EPR experiments in the one-dimensional salt $(CH_3)_4NMnCl_3$ (TMMC) at temperatures between 4.2 and 70 K

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EPR experiments at low temperatures have been performed in the one-dimensional antiferromagnet $(CH_3)_4NMnCl_3$. Two resonances have been observed: one due to the manganese ions in the linear chains and a second of unknown origin. The temperature dependences of the positions and linewidths of the resonance lines have been analyzed in terms of the available theory.

I. INTRODUCTION

Tetramethyl ammonium trichloromanganate $(CH_3)_4NMnCl_3$ (TMMC) is one of the best one-dimensional antiferromagnets[1,2] and probably the better known. The ratio of the interchain to the intrachain exchange constants $|J'/J|$ is of the order of $10^{-4}-10^{-5}$ (Refs. 3 and 4) and the intrachain exchange constant J has a value between 6.3 and 6.7 K.[4,5]

Since the pioneer work of Dingle *et al.*,[1] many experiments have been performed on this salt. The static properties have been studied by magnetic susceptibility and specific-heat measurements.[1,6,7] The low-temperature magnetic susceptibility shows an anisotropic behavior[6] as a consequence of the dipolar interactions between Mn^{2+} ions within the chain, and the system shows a crossover from isotropic Heisenberg ($n=3$) to XY ($n=2$) behavior at $T \lesssim 20$ K.[8]

The occurrence of the three-dimensional ordering at $T_N \simeq 0.85$ K has been observed by several techniques.[3,6] The magnetic field dependence of the Néel temperature has been studied by Dupas and Renard[3,4] at low magnetic fields, and by Borsa *et al.*[9] at higher fields. Recently, this dependence has been compared with other one-dimensional magnetic materials.[10]

The dynamic properties of TMMC have been studied by neutron diffraction experiments.[5]

The antiferromagnetic resonance (AFMR) has been observed by Okuda *et al.*[11] below 1 K, and above 1 K at higher frequencies by the present authors.[12] EPR experiments[13–15] in this one-dimensional magnetic system show interesting effects:

(i) A large shift in the position of the EPR signals at low temperatures, due to the effect of the short-range order characteristic of one-dimensional systems, was observed by Nagata and Tazuke.[13]

(ii) An angular dependence of the linewidth and line shape at high temperature is found and differs drastically from the one observed in three-dimensional exchange-narrowed paramagnets.[16] The observed behavior is explained taking into account the especially long time persistence of spin correlations in a one-dimensional magnetic material.[14]

(iii) The temperature dependence of the linewidth has been observed and explained quantitatively by Cheung *et al.*[125] between 40 and 300 K.

Discrepancies exist between the low-temperature results:

(a) No shift in the position of the EPR signals has been observed in Ref. 15 at temperatures as low as 1.5 K, in contradiction with the previous results of Ref. 13 and with the shifts observed in other one-dimensional magnets.[17]

(b) The linewidth observed in TMMC by Cheung *et al.*[15] increases when the temperature decreases in the temperature range $40 < T < 100$ K, and decreases at temperatures lower than 40 K. This temperature dependence is different from that observed in the one-dimensional magnet $CsMnCl_3 \cdot 2H_2O$ by Tazuke *et al.*[18] In this work the linewidth increases in the whole temperature range $10 < T < 100$ K as the temperature decreases.

We report here EPR experiments at high frequencies of the order of 100 GHz, and in magnetic fields up to 60 kG. We have studied, in the temperature range $4.2 < T < 70$ K, the temperature dependence of the positions and of the linewidths of the resonances of the Mn^{2+} ions with the external magnetic field applied parallel and perpendicular to the chain axis.

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II. EXPERIMENTAL SET-UP AND SAMPLES

The microwave set-up is a simple transmission system. The microwave transmitted through the sample is measured by a carbon bolometer as a function of the steady magnetic field. The power of the microwave source is modulated at 85 Hz, and the signal detected by the bolometer is proportional to the power transmitted through the sample. A lock-in amplifier is used for the amplification of the signal. The amplified signal is plotted as a function of the magnetic field on an X-Y recorder.

