Perturbed Angular Correlation Measurements in 2D Spin-Frustrated $CuFeO_2$

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(Received 31 October 1995; revised manuscript received 5 March 1996)

We report on first perturbed angular correlation (PAC) measurements in the 2D triangular antiferromagnet $CuFeO_2$. The implanted ^{111}In PAC probes resides on Fe sites and sense the combined hyperfine interaction of the structural electric field gradient and an antiferromagnetic internal field which is surprisingly small as compared to other ferromagnetic or antiferromagnetic oxides. This is explained by a local change in the frustrated triangular lattice leads to a perfect cancellation of the magnetic hyperfine fields of the probe's next-neighbor hexagon. As a consequence the observed small magnetic hyperfine field gives access to second-neighbor and/or interplane interactions in the frustrated lattice. [S0031-9007(96)00457-7]

PACS numbers: 72.25.+z, 75.50.Ee, 76.80.+y

The frustration of spin-spin interactions plays an important role in the ordering of low dimensional antiferromagnets. Using a 2D triangular-lattice Anderson introduced the concept of a spin liquid ground state with high degeneracy [1]. The lower part of Fig. 1 shows immediately that a macroscopic number of states is possible with exactly the minimum number of parallel spins. In a simple description of the frustrated ground state one can state the following: In the 2D plane no unit triangle exists with three parallel spins [1]. In most real cases, an additional interaction such as a second-neighbor interaction or interlayer interaction lifts the degeneracy and gives rise to complex magnetic ordering at a finite temperature [2]. Nevertheless, a fully frustrated 3D system was found in crystals of the spinel structure with the magnetic ion on the B sites [1]. A rather close approximation to 2D triangular-lattice antiferromagnets can be found in the class of ABO_2 compounds with the delafossite structure which contains magnetic B ions [3]. Figure 1(a) shows the lattice structure of $CuFeO_2$ [3]. The trivalent B cations (Fe) are at the center of regular oxygen octahedra which are connected by monovalent A ions (Cu). The cations A^{1+} and B^{3+} form triangular lattices which are stacked alternately with an intervening oxygen layer. Consequently, magnetic B^{3+} layers are separated from each other by two O^{2-} layers and an A^{1+} layer. Moreover, B^{3+} ions are not sitting right above the B^{3+} ions in the adjacent layer, but above the center of the triangle formed by B^{3+} ions, so that the magnetic lattice is nonbipartite in each layer as well as among the layers. Thus, from geometrical considerations, spins are expected to be highly frustrated between neighboring layers as well as within a layer [3,4].

In the present study we report on the first perturbed angular correlation (PAC) experiments in such a 2D antiferromagnetic triangular lattice. Among hyperfine interactions methods like nuclear magnetic resonance (NMR), Mössbauer spectroscopy (MS), and electron-nuclear double resonance (ENDOR), the PAC of γ rays provides information on the local electric and/or magnetic environment of a nuclear probe which has to be introduced as a trace element into the matrix. Such measurements in magnetically ordered systems are easy to analyze, if no electric field gradient is present as in cubic defect-free lattices of the ferromagnets Fe, Co, and Ni, but also in most transition metal monoxides which crystallize in the NaCl structure, like NiO [5–7], CoO [8,9], FeO [10], and MnO [11]. In these oxides the strong antiferromagnetic coupling is due to supertransfer via the $2p_\sigma$ orbitals of the oxygen ions [12]: The six second-next cation neighbors have parallel spins and produce the magnetic hyperfine field (MHF) at the probe. Indeed, PAC probes in cubic antiferromagnets (AF's) show effects which are similar to those in ferromagnets: Below T_N probes on substitutional cation sites sense a MHF whose temperature dependence follows a modified Curie-Weiss law: $B(T)/B_0 = (1 - T/T_N)^\beta$ [13].

