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# Temperature dependence of spin dynamics in the impurity-doped quasi-two-dimensional antiferromagnet $C_2H_5(NH_3)_2MnCl_4{}^{2+}$:$Cu^{2+}$

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We have studied the temperature dependence of linewidths in the quasi-two-dimensional magnetic crystals $C_2H_5(NH_3)_2MnCl_4$:$Cu^{2+}$ with different concentrations of paramagnetic $Cu^{2+}$ ions with the use of electron spin resonance between 295 and 30 K. We have measured the linewidths at $X$-band microwave frequency at $\theta=0°$ and 55° where $\theta$ is the angle between the steady magnetic field $\mathbf{H}_0$ and the normal to the plane of the crystal. The linewidths initially decreased as the temperature was lowered from room temperature towards the antiferromagnetic ordering temperature $T_N$, passed through a minimum, and then increased rapidly as $T_N$ is approached. We have interpreted our results in the light of the theory which assumes the diffusive motion of spins for the longtime dependence of the time correlation functions. We have studied also the line shapes in the four samples, including the one with no impurity present, at room temperature, and at $\theta=0°$, 55°, and 90°. At all three angles of orientation $\theta$, the line shapes in all four samples were observed to be pure Lorentzian for up to 1.5–2.5 linewidths from the center of resonance line. However, the non-Lorentzian character was observed to increase with the impurity concentration at all three angles of orientation $\theta$ in all four samples.

## INTRODUCTION

We have measured the temperature dependence of the linewidths ($\Delta H$) in the quasi-two-dimensional (2D) antiferromagnetic crystal $C_2H_5(NH_3)_2MnCl_4$ (Refs. 1–4) doped with different concentrations of paramagnetic $Cu^{2+}$ ions with the use of electron spin resonance (ESR) at the $X$-band microwave frequency, between 30 and 295 K. We have studied the linewidths as a function of temperature at $\theta=0°$ and 55° where, $\theta$ is the angle between the steady magnetic field $\mathbf{H}_0$ and the normal to the magnetic plane of the crystal. In the four crystals containing 0, 3.0, 8.0, and 30 at. % of $Cu^{2+}$ impurity concentrations (hereafter referred to as samples 1, 2, 3, and 4, respectively), we have observed the linewidths initially to decrease as the temperature is lowered from room temperature (295 K) towards the antiferromagnetic ordering temperature $T_N$ which is about 50 K for a pure crystal (sample 1), pass through a minimum (between 60 and 55 K) and then increase very rapidly as $T_N$ is approached. Such a temperature dependence of ESR linewidths was observed in pure 2D antiferromagnet $K_2MnF_4$ by Richards *et al.*,[4] and in $Rb_2Mn_cMg_{1-c}F_4$ by Walsh *et al.* Richards' theory[4] to explain the results in $K_2MnF_4$ was based on spin diffusive motion for the long time dependence of the time correlation functions. There is a good agreement between the theory and the experimental results in $K_2MnF_4$. At room temperature we have measured the linewidths ($\Delta H$) in all four samples as a function of $\theta$ and all four were observed to have the following $\theta$ dependence[4]

$$\Delta H=\alpha+\beta(3\cos^2\theta-1)^2 , \tag{1}$$

where $\alpha$ and $\beta$ are constants, characteristic of a quasi-2D magnetic crystal. Walsh *et al.*[5] had to add another term