The microwave sources consist of several carcinotrons (backward wave oscillators) and the magnetic field is produced by a superconducting magnet which can be swept up to 60 kG. Inside the Dewar, which contains the superconducting magnet, there is another Dewar which can be isolated from the previous one. The sample holder (Fig. 1) is mounted in this inner Dewar which fits in the core of the magnet. Experiments can be performed at temperatures between $1.4 < T < 70$ K. A heater mounted around the sample holder maintains the sample temperature via the use of a temperature sensor (carbon resistor) and P.I.D. (proportional integral differential) system. The temperature is measured with an adjacent carbon resistor. Using a rotating device,[19] the sample in any crystallographic direction in a plane can be set parallel to the external magnetic field. From the sources to the sample, the microwave propagates along oversized wave guides. It is directed on to the front of the sample, a crystallographic plane, through a coupling hole. The bolometer is an Allen-Bradley resistor thinned down to 0.2 mm.

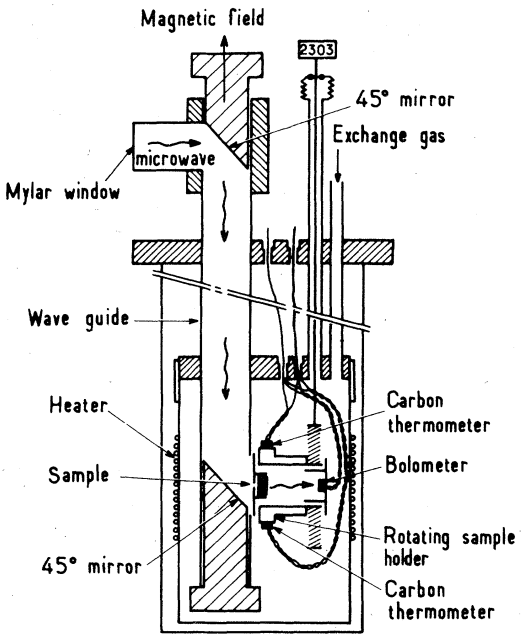

FIG. 1. Sample holder.

The samples used in this study were grown by slow evaporation of saturated solutions prepared with stoichiometric amounts of $N(CH_3)_4Cl$ and $MnCl_2 \cdot 4H_2O$.

TMMC is hexagonal at high temperatures.[20] A structural phase change occurs at a temperature of 126 K[5,20] below which the structure is monoclinic. Several crystals were mounted in the rotating device previously described with the magnetic field in the (c,a) plane or in the (a,a) plane, so that any direction in these planes could be set parallel to the direction of $\vec{H}$.

III. EXPERIMENTAL RESULTS

Typical recorder traces are shown in Figs. 2 and 3. At temperatures between 4.2 and 10 K, only one resonance signal previously reported at temperatures $1.5 < T < 4.2$ K (Ref. 12) is observed. The g value for this resonance was measured at 1.7 K at several frequencies between 73 and 135 GHz. The value is $g = 2.0 \pm 0.05$. The linewidth measured for $\vec{H} \perp \vec{c}$ at $T = 4.2$ K is $\Delta H = (900 \pm 200)$G. No angular variation of the linewidth is observed for $\vec{H}$ in the (c,a) plane.

As shown in Fig. 2 for $\vec{H} \perp \vec{c}$ and $T \gtrsim 10$ K a new, large, resonance is observed at higher fields than the resonance line described above. For $\vec{H} \parallel \vec{c}$, this new resonance is observed also for $T \gtrsim 10$ K, but at lower fields than the other resonance.