In the present experiments we used $CuFeO_2$, the prototype of delafossites, whose antiferromagnetic order has been investigated by different techniques: Powder neutron diffraction established two successive magnetic transitions at $T_{N1} = 16$ K and $T_{N2} = 11$ K [3]. The orthorhombic magnetic structure below T_{N2} is plotted in Fig. 1(b), the spins in the triangles are ordered up and down alternately along the c axis [3]. Mössbauer spectroscopy experiments down to 4.2 K proved that the Fe planes consist of Fe^{3+} ions. At intermediate temperatures (below T_{N1}) $CuFeO_2$ has a monoclinic unit cell [3]. Our experiments were performed using the

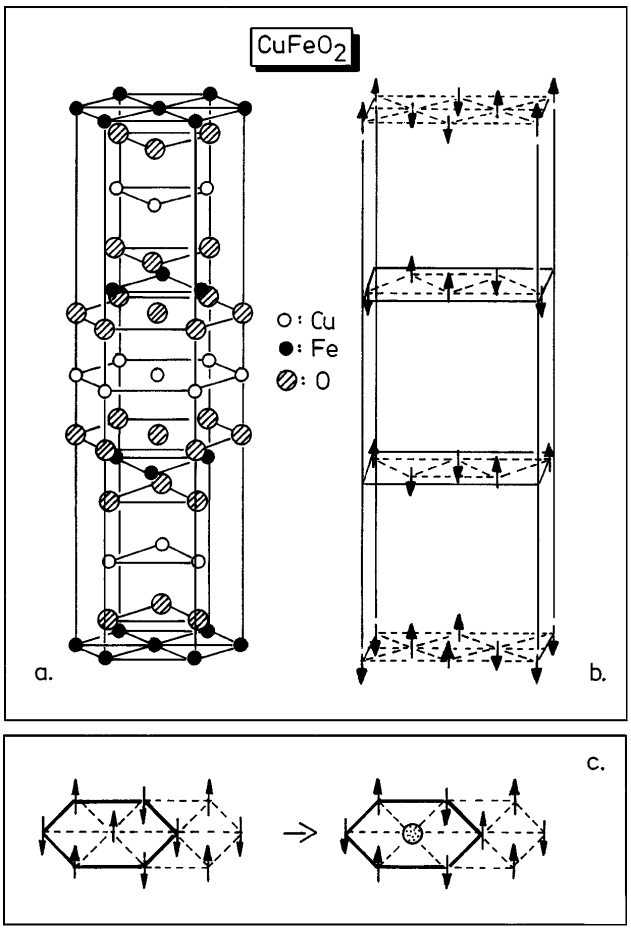

FIG. 1. (a) Crystalline structure of the delafossite $CuFe_2$ [3]. (b) Spin directions in the triangular Fe planes of $CuFeO_2$, as deduced from neutron diffraction measurements [3]. The 2D planes correspond to the structure model given in (a). (c) The smallest representation of the frustrated ground state of the triangular plane shows two possible spin arrangements for the central spins [1]. If we insert a nonmagnetic probe (dotted, in the right side of the figure) in one of these sites, the spin frustration is locally released and the next-neighbor hexagon can realize the antiferromagnetic order.

standard PAC probe atom ^{111}In which decays within a half-life of 2.8 d via electron capture (EC) to ^{111}Cd. The ^{111}In ions were implanted at 400 keV into pressed powder samples which were produced in solid state reactions according to [3,14–16]. The perturbation was observed using a setup of 4 BaF_2 or NaI(Tl) scintillation counters at 90° angles [17]. Experimentally, the perturbation is seen as a modulation of the measured time spectra between the ^{111}Cd γ quanta with typical interaction frequencies. In the case of MHF these are the Larmor frequency $\omega_L = \mu B_{\mathrm{HE}}/\hbar = 14.23 B_{\mathrm{HF}}$ $[T]$ and its first harmonic. In case of an EFG there are three frequencies which depend on the coupling constant $\nu_Q = eQV_{zz}/h$ and the asymmetry parameter η [7,18]. Fourier transforms of the PAC spectra show these frequencies as on the right hand sides of Fig. 2. Finally, a combined interaction of a MHF and an electric field gradient (EFG) acting on the same probe nucleus causes a complicated PAC pattern [19,20] if both interactions are of similar strengths. In the simpler cases where either $\omega_L \gg 2\pi\nu_Q$ or vice versa [7], the weak component of the hyperfine interaction causes a broadening of the frequencies of the strong component, as observed in the present work.