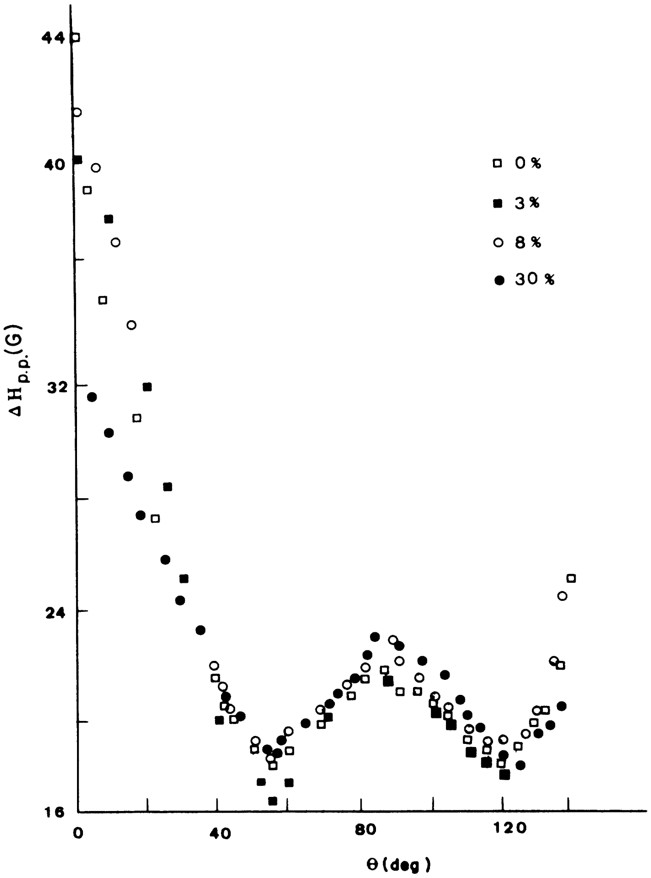

FIG. 1. Linewidth $\Delta H_{\text{p.p.}}$ (peak-to-peak width) of the derivative of resonance line as a function of $\theta$ at room temperature 295 K.

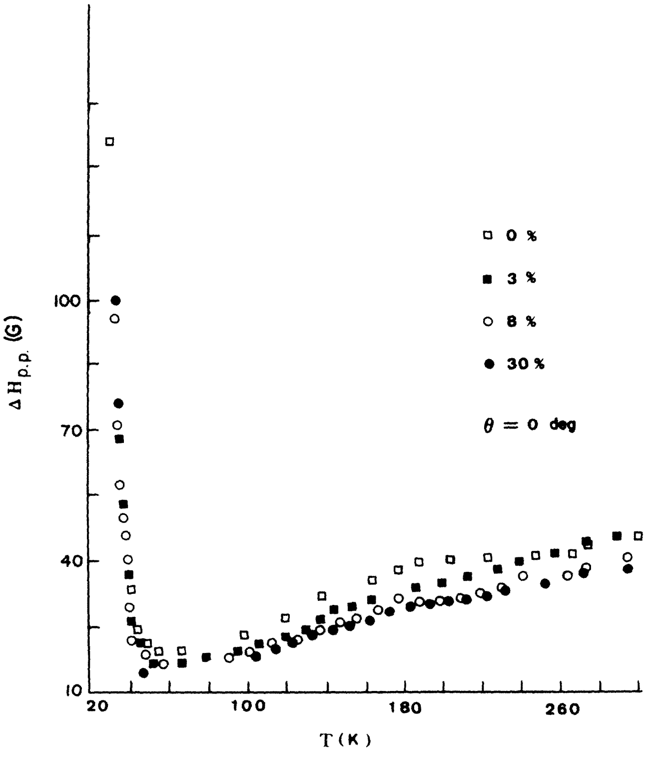

FIG. 2. Linewidth $\Delta H_{\mathrm{p.p.}}$ (peak-to-peak) width of derivative of resonance line as a function of temperature $T$(K) at $\theta=0°$.

to Eq. (1) to explain their results in $Rb_2Mn_cMg_{1-c}F_4$ at very low temperatures, when the concentration of Mn is at the percolation threshold. As the temperature of the crystal was lowered they[5] observed the onset of antiferromagnetic correlation in the percolation clusters. The additional term in Eq. (1) was to account for this effect. They[5] have observed $\alpha$ to be very nearly temperature independent in $Rb_2Mn_cMg_{1-c}F_4$, which seems to agree with our results in $C_2H_5(NH_3)_2MnCl_4$:Cu. However, in $Rb_2Mn_cMg_{1-c}F_4$, they have observed $\alpha$ to have a moderate increase with decreasing temperature $T$. On the other hand, in our samples we observed $\alpha$ to decrease slightly with decreasing temperature. $\beta$ contributes significantly to the linewidth $\Delta H$ from the room temperature 295 K to fairly low temperature 60 K in $Rb_2Mn_cMg_{1-c}F_4$ (Ref. 5) which seems to agree with our results in $C_2H_5(NH_3)_2MnCl_4$:Cu crystals. Therefore, we have interpreted our results on the basis of Richards theory[4] and Eq. (1) without the additional term of Walsh *et al.*[5] One important difference between the two 2D magnetic crystals $Rb_2MnF_4$ and $C_2H_5(NH_3)MnCl_4$ is that the former was doped with a diamagnetic impurity $Mg^{2+}$ unlike the paramagnetic $Cu^{2+}$ impurity in $C_2H_5(NH_3)_2MnCl_4$. Walsh *et al.*[5] have assumed the line shapes in $Rb_2Mn_cMg_{1-c}F_4$ to be qualitatively Lorentzian, and no special effort was made to study the deviations of line shapes from the Lorentzian character. In this present work, we have studied also the line shapes in all four samples at room temperature which were observed

