 1. Because of the vacancies, this structure does not have the full space group $S^2_4$. Rather, we can assign this structure the $I4$ symmetry. The positions of Te’s are zinc-blende type, i.e. two inter-penetrating fcc lattices shifted one-fourth of the way along a body diagonal. The values of the lattice parameters $a$ and $c$ are taken from experiment to be 6.11Å and 12.22Å respectively as reported by Hahn and Ozaki [2, 3]. The positions of the atoms within the unit cell is shown in table 1.
Electronic and Optical Properties of ZnIn$_2$Te$_4$

| Atom type | Positions   | Atom type | Positions   |
|-----------|-------------|-----------|-------------|
| Zn        | 0.00 0.50 -0.50 | In1       | 0.00 0.00 0.00 |
| In2       | 0.50 0.00 -0.50 | Te        | 0.25 0.25 0.25 |
| Te        | 0.25 -0.25 -0.25 | Te        | -0.25 0.25 -0.25 |
| Te        | 0.25 0.25 -0.75 | E1        | 0.00 0.00 1.00 |
| E2        | 0.25 0.25 -0.25 | E2        | 0.25 -0.25 0.25 |
| E2        | -0.25 0.25 0.25 | E2        | 0.25 0.25 -1.25 |
| E3        | 0.50 0.00 0.00 | E3        | 0.00 0.50 0.00 |
| E4        | 0.00 0.00 0.50 | E4        | 0.00 0.00 -0.50 |

Table 1. Positions within the unit cell of atomic basis, including the empty spheres to take into account the voids within the structure.

2. Results and Discussion

2.1. Electronic Structure Calculations

To start with, for our electronic structure calculations we have used the well established tight-binding linearized muffin-tin orbitals method (TB-LMTO), discussed in detail.

Figure 1. Crystal structure of defect-chalcopyrite-type semiconductor ZnIn$_2$Te$_4$. Here an orthorhombic primitive cell is shown.
elsewhere \cite{16, 17, 19}. Electron correlations are taken within local density approximation of density functional theory \cite{14, 15}.

The TB-LMTO energy bands in several high symmetry directions in reciprocal space is shown in figure 2. Let us examine this in some detail. The basis of the TB-LMTO starts from the minimal set of muffin-tin orbitals of a KKR formalism and then linearizes it by expanding around a ‘nodal’ energy point $E_{\nu l}^\alpha$. The wave-function is then expanded in this basis:

$$\Phi_{jk}(\mathbf{r}) = \sum_L \sum_\alpha c_{La}^{jk} \left[ \phi_{\nu L}^\alpha(\mathbf{r}) + \sum_{L'} \sum_{\alpha'} h_{LL'}^{\alpha\alpha'}(\mathbf{k}) \phi_{\nu L'}^{\alpha'}(\mathbf{r}) \right]$$

and,

$$\phi_{\nu L}^\alpha(\mathbf{r}) = i^\ell Y_L(\hat{\mathbf{r}}) \phi_{\nu L}^\alpha(\mathbf{r}, E_{\nu l}^\alpha)$$

$$\dot{\phi}_{\nu L}^\alpha(\mathbf{r}) = i^\ell Y_L(\hat{\mathbf{r}}) \frac{\partial \phi_{\nu L}^\alpha(\mathbf{r}, E_{\nu l}^\alpha)}{\partial E}$$
Electronic and Optical Properties of ZnIn$_2$Te$_4$

\[ h_{LL'}^{\alpha\alpha'}(k) = (C_L^{\alpha} - E_{\nu\ell}^{\alpha}) \delta_{LL'} \delta_{\alpha\alpha'} + \sqrt{\Delta_L^{\alpha}} \ S_{LL'}^{\alpha\alpha'}(k) \sqrt{\Delta_L^{\alpha'}} \]

\( C_L^{\alpha} \) and \( \Delta_L^{\alpha} \) are TB-LMTO potential parameters and \( S_{LL'}^{\alpha\alpha'}(k) \) is the structure matrix.

