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Potentiality of $CuFeO_2$-delafossite as a solar energy converter

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ABSTRACT

The $CuFeO_2$ semiconductor, a delafossite compound with a lower band gap, has electronic and optical properties of interest for absorbing solar radiation in solar converters. In order to evaluate its potential the optical properties and their decomposition into atomic contributions are obtained using first-principles. Both ferromagnetic and antiferromagnetic spin alignments are considered. According to the results the structure, the Fe-Cu transitions makes almost no contribution to the absorption. Then, by using the absorption coefficient, the maximum absorption efficiencies, voltages, and currents of the solar conversion are found. The results indicate it as being a good candidate for solar cells but it does not generate enough output voltage for water-splitting.

1. Introduction

In oxide M_xO_y semiconductors, the valence band (VB) edge states are usually made up mainly of p(O) states and the conduction band (CB) of s(M) or d(M) states. On the other hand, $CuMO_2$ delafossite compounds, where M is a trivalent transition-metal cation, the VB edge states mostly come from d(Cu) states. From the ionic picture, the Cu^{2+} ions have a d^{10} configuration resulting in a higher energy VB edge and therefore, a smaller band gap. Furthermore, substitutional doping of the trivalent metal site with a divalent metal is known to increase bulk conductivity. For example, Mg^{2+} dopant is found to improve the $CuFeO_2$ conductivity (Gu et al., 2013).

The solar energy can be converted into electricity using photovoltaic converters (PVC), i.e. solar cells. A fundamental problem with the solar cells is currently the lack of a viable storage system. An alternative is galvanic battery storage. However it is expensive and requires a lot of space for installation. Another alternative are the photoelectrochemical converters (PEC) in which the solar energy is transformed and stored as chemical energy in the photoproducts via photodecomposition reactions. The photoproducts can later be mixed to recover the stored energy. One interesting example is the photosensitized decomposition of water into H_2 and O_2. These photoproducts may recombine at a later stage when energy is required in a fuel cell to generate electrical energy. Alternatively H_2 burns in air to produce water again releasing a large amount of heat.

The delafossite compounds with lower band gap are of interest for absorbing the solar radiation in the solar converters, photovoltaic (PVC) or photoelectrochemical (PEC). With a band gap within the visible region $CuFeO_2$, $CuRhO_2$, and $CuGaO_2$ delafossites are appropriate for the sunlight absorption component of PEC or PVC. $CuFeO_2$ and $CuRhO_2$ delafossites have been investigated as a photocathode for the splitting of water (Abdi and Berglund, 2017; Sullivan et al., 2016), and Mg-doped $CuFeO_2$ was investigated for the reduction of CO_2 (Gu et al., 2013). Wide bandgap delafossites ($CuBO_2$, $CuCrO_2$, $CuGaO_2$, $CuInO_2$, $CuScO_2$, and $CuYO_2$) are not efficient sunlight absorbers. However they may be useful for PEC applications as transparent p-type conducing oxides layers (Abdi and Berglund, 2017).

The absorption efficiency depends on the characteristics of the absorbent material (absorption coefficient and thickness) and the incident spectrum. The overall efficiency will be lower than the absorption efficiency because of transport losses, surface recombination, charge transfer in interfaces, etc. But if the absorption efficiency is small then the global efficiency of the solar energy converter will also be small and the material used to absorb the solar radiation will not be suitable.

$CuFeO_2$ delafossite is made up of abundant elements and is attractive as an absorbent of sunlight radiation in PVCs and as a photocathode material (Abdi and Berglund, 2017; Prévot et al., 2015; Read et al., 2012) in PECs. However, as a photocathode, it is limited by poor efficiency and photocurrent (Jang et al., 2016; Prévot et al., 2015; Read et al., 2012) which may be due to its poor charge transport properties (Jang et al., 2016) although the reasons for it have not been determined specifically. Therefore further research is needed to evaluate the main factors that affect its efficiency and photocurrent.

In this work we approach two seemingly different aspects, even though they are closely related. First, we carried out a study of the $CuFeO_2$ delafossite electronic and optical properties from first-principles, focused mainly on the absorption coefficient and the analysis of the main contributions. Later, using the absorption coefficient, the absorption efficiencies, photocurrents, and photo-voltages of the solar energy converters based on this compound were evaluated.

