Half-field EPR transition in the one-dimensional paramagnet tetramethylammonium-manganese-trichloride (TMMC)*

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We report the observation of a half-field transition in the EPR spectrum of tetramethylammonium-manganese-trichloride (TMMC). The observation of this new resonance is a direct consequence of the one-dimensionality of the spin dynamics of this manganese salt. We present a theory which accounts for many of the observed features in a very satisfactory way. The experiments are performed with the microwave field parallel to the static magnetic field. The most important characteristics of the transition are the scaling of the linewidth with the EPR spectrum obtained with the microwave field perpendicular to the static magnetic field, and its highly anisotropic intensity.

I. INTRODUCTION

Only the magnetic resonance techniques are able to reveal the dynamic properties of one-dimensional magnets at high temperatures. These techniques sample only $k\approx 0$ modes. However, in this region the effect of the lower dimensionality is most dramatic. This was shown for the first time by Dietz *et al.*,[1] who studied the EPR spectrum of TMMC (tetra-methyl-ammonium-manganese-chloride), the best one-dimensional Heisenberg magnet known. The experimental proof of the existence of spin diffusion of two-spin correlation functions in a one-dimensional magnet has been given recently, using NMR spectroscopy.[2] Similarly, the existence of spin diffusion of four-spin correlation functions has been demonstrated with EPR.[3] All magnetic resonance studies of one-dimensional systems reported so far, refer to the resonance at the (nuclear or electronic) Larmor frequency. We wish to report here a new resonance in the EPR spectrum of a one-dimensional Heisenberg magnet. The fact that this resonance can be observed is a consequence of the low dimensionality of the spin dynamics. It cannot be observed in exchange-coupled three-dimensional magnets. The fact that the resonance should exist can be understood readily, although the quantitative interpretation of the experimental results is very difficult. The phenomenon can be understood most easily by explaining why it is not present in a three-dimensional paramagnet, and identifying the parameters which prohibit the observation of the resonances in this case.

In the next section, we will present the theory of EPR absorption in three-dimensional paramagnets using a formalism which is very suitable to treat one-dimensional cases, too. In a natural way, the theory will then be extended to discuss the magnetic resonance absorption in one-dimensional systems. In Sec. III, the experimental details are presented. The experimental results and their discussion will be found in Secs. IV and V, respectively. The sections are presented in that order because it represents our work in chronological order.

II. THEORY

We want to describe the EPR spectrum of a three-dimensional paramagnet at high temperatures. The total Liouville operator of the system is

$$L=L_Z+L_D+L_H, \tag{1}$$

where L_Z, L_D, and L_H are the Liouville operators of the Zeeman interaction, the dipolar interaction, and the Heisenberg exchange coupling, respectively. The fact that we take into account the dipolar interaction in order to describe the spin dynamics is because we want to represent the $\vec{k}=0$ mode. For the other modes, the dipolar interaction can be neglected because we assume to deal with strong exchange coupling. We will need the spin-wave coordinates

$$S(\vec{k},t)=N^{-1/2}\sum_j S_j(t)\exp(-\vec{k}\cdot\vec{r}_j), \tag{2}$$

and denote the Kubo relaxation function by[4]

$$\langle S^\alpha(\vec{k},t)\,|\,S^\alpha(\vec{k})\rangle =\int_0^\beta d\lambda\,\langle\!\langle S^{-\alpha}(-\vec{k},t)\exp(-\hbar L\lambda)S^\alpha(\vec{k})\rangle\!\rangle\,, \tag{3}$$

where α is 0, + or − corresponding to S_z, S^+ or S^-, respectively, and the double brackets indicate thermal averaging. The Mori projection operator method will be used.[5] P^α is the projection operator which projects onto the single spin states,

$$P^\alpha=\sum_{\vec{k}}|S^\alpha(\vec{k})\rangle[\chi^\alpha(\vec{k})]^{-1}\langle S^\alpha(\vec{k})|, \tag{4}$$

in which $\chi^{\alpha}(\vec{k})$ represents the susceptibility, $\langle S^{\alpha}(\vec{k})|S^{\alpha}(\vec{k})\rangle$. Q^{α} projects onto the complementary space,

