^{55}Mn NMR Study of the Collective Excitations in Spin-Glasses

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The first direct observation of zero-field NMR spectra of ^{55}Mn in *Cu*Mn, *Ag*Mn, and *Au*Mn spin-glasses allows a detailed study of the concentration and T dependence of the Mn local magnetization for $T \lesssim 0.2T_g$. The quantum reduction of the local spin is found smaller than numerical estimates, while the thermal part is found quadratic in T. Such a result agrees with expectations for magnons with a linear dispersion relation and a large stiffness constant, at short times, for the spin system.

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Spin-glasses (SG) are known to exhibit many degenerate ground states, and experiments have demonstrated that at $T << T_g$, the spin system is trapped for a long time in a given stable or metastable energy well. The magnetic $q=0$ modes and the influence of anisotropy have been studied in great detail.[1] Although theoretical efforts have been made to characterize in-well excitations in SG, these dynamical properties are far from being understood.[2] Hydrodynamic theories yield propagating magnons as long as a nonnegligible stiffness constant ρ is assumed.[3] However, the existence of such modes has not been proved in real Heisenberg systems. Walker and Walstedt (WW) have computed the eigenmodes of the ground states of Ruderman-Kittel-Kasuya-Yosida (RKKY) spin-glasses in a harmonic approximation.[4] The specific-heat and resistivity data[5] can be explained with their density of modes in the intermediate T range. Their lowest energy modes, although spatially extended, could not be identified with propagating magnons. Sample-size limitations have further restricted the significant information from computer simulations to $T \gtrsim 0.1T_g$. As in ordered magnetic materials, collective excitations are expected to induce a low-T reduction of the local spin $\Delta S_i(T) = |\langle \mathbf{S}_i \rangle| - S$, which can be written in the notation of WW

$$\Delta S_i(T) = \textstyle\sum_\nu W_{i\nu}/2 + \sum_\nu W_{i\nu} n_\nu = \Delta S_i^0 + \Delta S_i^T, \quad (1)$$

where $W_{i\nu}$ characterizes the amplitude of the spin oscillations on site i for the mode of energy $h\nu$ and n_ν is the Bose population of the mode. Here ΔS_i^0 is the zero-point quantum reduction and ΔS_i^T the thermal part.

In this Letter we present zero-field NMR experiments which allow accurate determination of $\Delta S_i(T)$ and provide the first experimental evidence favoring the existence of propagating magnons in RKKY spin-glasses. Observation of the ^{55}Mn NMR is made possible through the existence of a large enhancement of the signal intensity in the presence of a remanent magnetization M_r.[6] Therefore a specific pulsed NMR setup has been designed, with wideband transmitter and receiver, and a helix resonator mechanically tuned in the ^{4}He bath, which allows one to span a frequency band of about 200 MHz in the range 100–600 MHz. The sample is inserted in a glass cryostat, and data can be taken above 4.2 K or in liquid ^{3}He down to 0.35 K. After field cooling the sample, a nuclear spin-echo signal is detected in zero field. The ^{55}Mn NMR spectra which have been studied in *Cu*Mn, *Ag*Mn, and *Au*Mn[7] are obtained as a plot of the frequency dependence of the signal intensity. In most cases they consist of several resonance lines (Fig. 1).

For a given ^{55}Mn nucleus **I** at site i, the resonance frequency is $\omega_n^i = \gamma_n |\mathbf{H}_L(\mathbf{R}_i)|$, where $\mathbf{H}_L(\mathbf{R}_i)$ is the local field induced on the Mn nucleus by all the Mn electron spins $\mathbf{S}_j$. If only scalar contributions to the hyperfine couplings are considered

$$\hbar\gamma_n \mathbf{H}_L(\mathbf{R}_i) = A_0(\mathbf{R}_i)\langle \mathbf{S}_i \rangle + \sum_{j\neq i} A(\mathbf{R}_i - \mathbf{R}_j)\langle \mathbf{S}_j \rangle, \quad (2)$$

where $A_0(\mathbf{R}_i)\mathbf{I}_i \cdot \mathbf{S}_i$ is the internal d hyperfine coupling of the ion, which is the major contribution to $\mathbf{H}_L(\mathbf{R}_i)$, and $A(\mathbf{R}_i - \mathbf{R}_j)\mathbf{I}_i \cdot \mathbf{S}_j$ are the transferred hyperfine couplings.