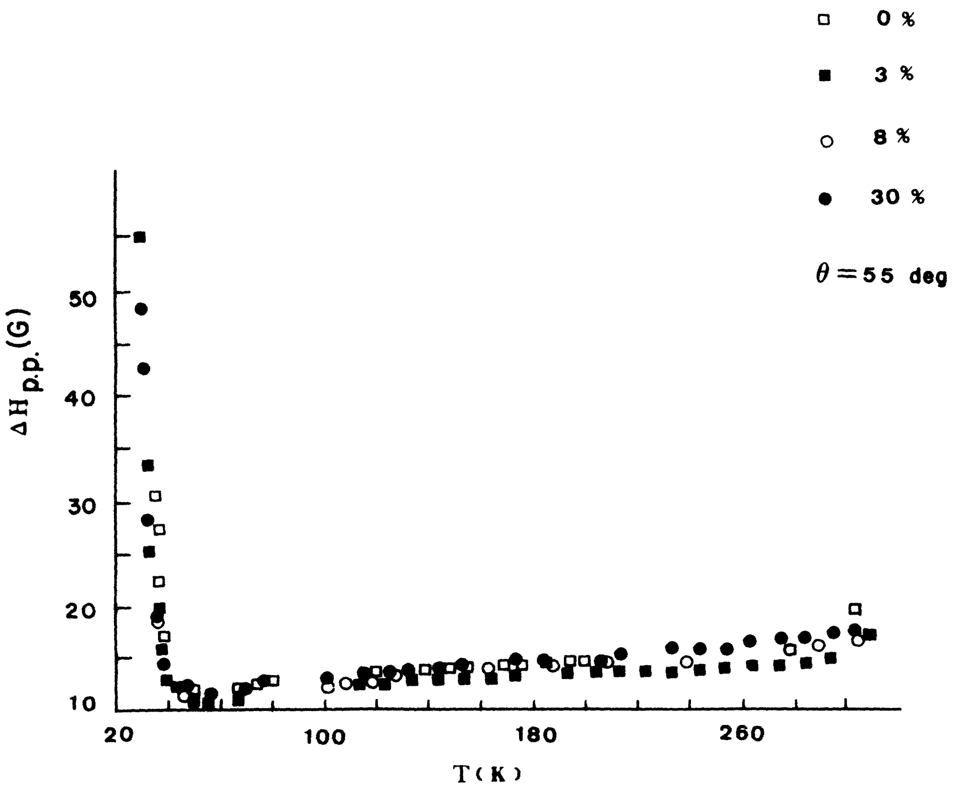

FIG. 3. Linewidth $\Delta H_{\mathrm{p.p.}}$ (peak-to-peak) width of the derivative of resonance line as a function of temperature $T$(K) at $\theta=55°$.

to be Lorentzian in character at long times which again is the characteristic of diffusive motion of spins.[4] The presence of impurities alters the spin-diffusion constant $D$ and has an effect on the line shapes in 2D systems unlike the Richards[6] model for 1D systems. The non-Lorentzian character was observed to increase with the increase in impurity concentration at all three angles of orientation $\theta$ in all four samples. In addition, we have observed the line shapes at $\theta=90°$ to be more Lorentzian than those at $\theta=55°$ in all four samples. At $\theta=0°$, the non-Lorentzian character in all four samples was observed to be very pronounced as the diffusive model of Richards'[4] predicts.

## EXPERIMENT

Single crystals of $C_2H_5(NH_3)_2MnCl_4$ with different concentrations of $Cu^{2+}$ ion impurity were grown by slow evaporation of solution of manganese chloride, ethyl alcohol, and copper chloride following the method suggested by Boesch[2] and Van Amstel.[3] The crystals were chemically analyzed by atomic absorption spectrometry to determine the impurity concentrations. The crystals studied here by ESR have the following concentrations of $Cu^{2+}$ impurity 0, 3, 8, and 30 at. % (samples 1–4). The crystals were of size $1.5\times1.5\times0.3$ mm$^3$. These crystals are isomorphous with $C_2H_5(NH_3)_2MnCl_4$ (Ref. 7) and from the x-ray data of these crystals, the lattice constants $a$, $b$, and $c$ (where $a$ plane contains $Mn^{2+}$ or $Cu^{2+}$ ions) are shown to be 7.35, 7.47, and 21.18 Å, respectively, and where we chose the $c$ axis to be normal to the plane. We have recorded the derivatives of the absorption mode of ESR lines for the measurement of the linewidths using magnetic field modulation and at an $X$-band microwave frequency of 9.6 GHz. We let the helium vapor circulate around the sample for sufficiently long time until a steady value of temperature of the crystal is reached before any ESR line was recorded.

