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Supertransferred Hyperfine Magnetic Fields at ^{111}Cd Impurity sites in $Cd_xFe_{3-x}O_4$ and $Zn_xFe_{3-x}O_4$

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Abstract. The hyperfine magnetic field at ^{111}Cd impurities substituting iron in the mixed spinels $Cd_xFe_{3-x}O_4$ and $Zn_xFe_{3-x}O_4$ has been determined by means of the Perturbed Angular Correlation technique. Compounds with different concentrations x were investigated as a function of temperature. The possibility of determining the lattice location of probes at octahedral or tetrahedral sites through the magnitude of the electric field gradient is analyzed. The measured hyperfine magnetic field at impurities in tetrahedral sites is discussed in terms of the populations of magnetic ions in the nearest neighbor sites.

Key words: magnetic fields, ferrites, spinels.

1. Introduction

The magnetic hyperfine fields in mixed ferrites of the type $M_xFe_{3-x}O_4$ where M is Zn or Cd have been the subject of several investigations in the past, specially using Mössbauer spectroscopy [1–5]. Analysis of the Mössbauer data in terms of the local configurations of M ions at tetrahedral sites has permitted to monitor the influence of the conduction electrons on the electrostatic and magnetic interactions. Significant change in the electronic properties of the systems have been observed around $x = 0.5$. The samples with low values of x retain the characteristics of magnetite (Fe_3O_4) while those with high values of x behave as semiconductors as the sixth 3d electron of ferrous iron becomes localized. Fast electron exchange occurs among the Fe^{+2} and Fe^{+3} ions in octahedral sites. The replacement of Fe^{+2} ions by diamagnetic ions in the octahedral sites interferes with this electron hopping but the phenomenon persists to some concentration near the middle of the composition range [5]. In the present work the replacement of ferric ions takes place in tetrahedral sites due to the preference of the closed d shell ions Zn^{+2} and Cd^{+2} for tetrahedral sites. The aim is to establish the influence of this replacement on the supertransferred hyperfine field at the diamagnetic ions in the tetrahedral sites. The hyperfine fields at ^{111}Cd impurity sites were measured by means of the Perturbed Angular Correlation (PAC) technique.

PAC studies of supertransferred hyperfine magnetic fields at ^{111}Cd in ferrimagnetic oxides with the spinel structure have been carried out in the past [6–10]. According to these and others studies [11, 12], the magnetic hyperfine field at the probe site arises from spin density transferred mainly into the 4s and to a lesser extent into the 5s orbitals of the probe.

In the case of the spinels $M_xFe_{3-x}O_4$ (M = Cd, Zn), the compounds at both ends of the concentration range ($x = 0$ and 1) were studied by PAC before [7–10, 13]. This paper presents results for the concentrations $x = 0$, 0.2, 0.4, 0.5, 0.6 and 0.8. The main focus of this work is the concentration dependence of the supertransferred magnetic field at the probe nucleus at low temperatures.

2. Crystal and magnetic structure

We begin with a description of magnetite ($x = 0$ case). The ionic order corresponds to the inverse spinel structure in which Fe^{+3} occupies the tetrahedral A sites while the octahedral B sites are occupied by both Fe^{+2} and Fe^{+3} ions. The Fe ions on A sites are assumed to be antiferromagnetically coupled to those in sites B, leading to a ferrimagnetic spin arrangement with the net magnetization along the [111] direction [14].

The magnetic moments of iron at octahedral and tetrahedral sites give place to a dipolar contribution to the magnetic field at the lattice sites. The dipolar field is found to vanish at tetrahedral sites. For the octahedral sites one expects two magnetically non-equivalent ions, with a population ratio of 3 : 1 [15]. Additionally, at the octahedral sites there exists an electric field gradient (EFG), at the tetrahedral sites the EFG vanishes.

In the case of the compounds $M_xFe_{3-x}O_4$ (M = Cd, Zn) the tetrahedral ferric ions are progressively replaced by the diamagnetic ions. The atomic order changes with x from an inverse spinel at $x = 0$ (all the bivalent ions at octahedral sites) to a normal spinel (all the bivalent ions at tetrahedral sites) at $x = 1$. The M ions preferentially occupy the tetrahedral A-sites because of their tendency to form covalent bonds involving sp^3 orbitals. This distribution on the tetrahedral sites is normally assumed to be at random [3–5]. At small values of x the average magnetic moment of the B-sublattice is expected to increase with increasing substitution x because of the change in the ratio Fe^{+3}/Fe^{+2} on the octahedral sites. The average magnetic moment of the A-sublattice decreases, increasing the net magnetic moment per molecule. At larger x-values, the magnetic moments at the B sites begin to make random canting angles with the magnetization direction [4].