The shifts between the two resonances for $\vec{H} \parallel \vec{c}$ and $\vec{H} \perp \vec{c}$ decrease when the temperature is increased,

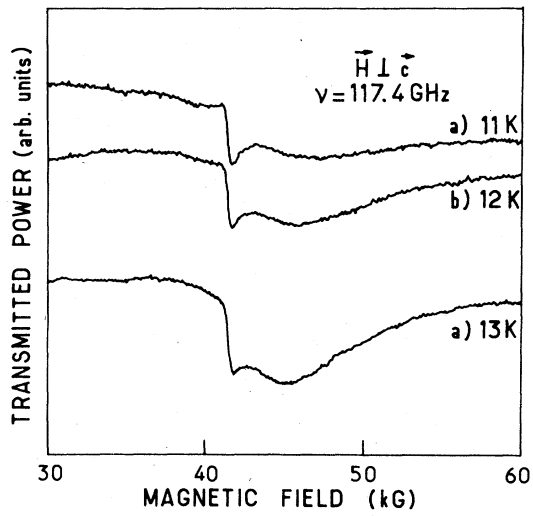

FIG. 2. Typical recording traces at three temperatures. The center of the resonance lines is identified as the minima of the transmitted power.

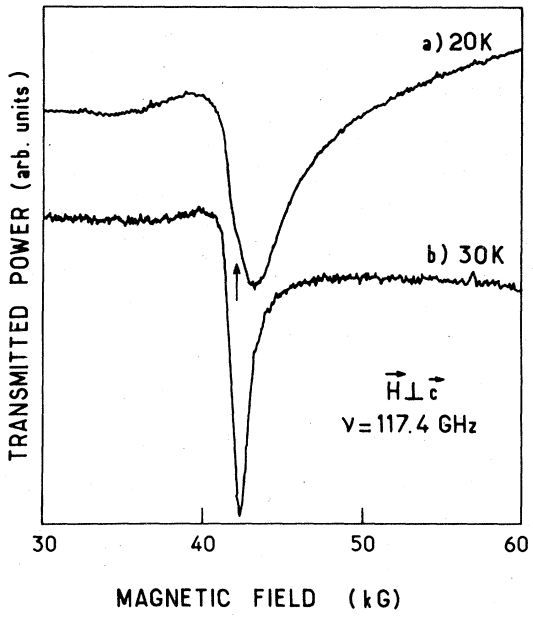

FIG. 3. Typical recording traces at 20 and 30 K. The center of the resonance lines is identified as the minima of the transmitted power.

and at temperatures higher than 20 K only one resonance can be observed (Fig. 3). At temperatures higher than 60 K, no significant variation in the position of the resonance field can be observed for both $\vec{H} \| \vec{c}$ and $\vec{H} \perp \vec{c}$.

The temperature dependences of the positions in field of the new resonance line are shown on Figs. 4 and 5 for $\vec{H} \| \vec{c}$ and $\vec{H} \perp \vec{c}$, respectively.

The temperature dependence of the full linewidth at half-height is shown for $\vec{H} \| \vec{c}$ and $\vec{H} \perp \vec{c}$ in Figs. 6 and 7. In both cases the linewidth decreases when the temperature increases for the resonances observed at $T > 10$ K. The observed values at $T = 60$ K are $\Delta H = (900 \pm 200)$ G for $\vec{H} \perp \vec{c}$ and $\Delta H = (2100 \pm 300)$ G for $\vec{H} \| \vec{c}$. For the resonance observed at 4.2 K only a slight variation is observed for the linewidth in the range $4.2 < T < 14$ K for the two orientations of $\vec{H}$.

