First principles characterization of direct transitions for high efficiency new photovoltaic materials

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Abstract

Some alloys containing a transition metal atom in an III–V host semiconductor show an intermediate half filled band in the middle of the usual semiconductor band gap. The presence of this intermediate band allows to use this material in high efficiency solar cells due to its capability of absorbing low energy photons. In the current work a study of the optoelectronic properties is presented. We mainly focus the work in the obtaining the matrix elements that contribute to direct transitions. We also have analyzed some of the factors on which that process depends. We have also found that some low energy transitions can be found for several points inside the Brillouin zone.

1. Introduction

The high efficiency intermediate-band solar cell whose physical properties we study in this work, is based on a semiconductor alloy which presents an intermediate band of states within the host semiconductor band gap. It has been demonstrated [1] the possibility of increasing the efficiency of ideal semiconductor solar cells, exceeding the thermodynamic limits established by Shockley and Queisser [2], the proposed material is capable of absorbing two sub-band gap photons to create one electron–hole pair [3].

In a recent work [4] we have identified several semiconductor compound candidates for high efficiency photovoltaic materials using very precise first principle calculations. These compounds of the type Ga_4X_3M with $X = As$ or P, and $M = $ transition metal, are formed by the substitution of some atoms in several III–V semiconductors for transition atoms. Some of these compounds show an intermediate, isolated, narrow band in the middle of the semiconductor band gaps. Several factors such as the width values of the intermediate band (IB) and the two band gaps, density of states (DOS), photon absorption coefficients or non-radiative recombination must account for the effectiveness of the processes [5].

The influence of both the direct and indirect transitions have to be taken into account when calculating the absorption coefficients. For

characterizising the direct transitions, it is necessary to obtain previously the dispersion band diagrams, the DOS and the transition matrix elements. There are three kinds of transitions to be considered, one between the valence band and the IB, another between the valence band and the conduction band and finally on between the IB and the conduction band. Transition matrix elements are the main objective for the present work.

2. Matrix elements for direct transitions

The probability of having a direct transition between an initial state (which will be denoted as $|i, k>$), belonging to the band i and a final state $|f, k>$, in a band labeled as f, is:

$$P_{if}^{direct}(\vec{k}) = \frac{2\pi}{\hbar} |\langle f, k | H_{e-p} | i, k \rangle|^2 \delta(E_i(\vec{k}) - E_f(\vec{k}) - \hbar\omega_\beta)$$

(1)

where H_{e-p} represents the Hamiltonian for the interaction between the electron and the photon. For the purpose of this work, as usual, we will approximate this in terms of the Radiation–Matter interaction theory, yielding the next expression:

$$H_{e-p} = \frac{e}{m} \sqrt{\frac{\hbar}{2\omega_\beta \varepsilon \Omega}} e^{i\beta\vec{r}} \vec{e}_v \hat{p}$$

(2)

In which, e represents the electron charge, m represents the effective electron mass, ε is used to denote the dielectric constant for the material, Ω is the volume, β is the wave vector for the photon, ω_β is the angular frequency for the photon, $\vec{e}_v$ is the polarization vector for the photon, and $\hat{p} = -i\hbar\vec{\nabla}$ is the momentum operator.

In order to characterize direct transition matrix elements it is necessary to connect the initial and final states for the electron involved in the interband direct transition having the wave vector ($\vec{k}$):

$$\langle f, k | H_{e-p} | i, k \rangle = \frac{e}{m} \sqrt{\frac{\hbar}{2\omega_\beta \varepsilon \Omega}} \langle f, k | \hat{p} | i, k \rangle$$

(3)

To obtain matrix elements such us the one presented in the Eq. (1), the wave function for a solid is built as a linear combination of localized

orbitals in the different atomic positions. These orbitals are known to be the basis representation for the wave function. The wave function has to include the translation symmetry of the solid being studied. It has to satisfy the Bloch's theorem

$$|j, k\rangle = \Phi_{j,k}(\vec{r}) = \sum_p \sum_{n_p} C_{p,n_p}^{j,k} |k, p, n_p\rangle$$

$$|k, p, n_p\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \phi_{n_p}(\vec{r} - \vec{R} - \vec{\tau}_p)$$

(4)

where, p is an index that labels every atom contained in the unit cell of the solid, n_p labels every basis function belonging to the atom p, $\vec{R}$ is a lattice vector and represents the position of each cell within the solid

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

(5)

The n's are integers and the $\vec{a}_i$'s are the lattice vectors. $\vec{\tau}_p$ represents the position of the pth atom within the unit cell, N is the number of cells under consideration and $C_{p,n_p}^{j,\vec{k}}$ is an expansion coefficient.

