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## Changes induced by the presence of Zn or Ni impurity at Cu sites in $\text{CuAlO}_2$ delafossite

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### Abstract

A semiconducting delafossite compound  $\text{CuAlO}_2$  containing either Zn or Ni impurity substituting for a Cu position has been investigated. The electronic structure and the electric field gradients (EFGs) for both donor (Zn) and acceptor (Ni) doped systems have been calculated using a full potential linear augmented plane-wave method with generalized gradient approximation accounting for the exchange and correlation effects. The results clearly indicate that the presence of Zn impurities changes the electric properties of  $\text{CuAlO}_2$  by producing n-type semiconductivity, in a similar way as we have previously shown for the Cd impurity. In the case when Ni substitutes Cu the results of calculations indicate p-type semiconductivity in the material. Despite the fact that both Zn and Ni exhibit a similar hybridization scheme for the bonding with neighboring oxygens, their d electron clouds have different shapes due to deficit (Ni) and excess (Zn) of the  $d_{z^2}$  electrons. This effect is responsible for the large difference between the EFG values calculated at the Ni and Zn nuclei in the compound. © 2003 Elsevier Science Ltd. All rights reserved.

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The semiconducting delafossite-type oxides (SDOs) have a chemical formula  $\text{ABO}_2$ , where A is either Cu or Ag, and B can be one of the many trivalent metal ions (Al, In, Cr, Co, Fe, etc.) [1]. Their crystalline structure belongs to the space group  $R\bar{3}m$ , and can be viewed as an alternative stacking of the A and  $\text{BO}_2$  layers perpendicular to the *c*-axis (Fig. 1). The A and B sites have a very different local neighborhood: while the A atoms are linearly coordinated by two oxygens along the *c*-axis, the B atoms are octahedrally surrounded by six oxygens.

Recently, the SDOs have attracted much attention due to their potential technological applications. Beside being transparent by virtue of their large band gaps, SDOs exhibit both p and n-type conductivities as shown recently in

several experiments [2–6]. These features qualify them as promising candidates for the construction of transparent semiconductor devices despite the limitation that the reported p-type conductivities are still too low to match the n-type ones.

In an attempt to study how the electrical properties of SDOs change in the presence of impurities, various experiments have been performed earlier. In majority of them the SDOs were doped with impurities that substitute the B atoms in the structure. The  $\text{AgInO}_2$  was found to be an n-type material after doping with the Sn which substitutes the In [2]. The  $\text{CuCrO}_2$  is reported to be a p-type material when doped with Mg which replaces Cr [3]. It has also been shown that the substitution of some In atoms with the Ca and Sn produces, respectively, p and n-type conductivities in the  $\text{CuInO}_2$  [4]. In the case of  $\text{CuScO}_2$ , intercalation with oxygen produces a p-type conductivity [5], while the  $\text{CuAlO}_2$  exhibits a p-type conductivity due to the presence of native defects in the structure [6]. On the other hand, effects induced by impurities introduced at the A site have not been investigated.

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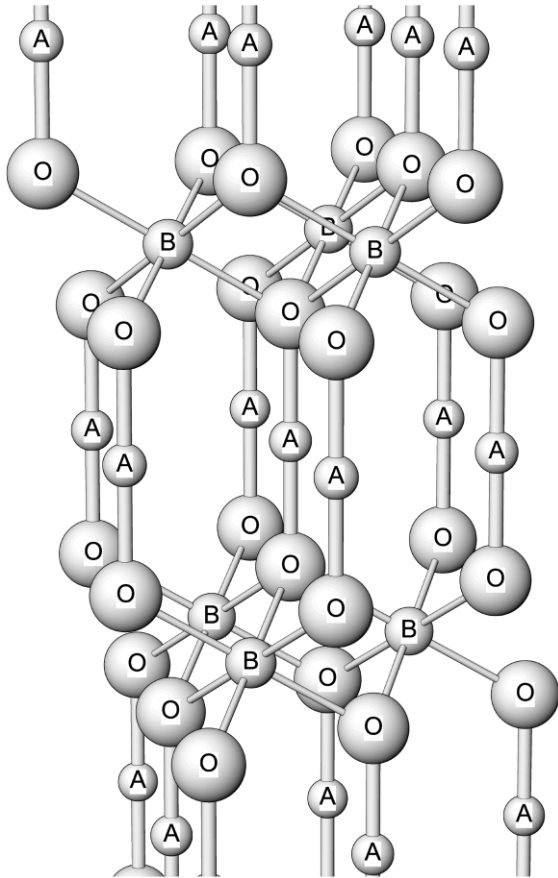


Fig. 1. Crystalline structure of the  $ABO_2$  delafossite compound.

