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Electron-spin resonance in the impurity-doped Heisenberg linear chain $(CH_3)_4NMnCl_3$:Cu[†]

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The room-temperature 23.4-GHz electron-spin-resonance linewidth and line shape are reported in a linear-chain crystal of $(CH_3)_4NMnCl_3$ (TMMC) containing 4-at.% Cu^{++} substituted for Mn^{++}. The width at $\theta = 0$ is 50% greater than for pure TMMC but is the same as in pure TMMC at $\theta = 55°$, where θ is the angle of applied field with respect to the chain axis. The line shapes are the same in pure and impure TMMC at both angles. These results are explained in terms of a model in which the only effect of impurities is to alter the rate of diffusion along the chain. The slower diffusion produces a marked increase in width at $\theta = 0°$, where long-time effects dominate the one-dimensional ($1d$) spin dynamics, but has no effect at the "magic angle" ($\theta = 55°$, $3\cos^2\theta - 1 = 0$), where there is no secular contribution to the broadening and thus the $1d$ character is unimportant. A continuum calculation is presented in which an impurity is replaced by a region in which the diffusion coefficient is D', compared with the host value D. The line shape is not altered in this model, in agreement with experiment, and the width, compared with pure TMMC, is related to D'/D. A relation is then assumed between D'/D and J'/J from which we estimate $|J'/J| = 0.06$, where J' and J are impurity-host and host-host intrachain interactions, respectively.

I. INTRODUCTION

Exchange-narrowed electron-spin resonance (ESR) has markedly different characteristics in low-dimensional systems than in three-dimensional ($3d$) systems. The differences are reflected in the magnitude of the linewidth ΔH, the angular dependence of ΔH, and the line shape and have been well-documented experimentally in both quasi-$1d$ and quasi-$2d$ materials.[1-3] Theories in terms of diffusive motion for the spin dynamics have generally been successful in giving quantitative interpretation to the results.

The effects are particularly strong in $1d$, where a physical explanation is also quite clear. The possible paths of diffusion are severely limited for $1d$ so that the rate at which spin polarization decays is greatly reduced compared with $3d$. A consequence of this persistence of spin correlation for long times is that exchange narrowing,[4-6] which occurs because of rapid fluctuations which tend to average the line-broadening mechanism (typically the dipole-dipole interaction) to zero, is much less effective in $1d$.

In the above context, it is particularly interesting to study the influence of a relatively small concentration of impurities on ESR in $1d$. Since the diffusion path cannot avoid an impurity placed on the chain, we expect impurities to have a far more pronounced effect in $1d$ than in $3d$ or $2d$. Hone and Petzinger[7] did a theoretical study of spin dynamics in impure chains and calculated the NMR width for two limiting cases: (i) diamagnetic impurities and (ii) paramagnetic impurities with rapid spin-lattice relaxation. In either case a simplification occurs since there is no diffusion across the impurity site so that only independent chains of finite length need be considered. In case (i), which is more nearly related to our studies of Cu^{++} in $(CH_3)_4NMnCl_3$ (TMMC), the impurities act as perfectly reflecting boundaries and therefore the spin polarization can never completely diffuse away. Consequently, the effective rate of decay of the spin correlations is slower than in an infinite $1d$ system, and exchange narrowing thus should be less effective.

In Sec. II we report room-temperature ESR measurements on a single crystal of TMMC in which 4 at.% of the Mn^{++} ions have been replaced by Cu^{++}, and on a single crystal of pure TMMC for comparison. TMMC is probably the best-documented and most nearly ideal quasi-$1d$ system with transition-metal-ion paramagnetism (as opposed to the organic solids) and thus is the logical choice for host crystal. The selection of Cu, rather than a diamagnetic ion, as the impurity was based strictly on availability of this particular mixed crystal. The linewidth at $\theta = 0°$ (θ is the angle of applied field with respect to the chain axis) is 50% greater in TMMC:Cu than in pure TMMC, but the linewidths are the same at $\theta = 55°$ ($3\cos^2\theta - 1 = 0$). Line shapes are also the same at both angles.

The theory of Hone and Petzinger is extended in Sec. III to a treatment of the ESR line and to the case, appropriate to Cu^{++}, of impurities which are not perfect reflectors. We find that all the observed features are consistent with this model, whose adjustable parameter is the Cu-Mn exchange interaction. The conclusions in Sec. IV reemphasize the relative importance of impurities in $1d$ and point out that ESR studies of this type give strong additional comfirmation of the effects of long-time diffusive decay in low-dimensional systems.

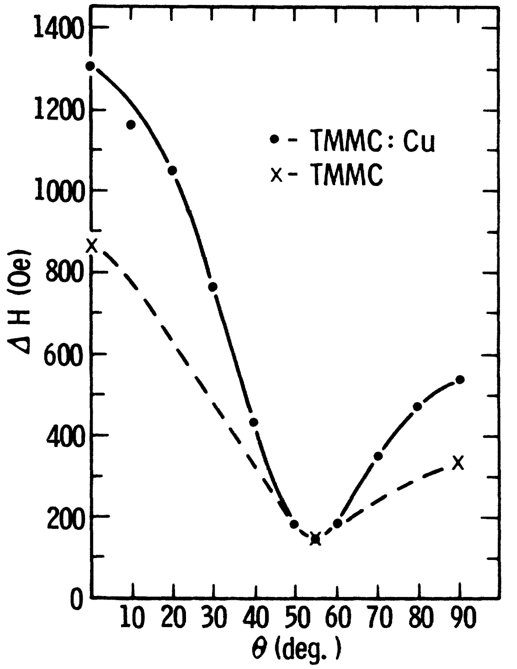

FIG. 1. Peak-to-peak derivative linewidth ΔH vs angle θ of applied field with respect to chain axis. Curves are aids to eye only. Data are for room temperature, 23.4 GHz.