Using this wave function the matrix elements have the following form:

$$\langle f, k | \hat{p} | i, k \rangle = \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \sum_p \sum_{n_p} \sum_q$$

$$\times \sum_{n_q} C_{p,n_p}^{f,k^*} C_{q,n_q}^{i,k} \int \phi_{n_p}^*(\vec{r}) \hat{p} \phi_{n_q}$$

$$\times (\vec{r} - \vec{R} + \vec{\tau}_p - \vec{\tau}_q) d\vec{r}$$

(6)

From this expression it is possible to observe that the matrix elements depend on several factors: the atomic basis of functions used (ϕ_{np}), the expansion coefficients of the band in the chosen $\vec{k}$ point, the number of cells used in the calculation and the integral containing the product of two basis functions. One of the basis functions is located in an atom, the other function being located in another atom within the considered cells. (This cell will be placed $\vec{R}$ with respect to the reference cell.) In order to characterize the direct transitions well we have to analyze each one of these factors.

The basis functions are obtained by solving a pseudo-atomic equation in which we confine the atomic orbital in a sphere with a finite radius. These pseudo-atomic orbitals finally take the form

of a numerical radial function multiplied by a real spherical harmonic.

$$\phi_\alpha(\vec{r}) = f_\alpha(r)Y_{l\alpha}^{m\alpha}(\theta,\phi) \qquad (7)$$

The numerical radial part is obtained by using the algorithm proposed by Sankey and Niklewski [6]. The main reason for using this basis set is because the atomic wave functions seems to be more confined in the solid than it is in the free atom, so a scheme of confined basis functions seems to be very suitable for representing the wave function. These pseudo-atomic orbitals are chosen in order to be continuous in the limiting confinement sphere. We use a parameter (ΔE) as a measure-
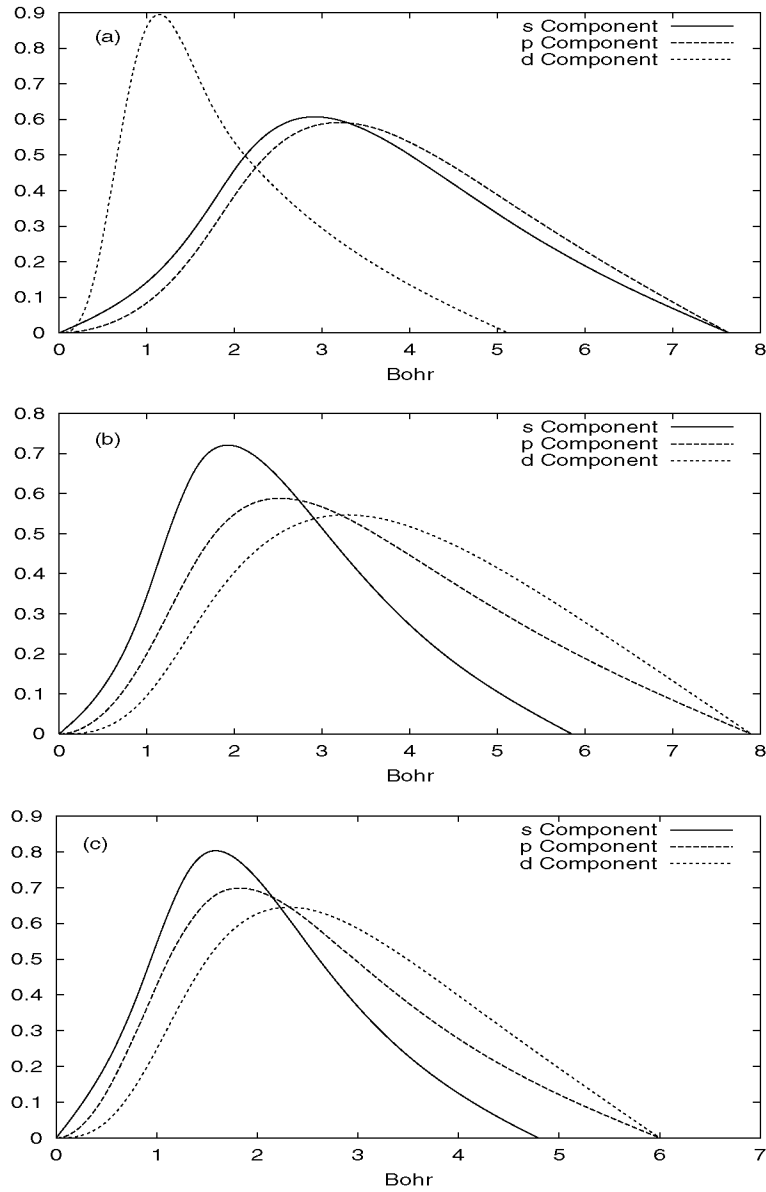