3. Experimental

The samples were prepared by solid state reaction of stoichiometric amounts of the oxides Fe_3O_4, Fe_2O_3 and CdO or ZnO. The mixed powders of the oxides were pressed and the resulting pellets were encapsulated in quartz tubes at reduced Ar pressure ($2 \cdot 10^{-2}$ Torr). The samples were then annealed at 1000°C during 10 hs. All the samples were found to be single-phase spinel by X-ray powder diffraction analysis. In each case, a solution of carrier-free ^{111}In was dropped onto a piece of the sample. After drying the material was again closed in Ar atmosphere and annealed at 800°C during 15 hs.

The PAC measurements were carried out on the 174–247 keV γ–γ cascade of ^{111}Cd. The PAC spectra were taken with a set-up of four BaF_2 detectors arranged in 90° geometry. $R(t)$ perturbation functions were determined from the twelve simultaneously measured PAC spectra. The spectra were recorded as a function of temperature. The ranges were 10–875 K and 77–875 K in the case of Cd and Zn compounds, respectively.

4. Results and discussion

Before describing our results we make some comments on the expected probe location. In the samples $M_xFe_{3-x}O_4$ the expected ion distribution is $(M_x^{+2}\ Fe_{1-x}^{+3})[Fe_{1-x}^{+2}\ Fe_{1+x}^{+3}]$, here the round and square brackets enclose ions located on tetrahedral and octahedral sites respectively [16, 17]. Doping with ^{111}In, the probe substitute for Fe as can be follow from the PAC results in the spinels with $x = 1$ [13]. The substitution takes place preferentially at tetrahedral sites (if there exist iron ions in such sites) as can be expected from the well known preference for such sites of d^{10}-impurities in spinels [18]. It has been corroborated by PAC measurements in magnetite at $T > T_N$ [10] where 80% of the probes were in a cubic environment. So, at least for the $x = 0$ case, the probe location in tetrahedral sites can be identified through the measured of a vanishing EFG. On the other hand, the observation of a fraction with non vanishing EFG can not be directly ascribed to probes at octahedral sites. Such a fraction could include probes at tetrahedral sites with point defects nearby, so the possible influence of defects must be considered. It is worth of mention that the introduction of M-ions does not involve creation of point defects due to charge compensation. The charge balance is obtained by conversion from Fe^{+2} to Fe^{+3} in the octahedral sites. Anyway some concentration of point defects is expected associated with oxygen–metal nonstoichiometry produced during the sample annealing.

The scenario becomes more complex when x takes a value in the middle of the range (0.4–0.6). The random distribution of the diamagnetic ions M in the tetrahedral sites give place to a distribution of the EFG at the lattice sites. The effect of this disorder must be more important at B-sites, since each A site has as first neighbors only octahedral sites. We expect large value of the distributions and strong damping in the spectra.

We begin with the description of the results discussing an intermediate concentration. In Figure 1 typical PAC spectra obtained with $Cd_xFe_{3-x}O_4$ ($x = 0.4$) at different temperatures are shown. The PAC spectra obtained with $Zn_xFe_{3-x}O_4$ for

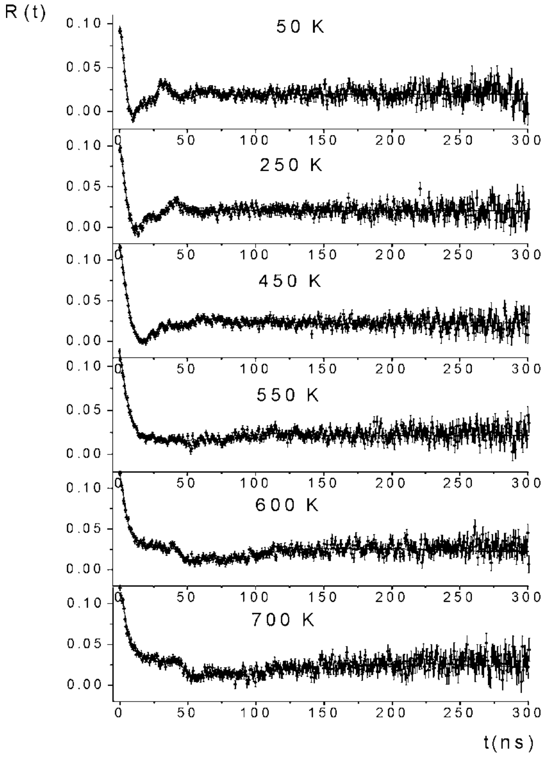

Figure 1. PAC spectra obtained at the indicated temperatures for $Cd_{0.4}Fe_{2.6}O_4$.