In Fig. (1) we have presented the angular ($\theta$) dependence of peak-to-peak linewidth $\Delta H_{\text{p.p.}}$ for all four samples at room temperature. In Figs. 2 and 3 we have presented the $\Delta H_{\text{p.p.}}$ as a function of temperature at $\theta=0$ and 55 K, respectively. In Figs. 4–6 we have presented the lineshapes of ESR lines in all four samples at $\Theta=55°$, 90°, and 0° at room temperature. For the line shapes we have recorded the pure absorption mode of ESR lines

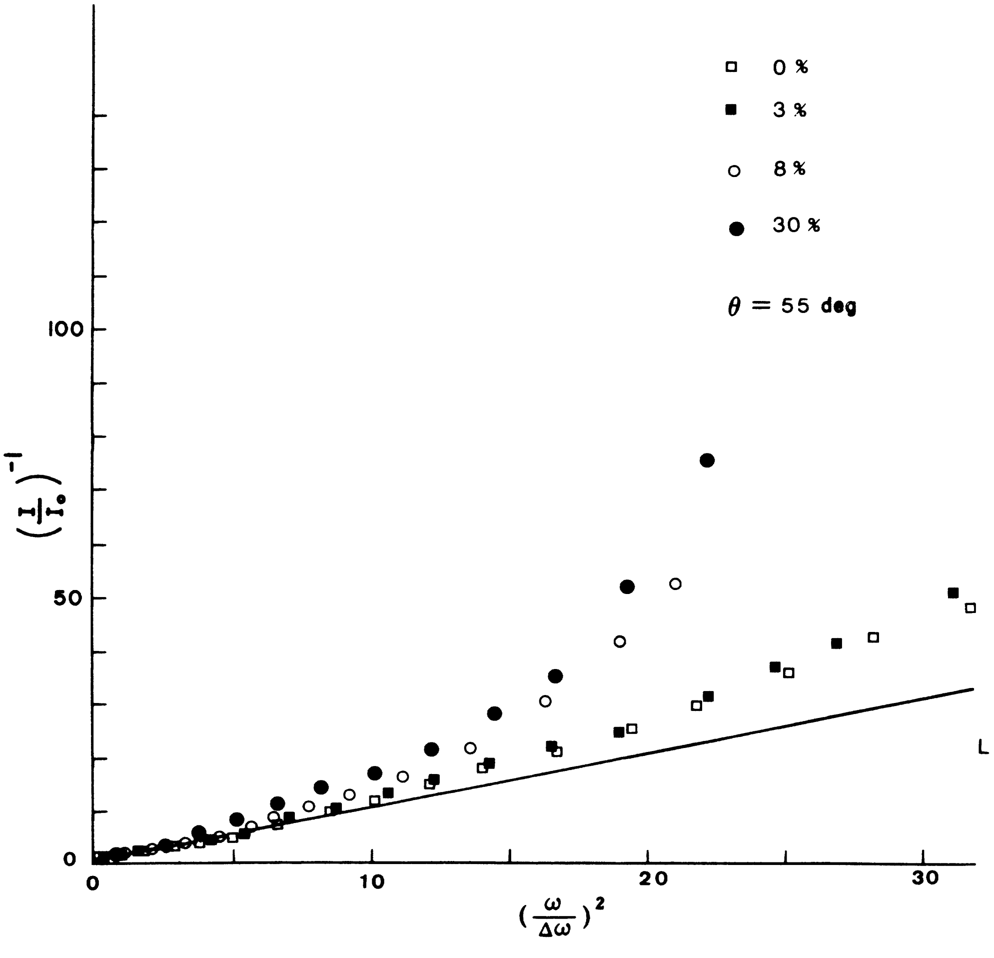

FIG. 4. Line-shape data at room temperature (295 K). The straight line is the Lorentzian line shape at $\theta=55°$. $\omega$ is the angular frequency of resonance, and $\omega=0$ is the center of the resonance absorption peak. The line width $\Delta\omega$ is half width at half maximum intensity of resonance line. $I$ is the height of the line at $\omega$ and $I_0$ is the maximum height of the line at $\omega=0$.

without the magnetic field modulation which causes the distortion of the line shape. In Table I we have presented the linewidths $\Delta H_{\text{p.p.}}$ measured at different values of $\theta$, at different temperatures in all four samples.

## RESULTS AND DISCUSSION

At room temperature we have observed the linewidths $\Delta H_{\text{p.p.}}$ in all four samples (Fig. 1), to have $\theta$ dependence as given by Eq. (1) (within 10% experimental error) which is the characteristic of 2D systems. The values of $\beta$ in Eq. (1) at $\theta=0°$ and 90° in each sample differ by about 20%, and therefore we have listed only the values of $\beta$ at $\theta=0°$ in Table I. As the temperature was lowered from 295 to 60 K all four samples maintained the 2D character, although both $\alpha$ and $\beta$ decreased in value, the former by about 25% and $\beta$ by a very large factor from a value of 5 at 295 K to less than half at 60 K (Table I).