After an appropriate annealing procedure of the ^{111}In-doped $CuFeO_2$ pellet only one EFG was observed in the temperature range $T_m = 20$–873 K which has a weak dependence on the measuring temperature T_m[$\nu_Q(273\ \mathrm{K}) = 125(1)$ MHz, $\nu_Q(873\ \mathrm{K}) = 131(1)$ MHz]. This EFG had axial symmetry ($\eta = 0$) [14]. The amplitude ratio of the three frequencies in the Fourier spectrum was not typical for a polycrystalline material. As discussed in [14] the sample consisted of tiny flakes according to the planar structure of the lattice which caused a texture also after pressing and heating the sample. This texture was confirmed by separate measurements in [14]. At still higher temperatures (973, 1073 K) a small fraction of a second EFG [$\nu_Q = 157(2)$ MHz, $\eta = 0$] was observed which, most probably, indicates the trapping of an intrinsic defect at the probe [14]. Typical spectra taken above T_N are shown in Figs. 2(a) and 2(d). The low-temperature data of the present study were taken at 4.2 K in a bath of liquid He in an open cryostat, using BaF_2 detectors. Measurements between 12 K and RT were performed with the help of a closed-cycle He cryostat and NaI detectors. A clear damping of the perturbation function $R(t)$ was observed below T_{N2} [see Fig. 2(b)] leading to line broadenings in the Fourier spectra. The damping was less pro-

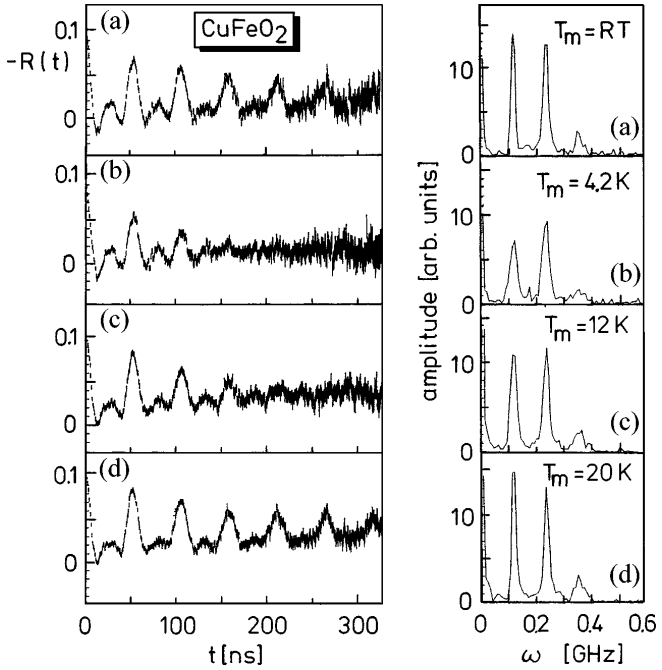

FIG. 2. Temperature dependent PAC spectra of $CuFeO_2$, taken with BaF_2 (a), (b) or with NaI detectors (c), (d). For (b) the sample was suspended in liquid He.

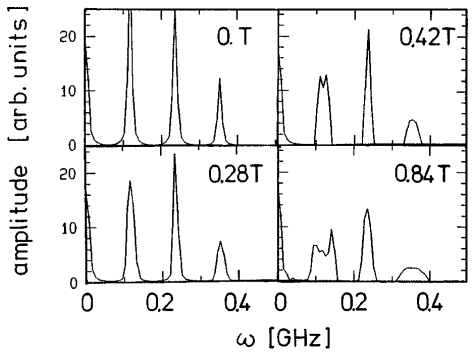

FIG. 3. Simulations of the combined interaction of the structural EFG in $CuFeO_2$ with a small, randomly oriented MHF. The field strengths are given in the figures.

nounced between T_{N2} and T_{N1} [Fig. 2(c)] and the spectrum at 20 K [Fig. 2(d)] had already the same parameters as the RT spectrum. The following conclusions can be drawn immediately: (1) The PAC spectra of $CuFeO_2$ change their shapes at the highest Néel temperature T_{N1}. Thus we observed hyperfine fields due to antiferromagnetic ordering. (2) The broadening of the EFG patterns in the Fourier spectra is a result of the combined interaction of the *dominating* structural EFG and a *weak* magnetic field. Using the approximation of [7] we evaluated for $CuFeO_2$ the MHF $B_{\mathrm{HF}} = 0.3(1)$ T at 4.2 K. Higher MHFs would split the first Fourier peak as can be seen in the simulated Fourier spectra shown in Fig. 3.

