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**Concentration dependence of the electron-spin-resonance linewidth in  $(\text{CH}_3)_4\text{NMn}_{1-x}\text{Cu}_x\text{Cl}_3^\dagger$** 

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The electron-spin-resonance linewidth  $\Delta H$  has been measured in  $(\text{CH}_3)_4\text{NMnCl}_3$  (TMMC) samples having a fraction  $x$  of  $\text{Cu}^{++}$  substituted for  $\text{Mn}^{++}$ , with  $x$  up to 0.22. For the applied field along the chain axis,  $\Delta H$  increases with  $x$  in a manner consistent with predictions of one-dimensional spin dynamics.

**I. INTRODUCTION**

In a paper<sup>1</sup> referred to as I, we studied electron spin resonance (ESR) in a linear chain crystal of  $(\text{CH}_3)_4\text{NMnCl}_3$  (TMMC) which contained 4-at. %  $\text{Cu}^{++}$  substituted for  $\text{Mn}^{++}$ . The main result of I was that the linewidth  $\Delta H$  of TMMC:Cu was greatly enhanced when the field was applied along the chain axis, and this enhancement of 50% could be explained in terms of the  $\text{Cu}^{++}$  slowing down the rate of spin diffusion along the chain and was consistent with the peculiar features of ESR caused by one-dimensional spin dynamics.<sup>2</sup> Here we report measurements on a number of  $(\text{CH}_3)_4\text{NMn}_{1-x}\text{Cu}_x\text{Cl}_3$  samples with  $x$  between  $3.4 \times 10^{-4}$  and 0.22. The results further confirm the basic conclusions presented in I.

**II. THEORY**

According to the theory in I, the concentration dependence of  $\Delta H$  is given by

$$\Delta H(x)/\Delta H(0) = (1-x)^{2/3} [D(0)/D(x)]^{1/3} \quad (1)$$

for the field applied along the chain axis. The factor  $(1-x)^{2/3}$  comes from a reduction of the second moment  $M_2$  due to substitution of  $\text{Mn}^{++}$  by the much lower moment  $\text{Cu}^{++}$ . [See Eq. (27) of I and surrounding discussion. The  $\frac{2}{3}$  power results because  $\Delta H \propto M_2^{2/3}$  for a one-dimensional system.] It produced a negligible effect for the  $x = 0.04$  sample measured in I and thus was not included in Eq. (30) of I. For the larger concentrations

studied here, however, its effect can be significant. The quantity  $D(x)$  is the spin-diffusion coefficient of the chain at concentration  $x$ , and the  $\frac{1}{3}$  power results, once again, from the one-dimensional characteristics of the problem.

A model was employed in I whereby the chain is made up of segments of length  $2c$  ( $c$  is the nearest-neighbor intrachain distance) in which the spins diffuse at the rate  $D'$  proportional to the Mn-Cu exchange interaction and ones of length  $l-2c$  ( $l = c/x$ ) in which the diffusion coefficient is  $D(0)$ . From this model we obtain

$$\frac{D(0)}{D(x)} = 1 + 2x \left( \frac{D(0)}{D'} - 1 \right). \quad (2)$$

Equation (2), which is valid for an arbitrary ratio of  $D/D'$ , agrees with Eqs. (29) and (35) of I for  $D/D' \gg 1$ , the conditions under which these equations were derived. Note that (2) correctly gives  $D(x) = D'$  at  $x = \frac{1}{2}$ , which corresponds to an alternating chain of  $\text{Mn}^{++}$  and  $\text{Cu}^{++}$  ions. The model clearly breaks down for  $x > \frac{1}{2}$  since no account is taken of Cu-Cu interactions. Use of (2) in (1) then gives the predicted concentration dependence

$$[\Delta H(x)/\Delta H(0)]^3 (1-x)^{-2} = 1 + \lambda x, \quad (3)$$

where  $\lambda$  is a constant.

