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Semiconductor properties of Cu-based delafossites revealed by an electric field gradient study

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Abstract

In this paper we offer an interpretation of the previously observed trend of the electric field gradient (EFG) values measured in a group of semiconducting delafossites CuBO_2 ($B = \text{Al, Fe, Cr, Nd}$) at Cd impurities which substitute either Cu or B atoms. Our theoretical study indicates that this EFG trend reveals one of the most subtle details in the electronic spectrum of the compounds, namely whether the impurity states are formed within or out of the band gap. When Cd substitutes the Cu, it exhibits a larger EFG value in CuAlO_2 and CuFeO_2 than in CuCrO_2 and CuNdO_2 . This occurs because the Cd states form in the first two compounds a shallow band within the gap, but in the second two compounds they do not. When Cd substitutes the B atom it exhibits almost the same EFG in all delafossites. In this case, Cd states are not formed within the gap in any of the compounds. The same interpretation can be applied to the whole family of CuBO_2 delafossites, whatever the B atom is. To arrive at these conclusions we analysed and calculated various systems (Cd-doped CuAlO_2 and CuCrO_2 compounds, and molecular clusters) using the full-potential linear augmented plane wave method.

1. Introduction

The semiconducting delafossite-type oxides (SDOs) have chemical formula ABO_2 , where A is either Cu or Ag, and B can be one of many trivalent ions (Al, In, Cr, Fe,...) [1]. Their crystalline structure belongs to space group $R\bar{3}m$, characterized by very different neighbourhoods seen from the A and B sites. The A atoms are linearly coordinated by two nearest-neighbour (NN) oxygens along the crystalline c -axis and by six second-NN A atoms in the basal plane, while the B atoms are octahedrally surrounded by six NN oxygens (see figure 1 in [2]).

Recently, the SDOs have attracted much attention due to their potential technological application. Besides being transparent by virtue of their large band gaps, SDOs exhibit both p- and n-type conductivities, as shown in several experiments [3–5]. These features qualify

Table 1. The EFG values measured at the isolated Cd impurities occupying either Cu or B positions in a group of CuBO₂ delafossites, taken from [8]. EFG units: 10²¹ V m⁻².

Delafossites	Cu site	B site
CuBO ₂	$ V_{zz} $	$ V_{zz} $
CuAlO ₂	27.44	7.47
CuCrO ₂	20.84	6.28
CuFeO ₂	27.96	6.21
CuNdO ₂	20.97	6.98
CuYO ₂	14.43	6.68

them as promising candidates for transparent semiconductor devices, despite a limitation that reported p-type conductivities are still too low to match the n-type ones [6].

One of the efficient ways to study the microscopic properties of solids is to measure the hyperfine interaction between the nuclear and the electronic subsystems [7]. By this way the electric field gradient (EFG) tensor can be determined, defined as a second spatial derivative of the crystalline potential at the nucleus. Its principal component is given by the formula

$$V_{zz} = \left(\frac{\partial^2 U}{\partial z^2} \right)_{r=0}$$

where z denotes the principal axis of the EFG tensor. The EFG is an important ground-state quantity of any crystal. Since it is always measured at the position of a specific nucleus (probe), it is predominantly determined by the electrostatic influence of its neighbourhood. It contains valuable information about the electronic charge distribution in the vicinity of the probe, and can be measured by various nuclear methods, such as Mössbauer spectroscopy, perturbed angular correlation (PAC) or nuclear magnetic resonance.

In the experiment whose results we shall discuss here, the five SDOs with formula CuBO₂ (B = Al, Fe, Cr, Nd, Y) were studied via hyperfine interaction measurements, utilizing the PAC method [8]. The objective was to determine the V_{zz} values at the isolated Cd probes which substitute either Cu or B atoms in SDOs (in the delafossite structure the z -axis corresponds to the crystalline c -axis, while the xy plane lies in the basal plane). The results showed two very distinct EFG trends, depending on the probe position. When Cd occupies the B site, it exhibits similar EFG values in all compounds, contrary to the situation when Cd occupies the Cu site, in which case its EFG exhibits peculiar oscillations (table 1). The CuYO₂ is an exception from this pattern since its structure belongs to a space group $P6_3/mmc$, polymorphic to $R\bar{3}m$. These two structures are characterized by a different nearest neighbourhood around the Cu site, but the same around the B site.