Fig. 1. Representation of the localized pseudo-atomic orbitals for the Ti (a), Ga (b) and P (c) atoms.

ment for the confinement of the pseudo-orbitals. This parameter represents the increasing energy that each orbital undergoes when confined in a finite sphere. In Fig. 1, we show the radial part for the confined pseudo-orbitals for the Ga, P and Ti atoms.

To obtain the coefficients to expand the wave function of the solid in our basis set, we have used first principles quantum-mechanical calculations. We have used a FORTRAN code called SIESTA [7]. This code is based on the formalism of the density functional theory (DFT). It uses norm conserving non-local pseudo-potentials to reproduce the core of the atoms, thus reducing the computational cost. We have used the Perdew, Burke and co-workers [8] parametrization for Generalized Gradient Approximation to introduce the exchange and correlation potential into the calculation.

In Fig. 2 we show the dispersion band diagram for the Ga_4P_3Ti system. In this figure we observe the half filled IB needed to obtain the IB material. From these diagrams we have also calculated the corresponding DOS (Fig. 3). This will allow us, bearing in mind the matrix elements, to characterize the direct transitions.

We add up on $\vec{R}$ in order to represent the interaction between the different cells in this material. This sum is infinite. However, $\vec{R}$ only appears

in the integral connecting two different basis functions by means of the momentum ($\vec{p}$) operator. If we apply this expression to two different
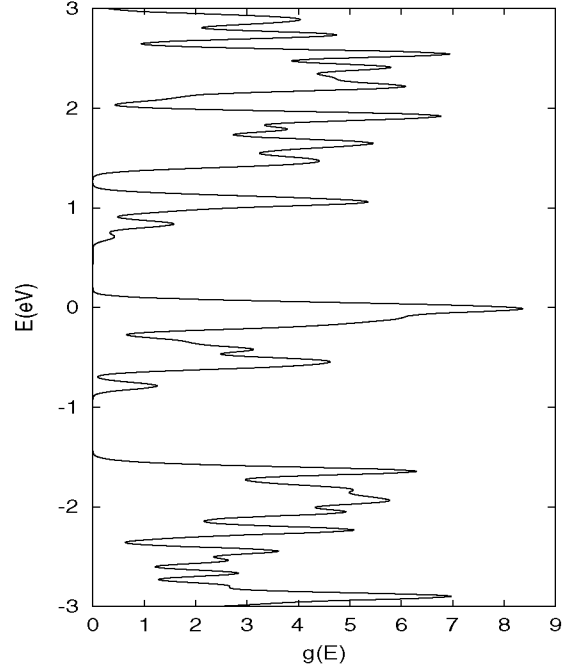

Fig. 3. DOS representation corresponding to the dispersion band diagram shown in Fig. 2.
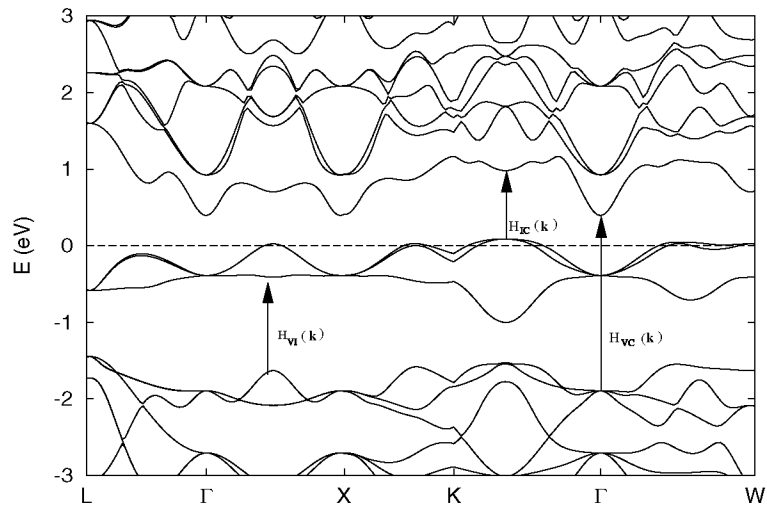

Fig. 2. Dispersion band diagram for the Ga_4P_3Ti. In the figure we show some of the possible direct transitions, with arrows.

functions that are quite distant from each other, this integral will vanish. Moreover, this effect is stressed when using confined basis functions. In this scheme, if the separation between the two functions is greater than the sum of the two confinement radius the integral will be negligible. To have a reasonable idea when this infinite sum has converged it is necessary to do a previous test in order to fix the truncation limit for this sum correlatively with the desired precision in the calculation.