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2. Methodology section

The electronic and optical properties have been obtained using the density function theory (Kohn and Sham, 1965; Soler et al., 2002) with the incorporation of an effective U parameter (DFT + U (Anisimov et al., 1993; Tablero, 2008, 2009)). It permits, at an intermediate level, the self-interaction problem to be partially avoided without excessively increasing the computational cost. In the methodology used (Tablero, 2008, 2009) the exchange and correlation interactions were treated with the functional proposed by Perdew-Burke-Ernzerhof (Perdew et al., 1996), with the Troullier–Martins (Troullier and Martins, 1991) pseudopotentials expressed in the Kleinman–Bylander (Bylander and Kleinman, 1990) form, using a basis set made up of localized pseudoatomic orbitals (Sankey and Niklewski, 1989), spin polarization and periodic boundary conditions. The crystal structure used in the study was taken from experimental ones: trigonal lattice (space group $R\bar{3}m$, no. 166) with lattice parameters $a = 3.02–3.04$ Å, and $c = 17.10–17.14$ Å) (Pavunny et al., 2010).

To obtain the optical properties we start by calculating the transition probabilities, proportional to the square of the momentum matrix elements $p_{\mu\lambda}$ between all bands. Then, the complex dielectric function is evaluated with the band energies $E_{\lambda,\mathbf{k}}$ and the band occupations $f_{\lambda,\mathbf{k}}$ at the $\mathbf{k}$-points in the Brillouin zone:

$$e_2(E) \sim \frac{1}{E^2} \sum_{\lambda>\mu} \int d\mathbf{k}[f_{\mu,\mathbf{k}} - f_{\lambda,\mathbf{k}}]|p_{\mu\lambda}|^2 \delta(E_{\lambda,\mathbf{k}} - E_{\mu,\mathbf{k}} - E) \tag{1}$$

Later the other optical properties are obtained using the Kramers-Kronig relationships. In addition, the transition probabilities and the optical properties have been split into atomic species and angular momentum contributions (Tablero, 2016). To do this, the momentum matrix elements are split into atomic species and angular momentum contributions: $p_{\mu\lambda} = \sum_A \sum_B p_{\mu\lambda}^{AB}$ with $p_{\mu\lambda}^{AB} = \sum_{l_A \in A} \sum_{l_B \in B} (p_{\mu\lambda}^{AB})_{l_A l_B}$. In these expressions $p_{\mu\lambda}^{AB}$ is the component that couples the basis set functions on A and B specie-atoms, and $(p_{\mu\lambda}^{AB})_{l_A l_B}$ couples the l_A shell-states on A specie-atom and the l_B shell-states on the B specie-atom. We will use the conventional s, p, d, etc. notation for $l = 0, 1, 2$, etc.

3. Results and discussion

3.1. Electronic structure

The $CuFeO_2$ crystal structure (Fig. 1) consists of magnetic Fe layers separated by non-magnetic Cu-O_2 layers where the Cu atoms are linearly coordinated with two oxygen atoms. The Fe atoms are situated in distorted FeO_6 octahedra. X-ray photoemission spectroscopy studies suggest that the Cu and Fe ions are in the +1 and +3 valence states with high spin S = 5/2 (Pavunny et al., 2010).

$CuFeO_2$ goes through several magnetic phase transitions which have been studied as a result of its interesting magnetic properties (Pavunny et al., 2010) in both ferromagnetic (FM) (Guo, 2015; Ong et al., 2007) and antiferromagnetic (AFM) (Pavunny et al., 2010; Terada et al., 2007; Zhong et al., 2010) spin orders. The experimental and theoretical band gaps in the literature have a large dispersion. Some experimental studies conclude that the band gap is 1.15 eV (Benko and Koffyberg, 1987; Joshi et al., 2015), and further optical transitions occur at 2.03 and 3.35 eV (Benko and Koffyberg, 1987). However other experimental results give values of between 1.4 eV (Gu et al., 2013) and 1.55 eV (Read et al., 2012). Theoretically, energy gaps of 0.15 eV (Guo, 2015) and 0.29 eV (Ong et al., 2007) have been reported for the FM spin order.

