Evidence of a large quantum shift of the antiferromagnetic resonance in three quasi-one-dimensional antiferromagnets

Jacques Tuchendler and José Margariño
Groupe de Physique des Solides de l'Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris 05, France*

Jean Pierre Renard
Institut d'Electronique Fondamentale, Bâtiment 220, Université Paris Sud, 91405 Orsay, France*
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Antiferromagnetic resonance experiments in three one-dimensional manganese compounds [$CsMnCl_3 \cdot 2H_2O$ (CMC), $(CH_3)_2 NH_2 MnCl_3$ (DMMC), and $(CH_3)_4 NMnCl_3$ (TMMC)] show disagreement with the classical antiferromagnetic resonance theory. In the three compounds we observe a positive shift in magnetic field of the resonance lines corresponding to the low-frequency mode. We show that this shift is larger for the compounds with smaller ratio $|J'/J|$ and try to explain this effect in terms of the quantum spin reduction of the magnon energy.

The dynamic properties of one-dimensional (1D) magnetic systems have been extensively studied in the last few years.[1] The high-temperature dynamics is now well understood, especially in 1D Heisenberg systems, where it is governed by a spin-diffusion process.[2] In particular, a great deal of experimental data have been obtained on tetramethylammonium trichloromanganate (TMMC), which well approximates the classical 1D Heisenberg antiferromagnet. The NMR and EPR results at high temperature are well explained by the simple model of 1D spin diffusion.[2,3]

On the other hand, the low-temperature dynamics, which is more complex, is not fully explained. In the intermediate temperature range, where static spin correlations start to develop, the EPR measurements[4] on TMMC are qualitatively explained by theory. At lower temperatures, close to the three-dimensional magnetic-ordering temperature T_N, the spin dynamics are essentially different. In large applied fields above T_N, magnetic solitons[5] seem to play an important role in the spin dynamics. In addition, magnon modes are observed above and below T_N by neutron scattering experiments. Their magnetic field dependence, recently studied by Heilman *et al.*[6] is not explained by spin-wave theory.

In this paper, we are concerned only by the uniform magnon modes ($\vec{q}=0$) observed in antiferromagnetic resonance. In a preliminary publication[7] we reported the frequency field dependence of the low-frequency mode, and the observation of crystalline domains on TMMC. We observed a sensitive magnetic field shift of the resonance lines to higher fields.

We report here new antiferromagnetic resonance (AFMR) results on high-quality TMMC crystals and on two other quasi-1D Heisenberg antiferromagnets: $(CH_3)_2NH_2MnCl_3$ (DMMC) and $CsMnCl_3 \cdot 2H_2O$ (CMC). The experiments were performed at temperatures between 1.5 and 4.2 K, in a large range of frequencies ($50 < \nu < 310$ GHz) and magnetic fields ($0 < H < 60$ kG). The microwave and cryogenic apparatus have been described elsewhere.[4] The single crystals used were grown from solutions.[8,9]

We first present the results on CMC. The crystal structure is orthorhombic. The Néel temperature at zero field is 4.89 K. The magnetic chains of Mn^{2+} ions are along the a (hard) axis. The spins are perpendicular to this axis and b is the easy magnetization axis. AFMR data at lower frequencies and fields[10,11] have been reported previously.

The experiments on this system were performed at two temperatures, $T=4.2$ and 1.8 K. At 4.2 K, we observed the expected antiferromagnetic resonances, but the lines were rather broad ($T \lesssim T_N$). The magnetic field was put in a ba plane or parallel to the c axis. We did not see any signal corresponding to $g \approx 2$ like those observed in TMMC.[7,12]