II. EXPERIMENT

Measurements of the ESR absorption derivative were performed at room temperature in a conventional K-band spectrometer at 23.4 GHz. Approximately the same size single crystals of TMMC : Cu and pure TMMC were used. The former crystal, which was grown by R. Dingle of Bell Laboratories, had a molar Mn : Cu ratio of 24 : 1 according to chemical analysis.

Figure 1 shows angular dependence of the peak-to-peak derivative linewidth. The values for pure TMMC, grown from solution at this laboratory, are in agreement with previous measurements.[1] The salient feature, to be discussed in Sec. III, is that TMMC : Cu has a 50% greater ΔH at $\theta = 0^\circ$ but the same width at $\theta = 55^\circ$. In Fig. 2 we plot the line shapes at $\theta = 0^\circ$ and 55°. For a Lorentzian shape, the quantity $|(H - H_0)/I(H)|^{1/2}$, where $I(H)$ is the absorption derivative at the field H and H_0 is the resonance field, is a straight line when plotted versus $(H - H_0)^2$. As treated elsewhere[1] (see also Sec. III), a Lorentzian shape is expected for $\theta = 55^\circ$ whereas, for a pure chain, the absorption at $\theta = 0^\circ$ is the Fourier transform of $e^{-t^{3/2}}$. The resulting $|(H - H_0)/I(H)|^{1/2}$, when $I(H)$ is the derivative of the Fourier transform of $e^{-t^{3/2}}$, is shown as the solid curve in Fig. 2. We see that the pure and impure crystals have identical line shapes, within experimental error, which conform to the theory for a *pure* (infinite) chain.

III. THEORY

A. General theory of ESR in linear chains

We review below the pertinent theory[1,4,8] of line shape as applied to a linear chain, either pure or impure. The exchange-narrowed ESR line in a low-dimensional system appears to be adequately described by the Kubo-Tomita formula[4,9]

$$\frac{\chi''(\omega)}{\omega} \propto \mathfrak{F}\left[\exp\left(-\int_0^t d\tau\,(t-\tau)g(\tau)\right)e^{-i\omega_0 t}\right], \quad (1)$$

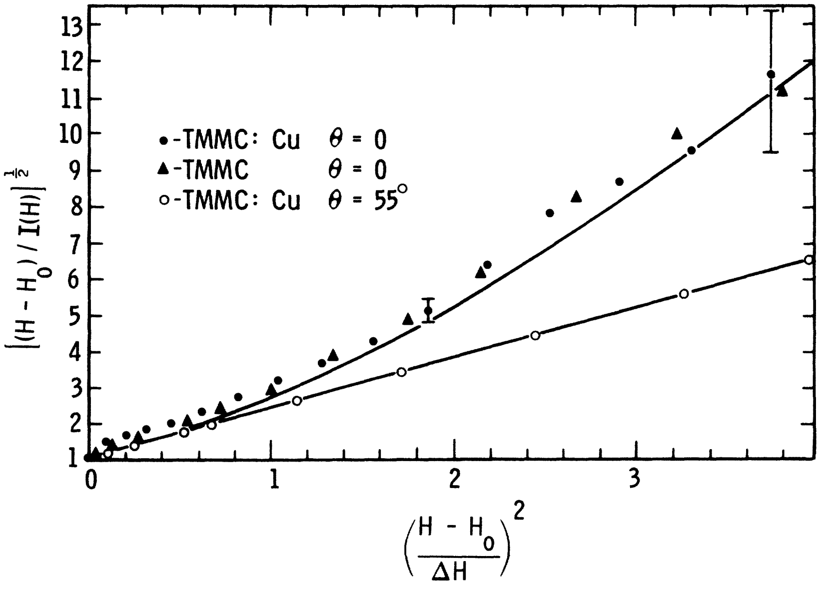

FIG. 2. Line shape data. Straight-line plot is indicative of Lorentzian line shape observed in both TMMC : Cu and pure TMMC (not shown) at $\theta = 55^\circ$. Curve is theoretical line shape for pure 1d chain at $\theta = 0^\circ$; $I(H)$ is the derivative of $\mathfrak{F}\{e^{-t^{3/2}}\}$.

where $\chi''(\omega)$ is the absorption at frequency ω, the symbol $\mathfrak{F}$ indicates Fourier transform at the frequency ω, and ω_0 is the angular resonance frequency. The quantity $\exp[-\int_0^t d\tau\,(t-\tau)g(\tau)]$ is the relaxation function, and its characteristic decay time and functional dependence determine the width and shape of the line. The relaxation function is governed by the spin-time-correlation function $g(\tau)$ which has the form

$$g(\tau)=\sum_M g_M(\tau)\,e^{iM\omega_0\tau}, \tag{2}$$

where $g_M(\tau)$ is related to that part of the line-broadening dipolar perturbation which produces a change M in Zeeman quantum number. Time dependence of $g_M(\tau)$ is with respect to the exchange modulation only. Modulation at the Zeeman frequency is explicitly accounted for by the $e^{iM\omega_0\tau}$ factors.