We have studied both the FM and AFM configurations. The band gaps obtained for the most stable AFM configuration are 1.16 eV and 1.70 eV for U = 0 and 3 eV respectively. For the FM configuration, with a total magnetic moment of 5 μ_B per formula in accordance with the $Fe^{3+}(d^5)$ configuration, the band gaps obtained for the spin down/up components are 1.02/1.75 eV for U = 0 eV and 1.56/1.75 eV for U = 3 eV. The AFM value of 1.16 eV is very close to the experimental value of 1.15 eV (Benko and Koffyberg, 1987; Joshi et al., 2015). Furthermore, the magnetic moments of the Fe atoms obtained for the FM and the AFM orders are similar: ~4.3 and ~4.5 μ_B for U = 0 and 3 eV respectively. These results agree with the experimental range 4.2 μ_B ("Successive Magnetic Ordering in $CuFeO_2$ –A New Type of Partially Disordered Phase in a Triangular Lattice Antiferromagnet–," 1993) and 4.4 μ_B (Muir and Wiedersich, 1967) reported from powder diffraction experiments.

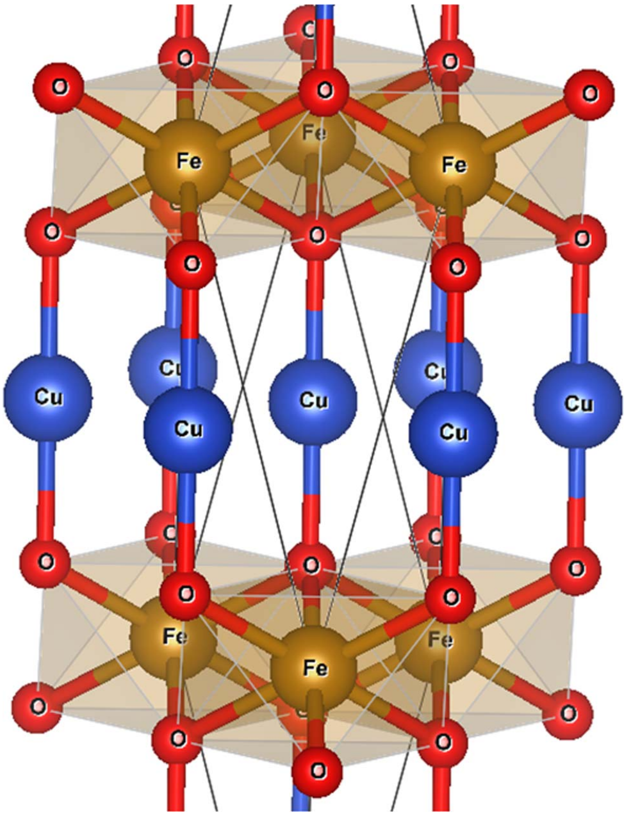

Fig. 1. Crystalline structure of the $CuFeO_2$ semiconductor. The structural figure was created using VESTA software (Momma and Izumi, 2011).

The AFM state is slightly more stable than the FM state by 0.13 eV per unit cell, similar to other results in the literature (Zhong et al., 2010). Although the AFM configuration is the most stable energetically, we will study both the AFM and FM configurations with U = 0 eV and with results very close to experimental ones.

In agreement with other experimental (Benko and Koffyberg, 1987) and theoretical (Guo, 2015; Kumar et al., 2013; Ong et al., 2007) results in the literature, the projected density of states (PDOS) analysis in Fig. 2 indicates that the VB edge states are made up mainly of d(Cu) and p(O) orbitals. The Fe does not contribute significantly to the VB. However, the CB edge states come mainly from the d(Fe) states (Guo, 2015; Ong et al., 2007).

3.2. Absorption coefficient

We have calculated the optical properties in order to identify additional transition peaks in the absorption spectrum and evaluate the absorption properties. The absorption coefficients (ACs) for the FM and the AFM configurations are detailed in Fig. 3. In this figure the shaded areas show the lowest experimental band gap (1.15 eV (Benko and Koffyberg, 1987; Joshi et al., 2015)), and further optical absorption experimental peaks at 1.55 (Read et al., 2012), 2.03 and 3.35 eV (Benko and Koffyberg, 1987). The comparison shows that our results are within