First note that for the calculation of the optical properties of the solid we need to span a large energy range, from the occupied valence to the unoccupied conduction states. For ZnInTe this spans a range from -15 eV to 10 eV. The “nodal” energies cluster below -5 eV in the valence band. Obviously, the conduction part of the band is not accurately reproduced. The third generation NMTO expands the wavefunction in term of a basis which is expanded as a Lagrange interpolation around a discrete set of nodal energies \( \{\epsilon_n\} \):

\[ \Phi_{jk}(r) = \sum_L \sum_{\alpha} c_{L\alpha}^{jk} \left[ \sum_{n=0}^{N} \phi_{nL}^{\alpha}(r) \mathcal{L}_{n,LL'}^{(N)}(k) \right] \quad (2) \]

The \( \mathcal{L}_{n,RL,R'L'}^{(N)} \) are Lagrange matrices which are such that the energy dependent partial wave basis \( \phi_{RL,R'L'}^{\alpha}(r,E) \) takes the values \( \phi_{nL}^{\alpha}(r) \) at the nodal energies. Unlike the LMTO, the nodal energies are independent of the indices \( L\alpha \). By choosing the nodal energies across the energy range of interest we can accurately reproduce the bands in that range. This was shown for GaAs in the range -15 eV to 20 eV by Andersen and Saha-Dasgupta [18].

The figure 3 shows the energy bands obtained from the NMTO using three nodal energies spread across the energy range of interest. In comparison with the figure 2, we note that the largest change occurs in the conduction band, away from the TB-LMTO nodal energies bunched below -5 eV. We have used the von Barth-Hedin exchange [20] with 512 \( k \)-points in the irreducible part of the Brillouin zone.

The calculated density of states within TB-LMTO and NMTO are shown in the figure 4. It is evident from these two figures that there is significant difference between these two only in the conduction band. From the band structure comparison, this was also evident for the reasons discussed earlier. These densities agree quite well with the experimental XPS measurements of Ozaki et al [5] and also with their parametrized tight-binding calculations. These results are shown in the figure 4. It must be noted here that since these calculations are based on the LDA, we do obtain a lower band gap. In this case the NMTO estimate of the band gap is around 1.3 eV, while the XPS data indicate a gap of around 2 eV. Nor can we have much confidence about the conduction bands. This problem can be tackled more accurately, for example, through by quasi-particle band structure within a GW type approximation [27]. These NMTO based calculations are a much better starting point of GW self-consistency iterations than the first or second generation LMTOs (see comments in [18]).

The TB-LMTO band structure gives us insight into the various structures in the density of states. At the lowest energies around -14 eV we have the states arising out of
the Te-s electrons. The sharp peak at -10 eV is due to the very narrow Zn-d bands. The next structures around -8 eV arise from the In-s and Zn-s electrons. The predominantly covalently bonded Te sp states gives rise to bonding and anti-bonding bands around -5 eV and 5 eV respectively. The band gap lies between these bands.

2.2. Optical Properties:

In recent years a number of methods have been proposed for calculating optical properties within the framework of the LMTO \cite{21, 22, 24, 26} for both metals \cite{21, 22} and semi-conductors \cite{23, 25, 26}. Upenski et al \cite{21} proposed a method for the accurate calculation of the optical matrix elements based on the continuity equation for the charge -density operator. They were able to calculate accurate optical matrix elements by including the combined correction term to compensate for inaccuracies in the wavefunction due to the basis set in LMTO theory being finite. This method and corrections were subsequently applied by other authors \cite{22, 23} to calculate accurate optical spectra of Ge, GaAs, InSb and CdTe.
Figure 4. Density of States for ZnIn$_2$Te$_4$ (top) calculated from the TB-LMTO and (bottom) calculated from NMTO with three nodal energies across the energy range.

In all the above calculations however, the gradient operator has been employed for the determination of the optical matrix. There is an alternative method developed by Hobbs et al [26] which avoids the determination of gradient operator. Their method allows for the inclusion of non-local potentials in the Hamiltonian. In their method they employed Green’s second identity and the commutation relation between the position and Hamiltonian operators. They finally wrote the momentum matrices in terms of Gaunt coefficients [28] and potential parameters which are defined within the LMTO method [16, 19]. The mathematics has been described in detail both by Hobbs et al and by Saha et al [30]. We shall indicate here the minor changes required for the calculation of the transition matrix element within the NMTO.
The expression for the imaginary part of the dielectric response remains the same, as derived from the Kubo formula:

$$
\varepsilon_2(\omega) = \frac{8\pi^2e^2}{m^*\Omega\omega^2} \sum_i \sum_f |\langle \psi_f|\hat{e}_\gamma \cdot \hat{p} |\psi_i \rangle|^2 F_i (1 - F_f) \delta(E_f - E_i - \hbar \omega)
$$

(3)

where, \(m^*\) is the effective mass of the electron, \(\Omega\) is the volume of the sample, \(i\) and \(f\) refer to the initial and final states respectively, \(\gamma\) refers to the direction of polarization of the incoming photon, \(\hat{p}\) is the momentum of the electron and \(F_{i,f}\) is the occupation probability of the initial and final states respectively. For semiconductors, \(i\) lies in the valence band and \(f\) in the conduction band and at 0\(^{0}\)K we have \(F_i = 1\) and \(F_f = 0\).