Recently we reported on first-principles electronic structure calculations of the  $CuAlO_2$  compound with Cd impurity occupying either Cu or Al position [7]. In this work we indicated a strong possibility that Cd, when substitutes a Cu, creates a shallow level inside the band gap and produces an n-type conductivity. In this way we demonstrated that the electrical properties of the SDOs can be changed by doping not just the B, but also the A site.

In the present work we continue to investigate the A site in SDOs by studying the effects induced by the presence of impurities at the Cu site in  $CuAlO_2$ . We have chosen the elements Ni and Zn as impurities that differ from the Cu by  $\Delta Z = \mp 1$  in atomic number. Our principal aim is to find out if Ni produces a p-type and Zn an n-type conductivity in the material, in order to further clarify the role of A site in the process of fabrication of the transparent p–n junction. For this purpose we performed the first-principles band structure calculations for two impurity-containing  $CuAlO_2$  systems: (1) with Ni at Cu position and (2) with Zn at Cu position. The full potential linear augmented plane-wave (FP-LAPW) method [8], embodied into the WIEN97 computer code [9], has been employed, with generalized-gradient approximation (GGA) [10] treating the exchange and correlation

effects. The calculations were performed in a supercell geometry, with the supercell consisting of 32 atoms in which one Cu atom has been replaced either by Ni or by Zn. Relaxation of all atomic positions in the supercell has been included. A self-consistency cycle was carried out until the stability of total energy was better than  $10^{-5}$  Ry, for both structures. The lattice parameters and all the other technical details of the calculations were the same as used in our recent study of Cd-doped  $CuAlO_2$  compound [7], since this study has been proved to give a realistic description of the impurity containing system on the basis of comparison with the experiment.

Analysis of the obtained results showed that most of the changes caused by the impurity are confined within a small cluster around the impurity atom. Relaxation of the atomic positions resulted in a substantial movement of just the two nearest neighbor (NN) oxygens along the  $c$ -axis, while the positions of the other atoms were not affected. Having a larger ionic radius than Cu, Zn pushed the NN oxygens significantly, increasing the Zn–O distance to 1.940 Å in comparison with Cu–O distance of 1.860 Å in the pure  $CuAlO_2$ . Despite the fact that Ni has a smaller ionic radius than Cu, it also pushed slightly the NN oxygen atoms, resulting in a Ni–O distance of 1.867 Å. The electronic structure changes have been studied by analyzing the partial density of states (PDOS) and the electric field gradient (EFG) for each inequivalent atom in both calculated structures. As a second spatial derivative of the crystalline potential at the nuclear position, EFG is a quantity that depends sensitively on the band-structure details [11,12]. It can be used, together with the PDOS, to characterize the ground state of the specific atoms in the compound. Both PDOS and EFG for each atom in the impurity-containing supercells have been compared with PDOS and EFG calculated for the same atom in pure  $CuAlO_2$  [7]. This procedure enabled us to make an estimate of the spatial extent of the impurity's influence in the material. It was found that majority of atoms in both supercells have their PDOS practically indistinguishable from the PDOS of the corresponding atoms in the pure compound, with the EFG differing by less than 5% in each case. The differences are found to be considerable only inside the cluster consisting of the impurity itself, its two NN oxygen atoms, and the six second NN copper atoms in the basal plane (see Fig. 1). Their PDOS, together with the DOS for both Zn and Ni-doped  $CuAlO_2$  delafossites are shown in Fig. 2.

