Electronic Structure of the n-Type Doped AgInO$_2$ and CuAlO$_2$ Delafossites: Similarities and Differences

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We performed the first-principles band-structure calculations for a pure and a Cd-doped AgInO$_2$ delafossite compound. The results are carefully analyzed and compared with the results obtained for a pure and a Cd-doped CuAlO$_2$ compound, calculated previously by our group. The electronic structures of both systems are found to be similar in many details, being characterized by the same hybridization scheme that occurs at both Cu and Ag positions. Introduction of Cd impurity into the Cu site produces a shallow band within the CuAlO$_2$ gap, while the Cd presence at the Ag site creates a wide band pinned at the Fermi level in the AgInO$_2$ spectrum. In both cases, however, the n-type conductivities are predicted.

1 Introduction

The semiconducting delafossite oxides (SDOs) have a chemical formula ABO$_2$, where A is either Cu or Ag, and B can be one of the many trivalent metal ions (Al, In, Cr, Co, Fe etc.). Their crystalline structure belongs to the space group $R\bar{3}m$, characterized by a linear coordination of the A atom with its two neighboring oxygens along the c-axis.

In the last few years the SDOs attracted much attention due to their potential technological applications. Besides being transparent by virtue of their large band gaps, SDOs can be doped both p- and n-type [1, 2]. This property separates them from other semiconducting oxides which can be doped merely n-type. Consequently, the SDOs are indicated as candidates for the construction of transparent semiconductor devices.

A number of experiments with the objective to study how the electric properties of the SDOs change in the presence of impurities were performed lately [3]. In most of them the impurities were introduced into the B sites of the structure, and dynamic properties, such as the p- or n-type conductivities, measured.

Recently, we demonstrated theoretically that doping of the A site could also produce either n or p-type conductivities in the SDOs. This conclusion emerged as a result of series of the first-principles full-potential linear augmented plane wave (FP-LAPW) calculations that we performed for the CuAlO$_2$ system containing Cd impurities [4], and the Zn or Ni impurities [5] at the Cu position. In this paper we continue to investigate the A site doping effects in the SDOs, but now in their Ag-based branch. Towards this aim, we performed the band-structure calculations for both pure and Cd-doped AgInO$_2$ compound. It is our intention to present their electronic structure features, to discuss them, and to compare them with the corresponding features of the pure and the Cd-doped CuAlO$_2$ compound.

The computational details were the same as published in the ref. [4]. The FP-LAPW method, as implemented in the WIEN97 computer code, has been used. Exchange and correlation effects were treated within the generalized gradient approximation. Parameters which determine the AgInO$_2$ crystal structure were taken from the ref. [6]. Calculations of the Cd-containing system were performed in a supercell geometry, with the supercell consisting of 32 atoms (8 original unit cells), in which one central Ag atom has been replaced by the impurity atom. Relaxation of all atomic positions in the supercell has been allowed.

In the section II, results for pure CuAlO$_2$ and AgInO$_2$ are presented, while in the section III we discuss the effects of the Cd presence in the compounds.

2 Pure compounds

Resulting density of states (DOS) for the pure CuAlO$_2$ and AgInO$_2$ compounds, as well as the projected DOS (PDOS) for each inequivalent atom, are presented in Fig. 1. In the case of CuAlO$_2$, the fundamental gap is found to be 1.97 eV, in fair agreement with the experimental value of $\sim$1.8 eV. The AgInO$_2$ gap is however difficult to determine since the slope of the conduction band bottom is extremely slight, and the possibility of making a numerical mistake significant. In any case, this gap is much smaller than in CuAlO$_2$, and range between 0.7 and 1.0 eV approximately (there is no experimental data in the literature). The electronic structure of both compounds is dominated by the O $2p$ and the Cu (or Ag) d states, while the Al and In states contribute very little to the DOS and do not play significant role in the compounds. A specific $s - d$ hybridization scheme, proposed for the cases when d^9 and d^{10} ions constitute the A site in delafossites [7], is seen to take place in both systems.

