

HYPERFINE INTERACTIONS AT ^{111}Cd IN DELAFOSSITE OXIDES ABO_2

(A = Ag, Cu; B = Al, Cr, Fe, In, Nd, Y)

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The time differential perturbed angular correlations of $^{111}\text{In}(\text{EC})^{111}\text{Cd}$ probes substituted into seven Ag and Cu-based delafossites ABO_2 have been observed and a systematic of the experimental shielding factors was obtained. The temperature dependence of the hyperfine interaction was measured between 4.2 and 1073 K. Combined interaction was seen in Fe and Cr based delafossites below their respective Néel temperatures.

1. INTRODUCTION

Perturbed Angular Correlation (PAC) experiments using $^{111}\text{In}(\text{EC})^{111}\text{Cd}$ probe nuclei have been extensively used to study microscopic properties in metal oxides. A compilation of many PAC measurements in oxides [1] showed that in ionic crystals the point charge model (PCM) can predict the experimental electric field gradients (EFGs), if the distance between probe and next neighbour oxygen atoms $d(\text{cation}-\text{O})$ is larger than 2.1 Å. In the PCM the EFG is proportional to a typical distance R^{-3} , which may be represented either by $d(\text{cation}-\text{O})$, the size of the cation or the lattice parameter. Such behaviour was in fact observed by A. Bartos et al. for M_2O_3 (bixbyite) [2] and $\text{M}_2\text{Cu}_2\text{O}_5$ [3] compounds. In both classes of substances a scaling of the EFG with the size of the M-cation was observed. The present study was performed to elucidate further this scaling behaviour. Delafossites and bixbyites have an oxygen octahedron with the same symmetry D_{3d} , however delafossites seem to present covalent bondings [4] and a different behaviour compared to the purely ionic compounds may occur. In addition the compounds CuFeO_2 , CuCrO_2 and AgCrO_2 have an interesting antiferromagnetic structure which has never before analysed in a PAC experiment. The magnetic ions are found in well separated planes which build a two-dimensional triangular lattice [5]. Below their respective Néel temperatures ($T_N=11\text{-}25\text{ K}$ [5-7]) the spins are highly frustrated.

2. EXPERIMENTAL

In general, the samples were obtained by mixing the constituent phases in the correct stoichiometric ratio and heating in a controlled atmosphere. X-ray diffraction analyses were performed for all samples before and after PAC measurements. Pellets of each substance were pressed to discs, which were implanted with a dose of 10^{12} $^{111}\text{In}^+$ ions at an energy of 400keV using the Göttingen implanter IONAS. After the

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implantation, annealing procedures were carried out to eliminate the radiation damage and PAC experiments were performed in the range $T_m=4.2$ -1073 K. Some spectra taken at room temperature are shown in the Fig. 1.

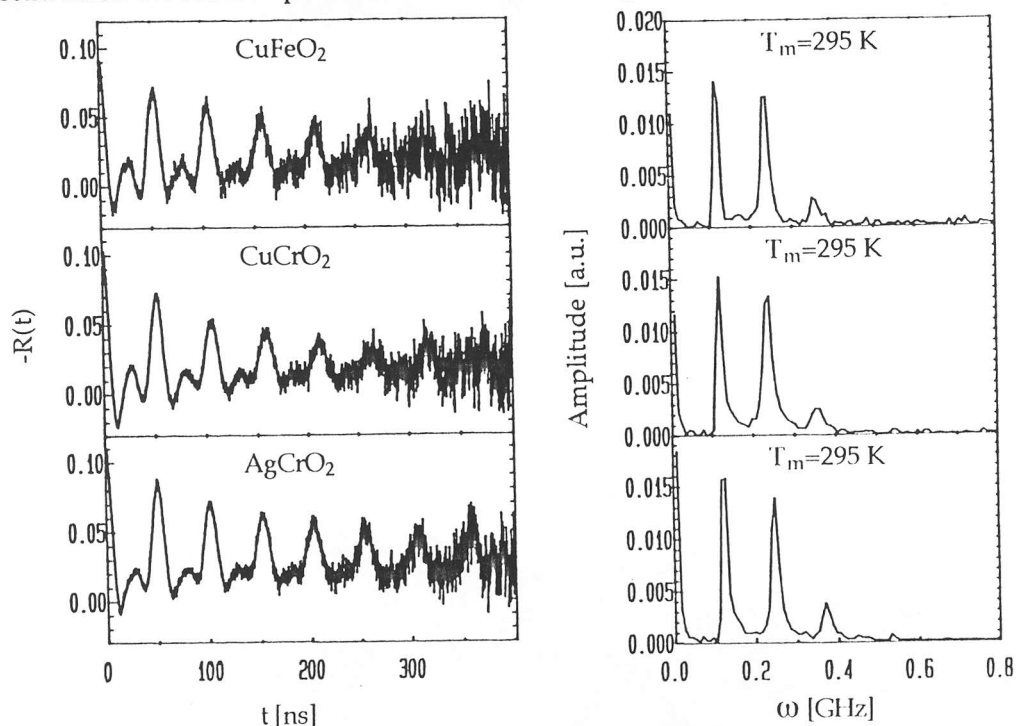


Fig. 1: Perturbation functions $R(t)$ and Fourier transforms of ^{111}In in delafossites taken at room temperature after annealing procedures