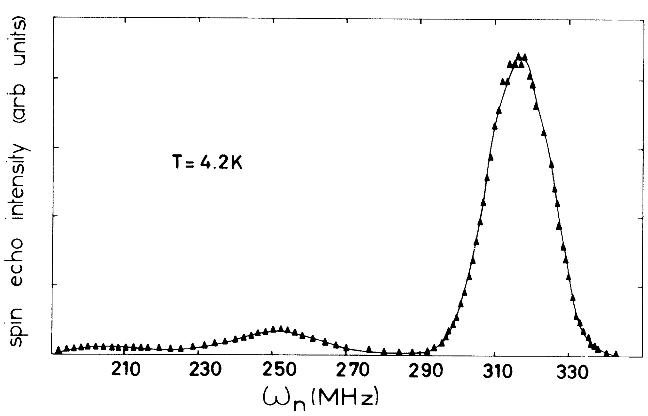

FIG. 1. ^{55}Mn NMR spectrum in 9.6 at.% *Cu*Mn. Apart from the main resonance, two satellite structures associated with ^{55}Mn nuclei with at least one nearest-neighbor Mn atom can be distinguished.

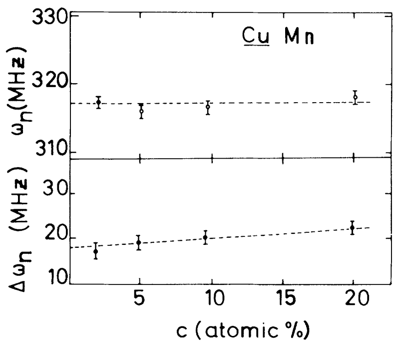

FIG. 2. Concentration dependence of the position and width of the main line at temperatures $T \lesssim 0.1\,T_g$. In this T range, the linewidth is T independent within experimental accuracy. The residual width at $c \to 0$ is not due to a distribution of zero-point motions ΔS_i^0, as can be seen in the text. It is then attributed to a small anisotropy of the single-ion hyperfine field.

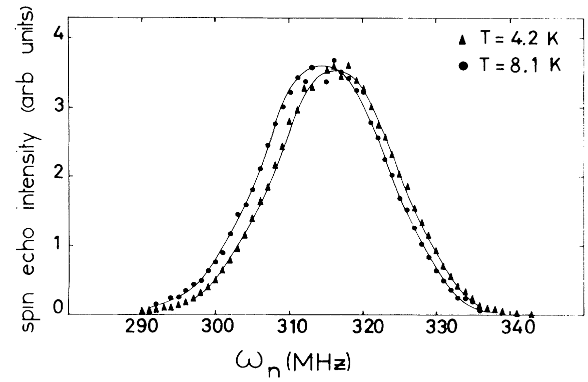

FIG. 3. T variation of the main NMR line in 9.6 at.% *Cu*Mn. An overall shift of the resonance is evidenced. The intensities have been normalized.

We shall mainly consider the most intense line of the spectrum, which has been found at $\omega_n = 317$ MHz in *Cu*Mn, down to the lowest c. It corresponds to ^{55}Mn nuclei for which the second term in Eq. (2) is small, as the linewidth is only slightly c dependent (Fig. 2). The large residual width obtained for $c \to 0$ ($\Delta\omega/\omega_n \sim 5\%$, Fig. 2) is dominated, as will be shown hereafter, by an anisotropic (orbital?) contribution to the single-ion hyperfine coupling. This large intrinsic width is unfortunately the main limitation of the experimental resolution. The other resonances, below 270 MHz, correspond to transferred hyperfine fields in excess of 50 kG, which can only be due to nearest-neighbor Mn atoms. A detailed study of this part of the spectra gives information on the chemical and magnetic short-range orders.[7]

As can be seen in Fig. 3, the main line, which corresponds to ^{55}Mn nuclei without nearest-neighbor Mn atoms, shifts to lower frequency with increasing T, without appreciable broadening. This means that the thermal reduction is not markedly site dependent, although its distribution cannot be deduced accurately because of the limited resolution. For instance, it would be impossible to account for the spectra of Fig. 3 by assuming that only 20% of the spins undergo a reduction while $|\langle \mathbf{S}_i \rangle| = S$ for the remaining 80%. This certainly excludes strongly localized excitations and would agree with the existence of extended modes.

In order to get a good accuracy on the T dependence of the resonance frequency $\hbar\omega_n = A_0 |\langle\langle \mathbf{S}_i \rangle\rangle_{\rm av}|$ (here $\langle\ \rangle_{\rm av}$ represents a site average), $\omega_n(4.2\text{ K}) - \omega_n(T)$ has been obtained by comparing two spectra taken at T and 4.2 K for a given value of M_r in the same experimental run. The sensitivity is limited at high T by the reduction of the spin-echo decay time. The data taken on the 9.6 at.% *Cu*Mn sample ($T_g \sim 45$ K) can be fitted with $\omega_n(T) - \omega_n(0) \propto T^\eta$ with $\eta = 2.0 \pm 0.4$. The best fit is, however, obtained for $\eta = 2$ as can be seen in Fig. 4.