In the case when Zn substitutes for a Cu (Fig. 2(a)), the most striking feature of the electronic spectrum is the occurrence of a narrow band within the fundamental gap near the bottom of the conduction band. This band is impurity induced, half-filled (one electron), and consists mainly of the Zn  $s$  and  $d_{z^2}$ , NN O  $p_z$  and second NN Cu  $d$  states with charges concentrated in the basal plane ( $z$ -axis is taken to be parallel to the crystalline  $c$ -axis). Since its corresponding electron density is widely spread over the crystal, the band can be considered as a shallow. Specific

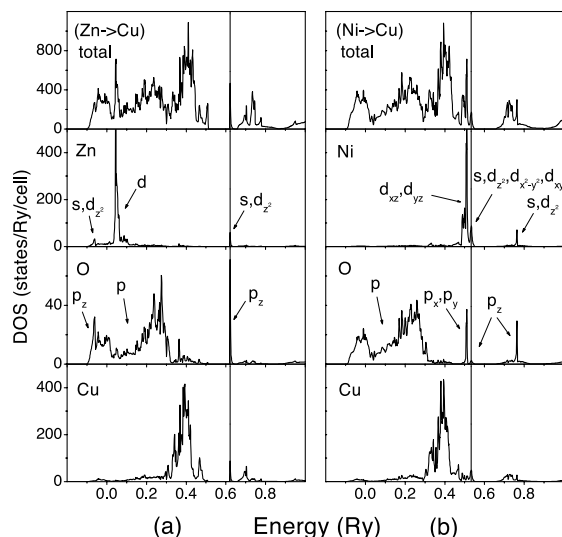


Fig. 2. The calculated DOS of the  $\text{CuAlO}_2$  compound containing (a) Zn, and (b) Ni as impurities that substitute for a Cu. PDOS of the impurity atoms and their first and second neighbors is also shown. Predominant orbital characters of some bands are indicated. The dashed line denotes Fermi level.

$s$ - $d$  hybridization scheme, proposed for the cases when  $d^9$  and  $d^{10}$  ions constitute the A site in delafossites [1,13], is seen to be valid for Zn located at the Cu site also. The antibonding Zn  $1/\sqrt{2}(s + d_{z^2})$  orbital is hybridized with the O  $p_z$  orbital, and builds a bonding hybrid located at the bottom of the valence band and an antibonding hybrid positioned within the band gap, 0.20 eV below the conduction band bottom. The band gap is found to be 2.00 eV, not much different from the band gap of 1.97 eV calculated for the pure compound [7]. In fact, the electronic structure shown in Fig. 2(a) is similar to that calculated for  $\text{CuAlO}_2$  with Cd substituting for Cu [7]. Therefore, the conclusion that can be drawn is the following: similarly to the case when Cd replaces a Cu, the electrical properties of  $\text{CuAlO}_2$  change when the system is doped with Zn substituting Cu, and an n-type semiconductivity is developed. In this manner we further reinforce our theoretical prediction that the Cu position (and the A position in general) in SDOs is sensitive to doping with the donor impurities, in the sense that they easily create a level within a band gap. We believe that this property deserves further experimental investigation.

When Ni substitutes Cu in  $\text{CuAlO}_2$ , a different physical situation is encountered (Fig. 2(b)). The  $\text{Ni}^{2+}$  ion has a  $d^8$  electron configuration and strictly speaking the  $s$ - $d$  hybridization scheme mentioned above should not be valid in this case. The present results, however, show that the Ni  $1/\sqrt{2}(s + d_{z^2})$  and the O  $p_z$  orbitals combine to form an antibonding hybrid in the conduction band and a bonding hybrid at the Fermi level. The bonding hybrid is mixed with the Ni  $d_x^2 - d_y^2$  and  $d_{xy}$  orbitals and almost overlaps in energy with the  $\pi$ -type hybrid consisting of the Ni  $d_{xz}$ ,  $d_{yz}$  and O  $p_x$ ,  $p_y$  orbitals. The states within the band gap are not formed,