Our experimental results show clearly the simultaneous existence of two resonance signals. The resonance observed for $T > 10$ K can be attributed as the EPR signal due to the Mn^{2+} ions in the magnetic chains along the c axis, as we show below. The second resonance observed at lower temperatures cannot be attributed to these Mn^{2+} ions. It can be an impurity signal. However, experiments on samples of TMMC with different purity, and on samples doped intentionally with Cu, show no important differences in the intensity and linewidth of this resonance. The origin of this resonance remains unclear.[12]

The existence of two resonance signals can explain

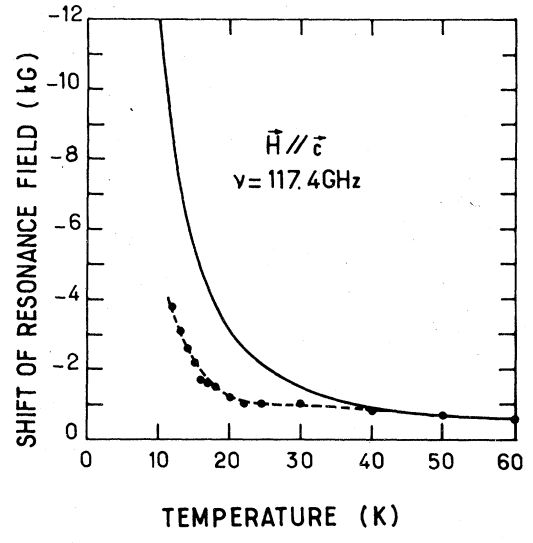

FIG. 4. Temperature dependence of the shift of the EPR positions for $\vec{H} \| \vec{c}$. • experimental points; —theoretical curve; - - - curve between the experimental points (a guide to the eye). The shift at $T = 60$ K has been made arbitrarily equal to the theoretical shift.

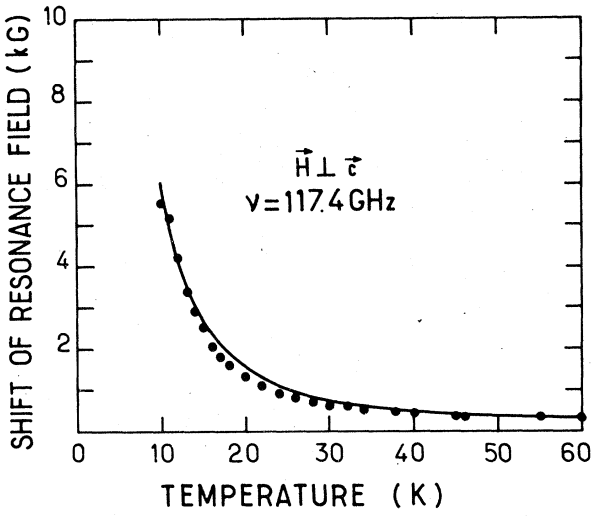

FIG. 5. Temperature dependence of the shift of the EPR positions for $\vec{H} \perp \vec{c}$. • experimental points; —theoretical curve.

the discrepancies between the previous experiments[13,15]:

(i) The shift observed in the positions of the EPR signals observed at $T > 10$ K are qualitatively in agreement with those observed by Nagata and Tazuke.[13] No shift is observed for the second resonance at $T = 4.2$ K. This explains why Cheung *et al.*[15] do not observe shifts in their resonance line at low temperatures.

(ii) The linewidth observed for the EPR signals observed at $T \gtrsim 10$ K always increases when the temperature decreases, in qualitative agreement with the temperature dependence of ΔH in the one-dimensional $CsMnCl_3 \cdot 2H_2O$.[18] For the second resonance the values of $\Delta H = 4.2$ K are in agreement with the value of Cheung *et al.*[15] at this temperature. The temperature variation of the linewidth reported by these authors seems to be a mixture of those reported for the two resonances observed in this work.

