Hyperfine Interactions (2004) 158:89–93
DOI 10.1007/s10751-005-9013-7

# Correlation between the EFG Values Measured at the Cd Impurity in a Group of Cu-based Delafossites and the Semiconducting Properties of the Latter

M. V. LALIC[1] and J. MESTNIK-FILHO[2]
[1]*Universidade Federal de Sergipe, Departamento de Física, P.O. Box 353, 49100-000, São Cristóvão, SE, Brazil; e-mail: mlalic@fisica.ufs.br*
[2]*Instituto de Pesquisas Energeticas e Nucleares, P.O. Box 11049, 05422-970, São Paulo, SP, Brazil*

**Abstract.** In this paper we analyze trend of EFG values measured at Cd impurity in a group of semiconducting delafossites with chemical formula $CuBO_2$ (B = Al, Fe, Cr, Nd). We conclude that this trend reveals one of the most subtle details in electronic spectrum of the compounds: if impurity states are formed within or out of the band gap. In $CuAlO_2$ and $CuFeO_2$ the Cd EFG exhibits larger value than in $CuCrO_2$ and $CuNdO_2$, when Cd substitutes the Cu atom. This occurs because in the first two compounds the Cd forms shallow band within the gap, and in the second two compounds does not. When Cd occupies the B position it exhibits almost the same EFG in all delafossites. In this case, Cd does not form its states within the gap in none of the compounds. To arrive to these conclusions we analyzed and calculated various systems (Cd-doped $CuAlO_2$ and $CuCrO_2$ compounds, fictitious molecules), using the FP-LAPW method.

**Key Words:** delafossites, density functional theory, electric field gradient.

## 1. Introduction

Ternary compounds $ABO_2$ (where A = Cu, Ag and B is trivalent metal ion) with delafossite structure (space group *R-3m*) attracted much attention recently owing to discovery that might be utilized as transparent semiconductors [1]. Knowledge of how the electronic spectrum of these materials changes under the doping is therefore of great importance, being a subject of many experiments so far [2]. In one of them [3], a group of $CuBO_2$ (B = Al, Cr, Fe, Nd) delafossites was studied by perturbed angular correlation (PAC) technique. Electric field gradient (EFG) was measured at Cd probes which substituted either Cu or B site, and results revealed interesting differences in EFG trends depending on position of Cd. When Cd occupies the B site its EFG exhibits almost the same value (6–7) in all compounds, while the EFGs of Cd residing at the Cu site oscillate, being 27–28 when B = Al, Fe and 21 when B = Cr, Nd, in units $10^{21}$ V/m$^2$ (see Table II in ref. [3]).

In this paper our aim is to interpret this EFG trend and to connect it with the semi-conducting properties of compounds if possible. The task was too complicated to be done directly, by performing the calculations for all compounds, since all of them except the $CuAlO_2$ are anti-ferromagnets with complicated alignments of magnetic moments (a fact which is difficult to treat accurately in the theory). Instead, we achieved the goal indirectly, in three consecutive steps:

1) by analyzing results of our previous theoretical study of doped $CuAlO_2$ compound [4] which exhibits an elevated EFG when Cd substitutes the Cu site, and performing some additional EFG decompositions;
2) by calculating EFGs in group of molecules constructed in a way which simulate the Cd neighborhood in delafossites;
3) by calculating electronic structure and the EFG in Cd-doped $CuCrO_2$ compound, which exhibits the smaller EFG at Cd occupying the Cu site.

All calculations were performed using the full potential linear augmented plane wave (FP-LAPW) method [5], as embodied in WIEN2k computer code [6].

## 2. Calculations and interpretation of the results

In ref. [4] we presented band-structure calculations for $CuAlO_2$ compound with an isolated Cd impurity substituting either Cu (Cd → Cu) or Al (Cd → Al) atom. In both cases Cd changes interatomic distances in its neighborhood. In Cd → Cu case the calculations performed with non-optimized interatomic distances (like in the pure compound) showed that Cd states are formed within the conduction band. By letting the atoms in the vicinity of Cd to relax (i.e., to reach optimized distances), the shallow band within the gap appears, near the conduction band bottom, converting the system into the *n*-type semiconductor. When Cd substitutes the Al atom, no states within the gap are observed, even with the optimized interatomic distances (figure 3 in ref. [4]).