although the gap itself is substantially reduced ( $\sim 1.50$  eV) in comparison with the gap in the pure  $\text{CuAlO}_2$ . The Ni d-band is merged into the top of the valence band where remained a space to put one more electron and thus a hole-type conductivity is enabled. The Ni d-states are strongly hybridized with the Cu d-states near Fermi level, i.e. in a region that is most important for determining the electrical properties of the compound. This hybridization induces a non-negligible Ni–Ni interaction mediated by the Cu atoms in the basal plane (through the sequences Ni–Cu–Ni, the Ni–Ni distance being 5.7 Å in our calculational model), which causes a significant broadening of the Ni d-band. Therefore, to find out what would happen in the isolated impurity limit (with no Ni–Ni interaction involved), more elaborate calculations that primarily involve a larger supercell need to be performed. These calculations would resolve the question whether the impurity band remains merged into the top of the valence band or appears inside the gap. In both cases, however, there will exist some hole states at the top of the valence band, and we can conclude that our calculations indicate a p-type conductivity in Ni-doped  $\text{CuAlO}_2$ .

From Fig. 2 it can be seen that both Zn and Ni impurities form similar hybrids (bonding and antibonding) consisting of their  $s$  and  $d_{z^2}$  orbitals and the NN O  $p_z$  orbitals, whose nature has been discussed in details elsewhere [1,7]. These hybrids are, however, positioned differently on the energy scale. While Zn antibonding hybrid is located at the Fermi level and half populated, the Ni antibonding hybrid makes part of the conduction band, thus being completely empty. As a consequence, a considerable difference between the shapes of the Zn and the Ni d electron clouds arises. In the case of Ni for example, the  $d_{z^2}$  orbital is less populated than the other d-orbitals, while in the case of Zn the opposite is true. The resulting d shell of Ni is thus more condensed in a basal plane and stretched towards the neighboring Cu atoms, while the d shell of Zn is more peaked towards the neighboring O atoms along the  $c$ -axis of the crystal. This effect can be described quantitatively by calculating the anisotropy count  $\Delta n_d = (n_{d_{xy}} + n_{d_{x^2-y^2}}) - 1/2(n_{d_{xz}} + n_{d_{yz}}) - n_{d_{z^2}}$ , defined as a specific combination of the subshell occupation numbers which estimates the degree of deviation of the d electron density from the spherical symmetry. Our calculations resulted in  $\Delta n_d = -0.035$  for the Zn and  $\Delta n_d = +0.405$  for the Ni d densities, showing that their departures from the spherical symmetry develop in the opposite directions.

Calculated EFGs at both Zn and Ni nuclei in  $\text{CuAlO}_2$  are listed in Table 1. As can be seen, very different EFG values are predicted for these two impurities, mostly due to differences between their d electron shells (which cause distinct d–d contributions to the EFG). The EFG depends sensitively on the asphericity of the electron shells, and the signs of its p–p and d–d contributions follow the signs of the corresponding electron shell anisotropy counts  $\Delta n_p = n_{p_z} - 1/2(n_{p_x} + n_{p_y})$  and  $\Delta n_d$ , respectively [12]. This is the reason why in the case of Ni the d–d contribution is

Table 1

Theoretical prediction for the EFGs at the Zn and the Ni impurities residing at the Cu site in CuAlO<sub>2</sub>, calculated by the FP-LAPW method.  $V_{zz}$  is the main component of the EFG tensor, directed along the  $c$ -axis of the crystal. It is further decomposed into the contributions from  $p$  and  $d$  electronic shells. A minor  $s$ - $d$  contribution, which was not considered important, is not presented. All the numbers given in the table are in units  $10^{21}$  V/m<sup>2</sup>

	$V_{zz}$	$p$ - $p$	$d$ - $d$
Zn	-15.08	-12.59	-2.53
Ni	0.16	-17.85	17.96

positive (canceling the  $p$ - $p$  contribution and resulting in almost zero total EFG), while in the case of Zn this contribution is negative (thus adding to the  $p$ - $p$  contribution and resulting in a significant EFG value). In this way, the calculated EFGs for Zn and Ni impurities in CuAlO<sub>2</sub> reflect their electronic structure properties described above.

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