

## Field-Induced Staggered Magnetization and Magnetic Ordering in $\text{Cu}_2(\text{C}_5\text{H}_{12}\text{N}_2)_2\text{Cl}_4$

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We present a <sup>2</sup>D NMR investigation of the gapped spin-1/2 compound  $\text{Cu}_2(\text{C}_5\text{H}_{10}\text{N}_2\text{D}_2)_2\text{Cl}_4$ . Our measurements reveal the presence of a magnetic field-induced transverse staggered magnetization (TSM) which persists well below and above the field-induced 3D long-range magnetically ordered (FIMO) phase. The symmetry of this TSM is different from that of the TSM induced by the order parameter of the FIMO phase. Its origin, field dependence, and symmetry can be explained by an intradimer Dzyaloshinskii-Moriya interaction, as shown by DMRG calculations on a spin-1/2 ladder. This leads us to predict that the transition into the FIMO phase is not in the BEC universality class.

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Since the pioneering work of Haldane for  $S = 1$  anti-ferromagnetic (AF) chains [1], the existence of collective singlet ground states separated by an energy gap from the first triplet excited states has triggered a very large number of theoretical and experimental studies in low-dimensional quantum AF systems, as well as in 3D AF coupled dimers [2]. Applying an external magnetic field  $H$  lowers the energy of the  $M_S = -1$  component of the triplet band, inducing at some critical field value  $H_{c1}$  a quantum phase transition from a nonmagnetic phase to a field-induced 3D long-range magnetic ordered (FIMO) ground state, which has been recently described in several cases as a Bose-Einstein condensation (BEC) of triplet excitations [3–6]. However, anisotropic terms in the spin-Hamiltonian, like Dzyaloshinskii-Moriya (DM) interactions or staggered  $g$  tensors, often open a gap at  $H_{c1}$ , and change the universality class of the transition [3,7,8]. Among numerous spin-liquid systems,  $\text{Cu}_2(\text{C}_5\text{H}_{12}\text{N}_2)_2\text{Cl}_4$  [Cu(Hp)Cl in short] [9] has long been considered as the prototype of a  $S = 1/2$  two-leg spin ladder in the strong coupling limit ( $J_{\perp} \gg J_{\parallel}$ ) [10]. Its phase diagram in the  $H$ - $T$  plane consists of a gapped spin-liquid phase below  $H_{c1}$ , a 3D ordered magnetic phase between  $H_{c1} = 7.5$  T and  $H_{c2} = 13$  T, and a fully polarized, gapped phase above  $H_{c2}$ . In the intermediate phase, between  $H_{c1}$  and  $H_{c2}$ , the interactions between the “magnetic ladders” lead to the FIMO phase [11–13]. Close to the first quantum critical point ( $H = H_{c1}$ ,  $T = 0$ ),  $T_{\text{FIMO}}(H)$  varies as  $(H - H_{c1})^{1/\alpha}$ , where  $\alpha$  was found to be close to  $3/2$ , as expected in a BEC description [4]. However, inelastic neutron scattering measurements [14] have shown that the exchange paths are not clearly identified in this system and are more complicated than in the ideal picture described above.

In this Letter, we present a <sup>2</sup>D NMR study of a Cu(Hp)Cl single crystal ( $0.35 \times 0.3 \times 0.15$  mm<sup>3</sup> size), in which the N-H groups have been replaced by N-D groups. <sup>2</sup>D spectra have been recorded in the field range 3.5–15 T, and in the temperature range 50 mK–50 K. From the study of the quadrupolar couplings as a function of  $T$  and  $H$ , we rule out previous interpretations of the origin of FIMO as being magnetoelastic [12,13]. We demonstrate the existence at low  $T$  of a sizable field-induced transverse staggered magnetization (TSM) which starts to grow several Tesla below  $H_{c1}$ , remains nearly constant within the FIMO phase, and decays within a few Tesla above  $H_{c2}$ . Within the FIMO, it coexists with another TSM of different symmetry corresponding to the order parameter of the FIMO. Such a behavior has never been reported so far. We show that the TSM outside the FIMO is well explained by density matrix renormalization group (DMRG) calculations on a  $S = 1/2$  spin ladder in the strong coupling limit if a DM interaction is introduced on the rungs.