In present paper we further analyzed the Cd EFG for both non-optimized and optimized geometries in Cd → Cu case, separating contribution from shallow band, and did the same for optimized geometry in Cd → Al case. We also calculated decomposition of these EFGs, tracing the information from which Cd shell, s- (s–d term), p- (p–p term) or d- (d–d term) the main contribution to the EFG arises. The results are summarized in the Table I.

Analysis of data in the Table I provides a clue to interpret experimental trend of Cd EFG in delafossites. When Cd occupies the Cu site in $CuAlO_2$, its EFG is approx. $-26$ (in $10^{21}$ $V/m^2$). From this number, approximately $-5$ originate from donor band within the band gap. If this band was formed as part of the conduction band, the resulting EFG would be approx. $-21$, like in $CuCrO_2$ and $CuNdO_2$. Thus, introduction of Cd impurity into the Cu site produces different effects in $CuAlO_2$ and $CuFeO_2$ on one hand, and in $CuCrO_2$ and $CuNdO_2$ on the other. It makes sense to assume that the first two compounds change their electric properties due to presence of Cd states within their fundamental gaps, and the last two compounds do not, since Cd forms its states within their conduction

*Table I.* Calculated principal values $V_{zz}$ of the EFG tensor at the Cd nuclei in $CuAlO_2$ compound

| | Non-optimized structure | | Optimized structure | |
|---|---|---|---|---|
| | $V_{zz}$ (at Cd ) | $V_{zz}$ decomposition | $V_{zz}$ (at Cd) | $V_{zz}$ decompositoion |
| Crystal $CuAlO_2$<br>(Cd → Cu case) | −33.90 | s–d: 0.78<br>p–p: −34.29<br>d–d: −0.39 | −25.73 | s–d: 0.26<br>p–p: −20.12<br>d–d: −5.87 |
| Shallow band → | | | −4.92 | s–d: −0.42<br>p–p: 0.64<br>d–d: −5.14 |
| The rest → | | | −20.81 | s–d: 0.68<br>p–p: −20.76<br>d–d: −0.73 |
| Crystal $CuAlO_2$<br>(Cd → Al case) | | | 5.63 | s–d: −0.12<br>p–p: 6.12<br>d–d: −0.39 |

$V_{zz}$ units: $10^{21}$ V/m$^2$.

bands. We postulated that the observed EFG trend just reflects this fact. When Cd substitutes the B atom, its EFG is stable. In this case formation of the shallow band within the gap is not expected, a fact which is confirmed by our calculations.

In order to support above interpretation we performed some additional calculations. Our aim was to investigate formation of Cd EFG in delafossites by studying the electrostatic influence of its closest neighborhood. Thus we constructed molecules which simulate the closest surroundings of Cd occupying either Cu or B site in delafossites, and performed series of molecular calculations. The molecules were designed using both types of $CuAlO_2$ supercells (Cd → Cu and Cd → Al) in which we removed all the atoms except the central Cd and its nearest neighbors (NN). Constructed this way, the molecular supercells preserved delafossite's symmetry, still containing enough empty space to substantially reduce interaction with molecules in neighboring supercells. Other calculational details were the same as in ref. [4]. The calculated EFGs at Cd we confronted with the Cd EFGs calculated in $CuAlO_2$ (Table I), and withdrawn conclusions.

To analyze situation in which Cd substitutes the B atom in $CuBO_2$ (Cd → B case) we constructed a molecule containing just Cd and six NN oxygens around B site, with the same Cd–O distances as in relaxed Cd-containing $CuAlO_2$. In order to simulate Cd → Cu case we considered two molecules. First one consisted of Cd and two NN oxygens around Cu site, and second one included six second NN coppers also. In both molecules interatomic distances were set to be the same as in Cd-doped $CuAlO_2$ with both optimized and non-optimized interatomic distances. Calculated EFGs at the Cd nuclei are presented in Table II.