At $T=1.8$ K, narrow antiferromagnetic resonances were observed. We studied the angular variation of these resonances in a ba plane. At a frequency $\nu=94.4$ GHz, we observed two resonances at magnetic fields 18.4 and 39.2 kG, respectively, for $\vec{H} \| b$. They correspond to the upper and lower frequency modes of AFMR given in Ref. 11. The first resonance line goes towards higher fields, and the second goes towards lower fields when $\vec{H}$ moves towards the a axis. The widths of both resonances increase and the lines disappear when the angle $(\vec{H}, b)$ is larger than 30°. The angular dependence of the lower mode is in qualitative agreement with equation[13]:

$$\frac{H_x^2}{C_1+(\omega/\gamma)^2} - \frac{H_z^2}{(C_2-C_1)-(\omega/\gamma)^2} = 1 \ , \qquad (1)$$

where $H_x = H \sin\theta$, $H_z = H\cos\theta$, θ being the angle between the external magnetic field and the hard axis (a axis). $C_1 = 2H_aH_E$ and $C_2 = 2H_AH_E$ are related to the in-plane and out-of-plane anisotropies[11]: $(2H_aH_E)^{1/2} = 16.85$ kG and $(2H_AH_E)^{1/2} = 34.8$ kG.

We have studied the frequency versus magnetic field dependences of the antiferromagnetic resonance modes when $\vec{H}$ is parallel to the easy b and to the intermediate c axis. This dependence of the resonance lines must be fitted with the values of the anisotropies given above, and with an *effective magnetic field* $H = H_{appl} - H_0$ as in TMMC.[7]

Let us now consider DMMC. The crystalline structure is monoclinic.[8] The three-dimensional ordering temperature is 3.6 K. The magnetic chains are along the c (hard) axis. The spins are in the c plane and a^* is the easy magnetization axis.[14] We report here the first AFMR experiments in this material.

The experiments on $(CH_3)_2NH_2MnCl_3$ were performed at temperatures between 1.5 and 4.2 K. The single crystals were cut in such a way that the magnetic field was parallel to a ca^* plane or a ba^* plane. At $T = 4.2$ K [$T > T_N(H=0)$] the antiferromagnetic resonance line is very broad. In addition, in the whole temperature range a $g \approx 2$ resonance signal is observed as in TMMC.[7,12] It may be due to Mn^{2+} ions in partially broken chains resulting from fast thermal variations.[12]

Figure 1 shows at $T = 1.7$ K the angular dependences of these resonance lines when the magnetic field is rotated in the ca^* plane and in the ba^* plane. When $\vec{H} \| a^*$, the AFMR resonance is observed at roughly 7.5 kG, higher in field than the $g = 2$ resonance of the Mn^{2+} ions. It goes rapidly towards higher fields when $\vec{H}$ moves towards c in the ca^* plane. In the ba^* easy plane, this same resonance goes towards lower fields when $\vec{H}$ moves towards b. These angular dependences are characteristic of the low-frequency mode AFMR for an easy c-plane antiferromagnet with a small in-plane anisotropy and with the easy magnetization axis parallel to a^*. This is indeed the case.[14] Such angular variations are similar to those observed in TMMC for one domain in the ca or aa planes.[7]

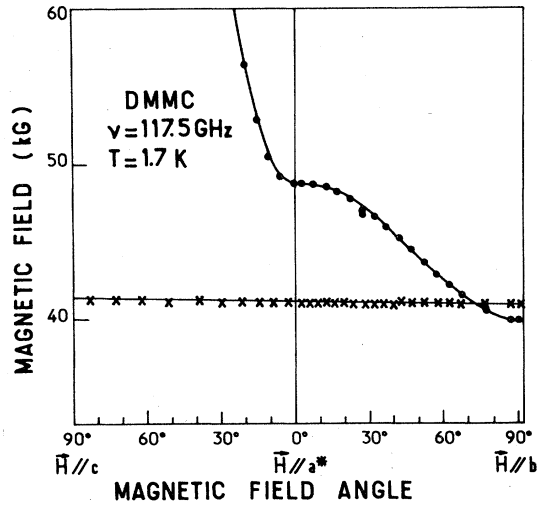

FIG. 1. Angular dependences of the resonances in DMMC at $\nu = 117.5$ GHz for $\vec{H}$ in ca^* and ba^* planes; dots: AFMR signal; crosses: Mn^{2+} paramagnetic signal at $g \approx 2$.