Although only one equivalent B^{+3} cation site exists in the delafossite structure, for most of the compounds more than one EFG are found. Using the knowledge on EFGs in oxides, as well as the X-ray analyses, the additional quadrupole frequencies could be identified in most cases as originating from contaminating foreign phases inserted during the production. Some have been attributed to defects. Details can be found in [8]. In Table I the EFG parameters for the delafossite phase in all studied materials are given. Only a mild variation of the hyperfine parameters with the

Compound	ν_{Q1} [MHz]	δ_1 [MHz]	η_1	$d_{\text{B}+3-\text{O}-2}$ [Å]
CuAlO_2	150.6(1.9)	2.2	0	1.912
CuCrO_2	126.0(1.4)	4.7(1.5)	0	1.990
CuFeO_2	124.6(1.1)	0.6	0	2.033
CuNdO_2	140(4)	3.6	0	2.374*
CuYO_2	134(2)	3.8(1.6)	0	2.276
AgCrO_2	131(1)	0.6	0	1.990
AgInO_2	91(6)	4	0	2.174

* calculated
according [9]

Tab. I: Hyperfine parameters taken at room temperature for the fractions attributed to the delafossite phases and the bond length $d(\text{B}-\text{O})$

measuring temperature (T_m) was observed. In many cases, texture has been seen in the $R(t)$ and Fourier spectra.

Within the antiferromagnetic phase, measurements were performed at 4.2 and 12 K for CuFeO_2 ($T_{N1}=16$ K; $T_{N2}=11$ K) [5], and at 15 K for CuCrO_2 ($T_N=25$ K) [6] and AgCrO_2 ($T_N=24$ K) [7]. The spectra can be seen in the Figure 2.

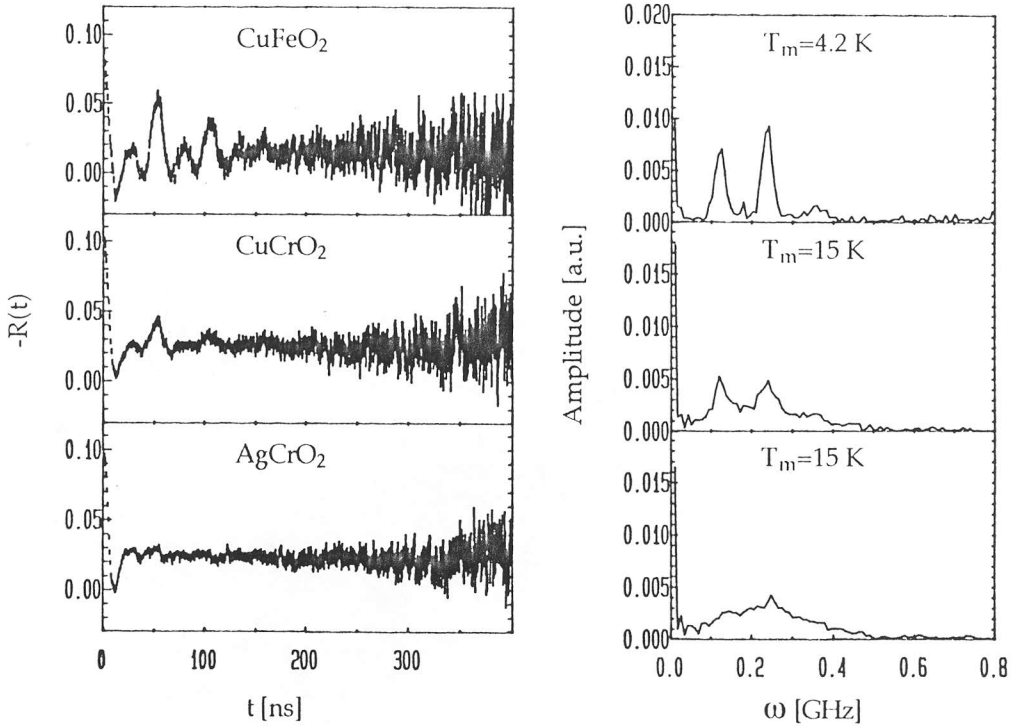


Fig. 2: Perturbation functions $R(t)$ and Fourier transforms of ^{111}In in delafossites taken below the Néel temperatures

3. DISCUSSION

Due to the valency +3 of the B-ion in delafossites, one expects the ^{111}In ions to substitute such a site. More arguments concerning the probe site, as well as the detailed discussion of the experiments are found in [8].