$$Q^{\alpha}=I-P^{\alpha}. \tag{5}$$

It can be shown,[4,5] that the one-sided Fourier transform of the equation of motion of the relaxation function can be written as

$$\langle S^{\alpha}(\vec{k})|(z-L)^{-1}|S^{\alpha}(\vec{k})\rangle=\chi^{\alpha}(\vec{k})[z-\omega^{\alpha}(\vec{k})-\Gamma^{\alpha}(\vec{k},z)]^{-1}, \tag{6}$$

where the self-energy

$$\Gamma^{\alpha}(\vec{k},z)=\langle Q^{\alpha}LS^{\alpha}(\vec{k})|(z-Q^{\alpha}LQ^{\alpha})^{-1}\times Q^{\alpha}LS^{\alpha}(\vec{k})\rangle[\chi^{\alpha}(\vec{k})]^{-1}, \tag{7}$$

and where the frequency

$$\omega^{\alpha}(\vec{k})=[\hbar\chi^{\alpha}(\vec{k})]^{-1}\langle\langle[S^{-\alpha}(-\vec{k}),S^{\alpha}(\vec{k})]\rangle\rangle. \tag{8}$$

We are interested in the $\vec{k}=0$ mode. In this case, the self-energy can be simplified in the following way:

$$\Gamma^{\alpha}(\vec{k}=0,z)=\langle L_D S^{\alpha}(\vec{k}=0)|(z-Q^{\alpha}LQ^{\alpha})^{-1}\times L_D S^{\alpha}(\vec{k}=0)\rangle[\chi^{\alpha}(\vec{k}=0)]^{-1}. \tag{9}$$

The fluctuation-dissipation theorem connects relaxation functions and correlation functions. One can make a high-temperature expansion of the fluctuation-dissipation theorem. As long as the frequencies of interest are much smaller than kT, the high-temperature form of the fluctuation-dissipation theory can be used,[4]

$$\langle A|B\rangle=\beta\langle\langle A^{+}B\rangle\rangle, \tag{10}$$

in which A and B are spin operators. This is not true in general, but it certainly is for the $k=0$ mode at high temperatures. The frequencies of interest in our case are, in temperature units, about 0.5 K, which is much smaller than the temperatures of interest here (room temperature). Consequently, we will assume that we can use Eq. (10) for the dynamic $k=0$ properties. We will expand the propagator of the self-energy $\Gamma^{\alpha}(\vec{k}=0,z)$ with the dipolar part as a small parameter

$$(z-Q^{\alpha}LQ^{\alpha})^{-1}=(z-L_H-L_Z)^{-1}+(z-L_H-L_Z)^{-1}\times[-P(L_H+L_Z)+QL_D](z-L_H-L_Z)^{-1}+\cdots \tag{11}$$

Inserting this expansion in expression (9), we find that an order of magnitude calculation shows that the contribution of the next nonzero term after the first is already smaller than the first one by a factor of $(\omega_D/\omega_{\mathrm{ex}})^2$, ω_D being the dipolar frequency scale, and ω_{ex} being the exchange frequency scale. This number is very small, and all terms except the first one can safely be neglected when we substitute expansion (11) in expression (9). This argument fails if it is applied to one-dimensional systems, because divergencies will show up. It is now a question of straightforward calculation to express the zero-wave-vector self-energies in terms of four-spin correlation functions of the pure (that is without dipolar propagators) Heisenberg system. The two self-energies $\Gamma^{+}(\vec{k}=0,z)$ and $\Gamma^{0}(\vec{k}=0,z)$ are given by

$$\begin{aligned}\Gamma^{+}(\vec{k}=0,z)=&-i\beta\hbar^{-2}N^{-1}[\chi^{+}(\vec{k}=0)]^{-1}\\&\times\int_0^{\infty}e^{izt}\sum_{j\neq k}\sum_{l\neq m}[\tfrac{9}{4}A(r_{jk})A(r_{lm})\langle\langle\{jk(t)\}_{-1}\{lm(0)\}_1\rangle\rangle e^{-i\omega_0 t}\\&\qquad+4B(r_{jk})B^{*}(r_{lm})\langle\langle\{jk(t)\}_{-2}\{lm(0)\}_2\rangle\rangle e^{-2i\omega_0 t}\\&\qquad+16B^{*}(r_{jk})B(r_{lm})\langle\langle\{jk(t)\}_0\{lm(0)\}_0\rangle\rangle\\&\qquad+4C^{*}(r_{jk})C(r_{lm})\langle\langle\{jk(t)\}_1\{lm(0)\}_{-1}\rangle\rangle e^{i\omega_0 t}]\,dt,\end{aligned} \tag{12a}$$