**III. RESULTS**

In Fig. 1 we plot  $[\Delta H(x)/\Delta H(0)]^3 (1-x)^{-2}$  vs  $x$  for data at room temperature, a frequency of 9.82 GHz and with the field along the chain axis. The

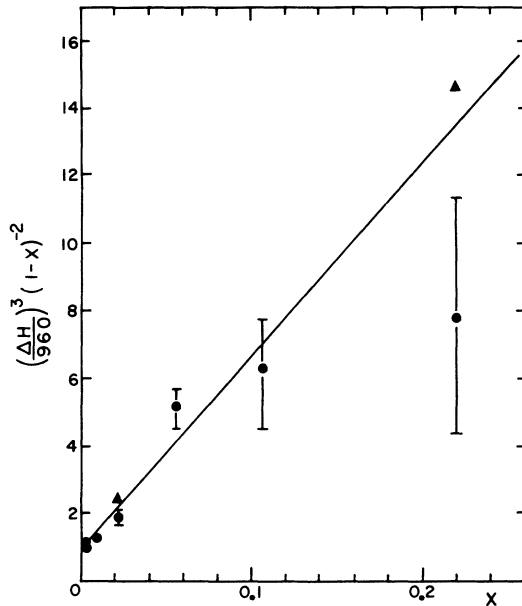


FIG. 1. Peak-to-peak linewidth  $\Delta H$  vs  $\text{Cu}^{2+}$  concentration  $x$ , plotted in manner to give straight line according to theory of Eq. (4). Circles are for  $\theta=0$ ; triangles are for angle at which  $\Delta H$  is a maximum, in cases where there is a shallow minimum in  $\Delta H$  at  $\theta=0$ .

peak-to-peak width at  $x=0$  is taken to be  $\Delta H(0) = 960$  Oe for normalization purposes. The large error bars at the most concentrated ( $x=0.22$ ) sample result from imprecision in measuring large linewidths ( $\Delta H \approx 2000$  Oe) and from taking the cube of the quantity. The values of  $x$  were obtained by chemical analysis at Huffman Laboratories, Wheatridge, Colorado. X-ray diffraction showed that the lattice constants decreased by about 0.7% in going from  $x=0$  to  $x=0.22$ .

The angular dependence of  $\Delta H$  in all samples was similar to that reported in I and thus showed the roughly  $3 \cos^2 \theta - 1$  ( $\theta$  is the angle of applied field with respect to the chain axis) variation characteristic of linear chain materials. In two of the samples ( $x=0.023$  and  $x=0.22$ ), however, there was a (10–15)% dip in  $\Delta H$  at  $\theta=0$ , the maximum  $\Delta H$  occurring at  $\theta \approx \pm 10^\circ$ . The effect was repeatable and just outside the experimental error. Data shown in Fig. 1 for these samples are both for  $\theta=0$  and the maximum observed  $\Delta H$ .

The peak-to-peak width at  $55^\circ$  ( $3 \cos^2 \theta - 1 = 0$ ) increased from 160 to 280 Oe as  $x$  varied between nearly zero and 0.22.

#### IV. DISCUSSION

The dependence of Eq. (3) is seen in Fig. 1 to be reasonably well verified up to at least  $x=0.1$ . The slope of the straight line gives  $\lambda=57$ , and this is in good agreement with the result in I based on comparison between  $x=0$  and  $x=0.04$ , and which

may be converted to  $\lambda=62$  in the present notation [comparison of Eq. (3) here and Eq. (36) of I, which approximated  $1-x \approx 1$ , shows that  $\lambda=3.7 \times |J/J'|$ , and the value  $|J'/J|=0.06$  was deduced in I]. If the maximum observed  $\Delta H$  is used for the  $x=0.22$  sample, then the agreement extends up to the highest concentration.

As noted in I, the linewidth at  $\theta=55^\circ$   $\Delta H_{55}$  should be nearly independent of  $x$  since it is not affected by the long-time features of spin dynamics in one dimension, whereas we observe a significant increase with  $x$ . If the source of broadening were purely dipole dipole,  $\Delta H_{55}$  should decrease with increasing  $x$ , and the observed 0.7% lattice contraction between  $x=0$  and  $x=0.22$  should be too small to have any significant effect on  $\Delta H$ . Two mechanisms for a  $\Delta H_{55}$  which increases with  $x$  are (i) a  $\Delta g$  broadening caused by the difference between  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$   $g$  factors and (ii) rapid spin-lattice relaxation of the  $\text{Cu}^{2+}$  ion. These are ruled out, however, by the following considerations. The  $\Delta g$  mechanism (i) should be strongly field dependent, but measurements on the  $x=0.22$  sample gave the same value of  $\Delta H_{55}$  at 22 GHz as at 9.8 GHz. Mechanism (ii) results in broadening only if the spin-lattice relaxation rate  $\delta$  is comparable to or larger than the impurity-host exchange frequency. As mentioned in I, this requires  $\delta \gtrsim 5 \times 10^{10} \text{ sec}^{-1}$ , which does not seem reasonable for  $\text{Cu}^{2+}$  ions in TMMC.

