REPRINTED FROM

journal of
magnetism
and
magnetic
materials

Volumes 15–18, Part II, January–March 1980

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pp. 681–682

NORTH-HOLLAND
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F^{19} NMR STUDY OF DISORDERED PARAMAGNETS $KMg_{1-x}Mn_xF_3$

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F^{19} NMR was studied in mixed crystals $KMg_{1-x}Mn_xF_3$ (x form 0.9 to 0.01) with the purpose of elucidating the electronic spin dynamics in a disordered paramagnet. Information is obtained about the spin correlation function of both the Mn ions belonging to the infinitely exchange-connected ensemble and to the ones belonging to isolated clusters.

In a previous communication [1] it was shown that measurements of the nuclear spin lattice relaxation rate T_1^{-1} and the linewidth of ^{19}F in $KMg_{1-x}Mn_xF_3$ mixed magnetic insulators afford a potentially powerful tool to investigate the spin dynamics in a disordered paramagnet. In the above system three well resolved ^{19}F resonances are observed, whose relative intensities are a function of x, which were identified as I_0, I_1 and I_2. These are associated according to the number of Mn^{2+} nearest neighbors (nn) to a given ^{19}F nucleus: I_0—no nn, I_1—one nn, I_2—two nn, with paramagnetic shifts of approximately 0, 1 and 2%, respectively, relative to the ^{19}F NMR in $KMgF_3$ [1].

The nuclear relaxation rate arising from the hyperfine and/or dipolar coupling to the magnetic ions is given in general by expressions of the form:

$$\frac{1}{T_1} = \sum_{j,j'} \alpha_j^{\pm,z} \alpha_{j'}^{\pm,z} \times \int_{-\infty}^{+\infty} \langle S_j^{\pm,z}(t) S_{j'}^{\pm,z}(0) \rangle \exp(-i\omega_{S,N} t)\, dt \tag{1}$$

with a similar expression for $1/T_2$. Here $\alpha_j^{\pm,z}$ are the tensor components of the appropriate hyperfine and/or dipolar interaction between the nucleus and the jth spin S_j and ω_S, ω_N are the electronic and nuclear Larmor frequencies, respectively.

The relaxation rate of the I_1 signal, in which the dominant interaction is the transferred hfs coupling to a single Mn^{2+} nn, becomes a direct measure of the zero frequency spectral density of the autocorrelation function ($j = j'$) in this random paramagnet. The experimentalal results for the linewidth δH of the I_1 resonance, extrapolated to $H = 0$ in order to eliminate inhomogeneous sources of broadening, are shown in fig. 1. Since the electronic spin fluctuations are fast and isotropic one has $\delta H \propto T_2^{-1} = T_1^{-1}$. The experimental results shown in fig. 1 give a direct evidence for the low frequency enhancement of the spectral density of the spin fluctuations in qualitative agreement with the theoretical predictions [2]. A quantitative comparison of theory and experiments was attempted by assuming for long times an autocorrelation function of the type $t^{-\alpha(x)}$ where the concentration dependent exponent $\alpha(x)$ was chosen to agree with the computer results by Klenin and Blume [3]. The short time behaviour was calculated by a moment expansion and matched to the long time behavior [4]: the long time behavior was truncated at a cut-off frequency ω_c in order to remove divergencies. The experimentally determined cut-off time $\omega_c^{-1} \approx 10^{-11}$ s is considerably longer than the exchange time $\omega_{ex}^{-1} \approx 2 \times 10^{-13}$ s which characterizes the decay of the correlation function in the undiluted paramagnet.

We turn now to the spin–lattice relaxation of the I_0 resonance. As previously [1] observed, the

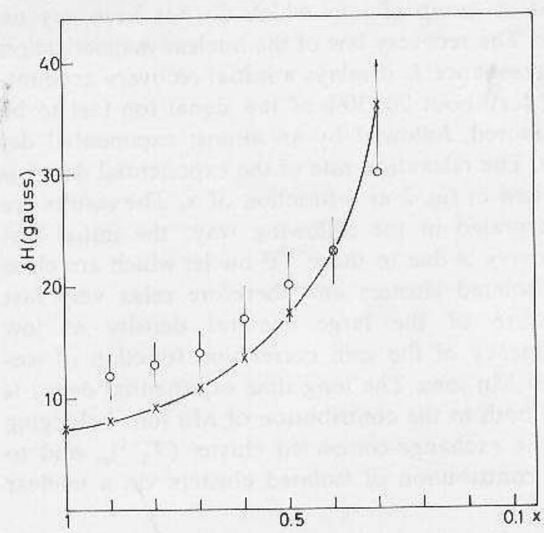

Fig. 1. (O) Zero field extrapolated linewidth of the ^{19}F resonance I_1 in $KMg_{1-x}Mn_xF_3$ as a function of Mn concentration. The crosses and the interpolation curve represent the results of the theoretical calculation described in the text.