The basic features of line shape and angular dependence of ΔH in 1d may be seen from the following arguments. If the spin dynamics are diffusive, then $g_M(\tau)\propto\tau^{-1/2}$ for long times. (This follows from the familiar result that the decay of particle density at the origin is proportional to $\tau^{-d/2}$ for classical diffusion, assuming an initial distribution confined to the origin.) The $M=0$ integral does not converge at the upper limit and is given by

$$\int_0^t (t-\tau)g_0(\tau)\,d\tau=\tfrac{4}{3}g_0(0)\,\tau_c^{1/2}t^{3/2}, \tag{3}$$

for $t\to\infty$, where the asymptotic form $g_0(\tau)=g_0(0)\times(\tau_c/\tau)^{1/2}$ has been assumed. The $M\neq 0$ integrations do, however, converge at the upper limits if $\omega_0 t\gg 1$, which is true for times of interest as long as $\omega_0 T_2\gg 1$ where T_2 is the decay time of the relaxation function. Hence we have, for $t\gg\tau_c$

$$\begin{aligned}\int_0^t d\tau\,(t-\tau)\sum_{M\neq 0} g_M(\tau)\,e^{i\omega_0\tau}\\ \approx t\int_0^\infty d\tau\sum_{M\neq 0} g_M(\tau)\,e^{i\omega_0\tau}=\eta t,\end{aligned} \tag{4}$$

where η is an appropriate relaxation rate which is of the order of $\sum_{M\neq 0}g_M(0)\tau_c$. (We assume that all g_M have the same characteristic decay time of the order of τ_c.)

The results (3) and (4) applied to (1) then show that

$$\frac{\chi''(\omega)}{\omega}\propto\mathfrak{F}\{\exp[-A(\theta)\,\tau_c^{1/2}t^{3/2}-B(\theta)\,\tau_c t]\,e^{-i\omega_0 t}\}, \tag{5}$$

where $A(\theta)$ and $B(\theta)$ are constants which have an angular dependence discussed below. Since the correlation time τ_c is of the order of $\hbar/J\ll T_2$ (J is the exchange interaction), we have $\tau_c\ll t$ in the region of interest so that the $t^{3/2}$ term dominates as long as $A(\theta)$ and $B(\theta)$ are comparable in size. The function $A(\theta)$ is proprotional to the $M=0$ (secular) part of the dipole interaction and is therefore given by

$$A(\theta)\propto(3\cos^2\theta-1)^2, \tag{6}$$

where θ is the angle of the applied field with respect to the chain axis. Hence the 1d line shape is given by the Fourier transform of $e^{-t^{3/2}}$ and the width shows a $|3\cos^2\theta-1|^{4/3}$ dependence. [From (5) it is evident that the decay rate T_2^{-1} is proportional to $|A(\theta)|^{2/3}$ in the region where $t^{3/2}$ is dominant.] At the "magic angle"—where $3\cos^2\theta-1=0$, $\theta\approx 55°$—$A(\theta)$ vanishes so that the line is Lorentzian (Fourier transform of e^{-t}). The angular dependence and line shape have been verified[1] in TMMC.

For further discussion it is necessary to write the specific form of $g_0(\tau)$ for classical dipolar coupling in a linear chain,

$$\begin{aligned}g_0(\tau)=\frac{9}{8}\,\frac{\gamma^4\hbar^2}{c^6}\,\frac{(3\cos^2\theta-1)^2}{N}\sum_{ij}{}'\sum_{kl}{}'\,|i-j|^{-3}\\ \times|k-l|^{-3}\,\langle S_i^z(\tau)S_j^+(\tau)S_k^z(0)S_l^-(0)\rangle\Big/\sum_i\langle S_i^{z^2}\rangle,\end{aligned} \tag{7}$$

where γ, the gyromagnetic ratio, is taken to be the same for all spins on the chain, $\vec{S}_i$ is the spin at the ith site on the chain, and N is the total number of sites separated by a distance c. Primes on the summations indicate $i\neq j$ and $k\neq l$, and the denominator $\sum_i\langle S_i^{z^2}\rangle$ assumes infinite temperature.

A major problem is the presence of four spin-time-correlation functions. These have generally been handled by the decoupling approximation,

$$\langle S_i^z(\tau)S_j^+(\tau)S_k^z(0)S_l^-(0)\rangle=\langle S_i^z(\tau)S_k^z(0)\rangle\,\langle S_j^+(\tau)S_l^-(0)\rangle, \tag{8}$$

whose validity is somewhat difficult to assess since there exist no exact results upon which to base comparison. Recent computer studies of classical spin dynamics in a linear chain,[10] however, suggest that the decoupling may be fairly reasonable, though not exact. We will assume Eq. (8) to hold henceforth.

