Zero-Field NMR in *Cu*Mn: New Viewpoint on Remanence in Spin-Glasses

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Zero-field Cu NMR of the first and fourth nearest neighbors of Mn in spin-glass Cu-Mn(1%) have been detected for $T \lesssim T_g/5$. The observed enhancement of rf field and signal intensity, associated with domain rotation, increases with the remanent magnetization and vanishes if the sample is zero-field cooled. A new description of the remanent properties of spin-glasses with no independent magnetic domains after zero-field cooling is proposed.

For experimentalists, the growing interest for the physical properties of spin-glasses is not only linked with the susceptibility cusp[1] and an eventual original phase transition,[2] but also with the appearance below T_g of remanent properties which obey scaling laws[3] with concentration.[4] The magnetic remanence has been often interpreted[5] using Néel's formalism developed for a collection of fine magnetic grains. This model relies upon the assumption of a spontaneous decomposition of the spin-glass in magnetic domains with random local magnetizations $\vec{\sigma}_i$ fixed by random anisotropy (or demagnetizing) fields $\vec{H}_A^{\,i}$.[5,6] Subsequent efforts have been aimed at demonstrating that the ac susceptibility cusp reflects the blocking temperature T_B of a fraction of the domains and varies with the frequency of the measurement.[7] This experimental point is still highly controversial[8] and neither is there, to my knowledge, any definite experimental evidence for the proposed domain structure.

In this Letter, I report the first observation of zero-field NMR in a spin-glass system. The characteristics of the signals were found to depend on the magnetic remanence and unveil new original features of spin-glasses. The starting point of this work is the general acceptance[9,10] that for $T \ll T_g$ the spin system is frozen and that the hyperfine fields on the impurity nuclei, or the Ruderman-Kittel-Kasuya-Yosida (RKKY) fields on a given shell of near-neighbor (nn) nuclei are well defined, although randomly distributed in direction. I have detected the signals of the first (A) and fourth (B) nn shells in zero (or small applied) field H_0 on a powdered (40-μm-thick) Cu-Mn(1%) sample at $T \ll T_g$ (=10 K). Let us consider first the zero-field signal detected at T =1.25 K after cooling the sample in a field $\vec{H}_c$ = 10 kG, which establishes a saturated remanent magnetization $\vec{\sigma}_s \parallel \vec{z}$. Spin echoes were generated with a two-pulse sequence (widths t_w, $t_{w'} \sim 2t_w$ separated by τ), in a single coil parallel to the $\vec{y}$ axis. The spectra displayed in Fig. 1 result of the overlap of the ^{63}Cu and ^{65}Cu resonances. Their width $\Delta\omega_{1/2}$ (due to the anisotropic coupling with the Mn spin plus the RKKY interaction with large-distance Mn impurities) and the deduced local fields H_L agree with expectations from the paramagnetic regime.[11] For a given resonance, the effective rf field $H_1^{\mathrm{eff}} = \eta H_1$ seen by the nuclei were enhanced in zero field, since the maximum spin-echo intensities were obtained for narrower pulses than for the bulk ^{63}Cu NMR detected for $H_0 = \omega/\gamma(^{63}\mathrm{Cu})$. The enhancement factors, deduced from the ratio of optimum t_w values, $\eta = 38 \pm 6$ and $\eta = 8 \pm 1$, respectively, for resonances A and B, scale with H_L. They will be coherently explained hereafter by domain rotation induced by the rf field, as in monodomain ferromagnetic materials.[12]

Let us consider an ensemble of Mn spins, rigidly bound together by strong RKKY forces, with a magnetization $\vec{\sigma}$ along the anisotropy axis $\vec{z}$. If the anisotropy energy is written as $K \sin^2\psi$, with $\psi = (\vec{\sigma}, \vec{z})$, a field with components $\vec{H}_0 \parallel \vec{z}$ and $\vec{H}_1 \parallel \vec{y}$ induces a rotation of $\vec{\sigma}$ around $\vec{x}$ of $\psi = H_1(H_0$

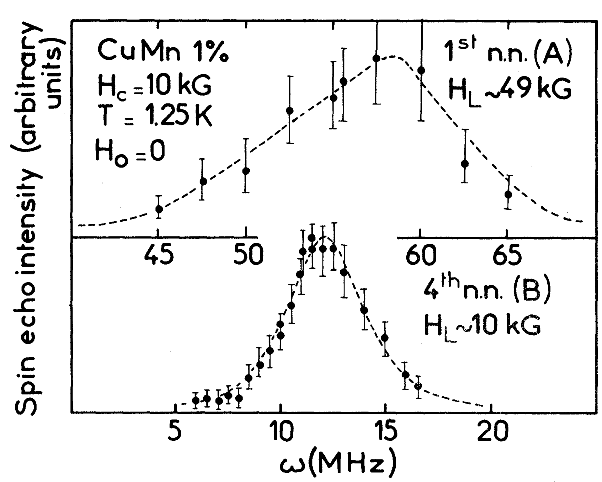

FIG. 1. A and B resonances: optimum spin-echo intensity, normalized at each ω to the bulk ^{63}Cu NMR intensity for a given H_1.