and

$$\begin{aligned}\Gamma^{0}(\vec{k}=0,z)=&-i\beta\hbar^{-2}N^{-1}[\chi^{0}(\vec{k}=0)]^{-1}\\&\times\int_0^{\infty}e^{izt}\sum_{j\neq k}\sum_{l\neq m}[B^{*}(r_{jk})B(r_{lm})\langle\langle\{jk(t)\}_1\{lm(0)\}_{-1}\rangle\rangle e^{i\omega_0 t}\\&\qquad+4C^{*}(r_{jk})C(r_{lm})\langle\langle\{jk(t)\}_2\{lm(0)\}_{-2}\rangle\rangle e^{2i\omega_0 t}+\mathrm{c.c.}]\,dt,\end{aligned} \tag{12b}$$

in which

$$A(r_{jk})=-\tfrac{1}{2}g_e^2\beta_e^2r_{jk}^{-3}(3\cos^2\theta_{jk}-1), \tag{13a}$$

$$B(r_{jk})=-\tfrac{3}{4}g_e^2\beta_e^2r_{jk}^{-3}\sin\theta_{jk}\cos\theta_{jk}e^{i\psi_{jk}}, \tag{13b}$$

and

$$C(r_{jk})=-\tfrac{3}{8}g_e^2\beta_e^2r_{jk}^{-3}\sin^2\theta_{jk}e^{2i\psi_{jk}} \tag{13c}$$

In Eqs. (12), Kubo and Tomita's notation $\{jk\}_n$ has been used to denote irreducible spin operators,[6] and the time dependence of the four-spin correlation functions in Eqs. (12) is due to the Heisenberg propagator.

It is known that at temperatures not too close to T_c (or T_N) all modes are highly damped,[7] which means that the four-spin correlation functions in Eqs. (12) are simple-decaying functions. Consequently, $\Gamma^+(\vec{k}=0, z)$ and $\Gamma^0(\vec{k}=0, z)$ possess several resonances. The resonances have a strength of the order ω_D^2/ω_{ex} and a width of the order ω_{ex}. In an ordinary magnetic resonance experiment, (that is the microwave field polarization perpendicular to the static magnetic field) one observes the normalized spectral function $I^+(\omega)$,[6]

$$I^+(\omega) = -2Im\langle S^+(\vec{k}=0)|(z-L)^{-1}|S^+(\vec{k}=0)\rangle$$
$$= -2Im\,\Gamma^+(\vec{k}=0, z)\,\{[z-\omega^+(\vec{k}=0)]^2 - 2[z-\omega^+(\vec{k}=0)]\,\mathrm{Re}\,\Gamma^+(\vec{k}=0, z) + |\Gamma^+(\vec{k}=0, z)|^2\}^{-1}, \tag{14a}$$

in which

$$z = \omega + i\epsilon.$$

and with the microwaves polarized parallel to the static magnetic field one observes

$$I^0(\omega) = -2Im\langle S^0(\vec{k}=0)|(z-L)^{-1}|S^0(\vec{k}=0)\rangle$$
$$= -2Im\,\Gamma^0(\vec{k}=0, z)\{z^2 - 2z\,\mathrm{Re}\,\Gamma^0(\vec{k}=0, z) + |\Gamma^0(\vec{k}=0, z)|^2\}^{-1}. \tag{14b}$$

Now we will study the structure of the spectral functions (14a) and (14b). Do these functions show resonances at other frequencies than the fundamental resonance $[\omega^+(\vec{k}=0)$ for $I^+(\omega)$, or 0 for $I^0(\omega)]$? The conditions for these resonances being observable are $\omega_D, \omega_{ex} \ll \omega_0$. However, this cannot be fulfilled for three-dimensional strongly exchange coupled systems. The reason is that the correlation time of the four-spin correlation functions is too short ($\tau_c \approx \omega_{ex}^{-1}$). In other words, the narrowing process in three-dimensional paramagnets is so effective that all details of the dipolar spectrum are washed out.

