Exchange Narrowing in One-Dimensional Systems

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Magnetic relaxation in one-dimensional exchange-coupled $(CH_3)_4NMnCl_3$ is found to be dramatically different than it is in three-dimensional exchange-narrowed paramagnets. A theory which accounts properly for the special long-time persistence of spin-correlation functions in one dimension is shown to explain the observed behavior.

We demonstrate here the dominant role of dimensionality in the spin dynamics of exchange-coupled systems as reflected in their magnetic-resonance properties. We have studied the Mn^{++} EPR in single crystals of the one-dimensional[1] antiferromagnet $(CH_3)_4NMnCl_3$ (TMMC). Although the Mn spins are strongly exchange coupled, the form of the line shape, the magnitude of the linewidth, and the anisotropy of both with magnetic field direction differ sharply from the predictions of standard three-dimensional exchange-narrowing theory. We can explain quantitatively each of these anomalous experimental results by taking account of the special long-time persistence of spin correlations in one dimension.

The single-crystal samples of TMMC used were grown from solution[2] and ground in the form of thin disks with a diameter-to-thickness ratio greater than 10. The c axis of the sample lay in the plane of the disk. Measurements were made at 24 GHz (K band) using a spectrometer consisting of a frequency source stabilized on an external cavity, a reflection-type cavity with variable coupling, and a crystal detector. A cylindrical TE_{011} cavity was used and the dc absorption signal recorded directly. In all cases the samples were oriented such that the dc magnetic field (H_{dc}) could be rotated in the plane, with the microwave field always perpendicular to the plane of the disk.

The half-power linewidth ΔH, obtained from the resonance data at 297°K, versus the angle θ (between H_{dc} and the c axis) is shown in Fig. (1) for 24.031 GHz. The X-band data were found to be almost identical, indicating the essential frequency independence of ΔH in this region. There is a small error in the linewidths in Fig. (1) since the microwave absorption signal was large enough to detune the cavity even when using the smallest practical sample size (~1.8 mm in diameter). However, a few profiles were recorded point by point where the oscillator frequency was adjusted to the cavity resonance at each H_{dc} setting. These line shapes were symmetric and centered about a value of $g = 2.01$. As seen in Fig. (1), the resulting linewidths (labeled "best data linewidths") do not differ greatly from those recorded without resetting the oscillator. At $\theta = 0$ ($H_{dc} \| c$), the observed linewidth is a factor of 5 larger than predicted by exchange-narrowing theory. Even more disturbing is the observation that the anisotropy of ΔH is in total disagreement with the $(1 + \cos^2\theta)$ dependence[3] of that theory.

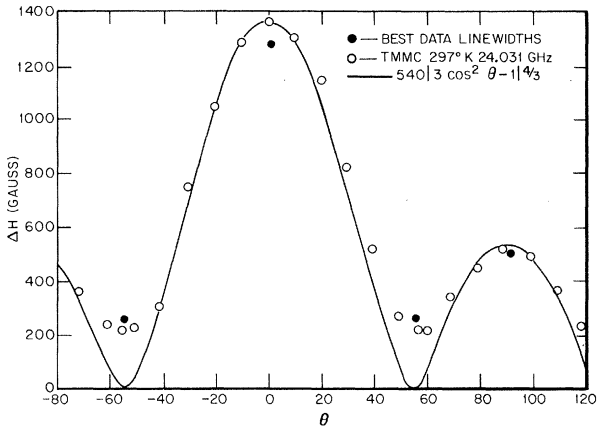

FIG. 1. The anisotropy of the full width at half-power, ΔH, of the K-band EPR absorption in TMMC at 297°K. Here θ is the angle between the linear-chain axis and the applied field.

The detailed line shapes observed at the extrema of the ΔH-vs-θ curve in Fig. (1) are shown in Fig. (2). To avoid distortion of the true line shape, the spectrometer was carefully adjusted to ensure square-law detection over the complete range of absorption levels. At $\theta = 0°$ and $\theta = 90°$, the shape departs significantly from the Lorentzian ordinarily expected. However, the line *is* Lorentzian at $\theta = 54°$ (where $3\cos^2\theta - 1 = 0$).

Low-temperature studies indicate that there is no significant change in the line shapes with temperature above about 80°K. Thus the data reported at 297°K may be considered representative of the infinite-temperature limit. The consequences of the strong one-dimensional correlations that occur below 80°K will be discussed in a subsequent publication.