In the present paper our intention is to interpret the EFG trend shown in table 1 by connecting it with the electronic and semiconductor properties of SDOs. Our ultimate objective is to understand how the electronic spectrum of SDOs changes under the doping, which is an issue of considerable importance for eventual opto-electronic technological applications of these materials.

A straightforward way to reach this objective is to perform first-principles calculations for all five Cd-doped SDOs given in table 1, and to analyse the resulting electronic structures and Cd EFGs. This strategy, however, is not appropriate since all compounds except CuAlO₂ are anti-ferromagnets with complicated alignments of magnetic moments [9, 10], a fact which is difficult to treat accurately in the theory.

In order to resolve the problem in a viable manner, we chose a different strategy, which consisted of several consecutive steps. In the first one, we analysed the results of our previous

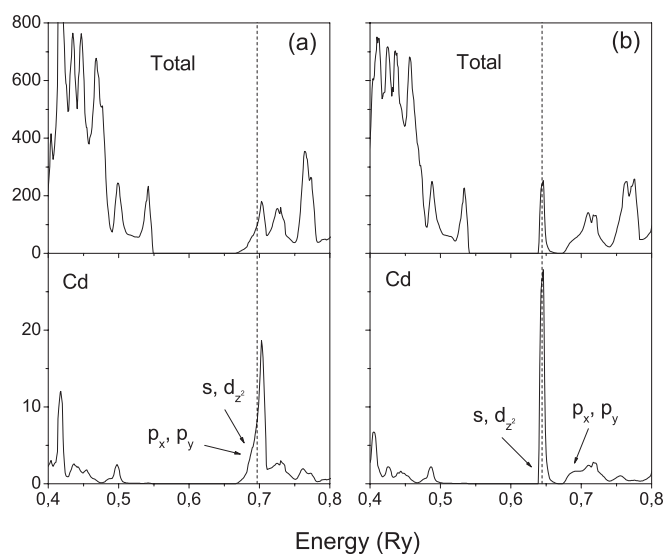


Figure 1. Calculated total and Cd-projected DOS in CuAlO_2 compound with Cd occupying the Cu position with (a) non-optimized and (b) optimized Cd–O distances (taken from [2]). The dashed line denotes the Fermi level. DOS units: states/Ryd/cell.

theoretical study of the doped CuAlO_2 compound [2] which exhibits an increased EFG when Cd substitutes Cu, and decomposed the Cd EFG. In the second step, we calculated the Cd EFG in two artificial molecular clusters constructed in a way which simulates the Cd nearest neighbourhood in SDOs. After that, we were able to draw conclusions and offer a possible interpretation of the Cd EFG trend in the whole family of Cu-based SDOs. Finally, in the last step, we tested this interpretation by calculating the electronic structure and the EFG in the Cd-doped CuCrO_2 compound, which exhibits a smaller EFG when Cd occupies the Cu site. The paper is organized in a way which follows and describes these steps.

All calculations were performed using the first-principles, density-functional based [11], full potential linear augmented plane wave (FP-LAPW) method [12], as embodied in the WIEN2k computer code [13].