In Fig. 4 the influence on the truncation size of the sum on $\vec{R}$, it is shown. As we can see, no so many qualitative changes are found, but there are some quantitative changes in the values of the obtained matrix elements.

Fig. 5 shows the characterization of the matrix elements corresponding to the IB system. This figure shows a large variation in the matrix elements when the direction in which the Brillouin zone is being inspected. As a consequence of these results, as well as by means of the results for the DOS, we can expect the higher transition probabilities in then zone close to the point K, where the minimal energy difference between the initial and final states is found.
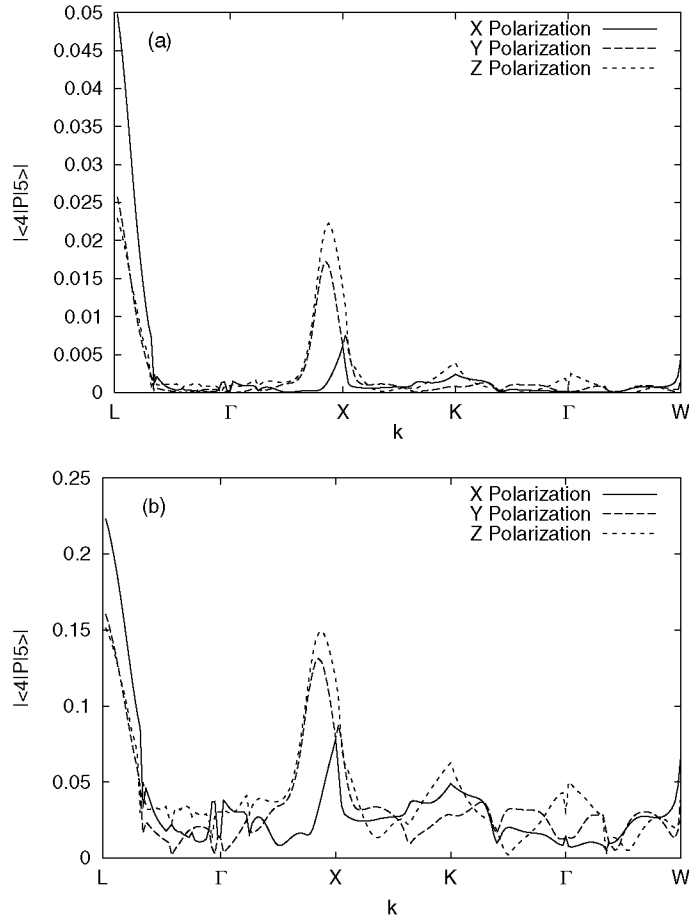