The frequency field dependence of the resonances has been studied in the range $60 < \nu < 310$ GHz for $\vec{H} \| a^*$ and $\vec{H} \| b$. Only the resonance corresponding to the low-frequency AFMR mode has been observed. These dependences can be fitted with an in-plane anisotropy $(2H_aH_E)^{1/2} = 18$ kG. As for the two other cases, an effective magnetic field must be included to fit the data as we show in more detail later on.

In addition we performed new experiments on high quality TMMC crystals. These experiments were made in the same range of temperatures and frequencies as before. The magnetic field was put in the ca or in the aa planes, c being the hexagonal high-temperature axis.[7] The angular dependences of the antiferromagnetic resonances are similar to those observed originally.[7] There are several groups of three resonances with a 120° periodicity. They are due to twinning at the structural transition which occurs in TMMC.

Figure 2 shows the frequency field dependences of

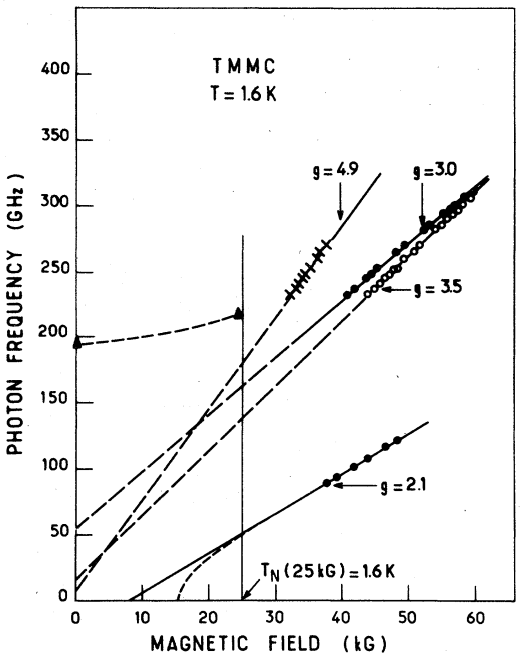

FIG. 2. Frequency vs magnetic field plot of the resonances in TMMC at $T = 1.6$ K for $\vec{H}$ parallel to the in-plane easy axis (for one domain); dots: low-frequency AFMR ($g = 2.1$); dots: high-frequency AFMR ($g = 3$); circles: two-magnon absorption ($g \approx 3.5$); crosses: two-magnon absorption ($g = 4.9$); triangles: high-frequency mode Refs. 6 and 15.