In spite of the large ratio (~10-100) of exchange to dipolar fields in TMMC, the linewidth and line-shape evidence presented above cannot be understood in terms of standard exchange-narrowing theory. These failures are particularly striking in light of the detailed success[3] of the theory in explaining paramagnetic resonance in three-dimensional systems. To understand the source of this difficulty, we examine the basic ideas of exchange-narrowing theory. Kubo has shown[4] that, if relaxation is governed by a Gaussian random process,[5] then the relaxation function $\varphi(t)$ (which is the Fourier transform of the line shape) has the form

$$\varphi(t) = \exp[-M_2 \int_0^t (t-\tau)\psi(\tau)d\tau], \qquad (1)$$

where $M_2 = \frac{1}{2}\ddot{\varphi}(0)$ is, by definition, the second frequency moment of the resonance line. Here $\psi(\tau)$ is the normalized $[\psi(0) = 1]$ correlation function between torques on the spins by the perturbing Hamiltonian H'. In the present case H' is the dipolar Hamiltonian and $\psi(\tau)$ is a sum of four-spin correlation functions of the form[6] $\langle S_{i+}(t) \times S_{jz}(t) S_{lz}(0) S_{m-}(0)\rangle$.

In the standard theory,[7] a finite correlation time $\tau_c \sim 1/\omega_e$, defined by $\tau_c = \int_0^\infty \psi(\tau)d\tau$, is assumed to exist, so that for times $t \gg \tau_c$ the integral in Eq. (1) is proportional to t. This exponential time dependence of $\varphi(t)$ implies a Lorentzian line shape. (Since usually the relaxation rate $M_2\tau_c \ll \tau_c^{-1}$, the line is Lorentzian throughout the region of experimental interest.) However, if $\psi(\tau)$ is governed by diffusion processes at long times ($\psi \sim \tau^{-d/2}$, where d is the dimensionality of the system), then in a one-dimensional system τ_c as defined above diverges, and both the central line shape and the width are given incorrectly by the standard theory.

Previous studies of NMR linewidths[3] and hyperfine contributions to EPR linewidths,[8] where $\psi(\tau)$ contains only simple two-spin correlation functions, indicate that the assumption of long-time diffusive behavior is essential to a proper interpretation of the data. We expect[9] that the more complex four-spin correlation functions of the dipolar problem will also exhibit long-time diffusive behavior. From Eq. (1) the consequent $\tau^{-1/2}$ asymptotic dependence of $\psi(\tau)$ leads[8] to a line shape which is the Fourier transform of $\exp(-A \times t^{3/2})$, intermediate between Gaussian and Lorentzian, as shown in Fig. (2). With this single diffusive assumption we obtain a universal curve with only one free scale parameter, the full width at half-maximum. The agreement with experiment when $H_{dc} \| c$ is striking.

The same simple model explains the angular anisotropy in both width and line shape. The time dependence of the operators in $\psi(\tau)$ is governed by the unperturbed (nonfluctuating) Hamiltonian —i.e., exchange plus Zeeman interactions. The former leads to decay of $\psi(\tau)$ (assumed above to be diffusive) at long times, but in general this is also sinusoidally modulated at integral multiples of the Zeeman frequency ω_0. In this regard it is convenient to make the standard separation of $\psi(\tau)$ into terms coming from the secular part of the dipolar Hamiltonian $[\sim(3\cos^2\theta - 1)(\vec{S}\cdot\vec{S} - 3S_zS_z)]$, whose Zeeman time dependence vanishes, and those from the nonsecular part, with time dependence $\exp(-i\Delta M\omega_0 t)$, where $\Delta M \neq 0$ is the change

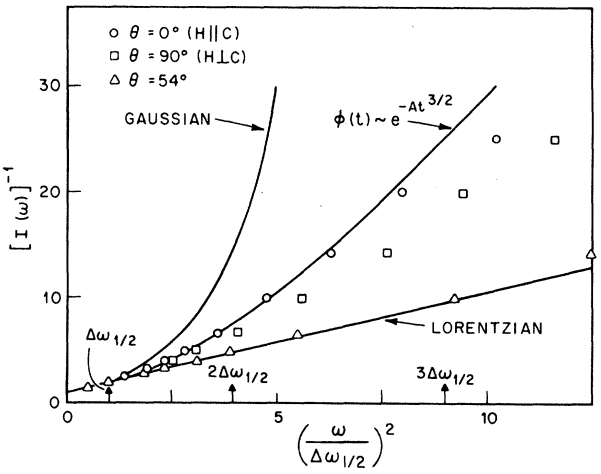

FIG. 2. The inverse of the line profiles for the points labeled "best data linewidths" in Fig. 1. Frequency is given in units of half-width at half-power, $\Delta\omega_{1/2}$. The parameter A in the expression for φ sets the absolute frequency scale.