2. CuAlO_2 study

In [2] we presented a detailed band-structure description of the CuAlO_2 compound with an isolated Cd impurity substituting either Cu ($\text{Cd} \rightarrow \text{Cu}$) or Al ($\text{Cd} \rightarrow \text{Al}$). When Cd replaces the Cu, the electronic structure of this compound is very sensitive on the Cd–O bond distance. If the crystal structure is not optimized (Cd–O distance the same as Cu–O distance in the pure compound) the Cd states are at the bottom of the conduction band (figure 1(a)). By allowing the two NN O atoms to relax (the second NN Cu atoms are fixed by symmetry), some of the Cd and O states (Cd s and d_{z^2} and O p_z) detach from the conduction band bottom and move inside the gap. When the Cd–O distance reaches its optimized value (at which the forces acting on the atoms are nearly zero), these states form the shallow band within the gap, converting the system into the n-type semiconductor (figure 1(b)). When Cd substitutes the Al, no states within the gap appear, either for optimized or for non-optimized Cd–O distances [2].

In this paper we present an analysis of the Cd EFG, that was not discussed in [2], as well as its connection with the electronic structure of the doped CuAlO_2 compound. In the $\text{Cd} \rightarrow \text{Cu}$

Table 2. V_{zz} values and their decompositions calculated at the Cd nuclei in Cd-doped CuAlO₂ compounds, for both non-relaxed and relaxed impurity–host distances. In the case when Cd occupies the Cu site, the total EFG is decomposed in two parts: one that originates from the valence band and other from the band situated at the Fermi level. V_{zz} units: 10^{21} V m⁻².

	Non-optimized structure		Optimized structure	
	V_{zz} at Cd nucleus	V_{zz} decomposition	V_{zz} at Cd nucleus	V_{zz} decomposition
CuAlO ₂ (Cd → Cu case)	-33.90	s-d: 0.78	-25.73	s-d: 0.26
↓		p-p: -34.29		p-p: -20.12
		d-d: -0.39		d-d: -5.87
Valence band	-35.00	s-d: 0.99 p-p: -40.04 d-d: 4.05	-20.81	s-d: 0.68 p-p: -20.76 d-d: -0.73
Band at Fermi level	+1.10	s-d: -0.21 p-p: 5.75 d-d: -4.44	-4.92	s-d: -0.42 p-p: 0.64 d-d: -5.14
CuAlO ₂ (Cd → Al case)			+5.63	s-d: -0.12 p-p: 6.12 d-d: -0.39

case we analyse the Cd EFG for both non-optimized and optimized geometries, since these geometries lead to essentially different electronic structures. In the Cd → Al case we analyse the Cd EFG just for optimized geometry, since the non-optimized one produces a similar electronic structure (with no shallow band). In our analysis the Cd EFG was decomposed in two parts. One part contains the EFG contribution from the occupied part of the band situated in the vicinity of Fermi level (the very bottom of the conduction band for the non-optimized, and half of the shallow band for the optimized structure). The other part contains the EFG contribution from the rest of the Cd valence states, which we shall refer to here as valence band, using the semiconductor terminology. We calculated the decomposition of both parts, by looking from which Cd shell, p (p–p term) or d (d–d term), the main contribution to the EFG comes [14] (the mixed s–d term, which also appears in the EFG decomposition, is usually of less importance). The results are summarized in table 2.

Analysing the Cd → Cu case, it can be seen that Cd EFG depends sensitively on changes of the Cd–O distance. Not just the total values, but also the values arising from the Fermi level band and valence band are very different comparing the optimized and non-optimized structure. The origin of these differences is difficult to trace for the valence band, whereas for the band situated at the Fermi level it is a possible task. When the Cd–O distance is not optimized, the occupied part of this band consists of s, d_{z^2} , p_x and p_y states of Cd (among the states of other atoms, principally p_z states of NN O), which all appear in the same proportion. All of these Cd states contribute to the total EFG at the Cd nucleus. The p_x and p_y states make a large positive contribution (+5.75) to the total EFG, almost cancelling the contributions from the s–d and d–d terms, which are negative. As a result, the total Cd EFG is very small. In the case of the optimized Cd–O distance, however, the band at the Fermi level is mainly composed from the Cd s and d_{z^2} states (apart from the states of other atoms), while the Cd p_x and p_y states are absent. This fact is reflected in the total EFG value, since now its p–p contribution is almost zero while the d–d and s–d contributions retain more or less the same values as in the case of non-optimized geometry.