We can obtain the real part of the dielectric function \(\varepsilon_1(\omega)\) from a Kramers-Krönig relationship.

$$
\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{(\omega' - \omega) \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'
$$

(4)
The transition probability which involves momentum matrix elements can be evaluated using a gauge independent formalism and commutation relation

\[ P = m_e \frac{dr}{dt} = \frac{m_e}{\hbar} [r, H] \]

Thus calculation of momentum matrix elements means calculation of the following integrals:

\[ \int \phi_{nL}^\alpha(r)^* r H \phi_{nL}^\alpha(r) \, d^3r \quad \& \quad \int \phi_{nL'}^\alpha(r)^* H r \phi_{nL}^\alpha(r) \, d^3r \]

By noting the relations:

\[ H \phi_{nL}^\alpha(r) = \epsilon_n^\alpha \phi_{nL}^\alpha(r) \]

and using Green’s second identity we may write the integrals as:

\[ \int \phi_{nL'}^\alpha(r)^* r H \phi_{nL}^\alpha(r) \, d^3r = \ell - \ell' \epsilon_n^\alpha \Gamma_{LL'} \int_0^{s_\alpha} \phi_{n\ell'}^\alpha(r) \phi_{n\ell}^\alpha(r) r^3 \, dr \]

\[ \int \phi_{nL'}^\alpha(r)^* H r \phi_{nL}^\alpha(r) \, d^3r = \ell - \ell' \epsilon_n^\alpha \Gamma_{LL'} \left\{ \epsilon_n^\alpha \int_0^{s_\alpha} \phi_{n\ell'}^\alpha(r) \phi_{n\ell}^\alpha(r) r^3 \, dr \ldots \right. \]

\[ \ldots + (\hbar^2/2m_e)s_\alpha^2 \phi_{n\ell}^\alpha(s_\alpha) \phi_{n\ell'}^\alpha(s_\alpha) \left( D_{n\ell'}^\alpha - D_{n\ell}^\alpha - 1 \right) \}

where, \( s_\alpha \) is the atomic sphere radius of the \( \alpha \)-th atom in the unit cell and \( \Gamma_{LL'} \) is a combination of Gaunt coefficients \[26\] :

\[ \Gamma_{LL'} = \sqrt{(2\pi/3)} \left[ (G_{\ell',1,\ell}^{-1,m}-G_{\ell',1,\ell}^{m',1,m}) \hat{i} + i \left( G_{\ell',1,\ell}^{m',-1,m} + G_{\ell',1,\ell}^{m',1,m} \right) \hat{j} + \sqrt{2} G_{\ell',1,\ell}^{m',0,0} \hat{k} \right] \]

\( D_{n\ell}^\alpha \) is the logarithmic derivative of \( \phi_{n\ell}^\alpha(r) \) at \( r = s_\alpha \).

The lattice for \( ZnIn_2Te_4 \) does not have cubic symmetry. If we take the \( c \)-axis to be the \( z \)-axis, it is clear that the three optical responses \( \epsilon_x, \epsilon_y \) and \( \epsilon_z \) are not the same.
In the top part of figure 6, we show the variation of the real and imaginary parts of $\varepsilon_\parallel = \varepsilon_z$ and $\varepsilon_\perp = \varepsilon_x + \varepsilon_y$ with the incident photon energy.

We first note that since our LDA-based calculations give a smaller band gap than experiment, we have applied the scissors operator, which involves a rigid shift of the conduction band with respect to the valence band, so that the band gap matches. This is frequently used by LDA practitioners, but cannot be fully justified. The correct procedure would be to carry out a full GW calculation which gives rise to an energy dependent self-energy, which shifts the bands unequally at different energies, resulting in a distortion of the shape of the densities of states as well. Given this, the agreement of the theoretical calculations with the experimental results of Ozaki et al. [5] available up to 10 eV photon energies, is not bad. The experiment does not align the crystal axis with the polarization of the electric field, so that we should compare the results the direction averaged response $(\varepsilon_\parallel + \varepsilon_\perp)/3$. The principal peak positions and heights are well reproduced.
We shall conclude with the remark on the two directions which we propose to take from here. The first point is to recognize that the NMTO calculations form a reasonable starting point of the more sophisticated many-body GW approaches. The second is related to the reason why we chose to study the defect chalcopyrite in the first place. We would like to fill the voids in the structure with various “impurities” and study the signal for these in the optical response. These will be the aim of our subsequent work in this area.

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