It has been shown[8] that the exchange narrowed ESR line in a pure 2D system $C_2H_5(NH_3)_2MnCl_4{}^{2+}$ will have a linewidth $\Delta\omega(\gamma\Delta H=\Delta\omega)$, where for a free electron $\gamma=1.76\times10^7\ \text{sec}^{-1}/\text{G}$ is of the form

$$\Delta\omega \approx \langle \Delta\omega^2\rangle \tau_c \ln(J/\langle\Delta\omega^2\rangle^{1/2}) \qquad (2)$$

(the $g$ value of $Mn^{2+}$ is very nearly 2 as that of a free electron), where $\langle\Delta\omega^2\rangle$ is the static second moment of the resonance line, $\tau_c$ is of the order of $\hbar/J$, $J$ is the exchange interaction constant, and $J/k_B \approx 5$ K, where $k_B$ is Boltzman's constant. The precise value of $\tau_c$ is related to the spin diffusion constant $D$ which, for large spin values and temperature $T$, is given by the following equation.[4,5]

$$D(T=\infty)=\tfrac{1}{3}(2\pi)^{1/2}Ja^2[S(S+1)]^{1/2} \qquad (3)$$

for a square lattice where the lattice constant $a=7.4$ Å and $S=\frac{5}{2}$ for a $Mn^{2+}$ ion. However, $D$ is a function of

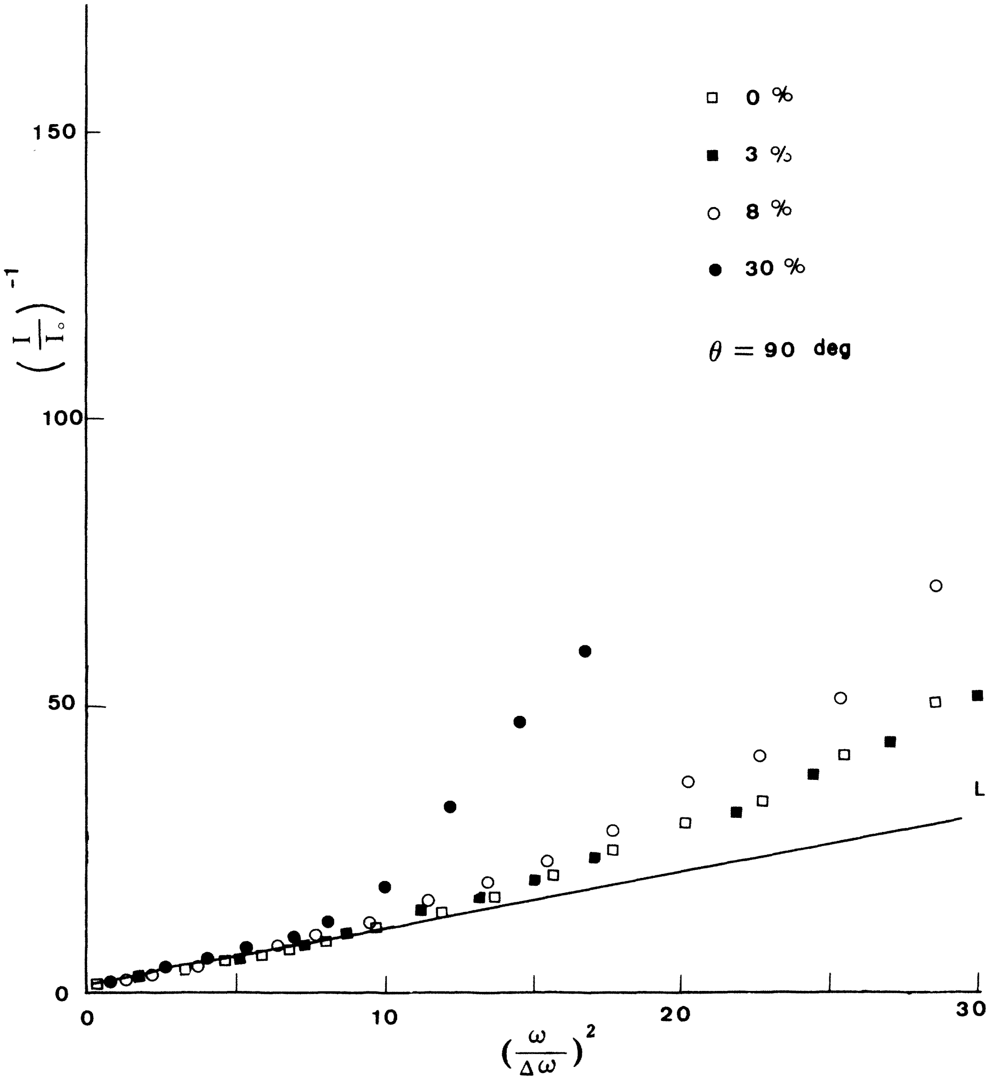

FIG. 5. Line-shape data at $\theta=90°$ and room temperature (295 K). The solid straight line is the Lorentzian line shape. $\omega$ is the angular frequency of resonance, and $\omega=0$ is the center of resonance absorption $\Delta\omega$ is half width of the resonance line at half maximum intensity. $I$ and $I_0$ are the heights of the line at $\omega$ and $\omega=0$, respectively, and $I_0$ is the maximum height of the resonance line.