The absence of Cd p_x and p_y states from the shallow band can be understood in terms of the specific hybridization scheme between Cd and its two NN oxygens, discussed in detail in [2].

When Cd occupies the Cu site, its $1/\sqrt{2}(s + d_{z^2})$ orbital makes a bonding and anti-bonding combination with the p_z orbital of NN oxygens. If the Cd–O distance is not optimized, the anti-bonding hybrid, highly directed along the z -axis, is situated at the bottom of the conduction band. There, it mixes with other electronic states, among them the Cd p_x and p_y states. As the Cd–O distance along the z -axis increases during the relaxation, the energy difference between bonding and anti-bonding hybrids decreases and the latter moves down into the gap. At the same time, the Cd p_x and p_y states, being concentrated in the xy plane, are not much affected by changing the Cd–O distance. Thus, they stay at the conduction band bottom even when the Cd–O distance reaches its optimized value (figure 1).

3. Molecular cluster calculations

According to our previous CuAlO₂ study [2], when Cd substitutes the Cu position it disturbs just a small cluster of atoms around it, namely the two NN O (along the c -axis) and six second-NN Cu (in the basal plane). When Cd substitutes Al, its presence affects only the six NN O around it. The calculations showed that just the quoted atoms exhibited significant differences in the projected DOS and the EFG values compared with the situation when the Cd impurity is not present [2]. Therefore it is reasonable to assume that in return the Cd EFG is mainly determined by the electrostatic influence of just these atoms.

Following this idea, we constructed artificial molecular clusters which closely simulate the surroundings of Cd (located either at Cu or B site) in CuBO₂ delafossites, and calculated the Cd EFG in these structures using the supercell approach within the FP-LAPW method. Molecular clusters were designed on the basis of supercells used to model a Cd-doped CuAlO₂ compound. Actually, we were using both types of CuAlO₂ supercells (Cd → Cu and Cd → Al) in which we removed all the atoms except the central Cd and its nearest neighbours. Constructed this way, the molecular supercells preserved delafossite's symmetry, still containing enough empty space to substantially reduce interaction with molecules in neighbouring supercells. Other calculational parameters, including the lattice constants, were exactly the same as adopted in the case of the CuAlO₂ study [2].

To analyse the situation in which Cd substitutes the B atom in CuBO₂ (Cd → B case) we constructed a cluster containing just Cd and the six NN oxygens around the B site, with the same Cd–O distances as in the optimized Cd-containing CuAlO₂ (Cd → Al case). In order to simulate the situation in which Cd substitutes the Cu atom in CuBO₂ (Cd → Cu case), we constructed a cluster from Cd, its two NN oxygens and six second-NN coppers. This cluster is calculated with two sets of Cd–O distances, the optimized one (optimized Cd–O distance as in the Cd-containing CuAlO₂) and non-optimized one (the same as the Cu–O distance in pure CuAlO₂). The calculated EFGs at the Cd nuclei are presented in table 3.

4. Interpretation of Cd EFG trend in CuBO₂ delafossites

4.1. Cd → Cu case

The cluster calculations, presented in the previous section, failed to completely reproduce the Cd EFG in the CuAlO₂ compound. The total Cd V_{zz} values, and especially their decompositions, differ significantly for both sets of Cd–O distances (tables 2 and 3). Obviously, considering just the first and second NNs of Cd is not enough to interpret its EFG. This is not a surprise, since otherwise the Cd EFG would be equal in all the CuBO₂ delafossites, whatever the B atom is (the Cd neighbours in question are O and Cu). However, we know from the experiment that the Cd exhibits two different EFG values (table 1). Thus we must

Table 3. Calculated EFGs at the Cd nuclei in clusters which closely simulate the Cd environment in Cd-doped CuBO₂ delafossites. The Cd + 6O cluster simulates the case when Cd occupies the B site (Cd → B), while the Cd + 2O + 6Cu cluster simulates the Cd presence at the Cu site (Cd → Cu). Interatomic distances in clusters are taken to be the same as in the CuAlO₂ compound with non-optimized or optimized Cd–O distances. V_{zz} units: 10^{21} V m⁻².