$+H_A)^{-1}$ for $H_1 \ll H_A$, where $H_A = 2K/\sigma$ is the anisotropy field (Fig. 2). In such a domain rotation, all the electron spins, and the local fields $\vec{H}_L$ on the nuclei of the domain rotate at the same angle ψ around $\vec{x}$. Therefore if the direction of $\vec{H}_L$ is given by $\theta = (\vec{H}_L, \vec{x})$ and $\varphi = (\vec{H}_L, \vec{y})$, the nuclei sense an rf field $\vec{H}_1 + \vec{H}_1'(\theta)$ where $\vec{H}_1'$ is transverse with respect to $\vec{H}_L$ and given by

$$H_1'(\theta) = H_1(H_0 + H_A)^{-1} H_L \sin\theta = \eta_\theta(H_0) H_1. \tag{1}$$

Similarly, the Larmor precession of the nuclear magnetization induces a precession of $\vec{\sigma}$ which correspondingly enhances the detected signal. If the $\vec{H}_L$ are oriented at random, a simple calculation of the total spin-echo intensity I for $t_w' = 2t_w$, neglecting $\vec{H}_1$ with respect to $\vec{H}_1'(\theta)$, shows that although a loss of signal intensity with respect to the ferromagnetic case ($\theta = \pi/2$) occurs, I has a well-defined maximum for $\gamma \eta_{\pi/2}(H_0) H_1 t_w \sim 0.55\pi$ which corresponds to an average enhancement factor

$$\bar{\eta}(H_0) \simeq 0.9\, \eta_{\pi/2}(H_0) = 0.9 H_L (H_0 + H_A)^{-1}, \tag{2}$$

and $H_1^{\text{eff}} \sim \bar{\eta}(H_0) H_1$. The number of spins which contribute to I is proportional to H_1^{eff} as $\gamma H_1^{\text{eff}} \ll \Delta\omega_{1/2}$ and therefore

$$I \propto \bar{\eta}(H_0) H_1^{\text{eff}} \propto [\bar{\eta}(H_0)]^2 H_1.$$

In Fig. 3, the data for the two independently measured quantities η and I are shown to agree with Eq. (2), for resonance A, with $H_A = 1.35 \pm 0.2$ kG as a *single fitting parameter*. Since the powdered sample is certainly a polydomain, the agreement with this single-domain model implies that (i) the angular distribution of anisotropy axes is peaked in the direction of $\vec{H}_c$ (η was indeed found smaller for $\vec{H}_1 \parallel \vec{H}_c$ than for $\vec{H}_1 \perp \vec{H}_c$), and (ii) the H_A^i do not vary drastically among the observed domains since $H_1^{\text{eff}} = \eta H_1$ is a well-defined experimental quantity. This could be seen as the variation of of I with the first pulse tipping angle where $\gamma H_1^{\text{eff}} t_w$ were identical for the zero-field and bulk ^{63}Cu resonance (for which $H_1^{\text{eff}} \equiv H_1$ is unique).

A quite surprising feature is *the absence of any detectable enhancement* on both A and B resonances *when the sample is zero-field cooled* (ZFC) which would correspond to $H_A^i \gtrsim 100$ kG, and therefore independent domains cannot be defined in this case. If a field H_i is applied on the ZFC sample and then reduced to 0, η increases as does the isothermal remanent magnetization, and saturates at the value obtained by field cooling (Fig. 4). These results contradict the models[5,6] for which the decomposition of the ZFC sample into domains is assumed *ab initio*, $\vec{\sigma}_s$ being associated with reversals of the $\vec{\sigma}_i$ along the individual anisotropy axes. Here the domain structure is induced by the magnetic field, which is consistent with (i).

These domains are not simple ferromegnatic clusters, but do involve a large amount of disorder as the signal I_{cc} detected in a crossed-coil geometry (detection coil $\parallel \vec{x}$) is 10 times weaker than the single-coil signal I_{sc} with the same H_1. Indeed contributions from nuclear spins with opposite $\vec{H}_L$ add in a single coil, while they are opposite in crossed-coil geometry. Then, I_{sc} is due to nn of all the Mn spins of the observed domains, while I_{cc} is associated only with those which contribute to $\vec{\sigma}_s$, and changed sign when $\vec{\sigma}_s$ was inverted after applying a reverse field H_0, which even allowed one to follow the displaced hysteresis loops.