B. Pure chains

In this part we derive an expression for $g_0(\tau)$ in a pure infinite chain which is cast in the form of Eq. (16) which we show in Sec. IIIC to be valid for the impure chain as well. For the pure chain in which each site i is occupied by the same type of spin S, it is convenient to work in terms of the wave-vector normal modes

$$S_q^z=N^{-1/2}\sum_n S_n^z e^{iqcn}, \tag{9}$$

since

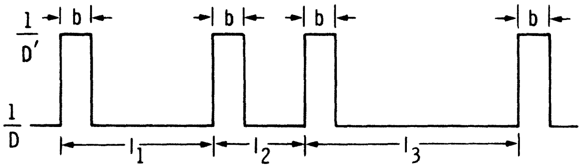

FIG. 3. Schematic of $1/D(x)$ for random impurities.

$$\langle S^z_q(\tau) S^z_{q'}(0)\rangle = \langle S^z_q(\tau) S^z_{-q}(0)\rangle\, \delta_{q,-q'} \tag{10}$$

for the translationally invariant periodic system. Use of Eqs. (8)–(10) then reduces Eq. (7) to

$$g_0(\tau) = \frac{3}{4}\,\frac{\gamma^4 \hbar^2}{c^6}\,(3\cos^2\theta - 1)^2 S(S+1) N^{-1} \times \sum_q f_q^2 [\phi_q(\tau)]^2 , \tag{11}$$

where

$$f_q = {\sum_m}' \,|\, m - n \,|^{-3} e^{iqc(m-n)}, \tag{12}$$

and

$$\begin{aligned} \phi_q(\tau) &= 3\langle S^z_q(\tau) S^z_{-q}(0)\rangle / S(S+1) \\ &= \tfrac{3}{2}\langle S^\pm_q(\tau) S^\mp_q(0)\rangle / S(S+1) . \end{aligned} \tag{13}$$

We assume exponential decay

$$\phi_q(\tau) = e^{-\Gamma_q \tau}, \tag{14}$$

[note that Eq. (13) shows $\phi_q(0) = 1$ at infinite temperature] where $\Gamma_q = Dq^2$ for $q \to 0$, with D the diffusion coefficient. As discussed in Sec. III A, the 1d anomalies are associated with long-time behavior, which corresponds to dominance by the slowly decaying $q \to 0$ modes; so it is permissible to replace f_q by its $q = 0$ value and thus the summation in Eq. (11) becomes

$$N^{-1} \sum_q f_q^2 [\phi_q(\tau)]^2 \approx N^{-1} f_0^2 \sum_q e^{-2\Gamma_q \tau} \tag{15}$$

for $\tau \to \infty$. At this point one normally replaces Γ_q by Dq^2, converts the sum to an integral over dq for $N \to \infty$, and observes that Eq. (15) is proportional to $\tau^{-1/2}$, the previously stated result for spin diffusion in 1d.

For later discussion, however, we maintain the form (15), which when combined with Eq. (11) gives

$$g_0(\tau) = \frac{3}{4}\,\frac{\gamma^4 \hbar^2}{c^6}\,(3\cos^2\theta - 1)^2 S(S+1) f_0^2 N^{-1} \sum_q e^{-2\Gamma_q \tau}. \tag{16}$$

It is useful to restate that Γ_q is the decay rate for the qth normal mode of the spin dynamics. We next argue below that Eq. (16), with the general interpretation of Γ and q just given, holds for the impure chain as well, apart from a trivial correction to account for the concentration dependences of the dipolar interaction and of $\sum_i \langle S_i^{z2}\rangle$.

C. Impure chains

The model to be treated is one in which a concentration x of impurity spins is distributed randomly among the magnetic-ion sites of the chain. We assume that the major effect of impurities is to alter the rate and manner of diffusion along the chain. Since we are primarily concerned with long-wavelength modes which are sensitive mainly to an averaged medium, it is reasonable that the description based on diffusion is still valid. Other possible effects, which are not peculiar to 1d, include altering ot the mean dipole field and additional broadening due to the impurity-host exchange interaction combined with impurity spin-lattice relaxation.[11] We do not believe these other effects are operable here to any significant degree, and they will be dismissed for the moment.

The problem reduces to finding the two-spin-correlation function which we write as

$$3\langle S^z_i(\tau) S^z_j\rangle / S(S+1) \equiv \phi_j(x_i, \tau) . \tag{17}$$

The function $\phi_j(x_i, \tau)$ represents the probability that a spin at position x_i on the chain has a given z component, say S, at time τ given that the spin at x_j has $S^z_j = S$ at $\tau = 0$. It satisfies the initial condition

$$\phi_j(x_i, 0) = \delta_{ij} . \tag{18}$$

Hone and Petzinger[7] set up a difference equation—which reduces to the diffusion equation in the long-wavelength limit—and determined $\phi_j(x_i, \tau)$ for the case of a single impurity with arbitrary impurity-host exchange interaction. They also solved the problem for diagmagnetic (perfectly reflecting boundaries) and rapidly relaxing (perfectly absorbing boundaries) impurities, as mentioned in the Introduction. Following their example, we assume that $\phi_j(x_i, \tau)$ obeys a diffusion equation of the general form[12]

$$\frac{\partial}{\partial x}\left(D(x) \frac{\partial}{\partial x}\, \phi_j(x, \tau)\right) = \frac{\partial}{\partial \tau}\, \phi_j(x, \tau), \tag{19}$$

for the slow spatial variations which are of interest. The diffusion coefficient $D(x)$ has a value D at the host sites and D' at the impurity sites, as sketched in Fig. 3.