As ω_n measures a short-time average of $|\langle \mathbf{S}_i \rangle|$, it certainly probes mainly intrawell excitations. We could then compare directly $\omega_n^2(T)/\omega_n^2(0)$ with the order paremeter $\tilde{q}(T) = (N_0 S^2)^{-1} \sum_i \langle S_i \rangle^2$ taken in a given energy well. The mean-field solutions of the Ising[8] and Heisenberg[9] spin-glass models yield $\tilde{q}(T) = 1 - \delta(T/T_g)^\eta$ with $\delta \sim 1$ and $\eta = 2$ (Ising) and $\eta = 1$ (Heisenberg) for infinite-range interactions.[2] In such infinite-range models no distinction between extended and localized modes can be made. We are not aware of any complete investigation of the excitations for finite-range models. However, for Ising spins, we would expect purely local excitations with a small fraction of spins experiencing small exchange fields,[2] and correspondingly a large thermal spin reduction. Although our data for $\tilde{q}(T)$ would agree with $\eta = 2$ and $\delta = 0.4$, the rather homogeneous spin reduction does not agree with this expectation. It would therefore be rather controversial from our point of view to

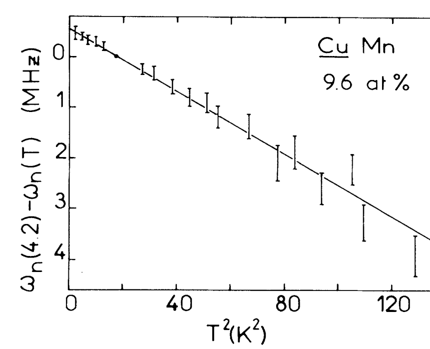

FIG. 4. The relative frequency deviation of the NMR line is plotted vs T^2. The full line represents the best linear fit.

associate the measured spin reduction with an Ising behavior induced for instance by anisotropic couplings in RKKY spin-glasses.

In the absence of theoretical advances beyond mean field in the relevant case of short-range Heisenberg models, it is natural to refer here to the realistic macroscopic approaches and to the numerical simulations introduced earlier. The zero-point-motion reduction ΔS_i^0 of Eq. (1) can be deduced from our data, as long as A_0S is known from other experiments. This can be obtained from nuclear orientation (NO) data taken in the saturated paramagnetic regime at about 10 mK, on very dilute (a few parts per million) ^{54}Mn dissolved in noble metals.[10] Although a reduction of ω_n is expected in the SG as compared to the paramagnet, no difference could be detected for *Ag*Mn and *Au*Mn (Table I). For *Cu*Mn, the larger value found in the SG state might be associated with incomplete saturation of the magnetization for NO data taken near the Kondo temperature $T_K \sim 10$ mK of Mn in Cu. Such a restriction does not hold for *Ag*Mn and *Au*Mn for which T_K is well below 1 mK.[13] Therefore, the accuracy of the NO data gives an upper limit of 2.5% for $\langle \Delta S_i^0 \rangle_{\mathrm{av}}/S$. With such a small average zero-point reduction, the residual width of Fig. 2 cannot be attributed to a distribution of ΔS_i^0, as a sizable fraction of sites would then correspond to $|\langle \mathbf{S}_i \rangle| > S$. This leads us to conclude that the residual linewidth is rather dominated by a small anisotropy of the single-ion hyperfine field.

The calculation of ΔS^T is easily achieved if we assume that the spin deviation $W_{i\nu}$, for a given excitation ν, is site independent and if we identify the excitations with magnons with a given dispersion relation. The anisotropy energy $-K\cos\theta$ can be included in the derivation of Halperin and Saslow and, in absence of remanence, three degenerate modes are obtained with[14] $h\nu = g\mu_B(\rho q^2/\chi + K/\chi)^{1/2}$, where χ is the isotropic spin-glass susceptibility. From ESR and transverse χ data, the corresponding anisotropy gap is $T_A = g\mu_B(K/\chi)^{1/2}/k_B \sim 0.5$ K for the present 9.6 at.% *Cu*Mn sample.[15] Therefore, above 1 K the anisotropy (and remanence in the present experimental conditions[14]) can be neglected, and the simple linear dispersion relation

$$\epsilon = h\nu = g\mu_B(\rho/\chi)^{1/2}|q| = \alpha |q| \tag{3}$$

is valid. We derive then

$$-\Delta S^T/S = (\chi N_0)^{-1} g^2 \mu_B^2 \textstyle\sum_\nu n_\nu / h\nu, \tag{4}$$