IV. COMPARISON BETWEEN EXPERIMENT AND THEORY

We have calculated the resonance frequencies according to the theory of Nagata and Tazuke.[13] In a linear chain of $N+1$ atoms of spin S described by the Hamiltonian

$$\mathcal{H} = -2J \sum_{j=1}^{N} [(1+\alpha)(S_j^x S_{j-1}^x + S_j^y S_{j-1}^y) + (1-2\alpha) S_j^z S_{j-1}^z] - g\mu_B \sum_{j=0}^{N} \vec{S}_j \cdot \vec{H} \ , \tag{1}$$

with

$$\alpha = -(g^2 \mu_B^2 / a^3)(1/2J) \ , \tag{2}$$

where a is the nearest-neighbor separation along the chain, J is the exchange constant, and H is the external magnetic field. The resonances frequencies, according to this theory, are for $\vec{H} \parallel \vec{c}$

$$\hbar\omega_{\parallel} = g_{\parallel}\mu_B H - \frac{12 J \alpha N \langle S_m^z S_{m+1}^z - S_m^x S_{m+1}^x \rangle}{\langle S^z \rangle} \tag{3}$$

and for $\vec{H} \perp \vec{c}$

$$\hbar\omega_{\perp} = g_{\perp}\mu_B H + \frac{6 J \alpha N \langle S_m^x S_{m+1}^x - S_m^z S_{m+1}^z \rangle}{\langle S^x \rangle} \ . \tag{4}$$

In this case, the correlations functions $\langle S_m^\alpha S_{m+1}^\alpha - S_m^\beta S_{m+1}^\beta \rangle$ can be calculated for a model of classical spins, and considering an isotropic Heisenberg Hamiltonian.[13,21] The result of this calculation is only valid, however, for low magnetic fields and the condition

$$g\mu_B HS(S+1)/kT << 1 \tag{5}$$

should be fulfilled. The results are

$$\hbar\omega_{\parallel} = g_{\parallel}\mu_B H - 12\alpha g \mu_B H \frac{1}{10x}\left(\frac{2+ux}{1-u^2} - \frac{2}{3x}\right) \ , \tag{6}$$

$$\hbar\omega_{\perp} = g_{\perp}\mu_B H + 6\alpha g \mu_B H \frac{1}{10x}\left(\frac{2+ux}{1-u^2} - \frac{2}{3x}\right) \ , \tag{7}$$

where

$$u(k) = \coth K - 1/K \ , \tag{8}$$

and

$$x = \frac{k_B T}{2|J|S(S+1)} = -\frac{1}{K} \ . \tag{9}$$

The theoretical curve for $\vec{H} \perp \vec{c}$ is plotted in Fig. 5.

We take the values $J = -6.5$ K and $a = 3.25$ Å. The agreement between the theoretical curve and the experimental points is fairly good. Nagata and Tazuke[13] have explained their experimental results in TMMC including a single-ion anisotropy term $-D \sum_{j=0}^{N} (S_j^z)^2$ with $D = 0.10$ cm^{-1}. In our work no D term has been included, in agreement with the recent experimental result reported by Tazuke[22] in TMCC: Mn^{2+} where $D \simeq 0.004$ cm^{-1}. However, it should be noted that in our work condition Eq. (5) is not verified for all magnetic fields and temperatures.

For $\vec{H} \parallel \vec{c}$, the theoretical curve is plotted in Fig. 4 for the same values of J and a. The agreement with the experimental points is not good particularly at low temperatures. The theoretical shift is about a factor of 2 the experimental value. Care should be taken as the calculation of the correlations is applied for an isotropic Heisenberg Hamiltonian, and cannot be applied directly at temperatures where the dipolar interaction and the magnetic field produce anisotropy. This is probably the cause of the discrepancy between experiment and theory.

The temperature variation of EPR linewidth has been calculated within Kubo-Tomita's framework.[23] As in the paper of Tazuke and Nagata,[18] the linewidth is divided into two parts: one is due to the Gaussian decay or short-time contribution, and the remaining part corresponds to the long-time diffusive decay

$$\Delta\omega = \Delta\omega_G + \Delta\omega_D \ . \tag{10}$$

The Gaussian part of the linewidth, which is predominant in the range of temperatures studied, is given by

$$\Delta\omega_G = \left(\frac{\pi}{2}\right)^{1/2} \left(\frac{M_2^3}{M_4}\right)^{1/2} \ . \tag{11}$$