Before we discuss this weak magnetic field in the context of spin frustration, we have to prove that the implanted ^{111}In probes substitute a *B* element (here Fe) in the delafossite lattice. [At the *A* site (Cu) only a weak supertransferred hyperfine field can occur.] In a preceding study [14] the dominant EFG for ^{111}In(EC)^{111}Cd in several delafossites Cu(Al,Cr,Fe,Nd,Y)O_2 and Ag(Cr,In)O_2 was measured in the temperature range 30–1073 K and attributed to probes residing at the *B* site. We will study shortly summarize the argumentation: As both inequivalent sites *A* and *B* will give an EFG with symmetry parameter $\eta = 0$, the symmetry of the EFG cannot differentiate between the sites, and additional arguments are needed to decide on the site location. After implantation into oxides, the trivalent ^{111}In ions usually come to rest on the site of the trivalent cations of the lattice, if there are any. ^{111}In was found to substitute only the M^{3+} site in the cuprates $M_2Cu_2O_5$ [21], a crystal-family correlated to the delafossites: At least $Y_2Cu_2O_5$ can be reduced to $CuYO_2$. More examples are given in [14]. If there are two trivalent sites, like in the orthoferrites *RE*FeO_3, ^{111}In can occupy both sites [20]. A conversion-electron Mössbauer experiment (CEMS) with ^{57}Fe was performed at RT with the $CuFeO_2$ samples. The observed quadrupole splitting showed the presence of a structural EFG at the Fe site. Its strength is in good agreement with the one measured by PAC. Futhermore, the systematics of the antishielding factors in the delafossite family may give an additional hint: $AgInO_2$ was one of the delafossites studied which fitted well in the trend of the observed EFG's [14]. Here the In probe resides on its natural *B* site. Finally, a PAC experiment was done with ^{111}Ag tracers which decay to the same PAC sensitive level in ^{111}Cd as the ^{111}In probes. The results obtained in $CuFeO_2$ and $AgInO_2$ proved that ^{111}Ag with its different valency, indeed, substitutes the monovalent *A* site, sensing there a 5 times higher EFG as compared to the *B* site [22]. We conclude that the ^{111}In probe substitutes a Fe cation in $CuFeO_2$ and that the EC decay does not change this location of the impurity.

In general, in frustrated systems the magnetic exchange fields cancel each other resulting in a vanishingly small molecular field at the magnetic ion site. A substituted nonmagnetic PAC probe is always the "center atom" of a hexagon and, now, its six next neighbors can easily arrange in the AF order. Therefore, the frustration is locally released by the nonmagnetic PAC probe as indicated in Fig. 1(c) inspired by [1]. It was calculated in [23] that such a configuration around an impurity reduces the total energy, leading to a more stable configurations. Usually, such a situation is discussed for the ground state of a frustrated system after diluting macroscopic amounts of a nonmagnetic impurity. We propose that the PAC technique observed locally just such a phenomenon in the range of the next neighbors. In a first-order description, in the triangular lattice the MHF vanishes at the PAC probe.

Nevertheless, in the present experiment we observe a small, but finite MHF of $B_{\mathrm{HF}} = 0.3(1)$ T. This MHF is remarkably small as compared with those at ^{111}Cd probes in Fe (38.2 T [24,25]), cubic monoxides (17–19 T [12]), oxide spinels (2.7–7 T [26]), and in the noncubic oxides α-Fe_2O_3 (6.8 T [19]) and CuO (2.7 [27]). If one accepts the next-neighbor cancellation, the PAC technique becomes extremely sensitive to the complex magnetic order via third-neighbor (J_3) or interplane interactions. One might object that fast fluctuations of neighboring spins could cause the damping of the PAC spectra. Such a type of dynamical interactions can lead to fully damped spectra as recently observed in La_2O_3 [28] and Cr_2O_3 [29]. However, the present data do not point to dynamical interactions which would affect all three Fourier components in a similar fashion. In the present case the first Fourier peak gets clearly broader and lowered in intensity, whereas the second one stays unchanged (see Fig. 2). This is expected from the simulations of the combined interaction shown in Fig. 3 and proves the presence of a combined hyperfine interaction. Independently, whether one accepts the picture of a local change in the frustrated triangular lattice around the probe or if one prefers a more dynamical interpretation of the damping in the spectra, it is shown here that the PAC is an appropriate technique which is able to investigate the complex magnetic order in a frustrated spin system.

The financial support by the Deutsche Forschungsgemeinschaft is greatly appreciated (Project No. Li325/2). The work of R. N. A. was supported by a fellowship from CNPq Brazil. It is a pleasure to thank Professor Dr. A. Zippelius for advice.