as for antiferromagnets. After integration for a density of modes

$$N(\epsilon) = (3N_0/8\pi^2 c)(a/\alpha)^3 \epsilon^2, \tag{5}$$

where a is the fcc lattice constant of Cu, we immediately obtain a T^2 dependence for $-\Delta S^T/S$ at low T, in agreement with the data of Fig. 4. With $\chi = 1.4\times 10^{-4}$ emu/g we deduce $\alpha = 12.6$ Å meV (or $\rho = 3.5$ meV). The deduced density of modes corresponds to a contribution $C_v/N_0 k_B = BT^3$ (with $B = 1.5\times 10^{-4}$ K^{-3}) to the specific heat, much smaller than the roughly linear in T, measured C_v. It is found quite comparable to the small T^3 term ($B = 1.16\times 10^{-4}$ K^{-3}) detected in a 10 at.% CuMn sample below 4.2 K.[16]

Therefore this implies that a large fraction of the modes which contribute to the low-T specific heat do not induce a detectable spin reduction. This would be the case for localized modes involving a small number of spins, which could escape observation, or for extra modes with long relaxation times (the NMR frequency is a short-time average of the magnetization, while C_v is measured on a long-time scale). In the latter case, which could be associated, for example, with activated processes, a time-dependent contribution to C_v should be detected. Further advances on this point rely upon a detailed knowledge of the dynamical properties of spin-glasses in this very-low-T range ($T \lesssim 0.2T_g$).

As for simulation experiments, although the data of WW for $N(\epsilon)$ are not accurate enough for low ϵ to support the existence of propagating magnons, similar computations for three-dimensional XY and planar models clearly yield $N(\epsilon) \sim \mu\epsilon^2$, where μ is further found in agreement with the stiffness computed independently.[17] Walstedt[18] has also calculated, for $c = 0.9\%$, both the bare stiffness ρ_b obtained by application of a uniform orientational gradient to an equilibrium spin configuration and the relaxed stiffness ρ_r obtained after spin reorientations and energy minimization. Scaling tentatively our data for ρ as $c^{4/3}$ yields a value comparable to ρ_b, while ρ_r would correspond to a spin deviation an order of magnitude larger than measured here. Such a large rigidity of the spin system on short times is not surprising in view of the excellent agreement found experimentally at $T << T_g$ with rigid-rotation models at $q = 0$.[1] We can then naturally wonder whether a counterpart of the experimental time scale can be introduced in the computer

TABLE I. ^{55}Mn NMR frequency in megahertz and NO data (Ref. 10) for the maximum value $\omega_n = A_0 S/\hbar$. The data of Ref. 10 have been slightly corrected, taking into account $\gamma^{54}/\gamma^{55} = (1.258 \pm 0.3)\%$ given by NMR/ON and NMR data (Ref. 11) in *Fe*^{54}Mn and *Fe*^{55}Mn, and the most recent value $\gamma^{55}/2\pi = 1.050$ kHz/G (Ref. 12).

Alloy	*Cu*Mn	*Ag*Mn	*Au*Mn
Spin glass (NMR) $T \lesssim 0.1T_g$	317 ± 1	348 ± 2	417 ± 2
Saturated paramagnet (NO)	296 ± 10	346.5 ± 6	422 ± 10

algorithms for $N(\epsilon)$ and ρ, which should also, as proposed recently[19] be a time-dependent property. Furthermore, a harmonic and Bose approximation is expected to fail for large times and large energy, certainly for $h\nu \sim k_B T_g$. This might explain why the zero-point spin reduction $\Delta S/S \sim 6\%$ for $S = \frac{5}{2}$ given by WW, which involves the whole excitation spectrum [Eq. (1)], is much larger than our upper estimate. It is not clear to us whether the computed $N(\epsilon)$ for the high-energy localized modes directly bears on this approximation.

In conclusion, the present ^{55}Mn NMR experiment has allowed a quite novel study of the local spin reduction in RKKY spin-glasses. Although the measured T^2 dependence of $\Delta S/S$ for $T < 0.2 T_g$ agrees with mean-field theory for Ising spins and infinite-range interactions, it is found in quite good agreement as well with expectations for magnons with a linear dispersion relation. Within this realistic approach, the approximate site independence of $\Delta S(T)$ and its small magnitude, imply a large stiffness for the spin system, at least for short times and in the long-wavelength limit. Further investigations are required in order to confirm the validity of this analysis, which revives the idea[20] that, as in glasses, harmonic processes coexist in SG with other excitations which dominate C_v at low T.

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