the same concentration are qualitatively similar. The spectra at low temperature can be fitted assuming a broadly distributed pure magnetic interaction. At 50 K the parameters are $\omega_L = 189(2)$ Mrad/s and $\delta = 46\%$. In spite of the distribution it is possible to see the decrease of the average Larmor frequency with the temperature. Between 550 K and 600 K the magnetic interaction vanished and at higher temperatures the probes appear subjected to pure quadrupole interactions. The spectrum at 700 K corresponds to 50% of the probes subjected to a large EFG ($\omega_Q = 24.7(7)$ Mrad/s, $\eta = 0.32(6)$ and $\delta = 34\%$) and the rest to a small EFG ($\omega_Q = 4.2(2)$ Mrad/s, $\eta = 0.43(1)$ and $\delta = 50\%$). Measurements carried out on the same sample at 650 and 800 K yield the same results. This fact gives an argument to exclude the influence of trapped defects. In PAC experiments (with ^{111}In/^{111}Cd as probe) performed in metal oxides where the presence of nearby trapped defects was observed, the spectra changed drastically in this temperature range. Rapid vacancy hopping was found in CeO_2 above 573 K [19] and defects which were static at room temperature are fast diffusing at 873 K in the case of tetragonal zirconia [20].

The question arises if these fractions can be associated with probes at tetrahedral and octahedral sites. The low value of the small EFG makes it a good candidate to be associated with the tetrahedral sites. The other component has parameters

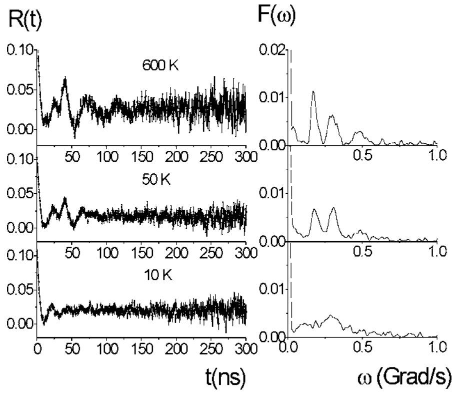

Figure 2. PAC data at the indicated temperatures and corresponding Fourier transforms obtained for $Cd_{0.8}Fe_{2.2}O_4$.

ω_Q and η quite similar to the ones observed in $CdFe_2O_4$ where the probes are only located at octahedral sites [13]. Therefore we associate the component under discussion mainly with probes at the octahedral sites. Certainly, the amplitude of this component increased with x. It can be seen in Figure 2 where a measurement obtained for $Cd_{0.8}Fe_{2.2}O_4$ at $T = 600$ K is shown. In this case, 80% of the probes are located at the octahedral site.

Coming back to the $x = 0.4$ case, the hyperfine field at each site cannot be resolved even at very low temperatures. The same occurs for $x = 0.5$. In the cases $x = 0$ and $x = 0.2$, the low temperatures spectra show better defined magnetic interactions. The populations of the tetrahedral sites are larger (65–90%), because there exists more Fe^{+3} for substitution. For example, in the case $x = 0$ and room temperature, we measured a well-defined Larmor frequency $\omega_1 = 173(1)$ Mrad/s, and $\delta_1 = 1.5\%$ for the majority site (population 65%). The other one corresponds to a more distributed magnetic interaction ($\delta_2 = 30\%$) $\omega_2 = 144(5)$ Mrad/s. The Larmor frequency ω_1 for the majority site corresponds to a magnetic field $B_A = 11.8$ T which is in good agreement with the values reported by Asai *et al.* [9] and the Göttingen group [7] for ^{111}Cd at the tetrahedral position. We must mention that after some years the Göttingen group discuss again their first interpretation and enumerates others possibilities for the site assignment [8]. The measure of a vanished EFG for the majority component at temperatures above T_N, corroborated in our experiment, is for us enough support for the tetrahedral site assignation. The second component could be attributed to probes at the octahedral sites. A field distribution can be expected for these sites due to the existence of different dipolar magnetic contributions in a fraction of them and also because of the existence of an electric field gradient which appears making angles of 0° and 70° with the magnetization direction. But the measured distribution seems to be too large for the mentioned effects. Probably this fraction includes probes interacting with lattice defects. Such interactions have been observed in samples prepared by implantation or diffusion of the probes [10, 13].