Molecules	Non-optimized Cd–O distance		Optimized Cd–O distance	
	V_{zz} at Cd nucleus	V_{zz} decomposition	V_{zz} at Cd nucleus	V_{zz} decomposition
Cd + 6O			+5.65	s-d: -0.17 p-p: 6.74 d-d: -0.94
Cd + 2O + 6Cu	-33.35	s-d: 0.41 p-p: -42.66 d-d: 8.90	-18.97	s-d: 0.42 p-p: -21.25 d-d: 1.86

conclude that the B atoms also participate in determining the Cd EFG, but in a more subtle way, which leads to two different V_{zz} values. Since these values sensitively reflect the properties of the electronic structure, it must be that Cd-doped CuBO₂ compounds exhibit two essentially different electronic structures, one for B = Al, Fe and the other for B = Cr, Nd.

Analysis of the data given in the table 2, resulting from the Cd-doped CuAlO₂ study, provides a clue about the basic differences of these electronic structures. When the Cd–O distance is not optimized, and no shallow band is formed, almost the whole Cd EFG value comes from the Cd valence band. This is due to the presence of the Cd p_x and p_y states at the occupied part of conduction band, as explained in section 2. When the Cd–O distance is optimized and a shallow band is formed, Cd has an EFG of approximately -26 (in 10^{21} V m⁻²). From this number, approximately -5 originate from the shallow band, due to the absence of Cd p_x and p_y states within it. If this band was not detached from the conduction band bottom, the resulting Cd EFG would be approximately -21 , like in CuCrO₂ and CuNdO₂. This statement is justified since the Cd p_x and p_y states are still present at the bottom of the conduction band (figure 1), but they do not contribute to the total Cd EFG, since they remain unoccupied. Consequently, we can draw the conclusion about the basic difference between the two electronic structures which result in two different Cd EFG values: in some delafossites the Cd states are formed within the conduction band and in others the Cd states form a shallow band within the band gap.

Our cluster calculations offer further support for this interpretation. One notices that these calculations correctly reproduce just the part of the Cd EFG that originates from the Cd valence band in the CuAlO₂ compound, for both the non-optimized and optimized Cd–O distances (compare the data in tables 2 and 3). The conclusion is valid not just for the total Cd EFG values, which are in good concordance, but for the EFG decompositions too. The fact that cluster calculations do not account for the part of the Cd EFG which originates either from the conduction band bottom or from the shallow band in CuAlO₂ is not surprising. Both of these bands are composed of the states from many atoms, and originate from collective effects occurring in the crystal. Our fictitious cluster is too simple to simulate the effects from these bands. It is, however, sufficiently complex to indicate the following: in any of the CuBO₂ delafossites the principal part of the Cd EFG, which originates from its valence band, is determined by the electrostatic influence of the first and second NNs only (which are common in all compounds). On the other hand, the CuAlO₂ calculations indicate that the total Cd EFG is practically equal to its valence part in the case when Cd does not form the shallow

band. Joining the above two indications, we finally put ourselves in a position to propose a reasonable interpretation of the experimentally observed Cd EFG trend in CuBO₂ delafossites.

When a Cd impurity occupies the Cu site, it should exhibit an EFG of approximately -21 (10^{21} V m⁻²) if the Cd states are positioned within the conduction band. This occurs in the case of Cd-doped CuCrO₂ and CuNdO₂ compounds (table 1). The difference between Cd EFG in these compounds and the Cd EFG measured in CuAlO₂ and CuFeO₂ originates from the contribution of the shallow band which is formed within the fundamental gaps of the latter.