The Van Vleck second and fourth moments M_2 and

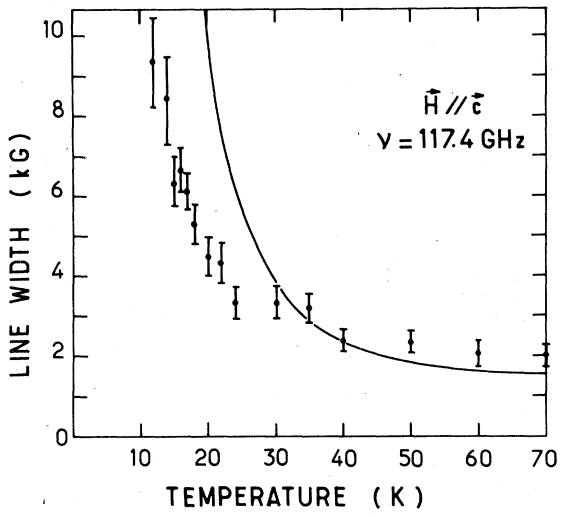

FIG. 6. Temperature dependence of the EPR linewidth for $\vec{H} \| \vec{c}$. ϕ experimental points; ——theoretical curve.

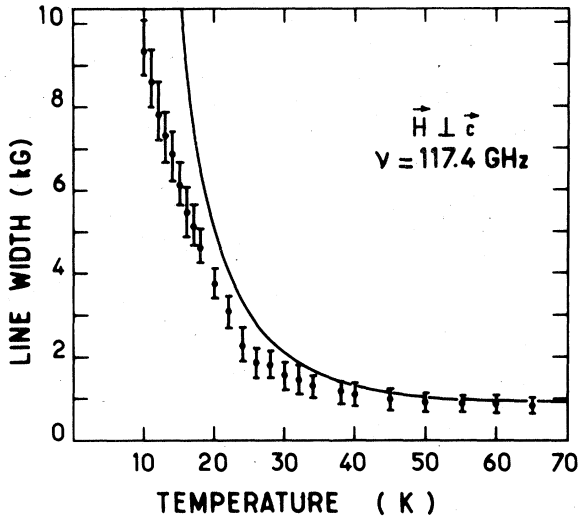

FIG. 7. Temperature dependence of the EPR linewidth for $\vec{H} \perp \vec{c}$. ϕ experimental points; ——theoretical curve.

M_4 can be calculated exactly by the use of classical spins[18]

$$M_2 = 3\zeta(6)\gamma e^4 \hbar^2 S(S+1)\frac{1+\cos^2\theta}{a^6} f(x) \quad , \tag{12}$$

$$M_4 = \tfrac{192}{5}\zeta(6)\gamma e^4 [S(S+1)]^2 J^2 \frac{1+\cos^2\theta}{a^6} g(x) \quad , \tag{13}$$

where

$$\zeta(6) = \sum_n n^{-6} = 1.05$$

and θ is the angle between the c axis and the magnetic field direction, and where

$$f(x) = \frac{1-u}{1+u}\left[\frac{12u^2}{5(1-v)} + \left[1 = \frac{v}{5}\right]\right] \quad , \tag{14}$$

$$g(x) = \frac{1-u}{1+u}\left[\frac{9vx(1-u)^2}{8} - 3ux\left[1 - \frac{3u+v}{4}\right]\right] \quad , \tag{15}$$

with x and u previously defined and $v = 1 + 3ux$. The temperature dependence of the second part $\Delta\omega_D$ has also been calculated as in Ref. 15.

In Figs. 6 and 7, we plot the theoretical curves for the values $J = -6.5$ K and $a = 3.25$ Å. In this case again, the agreement between experiment and theory is better for $\vec{H} \perp \vec{c}$ than for $\vec{H} \| \vec{c}$. As the theory for the linewidth has the same limitations as that for the resonance positions, we conclude that the theory available for the moment only qualitatively explains the experimental results.

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