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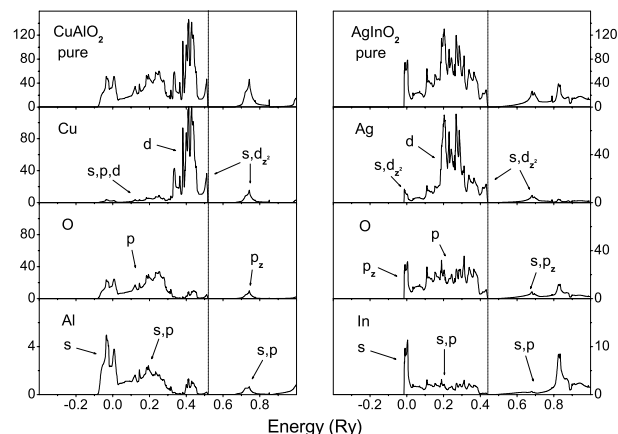
Figure 1. The calculated DOS for the pure $CuAlO_2$ and $AgInO_2$ compounds, in states/Ry/cell. Predominant orbital characters of bands are designated. The dashed line denotes Fermi level.

In order to stabilize the energy of a linear coordination, the Cu (or Ag) s and d_{z^2} orbitals hybridize, forming a filled bonding $1/\sqrt{2}(s - d_{z^2})$ and an empty anti-bonding $1/\sqrt{2}(s + d_{z^2})$ orbitals (the z-axis is parallel to the c-axis of the crystal). The bonding orbital has charges concentrated mainly in the basal plane, giving rise to anisotropy of the conductivity due to electron hopping between neighboring A ion orbitals. The antibonding orbital is used for mixing with neighboring O p_z orbitals, making a bonding complex that lies deep below the Fermi energy (E_F) and an anti-bonding complex that forms a conduction band. All of the three described hybrids are seen in Fig. 1 in case of $AgInO_2$. The peak positioned at the (E_F) consists of Ag s and d_{z^2} states, with negligible amount of O p_z states. It can be identified as a bonding $1/\sqrt{2}(s-d_{z^2})$ orbital of Ag. The first peak in the conduction band is builded from Ag s, d_{z^2}, and O p_z states mostly. It therefore corresponds to the antibonding combination of the Ag $1/\sqrt{2}(s+d_{z^2})$ orbital and O p_z orbital. The bonding combination of the same orbitals is situated deeply below E_F, at ~ 0 Ry. In the case of $CuAlO_2$ this combination can not be identified being smeared in the lower energy part of the valence band. The other two hybrids are, however, formed in exactly the same way as in $AgInO_2$ case.

3 Cd-doped compounds

When Cd replaces the Cu and Ag atoms in $CuAlO_2$ and $AgInO_2$, it causes significant changes: (1) in rearrangement of the atoms around the impurity, and (2) in the electronic structure of the compounds. We accounted for the first effect by allowing a relaxation of all atomic positions in the supercell. The largest changes were registered in immediate vicinity of Cd: its two nearest-neighbor (NN) oxygens were moved along the c-axis in both compounds. In $CuAlO_2$ they were pushed from the Cd, changing the Cd-O distance from 1.860 to 2.073 Å. In $AgInO_2$, on the contrary, Cd attracted the NN oxygens changing the Cd-O distance slightly, from

2.071 to 2.045 Å. The electronic structure changes are found to be considerable only within the cluster consisting of the Cd itself, its two NN O atoms, and the six second NN Cu (and Ag) atoms in the basal plane. Their PDOS is therefore presented in Fig. 2.

In the case when Cd substitutes the Cu in $CuAlO_2$ (Fig. 2a), a narrow band within the gap is created, near the conduction band bottom. This band is impurity induced, half filled (one electron), and consists mainly of the Cd s and d_{z^2}, NN O p_z and second NN Cu d states. Since its electron density is widely spread over the crystal [4], the band can be considered as shallow. Similarly to the Cu, the Cd d-shell also obeys the specific $s - d$ hybridization scheme. While the Cd bonding $1/\sqrt{2}(s-d_{z^2})$ orbital can not be recognized being smeared over the energies from ~ 0 to ~ 0.5 Ry, the Cd antibonding $1/\sqrt{2}(s+d_{z^2})$ orbital is clearly hybridized with O p_z orbital. Their bonding combination is recognized as a sharp resonance at the energy of ~ -0.1 Ry, while the antibonding combination is located at E_F. The present results clearly demonstrate that replacement of the Cu atom by the Cd impurity changes the $CuAlO_2$ electric properties in a fundamental way, producing the n-type conductivity.