Selective deuteration provides several advantages over proton NMR. First, it divides by 6 the number of sites contributing to the spectra. There are only 8 inequivalent sites for an arbitrary orientation of  $H$ , and 4 for  $H \parallel \vec{b}$  or in the  $(\vec{a}, \vec{c})$  plane, due to the symmetry of the space group  $P2_1/c$ . Secondly, the substituted <sup>1</sup>H are the closest to Cu atoms. Half of them are involved in the presumed exchange path  $J_{\parallel}$ . These <sup>1</sup>H sites show an anomalous shift at low  $T$ , which has been previously considered as a hint for the magnetoelastic character of the transition into the FIMO [13]. Finally, <sup>2</sup>D has a spin 1 and a quadrupolar moment. Therefore, each inequivalent <sup>2</sup>D site gives rise to two lines. Their average position depends on the magnetic hyperfine shift  $K$  due to the coupling with the electronic spins borne

by the  $\text{Cu}^{2+}$  atoms through the hyperfine tensors. Their splitting  $\delta\nu_Q$ , due to the quadrupolar coupling with the environment, is very sensitive to atomic displacements or structural distortions. Both  $K$  and  $\delta\nu_Q$  strongly depend on the orientation of  $H$  with respect to the crystalline axes. So, from the simultaneous determination of  $\delta\nu_Q$  and  $K$  versus  $H$  and  $T$ , one can decide whether the variations of  $K$  are due to atomic displacements or not. As a drawback,  $^2\text{D}$  NMR is much less sensitive than  $^1\text{H}$  NMR. All spectra were obtained by sweeping the frequency at fixed  $H$  value and summing the Fourier transforms of the echo [15]. As long as the hyperfine and the quadrupolar couplings are small perturbations with respect to the Zeeman energy,

$$\delta\nu_{\pm}^i = 2\gamma\delta h_z^i \pm \delta\nu_Q^i/2, \quad (1)$$

where  $\delta h_z^i = K^i H = \sum_{l,\alpha,\beta} A_{z\alpha}^{i,l} (g^{-1})_{\alpha\beta}^l \chi_{\beta z}^l H$ .  $K^i$  is the hyperfine shift of the deuteron site  $i$ ,  $A^{i,l}$  the hyperfine field tensor between copper site  $l$  and deuteron  $i$ , while  $\mathbf{g}^l$  and  $\chi^l$  are, respectively, the  $g$  and the susceptibility tensors of copper  $l$ . Both  $A^{i,l}$  and  $\mathbf{g}^l$  are  $T$  independent in the absence of structural change.

Before considering the  $T$  and  $H$  dependence of  $\chi(T)$ , we first demonstrate that the quadrupolar couplings are  $T$  independent below 10 K and  $H$  independent at  $T \sim 0$  (50 mK). Figure 1 shows  $^2\text{D}$  spectra as a function of  $T$  for  $H = 7.75$  T  $\parallel$   $[\bar{1}1\bar{1}]$ . In this particular orientation, the line A at the right-hand side of the spectra remains isolated in the whole  $T$  range 50 K–50 mK. Several approaches have been used to determine the  $T$  dependence of  $\delta\nu_Q$  for