[1] P. Fazekas and P. W. Anderson, Philos. Mag. **30**, 423 (1974).
[2] M. Shiga, in *Condensed Matter Studies by Nuclear Methods*, edited by K. Tomala and E. A. Görlich (Institute of Physics, Krakow, Poland, 1995), p. 57.
[3] M. Mekata, N. Yaguchi, T. Takagi, T. Sugino, S. Mitsuda, H. Yoshizawa, N. Hosoito, and T. Shinjo, J. Phys. Soc. Jpn. **62**, 4474 (1993).
[4] M. Mekata, N. Yaguchi, T. Takagi, S. Mitsuda, and H. Yoshizawa, J. Magn. Magn. Mater. **104–107**, 823 (1992).
[5] W. Bolse, M. Uhrmacher, and K. P. Lieb, Hyperfine Interact. **35**, 631 (1987).
[6] W. Bolse, M. Uhrmacher, and K. P. Lieb, Phys. Rev. B **36**, 1818 (1987).
[7] Th. Wenzel, M. Uhrmacher, and K. P. Lieb, J. Phys. Chem. Solids **55**, 683 (1994).
[8] Z. Inglot, D. Wegner, and K. P. Lieb, Hyperfine Interact. **50**, 785 (1989).
[9] Th. Wenzel, M. Uhrmacher, and K. P. Lieb, Philos. Mag. A **72**, 1099 (1995).
[10] Z. Inglot, D. Wiards, K. P. Lieb, Th. Wenzel, and M. Uhrmacher, J. Phys. Condens. Matter **3**, 4569 (1991).
[11] A. Bartos, D. Wiarda, Z. Inglot, K. P. Lieb, M. Uhrmacher, and Th. Wenzel, Int. J. Mod. Phys. B **7**, 357 (1993).
[12] H. H. Rinneberg and D. A. Shirley, Phys. Rev. B **13**, 2138 (1976).
[13] C. Hohenemser, T. Kachnowski, and T. K. Bergstresser, Phys. Rev. B **13**, 3154 (1976).
[14] R. N. Attili, M. Uhrmacher, K. P. Lieb, L. Ziegeler, M. Mekata, and E. Schwarzmann, Phys. Rev. B **53**, 600 (1996).
[15] H. Kadowski, H. Kikuchi, and Y. Ajiro, J. Phys. Condens. Matter **2**, 4485 (1990).
[16] Y. Oohara, S. Mitsuda, H. Yoshizawa, N. Yaguchi, H. Kuriyama, T. Asano, and M. Mekata, J. Phys. Soc. Jpn. **63**, 847 (1994).
[17] A. Bartos, K. Shemmerling, Th. Wenzel, and M. Uhrmacher, Nucl. Instrum. Methods Phys. Res., Sect. A **330**, 132 (1993).
[18] H. Frauenfelder and R. M. Steffen, in *Alpha-, Beta- and Gamma-Ray Spectroscopy*, edited by K. Siegbahn (North-Holland, Amsterdam, 1965).
[19] K. Asai, F. Ambe, S. Ambe, T. Okada, and H. Sekizawa, Phys. Rev. B **41**, 6124 (1990).
[20] T. M. Rearick, G. L. Catchen, and J. M. Adams, Phys. Rev. B **48**, 224 (1993).
[21] A. Bartos, M. Uhrmacher, L. Ziegeler, and K. P. Lieb, J. Alloys Compd. **179**, 307 (1992).
[22] R. N. Attili, A. W. Carbonari, R. N. Saxena, and M. Uhrmacher (to be published).
[23] M. Mekata, T. Tatsumi, T. Nakashima, K. Adachi, and Y. Ajiro, J. Phys. Soc. Jpn. **56**, 4544 (1987).
[24] F. Pleiter, C. Hohenemser, and A. Arends, Hyperfine Interact. **10**, 691 (1981).
[25] M. Neubauer, K. P. Lieb, P. Schaaf, and M. Uhrmacher, Phys. Rev. B **53**, 10 237 (1996).
[26] K. Asai, T. Okada, and H. Sekizawa, Hyperfine Interact. **34**, 435 (1987).
[27] A. Bartos, M. Uhrmacher, K. P. Lieb, and W. Bolse, Hyperfine Interact. **50**, 619 (1989).
[28] D. Lupascu, S. Habenicht, K. P. Lieb, M. Neubauer, M. Uhrmacher, Th. Wenzel, and ISOLDE Collaboration, Phys. Rev. B (to be published).
[29] M. Neubauer, A. Bartos, K. P. Lieb, D. Lupascu, M. Uhrmacher, and Th. Wenzel, Europhys. Lett. **29**, 175 (1995).