A possible explanation of both the variation of  $\Delta H_{55}$  with  $x$  and the anomalous minimum in  $\Delta H$  at  $\theta=0$  for the highest concentration could be an anisotropic Cu-Mn interaction which does not have a  $3 \cos^2 \theta - 1$  angular dependence. To be specific, consider an interaction of the form

$$\mathcal{H}' = 2GS_i^z s_{i+1}^z \quad (4)$$

between a  $\text{Mn}^{2+}$  spin  $\vec{S}$  and a neighboring  $\text{Cu}^{2+}$  spin  $\vec{s}$ . We take the principal axis  $z'$  to be in the direction of the  $g_{\parallel}$  axis of the  $\text{Cu}^{2+}$  ion, which should lie along one of the Cu-Cl bonds in the  $\text{Cl}_3\text{-Cu-Cl}_3$  octahedron.<sup>3</sup> A tetragonal distortion, common for  $\text{Cu}^{2+}$ , is expected to single out a particular Cu-Cl direction for  $z'$ . The direction  $z'$  will then be about  $63^\circ$  from the chain axis,<sup>3</sup> so that the interaction will be mostly secular at  $\theta=55^\circ$  and mostly nonsecular at  $\theta=0$  since the secular component varies as  $3 \cos^2 \alpha - 1$ , where  $\alpha$  is the angle between the applied field and the  $z'$  direction.<sup>4</sup>

The contribution of  $\mathcal{H}'$  to  $\Delta H$  may be estimated by assuming that  $\Delta H$  scales as  $M_2^{2/3}$ , where  $M_2$  is the second moment. Thus we have

$$\frac{\Delta H'}{\Delta H_D} \approx \left( \frac{J'c^3}{\gamma^2 \hbar^2} \right)^{4/3} \left[ \frac{S(S+1)}{S(S+1)} \right]^{2/3} \left( \frac{x}{1-x} \right)^{2/3}, \quad (5)$$

where  $\Delta H'$  is the linewidth at  $55^\circ$  due to  $\mathcal{H}'$ ,  $\Delta H_D$  is the linewidth at  $\theta=0^\circ$  due to intrachain dipolar

coupling, and  $\gamma$  is the  $\text{Mn}^{++}$  gyromagnetic ratio. One might expect to have an interaction  $G$  of the order of  $\frac{1}{2}(g-2)|J'|$ , where  $g$  is the  $\text{Cu}^{++}$   $g$  factor and  $J'$  is the Cu-Mn exchange constant. For  $|J'|/k_B = 0.4^\circ\text{K}$  ( $|J'| = 0.06|J|$ ,  $|J|/k_B \approx 7^\circ\text{K}$  for pure TMMC) and a typical value  $g = 2.2$  for  $\text{Cu}^{++}$ , we thus obtain  $\Delta H' \approx 80$  Oe at  $x = 0.22$ , which is nearly the amount by which  $\Delta H_{55}$  increases in going from  $x = 0$  to  $x = 0.22$ . Since the dominant secular contribution of  $\mathcal{H}'$  to  $\Delta H$  increases as  $\theta$  moves away from  $0^\circ$ , the small minimum in  $\Delta H$  observed when the field is along the chain axis could also be due to this mechanism.

Equation (5) assumes that the effective spin dynamics for the interaction (4) are the same as govern the Mn-Mn dipolar broadening. This is reasonable for the long times of interest where the strongly coupled system decays with the single diffusion coefficient  $D(x)$ .

In conclusion, we have established that the major point made in I about impurities affecting ESR in a Heisenberg linear chain by strongly altering the rate of spin diffusion is correct for a wide range of concentrations. In addition there are effects on the linewidth at the "magic angle" [ $\theta = \cos^{-1}(1/\sqrt{3})$ ] and near  $\theta = 0^\circ$  which are not yet fully understood and may be worthy of further investigation.

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<sup>1</sup>P. M. Richards, *Phys. Rev. B* **10**, 805 (1974).

<sup>2</sup>For reviews see D. Hone and P. M. Richards, *Ann. Rev. Mater. Sci.*, **4**, 337 (1974); P. M. Richards, in *Low-Dimensional Cooperative Phenomena*, edited by

H. J. Keller (Plenum, New York, 1975), p. 147.

<sup>3</sup>B. Morosin and E. J. Graeber, *Acta. Crystallogr.* **23**, 766 (1967).

<sup>4</sup>K. T. McGregor and Z. G. Soos, *J. Chem. Phys.* (to be published).