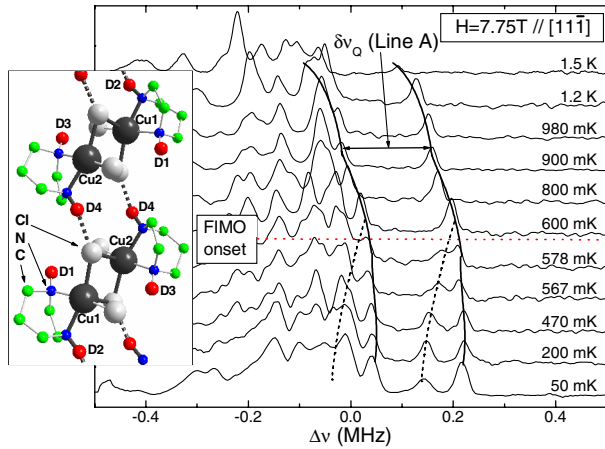


FIG. 1 (color online).  $T$  dependence of  $^2\text{D}$  spectra for  $H = 7.75$  T  $\parallel$   $[\bar{1}1\bar{1}]$ . The quadrupolar doublet corresponding to the line A at the right-hand side of the spectra is identified below 1.2 K. Its position is emphasized by solid lines, which are just a guide for the eyes. Below 600 mK, each component of the doublet splits into two lines (dashed versus solid line), due to the entrance into the FIMO phase. Inset: Structure of  $\text{Cu}_2(\text{C}_5\text{H}_{12}\text{N}_2)_2\text{Cl}_4$ . The 10 protons attached to the C atoms are not shown. The other ladders can be deduced by translation and rotation around the  $b$  axis.

this site. Between 50 to 10 K, where all the  $^1\text{H}$  lines have a similar  $T$  dependence, we made use of Eq. (1) by plotting  $\delta\nu_A(T)$  versus  $^1\text{H}$  shift  $\delta\nu_H(T)$ , which reflects directly the variation of  $\chi_S(T)$ . The extrapolation to  $\delta\nu_H = 0$  gives  $\delta\nu_Q^A = 170 \pm 8$  kHz. Below 1 K, the second line of the doublet involving line A also becomes isolated in the spectra and the value of  $\delta\nu_Q$  can then be directly determined. It is found constant through the 3D transition and its value  $175 \pm 6$  kHz [Fig. 1 and 2(a)] is consistent with that determined by the high  $T$  procedure. These results strongly support the absence of structural transition in the whole temperature range 50 K–50 mK, and, in particular, at  $T_{\text{FIMO}}$ . Let us now consider the  $H$  dependence of  $\delta\nu_Q$  at low  $T$ . For that purpose, we used the spectra recorded at 50 mK in the field range 6–14 T, with  $H \parallel c^*$ . In this case the symmetry reduces the number of inequivalent  $^2\text{D}$  sites to 4, and it is possible to fit the whole spectra. Figure 2(b) shows the values of  $\delta\nu_Q$  for the 4 sites as a function of  $H$ . They remain constant in the whole  $H$  range, in particular, throughout the two quantum transitions at  $H_{c1} = 7.5$  T and  $H_{c2} \approx 13$  T. This rules out the existence of a structural transition at  $T = 50$  mK associated with the quantum magnetic phase transition. This corrects our previous interpretation on the nature of the FIMO [13], and contradicts the recently published x-ray experiments [16]. Our experiments also show the absence of any hysteresis upon entering the FIMO by varying  $H$  at fixed  $T = 50$  mK.

We can now focus on the  $T$  and  $H$  dependence of the shift  $K$  which directly reflects that of  $\chi$ . In Fig. 3(a), we