Thus, we predict that introducing a Cd impurity at the Cu site produces different effects in CuAlO₂ and CuFeO₂ in contrast to CuCrO₂ and CuNdO₂. The first two compounds change their electric properties due to the presence of Cd donor states within their gaps (becoming n-type semiconductors), and the last two compounds do not. The experimentally observed EFG trend, given in the table 1, just reflects this fact.

4.2. Cd → B case

In the Cd → B case the cluster calculations (table 3) successfully reproduced the bulk EFG value calculated at Cd which occupies the Al site in CuAlO₂ (compare data in tables 2 and 3). Both EFG values have practically the same decomposition. This implies that Cd situated at the Al site in CuAlO₂ mainly senses the electrostatic influence of just the six NN oxygens around it, whereas the more distant neighbours have a negligible effect. Since Cd residing at the B position exhibits very similar EFG in any of the CuBO₂ delafossites (table 1), this conclusion can be generalized to the whole family. The CuYO₂ is no exception from this rule, since the Y atom has the same first neighbourhood as the B atoms in other delafossites.

The above EFG analysis allows us to conclude that the Cd → B doping case produces just one type of electronic structure, whatever the B atom is. Since our calculations for B = Al [2] resulted in the band structure with Cd states formed within the conduction band, we now predict that Cd → B doping will not produce the shallow band within the gap in any of the CuBO₂ delafossites.

5. CuCrO₂ study

In order to reinforce our conclusions presented in the previous section, we performed calculations for the CuCrO₂ compound in which an isolated Cd impurity substituted the Cu atom. According to experimental data (table 1), the Cd does not exhibit an elevated EFG value in this compound. Thus, if our interpretation is correct, the Cd electronic states should not appear within the band gap of the system.

CuCrO₂ is a semiconductor which exhibits a complicated arrangement of Cr magnetic moments. Actually, these moments form a non-collinear Heisenberg antiferromagnet on a triangular lattice, arranged with a 120° structure in the *ac* plane, with a moment of $3.1 \pm 0.2 \mu_B$ [10]. Without the possibility to treat this system accurately, we approximated its magnetic structure by the ferromagnetic order of Cr moments, aligned along the *c*-axis of the crystal. This approximation was sufficient to open a gap in the electronic spectrum of the pure compound (the non-magnetic calculations give a metallic solution) and to provide a good starting point for a treatment of the defect problem. For a rough analysis of Cd EFG properties, we found this approximation satisfactory. In calculations we used the experimental values of the lattice parameters taken from [15]. All the other computational details and parameters were the same as in [2], except that we took advantage of better computational resources and performed more accurate calculations: RKmax, the parameter which controls the size of the basis set, was set to be 8.0, in comparison to 7.0 in the case of Cd-doped CuAlO₂. After the convergence had

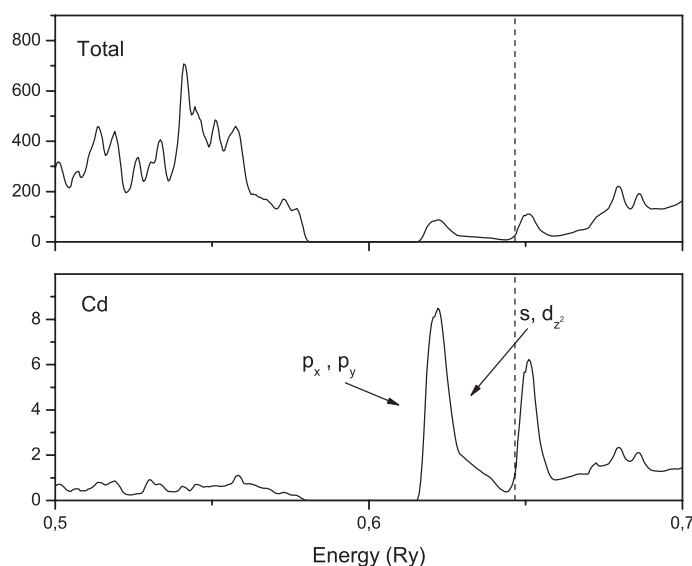


Figure 2. Calculated total and Cd projected DOS (spin up + spin down) in the vicinity of the Fermi level (dashed line) for the Cd-containing CuCrO_2 compound. Cd occupies the Cu position, and the Cd–O interatomic distance is relaxed. The shallow band within the gap is not formed, contrary to the case of the Cd-doped CuAlO_2 compound. DOS units: states/Ryd/cell.

