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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 ~ 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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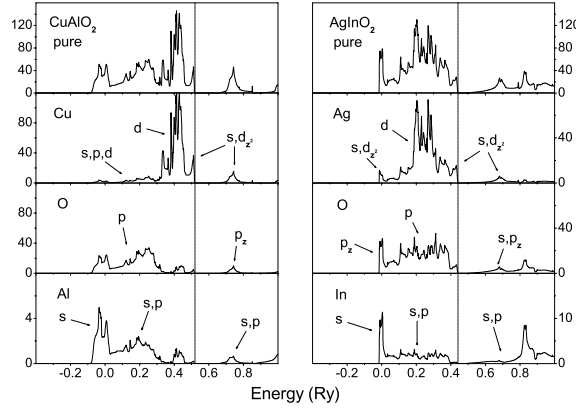


Figure 1. The calculated DOS for the pure CuAlO_2 and AgInO_2 compounds, in states/Ry/cell. Predominant orbital characters of bands are designated. The dashed line denotes Fermi level.

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 built from Ag s , d_{z^2} , and O p_z states mostly. It therefore corresponds to the anti-bonding 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.

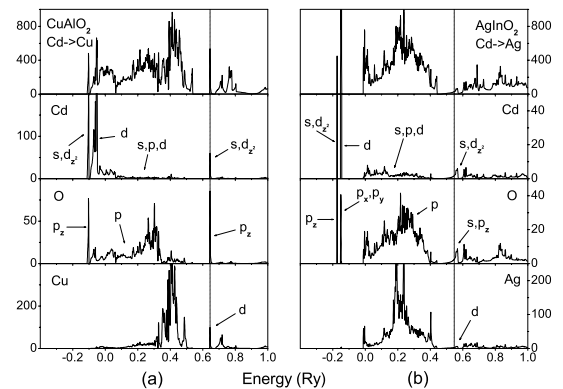


Figure 2. The calculated DOS for (a) CuAlO_2 compound in which Cd substitutes for the Cu, and (b) AgInO_2 compound in which Cd substitutes for the Ag. PDOS of Cd, its first NN O and second NN Cu (Ag) is also presented. The dashed line denotes Fermi level.

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	Theory
	$ V_{zz} $	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.

Acknowledgments

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