When Cd replaces the Ag in $AgInO_2$ (Fig. 2b), the electronic structure displays some relevant differences. The Cd impurity obeys the same $s - d$ hybridization scheme since its antibonding $1/\sqrt{2}(s+d_{z^2})$ orbital, together with NN O p_z orbital, builds a sharp bonding complex at ~ -0.18 Ry, and an antibonding complex positioned around E_F. The latter is, however, much broader than the corresponding one in $CuAlO_2$, which surprises since it does not seem that Cd-Cd interaction in $AgInO_2$ is stronger than in $CuAlO_2$. Indeed, the Cd-Cd distance in $AgInO_2$ (6.56 Å) is considerably larger than in $CuAlO_2$ (5.70 Å). Besides, majority of the Cd d-states are lying deeply below the Fermi energy, highly localized in space and without mixing with Ag states, which eliminates the possibility of propagation of the impurity-impurity interaction by the intermediate Ag atoms in basal plane, through the sequences Cd-Ag-Cd.
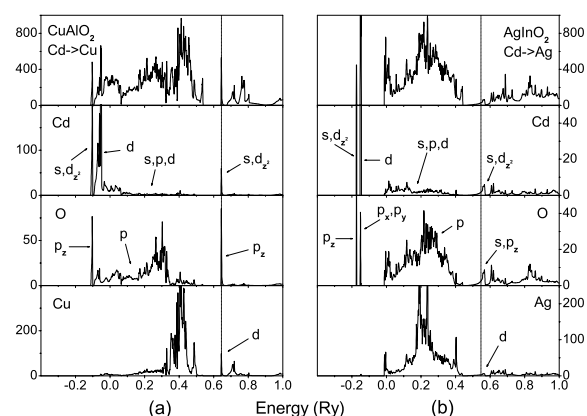

Figure 2. The calculated DOS for (a) $CuAlO_2$ compound in which Cd substitutes for the Cu, and (b) $AgInO_2$ compound in which Cd substitutes for the Ag. PDOS of Cd, its first NN O and second NN Cu (Ag) is also presented. The dashed line denotes Fermi level.

Table I. Experimental and theoretical V_{zz} values in the Cd-doped $CuAlO_2$ and $AgInO_2$ compounds. V_{zz} is the main component of the EFG tensor, directed along the c-axis of the crystal. The signs of the experimental V_{zz}'s have not been determined. All numbers given in the table are in units 10^{21} V/m^2.

	Experiment $|V_{zz}|$	Theory V_{zz}
Cd at Cu site in $CuAlO_2$	27.44	-25.74
Cd at Ag site in $AgInO_2$	31.34	-28.96

Very different widths of the bands positioned at E_F in $CuAlO_2$ and $AgInO_2$ can be explained on the basis of different relative positions of Cd and Cu, and Cd and Ag d-bands. In Cd-doped $CuAlO_2$ the Cd d-states are situated much deeper in energy than the Cu d-states. When Cd, as a donor, replaces a Cu it introduces an attractive potential for the host electrons and brings the conduction states of the nearest neighbors down in energy. Since formed from the conduction band bottom, the band situated at the E_F in $CuAlO_2$ includes therefore mostly the states which belong to the cluster composed of Cd and its first and second NNs ($\sim 60\%$). In Cd-doped $AgInO_2$ the energy difference between Cd and Ag d-states is smaller, so the impurity potential is less attractive for the host electrons. When the band at the E_F is formed, the participation of the states from the Cd and its first and second NN is halved ($\sim 30\%$), and the states from more distant atoms dominate. This effect delocalizes the band, which becomes considerably broader. Our calculations could not distinct if this band is merged to the conduction band bottom or detached from it. We registered a very small, but non-zero DOS between the band and the conduction band bottom, but this could be a consequence of approximation implemented into the calculations. In any case,

the impurity induced band at the E_F introduces some electron states at the bottom of the conduction band, and thus indicates the n-type conductivity in the Cd-doped $AgInO_2$.

In order to check reliability of the presented results, we calculated the electric field gradient (EFG) at the Cd impurities in both delafossites, and compared them with the experimental data [8]. Very good agreement between these values (Table 1) indicates that the presented calculations succeeded to describe the ground state of the impurity-containing systems correctly.

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