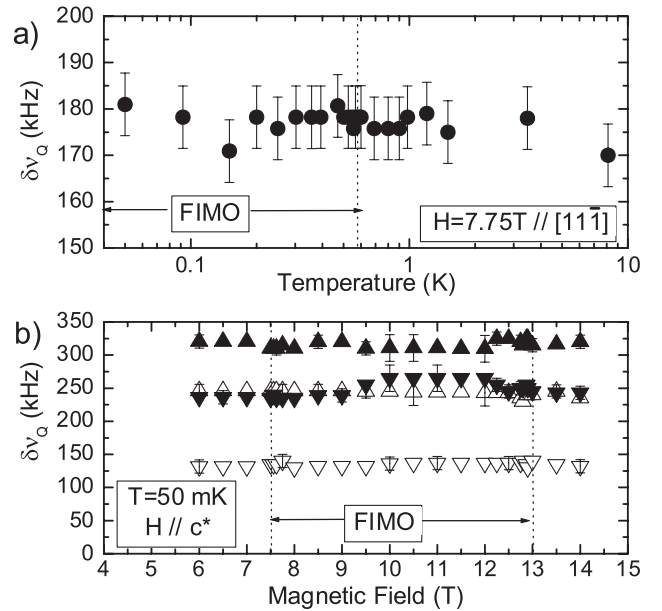


FIG. 2. (a)  $T$  dependence of  $\delta\nu_Q$  for the site corresponding to the line A for  $H = 7.75$  T and  $\parallel$  to  $[\bar{1}1\bar{1}]$  (b)  $H$  dependence of  $\delta\nu_Q$  of the 4 sites at 50 mK for  $H \parallel c^*$ . In both cases,  $\delta\nu_Q$  remains constant. These data demonstrate the absence of any structural transition at the quantum critical fields  $H_{c1}$  and  $H_{c2}$  at  $T \sim 0$ .

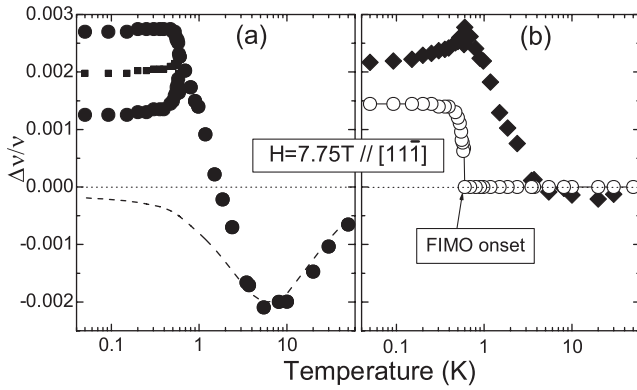


FIG. 3. (a) Comparison between the  $T$  dependence of  $A_{zz}\chi_{zz}$  (dashed line) [17] and the shift  $K$  (●) of the line A at  $H = 7.75$  T  $\parallel$   $[11\bar{1}]$ ,  $A_{zz} = -470$  G/ $\mu_B$ . Below  $T_{\text{FIMO}} = 600$  mK, the line splits into two components, and solid squares correspond to their average position. (b) The difference  $A_{zz}\chi_{zz}(T) - K(T)$  (◆) is due to the onset of a transverse magnetization (see the text). The splitting  $S(T)$  (○) of the A line below  $T_{\text{FIMO}}$  is proportional to the order parameter of the FIMO.

have reported the  $T$  dependence of the hyperfine shift  $K = \delta h_z/H$  of the A line and of the product of the longitudinal spin susceptibility  $\chi_{zz}(T)$  by the hyperfine field  $A_{zz}$  in the orientation  $[11\bar{1}]$  [17]. These two quantities are no longer proportional below 3 K, and this can only be explained by the growing of a transverse magnetization:

$$\delta h_z(T) = A_{zz}M_z(T) + \delta H_{\text{tr}}(T), \quad (2)$$

where  $\delta H_{\text{tr}} = A_{zx}M_x(T) + A_{zy}M_y(T)$ . In Fig. 3(b), the  $T$  dependence of the contribution of this transverse magnetization to  $K(T)$  is plotted. Below  $T_{\text{FIMO}}$  we consider the mean position of the split line (solid squares) and compare it to that of the splitting  $S$  which is proportional to the order parameter of the FIMO.

More information on  $\delta H_{\text{tr}}$  can be obtained by looking at its  $H$  dependence between 6 and 14 T at 50 mK, in the orientation  $H \parallel c^*$ . The experimental values of the shifts as a function of  $H$  are shown in Fig. 4 and compared with their expected variations in the absence of  $\delta H_{\text{tr}}$ , i.e.,  $A_{zz}^i M_z(H)$ . The solid and the dotted lines correspond to the extremal values of  $A_{zz}^i$  of the 4 hyperfine fields determined between 50 and 10 K. One clearly sees before  $H_{c1}$  the growing of two by two opposite values of  $\delta H_{\text{tr}}$ , which remain nearly constant within the FIMO, and then start to decrease to zero. This immediately points to the existence of a staggered magnetization, as in  $\text{SrCu}_2(\text{BO}_3)_2$  [19]. However, it must be noticed that for both orientations of  $H$  with respect to the crystal, the field-induced TSM does not split the NMR lines, as clearly seen outside the FIMO. This means that the number of inequivalent sites remains the same outside the FIMO (4 or 8 when  $H \parallel c^*$  or  $[11\bar{1}]$ ). This differs from the effect of the spontaneous TSM arising in the FIMO, which clearly splits them. The absence of splitting due to the field-induced TSM implies that this