Fig. 4. Representation of the matrix elements (in Rydbergs) for the transition bands 4 and 5 in the main directions of the Brillouin zone for the GaAs: (a) using three unit cells in the calculation and (b) using eight cells. In both figures we show the x, y, z polarization components.
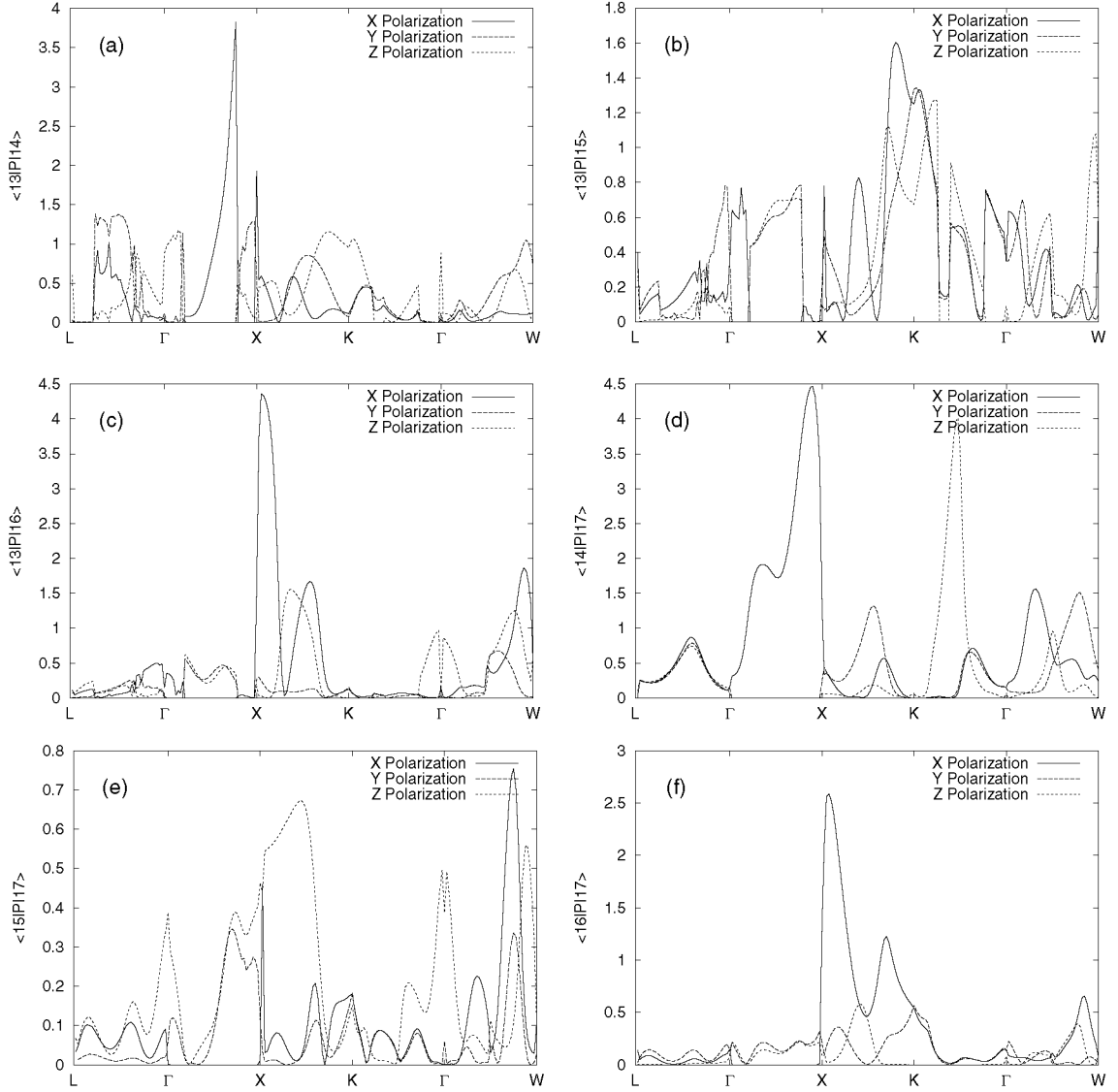
Fig. 5. Direct transition matrix elements for the Ga_4P_3Ti (in Rydbergs) for the direct transition between the valence state (13)—intermediate (14–15–16) bands and intermediate (14–15–16)—conduction (17) bands.

3. Conclusions

From the analysis of the direct optical transition matrix elements from the valence band to the IB, and from the IB to the conduction band we conclude that the presence of the IB band allows this material to absorb photons having lower energy than the photons usually absorbed in host semiconductor materials.

These matrix elements exhibit noticeable values in a wide range of k-points in the Brillouin zone. We also have demonstrated that the magnitude of the matrix elements depends on the polarization of the photon.

The magnitude of these matrix elements is also very sensitive to the basis set used to describe the wave function, and, also, to the number of cells considered in the calculation. We analyze the influence of these two factors and we found that the basis set used affects to the qualitative form of the spectrum obtained, so we correct this influence by improving the basis set from a SZ to DZ or DZP basis set. In reference to the influence of the other factor, being the number of cells used in the calculation not sufficient to account for the basis functions overlapping, we conclude that this influence in only quantitative. So when calculations with different number of cells are compared, we find quantitative differences.

In order to complete the description of the optical transitions in future works we have to regard to some features. We will have to include the indirect transition matrix elements, thus it will be necessary to take in account the electron–photon–phonon interaction. As it is a process in which three different particles are involved, we expect the contribution of the indirect transition matrix elements to be much lower than the contribution coming for the already studied transitions.

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