in magnetic quantum number associated with the spin operators in these terms. The modulation in the nonsecular terms washes out the anomalous contribution from the long-time diffusive tail. These terms then contribute a simple exponential to $\varphi(t)$. Thus

$$\varphi(t) \sim \exp[-A_1(3\cos^2\theta-1)^2 t^{3/2} - A_2 f(\theta) t]. \quad (2)$$

The dominant term in the exponent at most angles θ is the first one, in which the time t is scaled by $|3\cos^2\theta-1|^{4/3}$, and this is the principal angular dependence of the linewidth, as indicated in Fig. 1. The line shape is particularly simple at $\theta=0$, where $f(\theta)\propto\sin^2\theta$ vanishes [so $\varphi(t) = \exp(-4A_1 t^{3/2})$] and at $\theta=54°$, where $3\cos^2\theta-1=0$, so that we find a pure Lorentzian. The remarkable agreement of these predictions with experiment is shown in Fig. 2.

The only appreciable magnetic field dependence should be found at sufficiently low fields ($H_{dc} < \Delta H$). Then the Zeeman modulation of $\psi(\tau)$ sets in at such long times that the line shape at $\theta=54°$ will deviate increasingly (as H_{dc} is reduced) from a Lorentzian, with corresponding changes in linewidth anisotropy.

We can go further than this qualitative understanding of the experiments; we can calculate the *magnitude* of the linewidth. Determination of the second moment of M_2 is standard and straightforward.[10] The diffusion time ($\sim\hbar/J$) can also be estimated[11] from moment calculations. Proceeding as in Ref. (3) and using a value of $J=7.7°K$,[1] we find 1500 G for the full width at half-maximum for $\varphi=0°$ ($H_{dc}\|c$), in excellent agreement with experiment.

Thus the EPR measurements in TMMC can be understood only by recognizing the central importance of the long-time persistence of spin correlations for spin dynamics in less than three dimensions. With this long-wavelength, low-frequency probe of spin correlations we have independently obtained results as uniquely characteristic of the reduced dimensionality as those of neutron scattering. We have explained the magnitude of the linewidth, its dependence on magnetic field orientation, and the variation in line shape with field direction, all of which contrast sharply with exchange-narrowed resonance behavior in three dimensions.

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[1]Recent neutron-scattering experiments [R. J. Birgeneau, R. Dingle, M. T. Hutchings, G. Shirane, and S. L. Holt, Phys. Rev. Lett. 26, 718 (1971)] have revealed ideal one-dimensional behavior in TMMC with no detectable interchain exchange or dipolar interactions down to 1.1°K.

[2]R. Dingle, M. E. Lines, and S. L. Holt, Phys. Rev. 187, 643 (1969).

[3]J. E. Gulley, D. Hone, D. J. Scalapino, and B. G. Silbernagel, Phys. Rev. B 1, 1020 (1970).

[4]R. Kubo, in *Fluctuation, Relaxation, and Resonance in Magnetic Systems*, edited by D. ter Haar (Plenum, New York, 1962).

[5]Higher-order corrections to the form (1) are associated with successive terms in a cumulant expansion [see, e.g., Ref. 4, and M. Blume and J. Hubbard, Phys. Rev. B 1, 3815 (1970)], and we neglect them here. They vanish identically for a Gaussian random process. This is of some concern in a one-dimensional system, where the dominant independent perturbation sources include only the two nearest neighbors (as opposed to six or more in three dimensions). The random process may then be more accurately described as Markoffian than Gaussian.

[6]F. Carboni and P. M. Richards, Phys. Rev. 177, 889 (1969).

[7]P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. 25, 269 (1953).

[8]C. D. McElwee and P. M. Richards [Bull. Amer. Phys. Soc. 15, 269 (1970), and to be published; see also, C. D. McElwee, thesis, University of Kansas, 1970 (unpublished)], have independently made use of a diffusion argument to predict anomalously large hyperfine broadening of EPR in one-dimensional copper tetramine sulphate. Again the $\tau^{-1/2}$ behavior of the $\psi(\tau)$ and $\exp(-t^{3/2})$ form of $\varphi(t)$ are important.

[9]Briefly, arguments for diffusion include (i) a simple random-walk picture of the dynamics; (ii) numerical results in finite linear chains (see Ref. 6); and (iii) decoupling (factorization) of the four-spin correlation functions, leading to diffusive behavior. This last approach is supported by a comparison of two- and four-spin correlation functions in the exactly soluble *XY* model.

[10]J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

[11]See, e.g., R. A. Tahir-Kheli and D. G. McFadden, Phys. Rev. 178, 800 (1969).