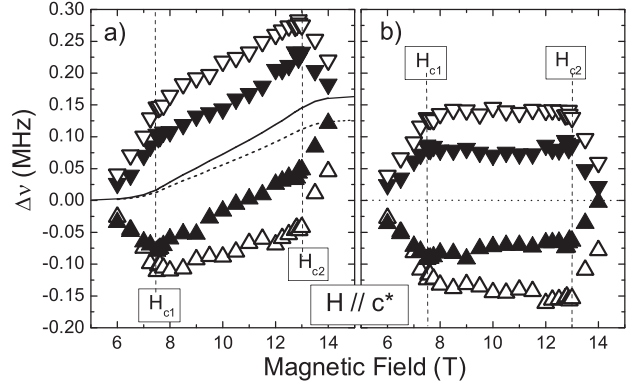


FIG. 4. (a)  $H$  dependence of the hyperfine experimental shift of the 4 sites (▼, ▲, ▽, △) for  $H \parallel c^*$ . Between  $H_{c1}$  and  $H_{c2}$ , the mean position of the split lines is plotted. The solid and the dotted lines are defined in the text. (b)  $H$  dependence of the fraction of the shift due to the field-induced TSM.

TSM respects the full symmetry of the crystal space group, while that corresponding to the order parameter of the FIMO does not, as expected in a phase transition.

The progressive appearance of a TSM upon approaching  $H_{c1}$  at low  $T$  must come from interactions that break the  $\text{SU}(2)$  symmetry and mix the  $S = 0$  ground state with the lowest triplet  $S = 1$  excitations. This can be due to DM interactions and/or staggered  $g$  tensors on dimers without inversion symmetry [19], which is the case for the shortest  $\text{Cu}_1$ - $\text{Cu}_2$  pairs [9]. To model the effects of DM interactions, we have performed DMRG calculations on a spin-1/2 ladder assuming a staggered distribution of DM vectors  $\vec{D}$  on the rungs, as the simplest model consistent with the presence of an inversion center between neighboring dimers [20]. Since the exchange paths are still debated, other geometries including, e.g., diagonal inter-rung couplings could in principle be realized. However, preliminary results show that, as far as the TSM perpendicular to  $\vec{D}$  is concerned, the field dependence is essentially the same up to an overall factor [21]. As seen in Fig. 5(a), the results reproduce the experimentally observed TSM fairly well for reasonable ratios  $\mathcal{D}/J_{\perp} = 0.05$  and  $J_{\parallel}/J_{\perp} = 0.2$ , with  $J_{\perp} = 13$  K. Furthermore, since  $\vec{m}_{\perp} \propto \vec{H} \times \vec{D}$  [21], it is easy to show, considering the symmetry transformations of a pseudovector in the group  $\text{P}2_1/c$ , that the field-induced TSM due to the DM interaction cannot split the  ${}^2\text{D}$  lines, whatever the orientation of  $H$ : the alternation of the DM vector from one rung to the adjacent one corresponds to the symmetry of the lattice so that, if  $\vec{S}_1$  and  $\vec{S}_2$  correspond, respectively, to  $\text{Cu}_1$  and  $\text{Cu}_2$  electronic spins,  $\vec{D} \cdot \vec{S}_1 \times \vec{S}_2$  remains invariant.