been reached (including optimization of interatomic distances), we analysed the resulting band structure details and verified that no states were detached from the conduction band bottom and were present within the band gap (figure 2). The Cd states at the occupied part of the conduction band bottom consist of s , d_{z^2} , p_x and p_y states, exactly as in the case of Cd occupying the Cu site in CuAlO_2 , for the non-optimized Cd–O distance (figure 1(a)).

The calculated EFG at the Cd nucleus is found to be in good agreement with the experimental value. Its decomposition is presented in table 4.

Although our computation model took into account the magnetic structure of the Cr sublattice only approximately, the calculated Cd EFG displays all basic features predicted by the present study. The EFG contribution from the Cd valence band is practically the same as the Cd valence band contribution in the case of CuAlO_2 (table 2, optimized structure). This is valid not just for the total values, but for their decompositions too. Accordingly, the difference between the total Cd EFGs in CuAlO_2 and CuCrO_2 compounds comes from the band situated at the Fermi level. In CuAlO_2 this band is detached from the conduction band bottom and does not contain Cd p_x and p_y states, a fact which results in significant EFG contribution which elevates the total Cd EFG. In CuCrO_2 this band is part of the conduction band and contains the Cd p_x and p_y states (figure 2). This fact causes the partial cancellation of the p – p and d – d contributions and results in a very small EFG contribution from this band, hardly affecting the total Cd EFG.

In conclusion, we found a connection between the Cd EFG and the basic features of the electronic structure of doped CuCrO_2 in perfect agreement with our interpretation presented in the previous section.

6. Conclusions

In this paper we discussed the experimental trend of EFG values measured at Cd impurities in a group of semiconducting delafossites with the chemical formula CuBO_2 ($B = \text{Al, Fe, Cr}$,

Table 4. Principal V_{zz} value and its decomposition calculated at the Cd atom occupying the Cu site in the CuCrO_2 compound, for relaxed impurity–host distances. The total EFG is decomposed into the parts which originate from the valence band and from the band situated at the Fermi level respectively. V_{zz} units: 10^{21} V m^{-2} .

	Optimized structure	
	V_{zz} at Cd nucleus	V_{zz} decomposition
CuCrO_2		s–d: 0.31
(Cd \rightarrow Cu case)	–22.58	p–p: –19.11
↓		d–d: –3.78
		s–d: 0.61
Valence band	–20.63	p–p: –20.44
		d–d: –0.80
		s–d: –0.30
Band at	–1.96	p–p: 1.32
Fermi level		d–d: –2.98

Nd, Y). We performed calculations and analyses of various systems (Cd-doped CuAlO_2 and CuCrO_2 compounds, and molecular clusters), using the first-principles FP-LAPW method.

Our conclusions strongly indicate that the trend of measured EFGs can be correlated with the differences in electronic structure of these compounds, in the sense that the EFG can detect whether or not the impurity states are formed within the band gap.

When Cd substitutes Cu, it exhibits a larger EFG value in CuAlO_2 and CuFeO_2 than in CuCrO_2 and CuNdO_2 . This happens because in the first two compounds the Cd forms the donor band within the band gap, while in the second two compounds it does not. When Cd substitutes the B site, it exhibits almost the same EFG in all delafossites. In this case, Cd does not position its states within the band gap in any of the compounds. Due to the specific symmetry of the delafossite structure, and the fact that the EFG at Cd is mainly influenced by its immediate neighbourhood, the same interpretation can be extended to the whole family of CuBO_2 delafossites.

Results of the present study have the following practical implications.