In one-dimensional systems the situation is quite different. The correlation time defined in the usual way would be infinite due to the $\omega^{-1/2}$ divergence characteristic for one-dimensional diffusion. The conclusions which can be drawn from this observation are that the narrowing will be ineffective and that the lineshape will deviate substantially from a Lorentzian shape. The theory of motional or exchange narrowing is always much more difficult if the observed lineshape is non-Lorentzian. In this case, it means that the dipolar Hamiltonian has to be kept in the propagator $e^{iQ^\alpha LQ^\alpha t}$ in order to suppress the divergence. The time-scale will be increased accordingly and we may expect the observation of satellite lines to be likely. The time-scale of the narrowing process is set by the interplay of dipolar interaction and exchange interaction, and it is of the order of the EPR linewidth.[8] This is called the region of intermediate exchange narrowing. Eqs. (14) shows that under favorable conditions the satellite lines have a width of the order of the correlation time, which is, in principle, observable in one-dimensional systems. In three dimensional systems these resonances are much too broad to be observable.

The one-dimensional case will now be discussed in detail. Eqs. (6)–(10) still hold, and we will again use them as our point of departure. Reiter and Boucher[8] have used mode-coupling arguments to treat the EPR spectrum of a one-dimensional paramagnet with only the secular part of the dipole interaction as the broadening mechanism. We extend this work by introducing the total dipolar interaction. This is necessary if we want to describe possible satellite lines in one-dimensional systems. Eqs. (12) show clearly that these satellite lines are a pertinent consequence of the nonsecular terms. These terms, however, do prevent us from applying the same strategy as Reiter and Boucher did, and we are forced to introduce additional approximations. The key-problem is that $\mathcal{H}_D$ does not commute any longer with $\mathcal{H}_Z$ if one keeps the nonsecular terms in $\mathcal{H}_D$. This is a complication which prevents simple manipulation of the relevant propagators. We know that $|S^+(k)\rangle$, $|S^-(k)\rangle$, and $|S^0(k)\rangle$ are eigenoperators of L_Z,

$$e^{iL_Z t}|S^\alpha(k)\rangle = e^{i\alpha\omega_0 t}\,|S^\alpha(k)\rangle, \tag{15}$$

and we would like to use this information. The following paragraph is meant to arrive at a situation where we can use property (15).

The four-spin correlation functions in Eq. (9) are decoupled according to

$$\langle\!\langle ABCD\rangle\!\rangle = \langle\!\langle AB\rangle\!\rangle\langle\!\langle CD\rangle\!\rangle + \langle\!\langle AC\rangle\!\rangle\langle\!\langle BD\rangle\!\rangle + \langle\!\langle AD\rangle\!\rangle\langle\!\langle BC\rangle\!\rangle, \tag{16}$$

where in the propagators of the decoupled correlation functions the projection operator P^{α} has of course been neglected. We do not wish to comment on the validity of this decoupling scheme, because many others have already done so.[9] However, we do want to point out that the four-spin correlation functions occurring here are a consequence of our approximation scheme, which is the Mori projection operator method. Consequently, these functions have nothing in common, except possibly at high frequencies, with the pure four-spin correlation functions of the Heisenberg magnet. In addition, this means that the statement that the EPR experiments sample pure four-spin correlation functions cannot be supported in general. When we use Eqs. (9) and (10), and apply decoupling (16) we are left with two types of two-spin correlation functions. One type is zero if we neglect the nonsecular terms in the propagator, like

$$\langle\langle S^{+}(k)e^{iLt}S^{+}(-k)\rangle\rangle\,, \tag{17}$$

because only the nonsecular terms in L can change the total spin-angular momentum. These terms start out to be zero at $t=0$, and cannot have long diffusive tails. The long diffusive tails dominate the low frequency spectral functions and all other terms decaying faster can be neglected. Correlations like (17) will be neglected for this reason. The next assumption is that the nonsecular part of the propagator e^{iLt} will be treated in a perturbative way. That is to say we can use expansions like expression (11), with the nonsecular part as a small parameter, and need to consider only a few terms. Actually, we will take all terms into account approximately, but we need the above assumption in order to treat the Zeeman interaction. In addition, we use our rule that, also in this case, only correlations with diffusive tails will be taken into account, because they force us to do the whole calculation self-consistently. Then we can show that the following simplification holds:

$$e^{iLt}=e^{iL_Z t}\,e^{i(L_H+L_D)t}\,, \tag{18}$$

whenever this propagator occurs in the self-energies. This approximation is crucial, because it permits proper treatment of the Zeeman interaction, as given by Eq. (15). We also get the resonance structure of $\Gamma^{\alpha}(k=0,z)$ we are looking for.