In Cd → B case the molecular calculations succeeded to reproduce almost completely the EFG value calculated at Cd occupying Al site in $CuAlO_2$

*Table II.* Calculated EFGs at Cd nuclei in molecules simulating the Cd environment in Cd-doped delafossites. First line corresponds to Cd → B case, second and third to Cd → Cu case

| Molecules | Non-optimized structure | | Optimized structure | |
|---|---|---|---|---|
| | $V_{zz}$ (at Cd) | $V_{zz}$ decomposition | $V_{zz}$ (at Cd) | $V_{zz}$ decomposition |
| Cd + $6O^{(1)}$ | | | 5.65 | s–d: $-0.17$<br>p–p: 6.74<br>d–d: $-0.94$ |
| Cd + $2O^{(1)}$ | $-41.02$ | s–d: 1.09<br>p–p: $-53.38$<br>d–d: 11.28 | $-28.74$ | s–d: 0.87<br>p–p: $-34.46$<br>d–d: 4.85 |
| Cd + $2O^{(1)}$ + $6Cu^{(2)}$ | $-33.35$ | s–d: 0.41<br>p–p: $-42.66$<br>d–d: 8.90 | $-18.97$ | s–d: 0.42<br>p–p: $-21.25$<br>d–d: 1.86 |

Interatomic distances are the same as in non-optimized and optimized geometries in the Cd-containing $CuAlO_2$. $V_{zz}$ units: $10^{21}$ V/m$^2$.

(Table I). Both EFG values have practically the same decomposition. It implies that Cd situated at the B site in any delafossite mainly senses electrostatic influence of just six NN oxygens around it, and negligible impact of more distant neighbors. This fact explains why Cd residing at the B position exhibits very similar EFG in all delafossites.

In Cd → Cu case molecular calculations reproduced the EFG of Cd residing at the Cu site in $CuAlO_2$ taking into accounts just Cd first and second neighbors, for non-optimized geometry. For optimized geometry, molecular EFG corresponds closely to the Cd EFG value in $CuAlO_2$ when the latter does not contain the contribution from the shallow band. This result is not surprising since creation of the shallow band is consequence of collective effects occurring in the crystal. We could not therefore expect that molecular calculations account for these effects exactly. A fact that just first and second Cd neighbors were considered in the molecule (and this Cd neighborhood is the same in any delafossite) leads to following interpretation of the experimental EFG trend. When Cd occupies the Cu site in Cu-based delafossites, it exhibits "regular" EFG of approx. $-21$ ($10^{21}$ V/m$^2$), as measured in $CuCrO_2$ and $CuNdO_2$ compounds. This EFG corresponds to situation when impurity states are positioned within the conduction band. The difference between "regular" EFG values and those measured in $CuAlO_2$ and $CuFeO_2$ arises from contribution of donor bands, formed within the fundamental gaps of these compounds.

Finally, in order to confirm our conclusions, we performed calculations for $CuCrO_2$ compound, with Cd substituting the Cu atom. In this case we should not expect formation of Cd states within the gap since measured EFG exhibits a "regular" value (approx. $-21$). In calculations we assumed ferromagnetic order of Cr moments although in the nature they are aligned antiferromagnetically. This approximation, however, was sufficient to open a gap in the pure compound and to provide a good starting point for a treatment of the defect problem. Other computational details were the same as in ref. [4]. After the self-consistency has been reached, we analyzed the resulting band structure details and verified the fact that no states were present within the band gap [7]. The calculated EFG at Cd (approx. −23) is found in good agreement with the experimental value (approx. −21). This result additionally enforced the evidences in favor of our explanation of the EFG trend in Cu-based delafossites.

## Acknowledgements

M. V. Lalic kindly acknowledges financial support provided by FAP-SE, CAPES and CNPq (Brazilian Foundation Agencies).

## References

1. Kawazoe H., Yasukawa M., Hyodo H., Kurita M., Yanagi H. and Hosono, H., *Nature* **389** (1997), 939.
2. Yanagi H., Hase T., Ibuki S., Ueda K. and Hosono H., *Appl. Phys. Lett.* **78** (2001), 1583.
3. Attili R. N., Saxena R. N., Carbonari A. W., Mestnik-Filho J., Uhrmacher M. and Lieb K. P. *Phys. Rev. B* **58** (1998), 2563.
4. Lalic M. V., Mestnik-Filho J., Carbonari A. W., Saxena R. N. and Moralles M. J., *Phys.: Condens. Matter* **14** (2002), 5517.
5. Andersen O. K., *Phys. Rev. B* **12** (1975), 3060.
6. Blaha P., Schwarz K., Madsen G. K. H., Kvasnicka D. and Luitz J. *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties*, Techn. Universität Wien, Austria, Karlheinz Schwarz, 2001.
7. Lalic M. V. and Mestnik-Filho J. to be published.