Before discussing the solution of Eq. (20) for the particular model of Fig. 3, we establish validity of Eq. (16). By the standard theory of partial differential equations with boundary values, there exists a complete set of orthonormal eigenfunctions to Eq. (19)

$$\psi_\lambda(x, \tau) = e^{-\Gamma_\lambda \tau} \psi_\lambda(x), \tag{20}$$

$$\frac{\partial}{\partial x}\left(D(x) \frac{\partial}{\partial x}\, \psi_\lambda(x)\right) = -\Gamma_\lambda \psi_\lambda(x) \tag{21}$$

into which $\phi_j(x,\tau)$ can be expanded,

$$\phi_j(x,\tau)=\sum_\lambda a_{j\lambda}\psi_\lambda(x)\,e^{-\Gamma_\lambda\tau}\ . \tag{22}$$

The initial condition (18) together with the completeness and orthonormality of the $\psi_\lambda(x)$ shows that

$$a_{j\lambda}=\psi^*_\lambda(x_j)\ . \tag{23}$$

If (22) and (23) are used in (17), together with (8), the summation in the numerator of (7) becomes

$$\begin{aligned}\sum_{ij}{}'\sum_{kl}{}' &|i-j|^{-3}|k-l|^{-3}\langle S^z_i(\tau)\,S^+_j(\tau)\,S^z_k(0)\,S^-_l(0)\rangle\\ &=\tfrac{2}{9}S^2(S+1)^2\sum_{ij}{}'\sum_{kl}{}'\ |i-j|^{-3}|k-l|^{-3}\\ &\quad\times\sum_{\lambda\lambda'}\psi^*_\lambda(x_k)\,\psi_\lambda(x_i)\,\psi_{\lambda'}(x_l)\,\psi^*_{\lambda'}(x_j)\,e^{-(\Gamma_\lambda+\Gamma_{\lambda'})\tau}\ . \end{aligned}\tag{24}$$

[We have used the fact that at infinite temperature $\phi_i(x_j,\tau)=\phi_j(x_i,-\tau)=\phi_j(x_i,\tau)$ so that $\sum_{\lambda'}\psi^*_{\lambda'}(x_l)\times\psi_{\lambda'}(x_k)=\sum_{\lambda'}\psi^*_{\lambda'}(x_k)\,\psi_{\lambda'}(x_l)$]. As before, the dominant contribution is expected to come from $\psi_\lambda(x)$ which have slow spatial variation since these are associated with small decay rates Γ_λ. Hence we have

$$|i-j|^{-3}\,\psi^*_{\lambda'}(x_j)\,\psi_\lambda(x_i)\approx|i-j|^{-3}\,\psi^*_{\lambda'}(x_i)\,\psi_\lambda(x_i), \tag{25}$$

as long as $\psi^*_{\lambda'}(x_j)$ does not change appreciably over the one or two lattice spacings for which $|i-j|^{-3}$ is important. A similar relation of course holds for the k, l terms, so that the final result is

$$\begin{aligned}g_0(\tau)=\frac{3}{4}\ \frac{\gamma^4\hbar^2}{c^6}\,&(3\cos^2\theta-1)^2S(S+1)\\ &\times f_0^2N^{-1}\sum_\lambda e^{-2\Gamma_\lambda\tau}\ ,\end{aligned}\tag{26}$$

upon using the orthonormality and definition of f_0 found in Eq. (12). This proves the important statement that Eq. (16), which was derived for the wave-vector normal modes of a pure chain, holds for the impure chain as well provided that the general interpretation of Γ_q and q, as given after (16), is used.

The above treatment has neglected the fact that in Eq. (7) not all sites i have the same spin value. An estimate of the error involved here can be obtained by considering the second moment $g_0(0)$. Since $\langle S^{z2}_i\rangle$ for a Mn⁺⁺ spin is $\frac{35}{3}$ greater than for a Cu⁺⁺ spin, we can simply replace S^z_i by zero at the sites occupied by Cu⁺⁺ impurities and therefore get for the average over all sites

$$\langle S^{z2}_i\rangle=\tfrac{1}{3}S(S+1)(1-x)\ , \tag{27}$$

where x is the impurity concentration. Use of Eq. (27) in (7) then shows that $g_0(0)$ is decreased by a factor $(1-x)^2/(1-x)=(1-x)$ from its value for the pure chain. This is the small effect on the mean dipole field mentioned earlier. It amounts to only a 4% reduction here and thus is not important.

D. Density of states and results

For an infinite chain we expect a continuous range of eigenvalues Γ_λ so that the summation in (26) can be replaced by an integral

$$\sum_\lambda e^{-2\Gamma_\lambda\tau}\to\int_0^\infty d\Gamma\left(\frac{d\lambda}{d\Gamma}\right)e^{-2\Gamma\tau}\ . \tag{28}$$

The problem thus reduces to finding the density of states $d\lambda/d\Gamma$ for small values of Γ. We are not aware of any such calculations for the random system described by Eq. (19) and Fig. 3; however, considerable work has been done on the very similar 1d random Kronig-Penny model in quantum mechanics.[13,14] In this model, δ-function potentials of equal strength are located at random with an average spacing l. The salient feature of the results for our purposes is that the density of states for small energies is the same as for an ordered lattice in which the potentials are regularly spaced a distance l apart. Only near band edges is there a significant difference between the density of states for the ordered and disordered lattices. This in fact appears to be a characteristic of random and amorphous systems in general.[15]

On the strength of the above argument we therefore assert that it suffices to compute the density of states for a model in which the impurities are regularly spaced a distance $l=c/x$ apart, i.e., $l_1=l_2=\cdots=l$ in Fig. 3. The result, derived in Appendix A, gives

$$\Gamma_\lambda=D(1+bD/lD')^{-1}q_\lambda^2\equiv\tilde{D}q_\lambda^2\ , \tag{29}$$

where q_λ is the wave vector of the Bloch function associated with the λth mode, and b (see Fig. 3) is the effective distance over which the diffusion coefficient is D'.