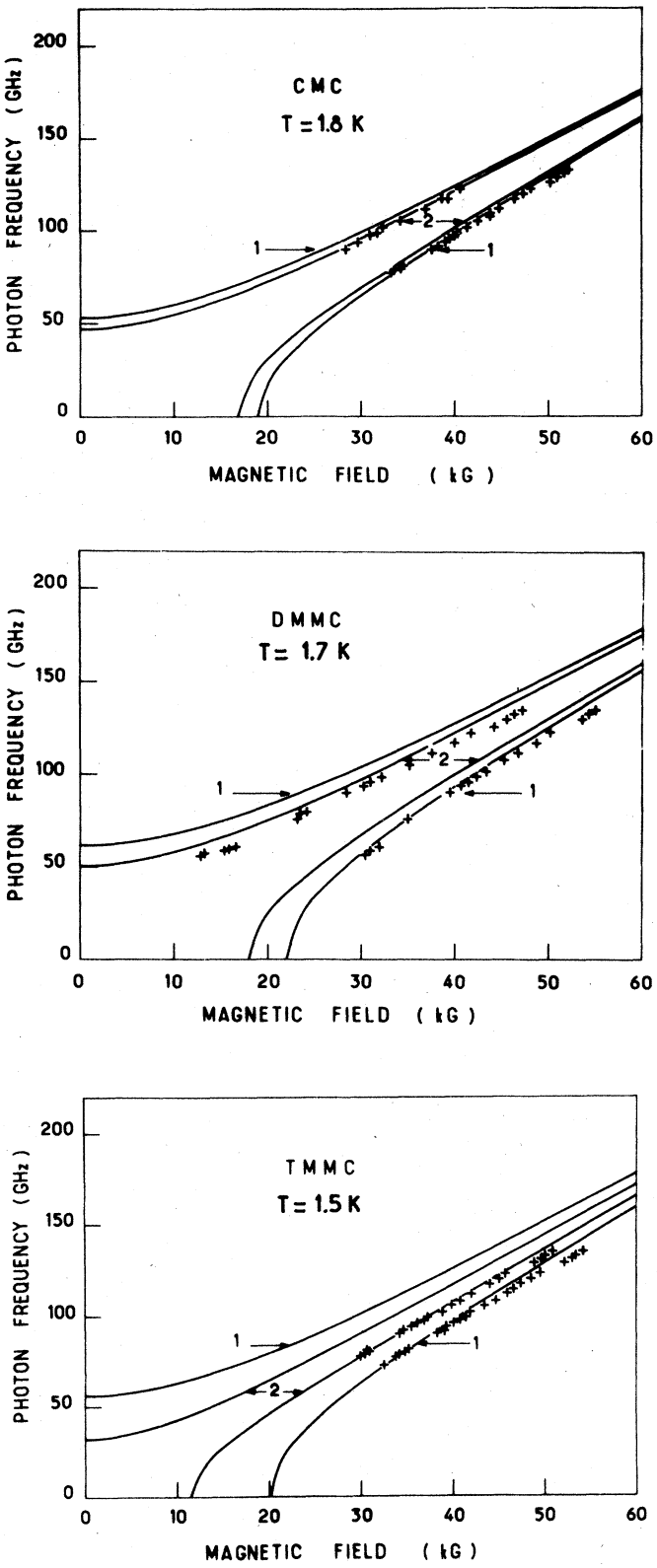

FIG. 3. Frequency vs magnetic field dependences of the low-frequency AFMR for CMC, DMMC, and TMMC. Crosses: experimental points. Continuous lines 1 and 2 are calculated as described in the text.

a high quality TMMC crystal at $T=1.6$ K for the resonance corresponding to one domain and for $\vec{H}$ parallel to the easy axis. The resonances observed in the range $90<\nu<120$ GHz correspond to the low-frequency AFMR mode. Three new resonances are observed in the frequency range $230<\nu<310$ GHz. The measured g factors are indicated in the figure caption. The resonances with $g\approx 3$ are more intense and correspond to the high-frequency AFMR mode observed by Heilman *et al.*[6] at $\nu\approx 190$ GHz for $H=0$. The signals corresponding to $g\approx 3.5$ are probably two-magnon absorptions at a frequency nearly twice that of the low-frequency AFMR modes. The fainter resonances with $g\approx 5$ are observed at a frequency which is the sum of that of the low and high AFMR modes. These resonances have also been observed in the more recent neutron scattering experiments.[15]

Finally, we compare the frequency field dependences of the low AFMR modes in these three compounds. This is shown in Fig. 3.

We tried to fit these experimental results[13] with equation

$$(\omega/\gamma)^2=H^2\pm 2H_aH_E\ , \tag{2}$$

where H_E is the exchange field, H_a the in-plane anisotropy field, and γ the magnetogyric ratio, and where the + and − signs apply to the case $\vec{H}$ parallel to the intermediate axis and easy axis, respectively.

Using accepted values[11,14,16,17] for $(2H_aH_e)^{1/2}$, $H_{sf}\approx(2H_aH_E)^{1/2}$, where sf represents spin flop, we obtained the calculated lines (2) shown in Fig. 3. In all three compounds, these lines are at lower fields than the experimental points when we take $H=H_{appl}$. If we use larger values for the parameter $(2H_aH_E)^{1/2}$, the calculated lines (1) cannot fit both the experimental points corresponding to $\vec{H}$ parallel to the easy and intermediate axes. One can see in this figure that the field shift between the calculated lines and the experimental points is larger in TMMC than in DMMC. This shift is smallest in the case of CMC.