The fraction n_σ of Mn sites which contribute

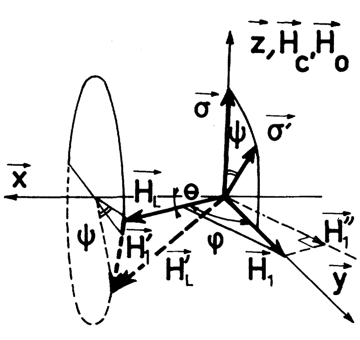

FIG. 2. Rotation of the domain magnetization $\vec{\sigma}$ and the local fields $\vec{H}_L$, induced by $\vec{H}_1$ applied perpendicularly to the anisotropy axis $\vec{z}$.

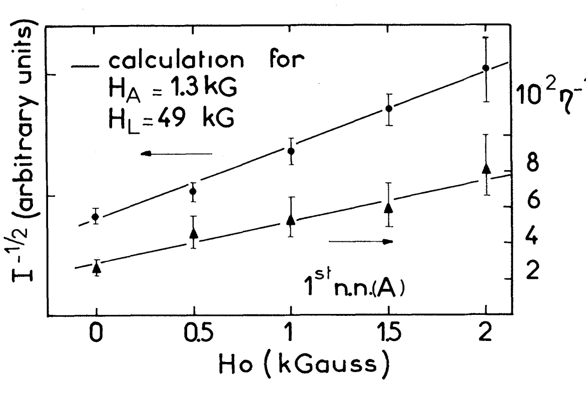

FIG. 3. Enhancement factor η, and $I^{-1/2}$ (normalized for the same H_1), for fields $H_0 < \Delta\omega_{1/2}/\gamma$, to avoid any broadening of the resonance. The full curves are obtained from Eq. (2) and $I^{-1/2} \propto \bar{\eta}(H_0)$.

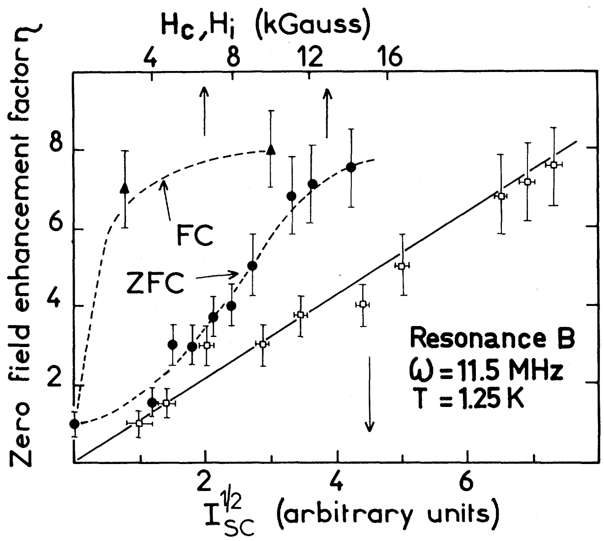

FIG. 4. Variation of η with H_c, or with the field H_i applied after ZFC. The single-coil signal intensity I_{sc} scales with η^2 even for $H_i = H_c = 0$.

both to $\vec{\sigma}_s$ and to the domains detected by NMR is directly related to the numbers $N_{cc}(B)$ and N(bulk ^{63}Cu) of Cu nuclei which contribute, respectively, to the crossed-coil zero-field resonance (24 sites on the fourth shell for B) and bulk ^{63}Cu resonance (isotopic abundance 0.69) and is given by $n_\sigma = 0.69 N_{cc}(B)/24cN(\text{bulk } ^{63}\text{Cu})$. These number of nuclei $N(\beta)$ are proportional to

$$I(\beta) \propto N(\beta)(\Delta\omega_{1/2}T)^{-1}\eta^2 H_1,$$

where $I(\beta)$ is the intensity of the spin-echo signal measured at given ω and temperature T, at the center of resonance β, which is assumed Lorentzian (width $\Delta\omega_{1/2}$).[13] For $c = 0.01$, $H_c = 10$ kG, $T = 1.25$ K, the results $\eta_{cc}(B) = 9 \pm 1$, $\Delta\omega_{1/2}(B)/\Delta\omega_{1/2}(\text{bulk } ^{63}\text{Cu}) = 3.3 \pm 0.4$, and $I_{cc}(B)/I(\text{bulk } ^{63}\text{Cu}) = 0.125 \pm 0.02$ yield $n_\sigma = (1.45^{+0.95}_{-0.6})\%$. Then σ_s *is essentially due to the domains detected here* since, for a saturation magnetization of $4.3\mu_B$/Mn atom, n_σ corresponds to $(0.062^{+0.038}_{-0.026})\mu_B$/Mn to be compared with $\sigma_s = 0.05\mu_B$/Mn, measured in the same conditions.[4]