Equation (29), together with Eqs. (16) and (26), shows that the impure chain behaves just like the pure chain for long times but with a reduced diffusion coefficient $\tilde{D}$. This result is to be expected on the basis of hydrodynamic behavior for the long-wavelength modes propagating through the random medium. Two conclusions may be drawn at once. First, one can show from Eqs. (5), (26), and (29) that the relaxation rate is proportional to $\tilde{D}^{-1/3}$ (assuming an $e^{-t^{3/2}}$) decay so that, in particular at $\theta=0°$, we have

$$\frac{\Delta H_{\text{impure}}}{\Delta H_{\text{pure}}}=(1+bD/lD')^{1/3}\ . \tag{30}$$

Second, the line shape is the same for both the pure and impure systems since the only effect of the impurities is to alter the diffusion coefficient.

It is of interest to compare the above results with those for a chain with diamagnetic impurities. In either case the width of the impure chain is expected to be greater at $\theta=0°$ than that of the pure chain, and for similar reasons. With perfectly reflecting diamagnetic impurities, spin polarization can never diffuse away completely so that the decay rate of $g_0(\tau)$ is obviously lessened, and in fact[7] $g_0(\tau)$ does not decay to zero for $\tau \to \infty$. If the impurities are less than perfect reflectors, then $g_0(\tau)$ will eventually decay to zero but at a slower rate than for a pure chain because of reflections. The line shapes for the two cases, however, are different. The fact that $g_0(\tau)$ remains finite at $\tau = \infty$ for the diamagnetic impurities does alter the line shape. In Appendix B we calculate and show curves of the line shape for this case of finite chains with perfectly reflecting boundaries.

E. Relation between D' and impurity-host exchange

We have employed a continuum model in which an impurity site is replaced by a region of size b with diffusion coefficient D' while the host sites have diffusion coefficient D. It is clearly desirable to make some connection between these parameters and the interaction constants J and J' of the microscopic exchange Hamiltonian, where J and J' are the nearest-neighbor host-host and host-impurity exchange interactions, respectively. (For a small concentration of impurities we neglect any impurity-impurity interaction.)

The diffusion coefficient D of a pure chain has been treated by several authors[16] who find that it is of the order of $Jc^2[S(S+1)]^{1/2}/\hbar \equiv \omega_e c^2$, where ω_e is the characteristic exchange frequency which also occurs in the short-time expansion of, for example, the pair-correlation function $\langle S_i^z(t) S_{i+1}^z(0)\rangle$. Thus the time required to diffuse one lattice spacing is of the same order as the characteristic time scale ω_e^{-1} on which short-time correlations vary. We make use of this fact to estimate D'/D in terms of J'/J by considering the short-time expansion of the function

$$\frac{3\langle S_{-1}^z(t)\, S_1^z(0)\rangle}{S(S+1)} = \tfrac{1}{24}\,(\Omega t)^4 + \cdots \qquad (31)$$

under two conditions. (A) The origin 0 is occupied by an impurity spin S' and the effective Hamiltonian for the short-time dependence is

$$H_A = 2J'(\vec{S}_{-1}\cdot\vec{S}_0' + \vec{S}_0'\cdot\vec{S}_1), \qquad (32a)$$

and (B) the origin is occupied by a host spin so that

$$H_B = 2J(\vec{S}_{-1}\cdot\vec{S}_0 + \vec{S}_0\cdot\vec{S}_1)\ . \qquad (32b)$$

In case (B) the characteristic frequency Ω_B should be of the order of D/c^2 as noted above, while for (A) it should be related to D'/c^2 since spin polarization must be transmitted through the impurity. We make the simple ansatz

$$D'/D = \Omega_A/\Omega_B \qquad (33)$$

from which straightforward calculation yields

$$\frac{D'}{D} = \left|\frac{J'}{J}\right| \left(\frac{S'(S'+1)}{S(S+1)}\right)^{1/4}\ . \qquad (34)$$

Note that for spins two lattice spacings apart as in (31), t^4 is the first nonvanishing term in the expansion at infinite temperature.

In the spirit of this model the effective distance for which the diffusion coefficient is D' (see Fig. 3) is given by

$$b = 2c\ , \qquad (35)$$

since $2c$ is the space over which we consider correlation in (31).