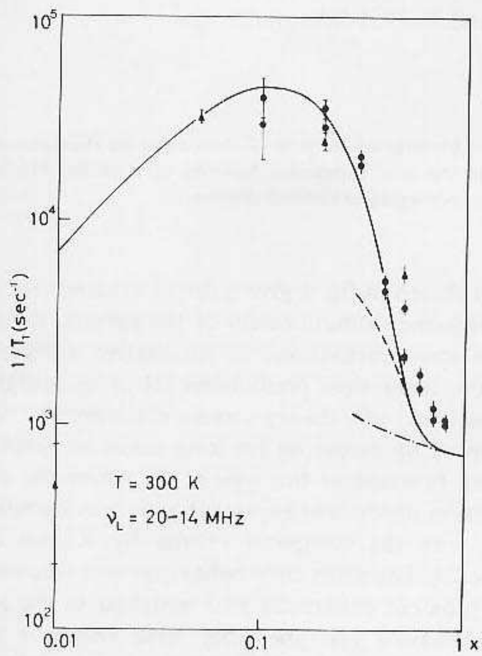

Fig. 2. Log–log plot of the relaxation rate for the [19]F nuclei of resonance I_0 in $KMn_xMg_{1-x}F_3$ (●) and $Zn_{1-x}Mn_xF_2$ (▲) as a function of Mn concentration. (–·–·–) Theoretical estimate for the contribution $(T_1^{-1})_{ex}$. Total theoretical estimate in the "diffusion limited" case, (______) and in the "diffusion vanishing" case (______).

$I_0T_1^{-1}$ is dominated by the interaction of the [19]F nuclei with isolated clusters of Mn^{2+} ions namely ions or group of ions which do not have any nn Mn. The recovery law of the nuclear magnetization of resonance I_0 displays a initial recovery accounting for about 20–30% of the signal too fast to be measured, followed by an almost exponential decay. The relaxation rate of the exponential decay is plotted in fig. 2 as a function of x. The results are interpreted in the following way: the initial fast recovery is due to those [19]F nuclei which are close to isolated clusters and therefore relax very fast because of the large spectral density at low frequency of the spin correlation function of isolated Mn ions. The long time exponential decay is due both to the contribution of Mn ions belonging to the exchange-connected cluster $(T_1^{-1})_{ex}$ and to the contribution of isolated clusters via a nuclear spin-diffusion mechanism $(T_1^{-1})_D$. The term $(T_1^{-1})_{ex}$ was calculated by considering the dipolar coupling of [19]F nuclei with Mn ions second nn and using for the spectral densities of the auto correlation functions the values calculated with the method described above for resonance I_1. The results for this contribution are shown in fig. 2. In order to calculate the main contribution $(T_1^{-1})_D$ we treat the isolated Mn ions as relaxing centers. For $x < 0.8$ the parameters are such that the solution to the problem of nuclear spin diffusion relaxation for the so-called "diffusion vanishing" case can be used. Lowe and Tse [5] found that in the limit of long times the nuclear magnetization decay exponentially with a relaxation rate given by:

$$(1/T_1)_D = \bar{\lambda}_0 \bar{C} N^2 + \bar{\lambda}(\bar{C}D)^{\frac{1}{4}} N^{\frac{4}{3}}, \qquad (2)$$

where $\bar{\lambda}_0 \approx 2$ and $\bar{\lambda} \approx 50$, N is relaxing centre concentration, D is the nuclear spin diffusion constant and $\bar{C}$ is an average interaction constant $\bar{C} \propto \tau_c^0 x^{-\frac{1}{2}}$. The correlation time τ_c^0 for the isolated Mn spin was computed as a spin–lattice relaxation due to the exchange modulated electron–electron dipolar interaction: $\tau_c^0 = 0.8 \times 10^{-8}$ s. For $0.8 < x < 1$ the solution for the "diffusion vanishing" case shouwl be replaced by the "diffusion limited" case [6] with the results of the two coinciding in this concentration range. The theoretical calculation for $(T_1^{-1}) = (T_1^{-1})_{ex} + (T_1^{-1})_D$ without adjustable parameters compares very well with the experiments as shown in fig. 2.

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