Before discussing the low temperature results, we would like to address the analysis of the spectra with combined interactions. We used a program developed for one of us (M. F.) to fit several combined interactions, including for each the angle β (between the magnetic field and the principal z-axis of the EFG tensor) and the angle γ (between the x-axis and the projection of the magnetic field in the plane xy). Result of such kind of fits are described below, but most of the data at low temperature can be fitted assuming only magnetic interactions. This is well justified in the cases $x = 0$ and $x = 0.2$ at all temperatures below T_N, because the majority of the probes populate the tetrahedral sites where the EFG is null or very small and the magnetic interaction is larger enough. A second component, which may involve probes at octahedral sites and probes associated with defects, is introduced to improve the fits without influencing the parameters associated with the well defined component. The $x = 0.4$ is one case where at temperatures below 300 K is achieved a good description of the data with only one distribution of pure magnetic interactions. This characteristic is achieved for $x = 0.5$ below 200 K. In these cases the broad distribution of the interactions makes no realistic to separate contributions from each kind of site.

The results with $x > 0.5$ require a different treatment. In Figure 2 PAC spectra obtained for $x = 0.8$ at different temperatures are shown. This composition shows a rather well defined pure quadrupole interaction above 50 K, with parameters which agree with those corresponding to the $x = 1$ composition [13]. At 600 K, 81(4)% of the probes are subject to a pure quadrupole interaction characterized by $\omega_Q = 24.3(2)$ Mrad/s, $\eta = 0.36(1)$ and $\delta = 19(1)\%$. The remanent fraction corresponds to $\omega_Q = 4.7(3)$ Mrad/s, $\eta = 0$ and $\delta = 100\%$. The change at 10 K is related to the increased magnitude of the magnetic interactions. The difference with the cases of smaller x is that the quadrupole interactions can not be neglected at this temperature. The attenuation corresponds to interactions with combined fields broadened by the cation distribution. The spectrum at 10 K is very well fitted fixing the amplitudes of the fractions, the values of ω_Q and η characterizing the EFG at both sites, in the values obtained at 600 K and allowing the existence of magnetic interactions. The same value of the magnetic field is obtained at both sites: $B = 3.0(2)$ T (corresponding to $\omega_L = 44(3)$ Mrad/s). For the most populated site the angle β was fitted as 48° (3) while γ was kept fix as zero. For the other site, both angles were kept fixed at zero. The distributions fitted at both sites were 28 and 67%, respectively. The values of β expected for octahedral sites in spinels with EFGs in the directions (111) and the magnetization in one of such directions, are $\beta = 0°$ for 25% of the sites and $\beta = 70.5°$ for the rest. To considerer only one angle β for such sites is an additional simplification of a situation which is more complex because the direction of the magnetic field at each probe site depends on the random distribution of the few magnetic ions in the neighborhood [4]. This fact contributes to the observed distributions. Computer simulations are underway to furnish a broader support to this explanation. It is worth of mention that "after-effects" of the preceding EC decay of ^{111}In at low temperatures in materials with

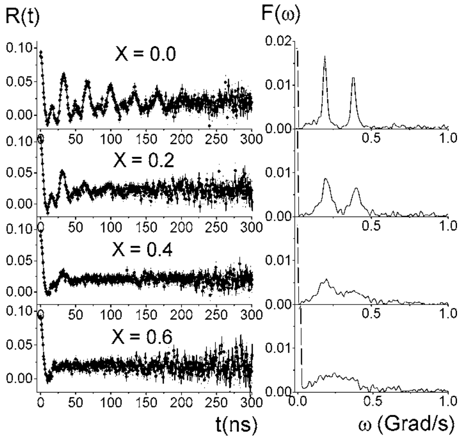

Figure 3. PAC spectra obtained at 10 K and corresponding Fourier transform for $Cd_xFe_{3-x}O_4$.

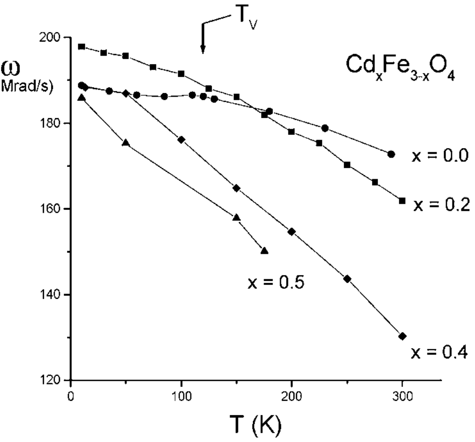

Figure 4. Temperature dependence of the Larmor frequency at majority sites. The temperature T_V for magnetite free of defects is indicated.

high resistivities could be an alternative explanation [8, 9] of the attenuation, but in the present case they can not be invoked because a similar attenuation is found at higher temperature (300 K) in the case of $x = 0.6$, where less resistivity is expected [5].