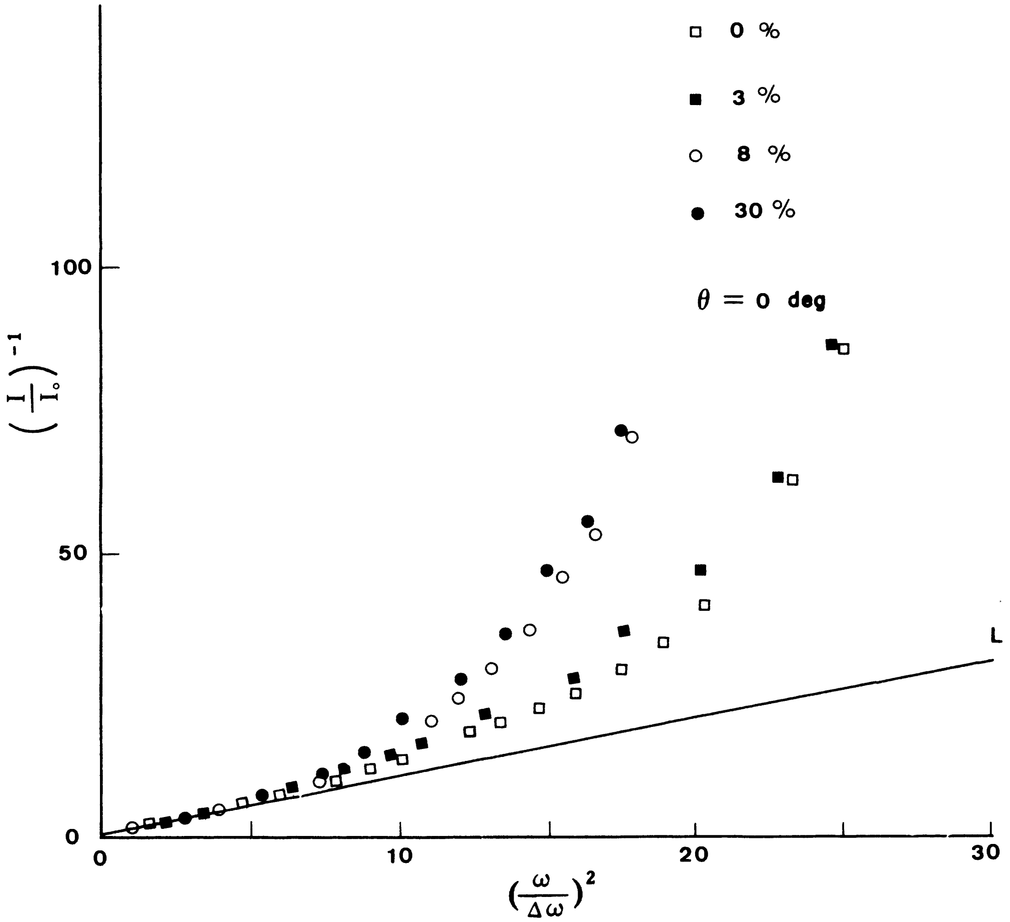

FIG. 6. Line-shape data at $\theta=0°$ and room temperature 295 K. The solid straight line is the Lorentzian line shape. $\omega$ is the angular frequency of resonance and $\omega=0$ is the center of the resonance absorption line. $\Delta\omega$ is the half width of the line at half maximum intensity. $I$ is the height of the line at $\omega$, and $I_0$ is the maximum height of line at $\omega=0$.

TABLE I. Line widths $\Delta H_{\text{p.p.}}$ measured at $T=295$ and 60 K in the impurity doped samples of $C_2H_5(NH_3)_2MnCl_4$:$Cu^{2+}$ at $\theta=0°$, 55°, and 90°. The error in the measured values of linewidths $\Delta H_{\text{p.p.}}$ is less than $\pm\frac{1}{2}$ G. The error in the measured values of temperature $T$ is about $\pm1$ K. The error in $\theta$ is $\pm1°$.