IV. COMPARISON WITH EXPERIMENT AND DISCUSSION

The combined results of Eqs. (30), (34), and (35) give

$$\Delta H_{\text{impure}}/\Delta H_{\text{pure}} = [1 + 2x\,|J/J'|\,(1.85)]^{1/3}\ , \qquad (36)$$

where $1.85 = [S(S+1)/S'(S'+1)]^{1/4}$ for $S = \frac{5}{2}$ and $S' = \frac{1}{2}$ and where $l = c/x$, with x the concentration. The above holds only near $\theta = 0°$ where the line shape is the $1d$ form $\mathfrak{F}(e^{-t^{3/2}})$. Since we observe the ratio to be 1.5 at $\theta = 0°$ for $x = 0.04$, it follows that (36) is consistent with a ratio of impurity-host to host-host exchange $|J'/J| = 0.06$. This ratio is perhaps surprisingly low and may cast doubt on the validity of our continuum model and the connection between D' and J'. General properties of long-wavelength modes lead us to believe that the impure chain acts as though it has an effective diffusion coefficient $\tilde{D}$, but making the precise microscopic connection between $\tilde{D}$ and D may be considerably more tenuous. However, in the absence of any independent measurements of $|J'/J|$ in this or similar compounds, it is difficult to draw any firm conclusions, especially in view of the complexities of the theory of superexchange.

The line shape at $\theta = 0°$ was found to be the same for the pure and impure crystals, and this is in agreement with theory. Here there is a definite distinction between the case of paramagnetic impurities with a finite J' and diamagnetic ones, for which the system breaks up into independent finite chains. The line shape would be quite different for a chain containing 24 spins on the average, as shown in Appendix B.

The linewidths at $\theta = 55°$ $(3\cos^2\theta = 1)$ are identical, and this is also consistent with theory for the following reason. At 55° the secular term $g_0(\tau)$ is rigorously zero so that the only contribution to broadening comes from the nonsecular $(M \neq 0)$ terms of Eq. (4). These terms are not affected by the long-time behavior because of modulation at the frequency ω_0. Hence alteration of long-time diffusion by the impurities is unimportant.

Indeed we regard the equality of linewidths at 55° as crucial to the interpretation that the only significant effect of the impurities is to alter the diffusion. If the widths differed at 55° we would have to worry about possible changes in the lattice or other effects which obviously would complicate the comparison. One such possible effect, mentioned earlier, is an increase of ΔH owing to the impurity-host interaction J'. This has been observed[11] in $3d$ paramagnets for impurities with rapid spin-lattice relaxation. The "bottleneck" can be broken and the interaction $2J'\vec{S}\cdot\vec{S}'$ broadens the observed host resonance provided the impurity spin-lattice relaxation rate δ is comparable to or greater than J'. Since this would give an isotropic contribution to ΔH, it does not seem to be operable here, as is reasonable because our estimate of $J' = 0.06\,J$ would require $\delta \gtrsim 5\times 10^{10}$ sec^{-1}, given the value[17] of J for TMMC, which is unlikely for the Kramers Cu^{++} ion.

In conclusion we have shown that a small concentration (4 at.%) of impurities has a large (50%) effect on the linewidth in TMMC at $\theta = 0°$ but no measurable effect at $\theta = 55°$. This is completely consistent with a picture in which the impurities alter the rate of diffusion along the chain but have no other influence. The observed line shapes are the same in pure and in impurity-doped TMMC which indicates that the basic mode of spin diffusion in an infinite chain still exists with the impurities. Detailed analysis of the problem predicts a variation of the effective diffusion coefficient with concentration and impurity-host intrachain exchange J' from which we estimate $|J'/J| = 0.06$, where J is the host-host (Mn-Mn) intrachain interaction.

The fact that alteration of diffusion by a small concentration of impurities can produce such a pronounced change in ΔH is clear evidence of the the importance of long-time correlations in $1d$. So dramatic an effect certainly would not be expected in $3d$ where (i) it is possible for the diffusing spin polarization to find paths which avoid an impurity and (ii) the characteristic time for decay of the spin-time correlations is much less than the average time for the correlation to diffuse to an impurity and therefore sense its presence.

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APPENDIX A: CALCULATION OF DIFFUSION MODEL

We calculate the eigenvalue spectrum for the model depicted in Fig. 3 in which the impurities are regularly spaced a distance l apart. Solutions to Eq. (21) are in the form of Bloch functions

$$\psi_k(x) = u_k(x)\, e^{ikx} , \tag{A1}$$

in which $u_k(x)$ has the periodicity l. In a region of length l the diffusion coefficient is

$$D(x) = \begin{cases} D, & -\tfrac{1}{2}l \le x < 0, \quad b < x \le \tfrac{1}{2}l \\ D', & 0 \le x \le b . \end{cases} \tag{A2}$$

Boundary conditions are that $\psi_k(x)$ and the current $D(x)\,\partial\psi_k/\partial x$ be continuous at $x = 0$ and $x = b$, and periodicity requires $u_k(-\tfrac{1}{2}l) = u_k(\tfrac{1}{2}l)$, and likewise for $\partial u_k/\partial x$. Apart from the fact that $D(x)\,\partial\psi_k/\partial x$ is continuous rather than $\partial\psi_k/\partial x$, the method of solution is the same as standard text book treatments[18] of the Kronig-Penny model.