To compare the EFGs found in delafossite oxides to the ones in the oxide classes collected in [1] we calculated, from our measurements, the experimental shielding factor $\beta(\text{exp}) = \nu_Q(\text{exp}) / \nu_Q(\text{PCM})$. The reference for the coordinates used in the PCM calculation are given in [8]. In Figure 3 this shielding factor $\beta(\text{exp})$ is plotted versus the distance in the octahedron around the B-ion ($d(\text{B-O})$). The general trend is in good agreement with the results in [1]. For the $d(\text{B-O}) \geq 2.1$ Å we find $\beta(\text{exp}) \approx 22$, close to the expected value $\beta_\infty = 30.27$ [10]. For closer distances $\beta(\text{exp})$ increases to about $2.5\beta_\infty$, similarly to the data collected from other oxide classes in [1]. There, it was proposed that EFG contributions from covalent bonding are the responsible. The present case of the delafossite oxides is now a first direct proof of that assumption, as here the influence of covalent bonding is well known [4].

The PAC measurements in the antiferromagnetic phase show a damping of the $R(t)$ spectrum taken at 4.2 K below the Néel temperature of CuFeO_2 (Fig. 2) compared

to the one taken at room temperature (Fig. 1). This effect is the result of combined interaction of the EFG with a weak magnetic field (~ 0.3 T) [11]. In contrast, with Mössbauer spectroscopy a strong magnetic field of 51.7 T [5] was observed at 4.3 K. To explain this different hyperfine interaction, it is proposed [11] that the PAC impurity probe $^{111}\text{In}(\text{EC})^{111}\text{Cd}$ on a Fe-site in the triangular lattice releases the spin frustration. Then the neighbouring Fe-ions can realize the antiferromagnetic ordering and no magnetic exchange field is found at the PAC probe site. The small remaining field may have intraplane or interplane origin. Similar behaviour was found for CuCrO_2 and AgCrO_2 (Fig. 2). In these cases the magnetic fields are also weak but clearly stronger than in CuFeO_2 . Both compounds with Cr present a different antiferromagnetic spin configuration. Details are discussed in [11].

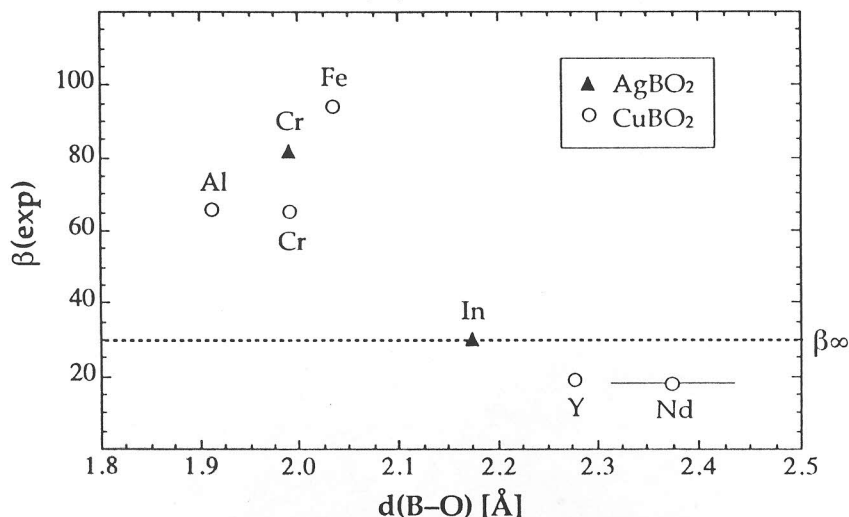


Fig. 3: The experimental shielding factor $\beta(\text{exp}) = \nu_Q(\text{exp}) / \nu_Q(\text{PCM})$ plotted versus the bond length

4. REFERENCES

- [1] D. Wiarda, M. Uhrmacher, A. Bartos and K.P. Lieb, J. Phys.: Cond. Matter 5 (1993) 4111
- [2] A. Bartos, K.P. Lieb, A.F. Pasquevich, M. Uhrmacher and ISOLDE Collaboration, Phys. Lett. A 157 (1991) 513
- [3] A. Bartos, M. Uhrmacher, L. Ziegeler and K.P. Lieb, J. All. Comp. 307 (1992) 179
- [4] J.P. Doumerc, A. Ammar, A. Wichainchai, M. Pouchard et P. Hagenmuller, J. Phys. Chem. Solids 48 (1987) 37
- [5] M. Mekata, N. Yaguchi, T. Takagi, T. Sugino, S. Mitsuda, H. Yoshizawa, N. Hosoi and T. Shinjo, J. Phys. Soc. Japan 62 (1993) 4474
- [6] H. Kadowaki, H. Kikuchi, and A. Ajiro, J. Phys.: Cond. Matter 2 (1990) 4485
- [7] Y. Oohara, S. Mitsuda, H. Yoshizawa, N. Yaguchi, H. Kuriyama, T. Asano and M. Mekata, J. Phys. Soc. Japan 63 (1994) 847
- [8] R.N. Attili, M. Uhrmacher, K.P. Lieb, M. Mekata, E. Schwarzman and L. Ziegeler, in preparation
- [9] T. Ishiguro, N. Ishizawa, N. Mizutani and M. Kato, J. Ceram. Soc. Japan 92 (1984) 25
- [10] F.D. Feiock and W.R. Johnson, Phys. Rev. 187 (1969) 39
- [11] M. Uhrmacher, R.N. Attili, K. Winzer, K.P. Lieb, in preparation