- (1) Since the chemical valence of Cd is +2, and that of Cu and B atoms +1 and +3, respectively, Cd behaves as a donor when substituting Cu, and as an acceptor when substituting the B atom. On the basis of the present study we predict that the presence of Cd can produce a donor band within the gap in some of the CuBO_2 delafossites, but not the acceptor band in any of them. This conclusion should also be valid for a Zn impurity, since it has the same chemical valence as Cd and its presence changes the CuAlO_2 electronic spectrum in a similar way as Cd does [16].
- (2) Nuclear experimental methods which investigate the hyperfine interactions in crystals (PAC, Mössbauer, NMR), combined with first-principles calculations, can be utilized to determine even subtle details in the electronic structure of doped delafossites through the EFG measurements.

In light of recent search for a proper wide-gap p–n junction, the above facts can help experimentalists to determine which of the doped delafossites can become p- or n-type semiconductors, and which cannot. We showed that this information is accessible from measurements of the impurity-induced EFG trend in candidate compounds.

Although the present work cannot be considered as a strict proof for the presented conclusions, mainly due to the approximate magnetic structure assumed in the CuCrO_2 calculations, it is at least a reasonable hypothesis, which could be verified by further experimental studies.

It is likely that a similar correlation between the impurity EFG values and the impurity states within a band-gap also exists in the Ag-based branch of delafossite semiconductors. There are, however, too few experimental data that can be analysed (just two Ag-based compounds were treated in [8]). We have already performed calculations of Cd-doped AgInO_2 [17] and plan to investigate this subject in more detail in the future.

References

- [1] Rogers D B, Shanon R D, Prewitt C T and Gilson J L 1971 *Inorg. Chem.* **10** 723
- [2] Lalić M V, Mestnik-Filho J, Carbonari A W, Saxena R N and Moralles M 2002 *J. Phys.: Condens. Matter* **14** 5517
- [3] Duan N, Sleight A W, Jayaraj M K and Tate J 2000 *Appl. Phys. Lett.* **77** 1325
- [4] Yanagi H, Hase T, Ibuki S, Ueda K and Hosono H 2001 *Appl. Phys. Lett.* **78** 1583
- [5] Yanagi H, Inoue S, Ueda K, Kawazoe H, Hosono H and Hamada N 2000 *J. Appl. Phys.* **88** 4159
- [6] Kawazoe H, Yasukawa M, Hyodo H, Kurita M, Yanagi H and Hosono H 1997 *Nature* **389** 939
- [7] Kaufmann E N and Vianden R J 1979 *Rev. Mod. Phys.* **51** 161
- [8] Attili R N, Saxena R N, Carbonari A W, Mestnik-Filho J, Uhrmacher M and Lieb K P 1998 *Phys. Rev. B* **58** 2563
- [9] Mekata M, Yaguchi N, Takagi T, Mitsuda S and Yoshizawa H 1992 *J. Magn. Magn. Mater.* **104–107** 823
- [10] Kadowaki H, Kikuchi H and Ajiro Y 1990 *J. Phys.: Condens. Matter* **2** 4485
- [11] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
- [12] Andersen O K 1975 *Phys. Rev. B* **12** 3060
Singh D J 1994 *Plane Waves, Pseudopotentials and the LAPW Method* (Dordrecht: Kluwer Academic)
- [13] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D and Luitz J 2001 *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Austria: Karlheinz Schwarz, Techn. Universität Wien)
- [14] Blaha P, Schwarz K and Dederichs P H 1988 *Phys. Rev. B* **37** 2792
- [15] Doumerc J P, Ammar A, Wichainchai A, Pouchard M and Hagenmüller P 1987 *J. Phys. Chem. Solids* **48** 37
- [16] Lalić M V, Mestnik-Filho J, Carbonari A W and Saxena R N 2003 *Solid State Commun.* **125** 175
- [17] Lalić M V, Mestnik-Filho J, Carbonari A W and Saxena R N 2004 *Braz. J. Phys.* **34** (2B) 611