In the limits $D' \to 0$ and $b \to 0$ such that b/D' is finite, we find the boundary conditions at $x = 0$, b lead to

$$\psi_k = [A(1 + \tfrac{1}{2}i\,\Delta - \tfrac{1}{2}i\Delta B]e^{i\kappa x} + [B(1 - \tfrac{1}{2}i\Delta) + \tfrac{1}{2}i\Delta A]e^{-i\kappa x}, \quad b < x \le \tfrac{1}{2}l \tag{A3}$$

if the solution for $-\tfrac{1}{2}l \le x \le 0$ is

$$\psi_k = Ae^{i\kappa x} + Be^{-i\kappa x} . \tag{A4}$$

In the above

$$\Delta = (D\Gamma_k)^{1/2}\, b/D' \tag{A5}$$

and

$$\kappa = (\Gamma_k/D)^{1/2} . \tag{A6}$$

Imposition of the periodicity conditions on $u_k = \psi e^{-ikx}$ then leads to the secular equation

$$\cos\kappa l - \tfrac{1}{2}\,\Delta\,\sin\kappa l = \cos kl . \tag{A7}$$

For κl, $kl \ll 1$ this reduces to

$$\Gamma_k = D(1 + bD/lD')^{-1}k^2 \tag{A8}$$

upon using (A6).

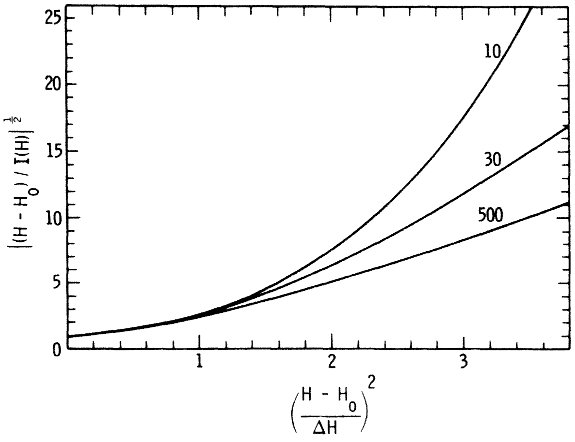

FIG. 4. Theoretical line shapes at $\theta = 0°$ for finite chains containing 10, 30, and 500 spins.

APPENDIX B: LINE SHAPE FOR DIAMAGNETIC IMPURITIES (FINITE CHAIN)

If there are diamagnetic impurities at positions $x=0,\ l$, then we effectively have a finite, independent chain of length l since no diffusion can take place across the boundaries. The eigenmodes to (21) are then simply

$$\psi_n(x)=\begin{cases}(2/l)^{1/2}\cos(n\pi x/l), & n=1,2,\ldots\\ (1/l)^{1/2}, & n=0\end{cases}\qquad\text{(B1)}$$

since the boundary conditions are $\partial\psi_n/\partial x$ at $x=0,\ l$ (zero current). The decay rates are

$$\Gamma_n=2(D/c^2)[1-\cos(n\pi c/l)],\qquad\text{(B2)}$$

where we have used the difference equation of Hone and Petzinger,[7] which reduces to the diffusion equation result for $n\pi c/l\ll 1$. The integrated correlation function at $\theta=0^\circ$ is then given by

$$\int_0^t (t-\tau)g_0(\tau)\,d\tau=\frac{6\gamma^4\hbar^2}{c^6}S(S+1)N^{-1}\int_0^t (t-\tau)\,d\tau\left[2+\sum_{n=1}^{N}\left(1+\cos\frac{2n\pi}{N}\right)e^{-2\Gamma_n\tau}\right]$$

$$=\frac{6\gamma^4\hbar^2}{c^6}S(S+1)N^{-1}\left[t^2+\sum_{n=1}^{N}\left(1+\cos\frac{2n\pi}{N}\right)\left(\frac{t}{2\Gamma_n}-\frac{1}{4\Gamma_n^2}\left(1-e^{-2\Gamma_n t}\right)\right)\right]\qquad\text{(B3)}$$

according to Eq. (11), where we have considered nearest-neighbor dipolar interactions only so that $f_q^2\approx 2(1+\cos 2qc)$ and $N=l/c$ is the number of spins on the chain.

Hone and Petzinger pointed out that Eq. (B3), which has essentially the same form for the NMR problem with diamagnetic impurities, leads to a Gaussian decay for very long times. However, they did not present detailed calculations of the line shape. The extent to which the line will actually appear to be Gaussian depends crucially on the size of $\Gamma_1 T_2$, where T_2 is the observed decay time of the magnetization. If $\Gamma_1 T_2\gg 1$ then all the $n\neq 0$ modes will have decayed to a small value at the times of interest and a Gaussian line will result. But if $\Gamma_1 T_2\ll 1$, then we must consider a large number of modes for the decay, and the line should be more nearly characteristic of an infinite chain.

The magnitude of $\Gamma_1 T_2$ depends on the dipole prefactor $6\gamma^4\hbar^2 S(S+1)c^{-6}$ as well as on D and N. In Fig. 4 we show the derivative line shape for $N=10$, 30, and 500 with $6\gamma^4\hbar^2 S(S+1)/D^2c^6=3\times 10^{-4}$, which is appropriate for TMMC. Curves were obtained by using Eqs. (B2) and (B3) in the derivative of Eq. (1). The shape for $N=500$ is indistinguishable from the infinite chain limit on the scale of the graph.

We have also computed the peak-to-peak width ΔH vs N and find that $\Delta H(N=30)\approx 1.5\Delta H(N\to\infty)$, which corresponds to the experimental data. Thus the linewidth by itself at $\theta=0^\circ$ is consistent with a finite chain of 30 spins, quite close to the average number of 24 spins between impurities in the sample. However, the shape for a chain containing only 30 spins is predicted to be significantly different from that of an infinite chain; so we feel that the model of the main text and Appendix A is much more appropriate.

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