| No. | Sample $Cu^{2+}$ conc. (at. %) | $T$ (K) | $\Delta H_{\text{p.p.}}$ (G) $\theta=0°$ | $\Delta H_{\text{p.p.}}(\alpha)$ (G) $\theta=55°$ | $\Delta H_{\text{p.p.}}$ (G) $\theta=90°$ | $\beta$[a] |
|---|---|---|---|---|---|---|
| 1 | 0 | 295 | 44[b] | 18 | 21 | 6.5 |
| | | 60 | 18[c] | 12.5[c] | | |
| 2 | 3 | 295 | 40 | 16.5 | 21.3 | 5.9 |
| | | 60 | 16 | 11 | | |
| 3 | 8 | 295 | 42 | 18.3 | 22 | 5.9 |
| | | 60 | 16 | 12.1 | | |
| 4 | 30 | 295 | 32 | 18.5 | 22.5 | 3.4 |
| | | 60 | 13 | 12.1 | | |

[a] Values of $\beta$ obtained at $\theta=0$ and 90° from Eq. (1) are not equal, and hence we used only the values calculated at $\theta=0°$. At $\theta=90°$ the $\beta$ values differ from those at $\theta=0°$ by 55% for pure sample (Ref. 1), by 18% for samples 2 and 4, and by 36% for sample 3.

[b] These 295-K values are in agreement with those measured by Boesch *et al.* (Ref. 2).

[c] At 80 K, those measured by Boesch *et al.* (Ref. 2) to be 18 and 13 at $\theta=0°$ and 55°, respectively.

temperature and $D(T)/D(T=\infty)\propto 1/T$ as well as a function of impurity spin ($S=\frac{1}{2}$ for $Cu^{2+}$ ion).[7] Therefore, the terms $\langle \Delta\omega^2\rangle\tau_c$, and $J$ in Eq. (2) will have to be modified in order to account for the presence of impurity ions. To account for the effect of impurity ions on the linewidth[4] in 1D tetramethyl manganese trichloride $(CH_3)_4NMnCl_3$ (Ref. 7) Richards has suggested that the $z$ component of $Cu^{2+}$ spin $S^z_{Cu^{2+}}$ be replaced by zero at the sites occupied by $Cu^{2+}$ ions, because the value of $\langle (S^z_{Mn^{2+}})^2\rangle$ is $\frac{35}{3}$ greater than that for $Cu^{2+}$ ion. As a result, the mean square value of $S^z$ of the $Mn^{2+}$ ion, when averaged over all sites, was shown to be

$$\langle (S^z_{Mn^{2+}})^2\rangle=\tfrac{1}{3}S(S+1)(1-x)\ , \tag{4}$$

where $x$ is the impurity ion concentration. Therefore, we have replaced $S(S+1)$ in the equation for the second moment of the resonance line[4] of the pure sample $\langle \Delta\omega^2\rangle_{\text{pure}}$ by $S(S+1)(1-x)$:

$$\begin{gathered}\langle \Delta\omega^2\rangle_{\text{pure}}=\tfrac{3}{10}\gamma^4\hbar^2 S(S+1)\sum_j (r_{ij}^{-3})^2(1-3\cos^2\theta)^2\ ,\\ \langle \Delta\omega^2\rangle=(1-x)\langle \Delta\omega^2\rangle_{\text{pure}}\ ,\end{gathered} \tag{5}$$

where $\langle \Delta\omega^2\rangle$ is the second moment of the resonance lines in impure sample due to secular part of the dipolar interaction.

However, the effect of impurities on the spin diffusion constant seems to be small as estimated from the measured linewidths at $\theta=0°$ in samples 1 and 4, with $x=0$ and 0.3 at. % concentration of impurity $Cu^{2+}$ ion. In Eq. (2), a 20% change in the term $J/\langle \Delta\omega^2\rangle^{1/2}$ results in less than 5% change in the logarithmic term $\ln(J/\langle \Delta\omega^2\rangle^{1/2})$. For a pure sample the value of $J/\langle \Delta\omega^2\rangle^{1/2}$ is approximately 127. Therefore the main contribution to the change in linewidth $\Delta\omega$ (observed) in Eq. (2) comes from the changes in the value of terms $\langle \Delta\omega^2\rangle$ and $\tau_c$ due to the impurity, and $\tau_c$ is inversely proportional to $D$:

$$\Delta H_{\text{imp}}/\Delta H_{\text{pure}}=(1-x)D/\tilde{D}\ , \tag{6}$$

where $\tilde{D}$ and $\Delta H_{\text{imp}}$, respectively, are the effective diffusion constant and the linewidth in the impurity doped sample. From the Eq. (6) our estimate of the ratio $\tilde{D}/D=0.96$ in the sample 4 at $\theta=0$, a 4% change in the value of $D$ and at $\theta=55°$ our estimate of $\tilde{D}/D=0.74$ nearly 36% change in $D$. In samples 2 and 3 the changes in the value of $D$ are much smaller. As the temperature $T$ is decreased, the linewidth too decreases but only slowly in all four samples because of the inverse $T$ dependence of diffusion constant $D$ as shown in Eq. C7 of Ref. 4 for the linewidth by Richards.[4] In addition, the angular part $3\cos^2\theta-1$ of the linewidth also decreases as the relative strength of wave vector $q=0$ modes decrease with the decrease in temperature. The observed decrease in linewidth by a factor of 2.4 when $T$ changes by a factor of 5 (295–60 K) at $\theta=0°$ suggests that the temperature dependence of angular term is not as strong as that of the diffusion constant in all four samples. It has been suggested by Huber[9] that as we approach $T_N$, the wave vector $q_0$ terms, characteristic of staggered susceptibility, become dominant and the angular dependence of the linewidth ($\Delta\omega$) close to $T_N$ was shown to be of the form

$$\Delta\omega\propto 1+\cos^2\theta\ . \tag{7}$$

Therefore, according to Eq. (7) no minimum in the linewidth is expected at $\theta=\cos^{-1}(1/\sqrt{3})$. However, we have observed minima in linewidths in all four samples at around 60 K. And also from Eq. (7), we have $\Delta\omega(\theta=0°)/\Delta\omega(\theta=55°)=1.5$. However, the observed value is about 1 at 60 K in all four samples.

## LINE SHAPES

The rapid modulation provided by $\cos(M\omega_0 t)$ terms in the nonsecular part of the dipolar interaction, where $M=1$ or 2 and $\omega_0$ is the Larmor frequency of resonance results in a Lorentzian line shape if the secular part of the interaction is zero in either 1D or 2D system. Therefore, we have recorded the line shapes at $\theta=55°$ at which secular contribution to the line width is very small in all four samples. The presence of impurity in the samples alters the spin diffusion constant $D$ by interrupting the spin diffusion and should have an effect on the line shape, unlike the 1D systems. However, the observed shapes at $\theta=55°$ (Fig. 4) are Lorentzian in character for up to 2.5 line widths from the center of resonance line in only the samples (1–3) with low impurity concentration. The non-Lorentzian character appears in sample 4 after only 1.5 line widths away from the center of the resonance line. The tendency to deviate towards Gaussian line shape increases with the increase in impurity concentration. Even in the pure sample the line shape is non-Lorentzian after only 2.5 line widths from the center. However, the line shapes at $\theta=90°$ (Fig. 5) in the samples 1–3 were observed to be Lorentzian for up to three line widths from the center of the resonance line. Even in the sample 4 at $\theta=90°$ the line shape is Lorentzian up to 2.5 line widths from the center of line. Here also, we have observed the effect of impurity concentration on the line shape, which tends then to be more non-Lorentzian with increase in impurity concentration. At $\theta=0°$ in all four samples (Fig. 6) the line shapes were observed to be Lorentzian only up to 1.5 line widths from the center of the line. The anomalies in line shape which occur primarily due to the secular part of the dipolar interaction are dominant in all four samples at $\theta=0°$ and the deviation toward Gaussian shape is much more pronounced. The line shapes of 3 and 4 (Fig. 6) samples are almost overlapping as they start deviating towards Gaussian shape from the point, three line widths away from the center of resonance line.

## CONCLUSIONS

The temperature dependence of linewidth in the quasi 2D system $C_2H_5(NH_3)_2MnCl_4{:}Cu^{2+}$ doped with different concentrations of $Cu^{2+}$ impurity was observed to be in qualitative agreement with the Richards model[4] where he assumed the diffusive motion of spins for the long time dependence of time correlation functions. However, the line shapes in all four samples at all three angles of orientation $\theta$, seem to be dependent on the presence of impurity ion. The higher the concentration of $Cu^{2+}$ ion was present, the more pronounced was the deviation of the line shape from Lorentzian to non Lorentzian character. We have observed the Lorentzian character to persist for much longer times (three line widths from the center of the resonance line) at $\theta=90°$ than at $\theta=55°$ or 0° in all four samples. However, at $\theta=0°$, where the secular part of the dipolar interaction is the primary cause of the anamolies in the line shapes of resonance lines in 1D and 2D systems, we have observed the line shapes to deviate from Lorentzian character at much lower angular frequencies in all four samples. This seems to be the case in $K_2MnF_4$ also where the line shape at $\theta=0°$ in Fig. 7 of Ref. 4 at room temperature, tends to deviate from Lorentzian shape at about 1.5 line widths away from the center of resonance line. Therefore, the diffusive model of Richards[4] seems to be the appropriate one to explain our experimental results in $C_2H_5(NH_3)_2MnCl_4$:$Cu^{2+}$.

## ACKNOWLEDGMENT

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