We can fit the experimental points of the frequency field dependences for the three compounds if we introduce in Eq. (2) the effective field $H=H_{appl}-H_0$. In each compound one can obtain two sets of parameters depending on the fitting procedure: either (a) one can use the value of H_{sf} or $(2H_aH_E)^{1/2}$ given by susceptibility or antiferromagnetic resonance experiments[13,15–17] and determine the value of H_0 which best fits the experimental results, or (b) one can also determine both parameters, H_{sf} and H_0, from the best fit of the frequency field dependences in the case of CMC, and from the frequency and angular dependences for $\vec{H}$ in the easy plane for DMMC and TMMC. The values of the parameters used in the fits of the frequency field dependences are shown in Table I.[18] One can see that *the shift H_0 is larger for the compounds where the ratio between interchain and intrachain interactions $|J'/J|$ is smaller.*

These experimental results can be understood in the following terms: The novel feature of our AFMR results is a sensible increase of the resonance

TABLE I. Magnetic parameters of these compounds after de Jonge *et al.* (Ref. 18). Parameters used in the frequency versus field dependence fits. (1) Values used to fit Fig. 3. The values noted (a) and (b) are explained in the text.

		$CsMnCl_3\cdot 2H_2O$	$(CH_3)_2NH_2MnCl_3$	$(CH_3)_4NMnCl_3$
$T_N(0)$ (K)		4.88	+3.6	0.85
J (K)		−3.0	−5.8	−6.7
$\lvert J'/J\rvert$		8×10^{-3}	10^{-3}	10^{-4}
(1)	$(2H_aH_E)^{1/2}$(kG)	16.85–19	18–22	11.5–20
	H_0 (kG)	0	0	0
(a)	$(2H_aH_E)^{1/2}$(kG)	16.85	18	11.5
	H_0 (kG)	1	3	3.7
(b)	$(2H_aH_E)^{1/2}$(kG)	17.6	19	13
	H_0 (kG)	0.8	2.75	4

field with respect to the prediction of the classical theory. Neglecting the anisotropy, the magnon energy gap at $\vec{q}=0$ is equal to $g\mu_B H$ for classical spins. In fact this gap is reduced by at least 10% in the best 1D antiferromagnet TMMC. This strongly suggests a quantum effect due to the finite value of the spin, $S=\frac{5}{2}$. Indeed, it is well known[19] that antiferromagnets exhibit a quantum spin reduction which is most important in lower dimensions.[20] Recently Maki[21] has developed a quantum theory for a 1D planar antiferromagnetic system. At 0 K the nonlinear excitations are solitons of mass m_0. The linear excitations are magnons with energy $\epsilon(q)=(c_0q^2+m_0^2)^{1/2}$ with

$$m_0 = g\mu_B H \exp\left[-\frac{G^2}{8\pi}\ln\alpha\right] , \tag{3}$$

where $G^2=8S^{-1}(1-D/2|J|S^2)^{1/2}$ and $\alpha=8\pi\sqrt{2}|J|S^2/g\mu_B H$. Here D is the planar anisotropy, J is the exchange integral, and H the applied field. In the case of TMMC, $G^2=3.16$ and $\alpha=1.2\times10^4/H$ (kG). The relative quantum spin reduction would be about 0.5 for $H=40$ kG, and nearly field independent in the range 30–50 kG. The relative experimental quantum reductions observed are 0.12, 0.09, and 0.075, for, respectively, 30, 40, and 50 kG.

In neutron[5] and NMR[22] experiments a quantum correction explains the experimental value of the energy of solitons. This correction is in qualitative agreement with the theory of Maki. However, more recent experiments[23] on the magnon energy gap are in agreement with our results and confirm the discrepancy with the theory. Further experiments in a wide range of fields and on antiferromagnets with lower spin value are needed to clarify this effect.

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