The situation is different for the TSM corresponding to the order parameter of the FIMO, which splits all the  ${}^2\text{D}$  lines whatever the field orientation. This means that it breaks the inversion symmetry between two adjacent rungs. An example of a possible pattern is shown in

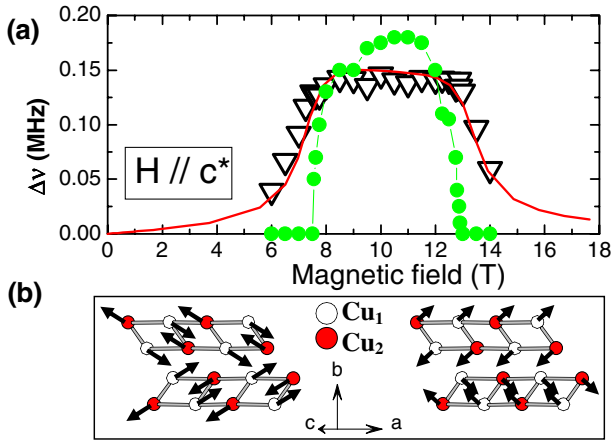


FIG. 5 (color online). (a)  $H$  dependence of the field-induced TSM ( $\nabla$ ) and the fit (solid line) by the DMRG calculation with  $J_{\perp} = 13$  K,  $J_{\parallel}/J_{\perp} = 0.2$ , and  $\mathcal{D}/J_{\perp} = 0.05$ . The order parameter of the FIMO is proportional to  $S(H)$  (solid circles). (b) Schematic representation of the two “ladders” and the Cu(1) and Cu(2) sites viewed from the  $c^*$  direction. Note an inversion symmetry between two successive rungs. Left: Schematic representation of the field-induced TSM. Its direction on one rung is fixed by  $\vec{H} \times \vec{\mathcal{D}}$  and the whole pattern can be deduced by applying the symmetry operations of the lattice. Right: TSM pattern consistent with the order parameter of the FIMO. The direction in the plane is unknown and fixed by the interdimer interactions.

Fig. 5(b). This would be consistent with a BEC in weakly coupled dimers systems into a uniform phase in which the TSM is the same on all rungs. However, the BEC description is here inadequate since, due to the field-induced TSM, the isotropy in the plane perpendicular to  $H$  is lost. So, the ordered phase can only break a discrete symmetry, and the phase transition into the FIMO cannot fall into the universality class of BEC. This is actually supported by the present data. Indeed,  $T_c(H)$  varies as  $(H - H_{c1})^{0.55}$ , consistent with the results reported in [13], but in slight disagreement with the BEC prediction  $(H - H_{c1})^{2/3}$  [22]. Moreover, the field dependence of the order parameter within the FIMO, as revealed by the splitting  $S$ , was found to be  $(H - H_{c1})^{\beta}$  with  $\beta = 0.34 \pm 0.04$  [23], instead of the mean-field value  $\beta = 0.5$  expected for a BEC in  $3 + 1$  dimensions. Unfortunately, the exponent for the transition as a function of  $T$  at fixed  $H$  could not be reliably extracted from the present data. So, the precise determination of the nature of the phase transition into the FIMO is left for future investigation. Finally, the presence of DM interactions is normally accompanied by a gap opening, corresponding to some kind of level anticrossing [19]. In Cu(Hp)Cl, a fast decrease of the nuclear spin-lattice relaxation  $T_1^{-1}$  has indeed been observed below 1 K in the field range of the FIMO, even at  $H = 7.75$  T for which  $T_{\text{FIMO}} = 300$  mK [13]. These data are consistent with the gap estimated by DMRG [21].

In conclusion, we have shown that in Cu(Hp)Cl two types of transverse staggered magnetization appear. The first one, which extends outside the 3D FIMO phase, is field induced and breaks the SU(2) symmetry, but not the crystal symmetry. We propose that it is due to the presence of a DM interaction  $\mathcal{D}$  on the strong dimers, and we have shown by an explicit calculation in a ladder geometry that a quantitative fit can be achieved for a reasonable value of the parameters ( $\mathcal{D}/J_{\perp} \approx 0.05$ ). The second one, which corresponds to the order parameter of the FIMO, breaks the inversion symmetry of the structure. We think that these features are generic for an assembly of interacting non-centro-symmetric dimers, and we suggest that they will change the universality class of the field-induced phase transition.

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