The intensity loss induced by the angular distribution of Eq. (2) prevents a reliable estimate of the fraction n_D of Mn involved in the domains at $T = 1.25$ K. However this purely geometrical reduction factor should be the same for large η and in the ZFC case($\eta \simeq 1$) for which, from Fig. 2, $H_1^{\text{eff}} = H_1'' = H_1 \sin\varphi$ has the same distribution as that of Eq. (2).[14] In this limit no further intensity loss is expected as long as all Mn spins are frozen, as is confirmed by preliminary data taken at 0.35 K. The fraction of Mn which contributes to the domains is obtained by comparing I_{sc} in the FC and ZFC limits. It can be seen in Fig. 4 that $I_{sc}^{1/2}$ scales with η within experimental error, which implies that n_D is independent of $\vec{\sigma}$, and (as this scaling holds down to $\eta \sim 1$) that most, if not all, Mn spins ($n_D > 0.5$) are involved in the domains.

From this ensemble of experimental evidences a new picture for the remanent properties of spin-glasses can be sketched. In the ZFC sample, although the total magnetization of the Mn included in a given volume might be nonzero, any coherent motion of these spins is forbidden by interactions with neighboring spins. An applied field, through rearrangements of the spin orientations, develops a remanent magnetization $\vec{\sigma}$ and favors coherent motion of spins in domains which nearly fill the sample volume. The anisotropy fields which restrict the domain rotations are nearly oriented along $\vec{H}_c$ and their magnitude H_A, which scales approximately (if not exactly) with σ^{-1}, is therefore a characteristic of the bulk material. All these results allow the inference that the domains are of macroscopic size, and that the large transverse susceptibility with respect to $\vec{H}_c$ measured by Kouvel in more concentrated samples[15] might be correlated with domain rotations through $\chi_\perp = \sigma/H_A$. Further complete comparisons with magnetization data which are presently undertaken should even allow confirmation of whether bulk samples behave as single domains, as can be assumed from the observation of sharp hysteresis loops.[16] The zero-field NMR technique evidenced here, which permits one to distinguish collective properties from local ones, should certainly help in the future to refine this description of spin-glasses and to answer pending questions concerning the origin of the anisotropy, the magnetic aftereffect, the spin dynamics, etc. Finally, the absence of domain structure in ZFC samples implies that the susceptibility cusp can hardly be described by blocking of domains in their anisotropy fields. However, a theoretical description of spin-glasses involving the absence of long-range magnetic order, the spin dynamics below T_g,[10] and the peculiar properties of the magnetic remanence does not seem presently at hand.

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[13]In the crossed-coil experiment, $\vec{H}_1$ is uniquely defined ($\theta=\varphi=\pi/2$) since the nuclear magnetization which contributes to I_{cc} is along $\vec{\sigma}_s \| \vec{z}$. It must also be pointed out that, although a reduction of I(bulk ^{63}Cu) due to relaxation effects has been detected even for $T \ll T_g$ (Ref. 11), in the present experimental conditions ($H_0 \sim 10$ kG), I(bulk ^{63}Cu) recovers its full intensity for $T \lesssim 1.5$ K.
[14]When η is not much larger than unity, the intensity loss should depend on η as $\vec{H}_1^{\text{eff}}=\vec{H}_1'' + \vec{H}_1(\theta)$ has an angular dependence which differs markedly from Eq. (2). However this effect is too weak to be detected within the accuracy of the data of Fig. 4.
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Specific Heat near the Critical Concentration for the Dilute Simple-Cubic Magnet $Co_pZn_{1-p}(C_5H_5NO)_6(ClO_4)_2$

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The specific heat of the diluted simple-cubic antiferromagnetic system $Co_pZn_{1-p}(C_5H_5NO)_6(ClO_4)_2$ has been studied for $0.11 \leq p \leq 1$. It is shown that for $p=p_c=0.31$ (the percolation threshold for the simple-cubic lattice) the specific-heat anomaly is excellently described by the prediction for a linear-chain antiferromagnet.

In this note we present the first specific-heat data on a random quenched-site-diluted simple-cubic (s.c.) magnetic system in the neighborhood of the critical concentration of magnetic atoms ($p_c = 0.31$) predicted theoretically[1] for the percolation problem on the s.c. lattice. We show that at p_c the experimental specific-heat curve is excellently described by the prediction for a linear-chain magnet. This supports current arguments that the behavior at p_c is mainly determined by one-dimensional links in the largest clusters of magnetic ions.

The present results are the completion of preliminary work[2] on the system $Co_pZn_{1-p}(C_5H_5NO)_6(ClO_4)_2$, that was restricted to $p \geq 1.1p_c$. The pure compound CoL_6X_2 ($L = C_5H_5NO$ and $X = ClO_4^-$)