In Figure 3 PAC spectra obtained at 10 K are shown. The spectrum for $x = 0.6$ shows the strong attenuation already mentioned. The spectrum for $x = 0$ is stronger attenuated ($\delta_1 = 8\%$) than the one at room temperature (see values above). This is probably due to fluctuations of the relative populations of Fe^{+2} and Fe^{+3} on the neighboring octahedral sites of the probe below 120 K (Verwey transition). At this temperature T_V occurs a cubic–orthorhombic distortion which is accompanied with the interruption of the B-site charge hopping process. Besides the increase in the distribution, the transition produces a small shift in the magnetic interaction at A-sites. In Figure 4 the frequencies measured between 10 and 300 K are shown for x, between 0 and 0.5, in the case of $Cd_xFe_{3-x}O_4$. Our results for $x = 0$ agree very well with those of Asai *et al.* [9], showing a less dramatic change at T_V than the one reported by the Göttingen group [7, 8]. A difference in these experiments is the method of doping (diffusion versus implantation) which is probably playing a role in the oxygen stoichiometry. In our experiments, the transition is observable only for the composition $x = 0$. The same occurs in related experiments quoted in the literature [1–5]. The presence of Zn or Cd in the structure prevents the formation of a crystallographically ordered valence structure which presumably provides the free energy for the cubic to orthorhombic transition [21]. The Verwey transition is linked to the ratio of divalent to trivalent iron occupying octahedral sites [16, 17, 22]. At the concentrations x used in this work such ratio differs enough from 1 to produce the disappearance of the transition. In the case of $Zn_xFe_{3-x}O_4$ no transitions were found with $x > 0.03$ [23] In the case $x = 0$, the nature of the transition changes from first to second or higher order with an increased degree of oxygen–metal nonstoichiometry [16]. This may explain the smaller shift in the frequency at T_V in the present paper as compared with the one reported by the Göttingen group. The transition disappears in $Fe_{3(1-\delta)}O_4$ for $\delta > 0.012$ [16] and this gives a limit for the defect concentration in our samples.

Values of the fields measured at 10 K and at 77 K for the lower concentrations are given in Table I. An interesting feature is the increase of the supertransferred field from $x = 0$ to $x = 0.2$. At a first view it might seem anomalous that the substitution of magnetic ions by non-magnetic ions can result in such an increase, but the substitution of the Fe^{+3} by Zn^{+2} or Cd^{+2} in the tetrahedral sites increases the amount of Fe^{+3} in the octahedral sites. And this produces an increase in the magnetic moment of the B sublattice. Larger concentrations of the non-magnetic ions in the A sublattice lead to a strong decrease of the exchange between the magnetic ions and the moment in B sublattice begins to be affected by canting and, eventually, spin reversal. This conduces to the reduction in the transferred field at both sites in the lattice. The fact that the increase from $x = 0$ to $x = 0.2$ is very similar for Zn and Cd-based compounds is easily understood: in both cases the

Table I. Magnetic field (in Tesla) of ^{111}Cd on tetrahedral sites of $Cd_xFe_{3-x}O_4$ and $Zn_xFe_{3-x}O_4$ as a function of the concentration x at different temperatures

Compound; temperature	$x = 0.0$	$x = 0.2$	$x = 0.4$
Cd 10 K	12.8 (1)	13.5 (1)	12.8 (2)
Cd 77 K	12.7 (1)	13.1 (2)	12.3 (2)*
Zn 77 K	12.7 (1)	13.4 (1)	13.3 (1)

*Interpolated between data corresponding to 50 and 100 K.

first nearest-neighbor environment of the probe is the same. Differences appear for larger x. For example, at 77 K and $x = 0.5$, the field for Cd-compound ($B = 11.6(4)$ T) is smaller than the field corresponding to $x = 0$, but the measured field for Zn-compound ($B = 13.1(1)$ T) remains above the value corresponding to $x = 0$.

5. Conclusions

We have measured the hyperfine interactions at ^{111}Cd impurities in the mixed spinels $M_xFe_{3-x}O_4$ (M = Cd, Zn) at different temperatures. At temperatures below 150 K and concentrations $x < 0.5$, we have identified the supertransferred magnetic field at ^{111}Cd impurities in tetrahedral sites. We have observed that the field at $x = 0.2$ increases at relative to the value at $x = 0$ in similar way for both substituents M. For $x > 0.3$, the field decreases with x.

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