The justification for treating contributions perturbative rather than self-consistently in these types of calculation can be given *a postiori*. If we wind up with divergencies we should do the computation self-consistently. If we do not end up with zero-frequency poles it should be simple to show that we have taken into account the major contribution.

It is now a question of straightforward calculation to find the two self-energies for the one-dimensional paramagnet. Guided by our results (12) concerning the three-dimensional paramagnets, it is easy to find that

$$\begin{aligned}\Gamma^{+}(k=0,z)=&-i\beta\hbar^{-2}\{\chi^{+}(k=0)N\}^{-1}\\&\times\int_0^{\infty}e^{izt}\sum_k\Big\{9|A(k)|^2e^{-i\omega_0t}\Sigma^0(k,t)\Sigma^{+}(k,t)+8|B(k)|^2e^{-2i\omega_0t}\Sigma^{+}(k,t)^2+32|B(k)|^2\Sigma^0(k,t)^2\\&+4|B(k)|^2\Sigma^{+}(k,t)\Sigma^{-}(k,t)+16|C(k)|^2e^{i\omega_0t}\Sigma^{-}(k,t)\Sigma^0(k,t)\Big\}dt\end{aligned} \tag{19a}$$

and

$$\begin{aligned}\Gamma^{0}(k=0,z)=&-i\beta\hbar^{-2}[\chi^{0}(k=0)N]^{-1}\\&\times\int_0^{\infty}e^{izt}\sum_k\Big\{4|B(k)|^2e^{-i\omega_0t}\Sigma^0(k,t)\Sigma^{+}(k,t)+8|C(k)|^2e^{-2i\omega_0t}\Sigma^{+}(k,t)^2+\text{c.c.}\Big\}\,dt,\end{aligned} \tag{19b}$$

where $A(k)$ is given by

$$A(k)=\sum_j e^{-ikr_{ij}}A(r_{ij}), \tag{20}$$

in which $A(r_{ij})$ is the one-dimensional counterpart of the geometrical coefficient (13a). The other coefficients $B(k)$ and $C(k)$ are defined accordingly. $\Sigma^{\alpha}(k,t)$ represents

$$\Sigma^{\alpha}(k,t)=\langle\langle S^{-\alpha}(-k)e^{-i(L_H+L_D)t}S^{\alpha}(k)\rangle\rangle\,. \tag{21}$$

These equations should be solved self-consistently. However, this is a formidable task and will not be attempted here. First, we will take the high-temperature limit of Eqs. (19). The simplifications in this limit are

$$\chi^{\alpha}(k=0)=(|\alpha|+1)(\tfrac{1}{3})S(S+1)\beta, \tag{22}$$

and

$$\omega^{\alpha}(k=0)=\alpha\omega_0. \tag{23}$$

In arithmetic expressions α represents 0, +1, or −1, depending on which spin operator is involved.

We will use a trial solution for $\sum^{\alpha}(k, t)$. The frequency independent parameters in this trial solution will be determined by solving Eqs. (19) for two relevantly chosen frequencies. The solution at other frequencies will be obtained by solving Eqs. (19) with the trial solution as input. In this way we obtain, what we would like to call, a first cycle of an iteration process. Such a calculation is much better than any perturbation calculation because there will not appear any diffusion poles.

The trial solutions we propose are

$$\Sigma^{\alpha}(k, t) = (|\alpha| + 1)(\tfrac{1}{3})S(S+1)e^{-(Dk^2+\Gamma^{\alpha})t} \qquad (24)$$

The influence of the dipolar interaction on the diffusion constant is very small and has been neglected in Eq. (24). Those wave-vectors for which Eq. (24) is not appropriate do not contribute to the wave-vector sums we will perform. This can be verified readily. We would like to emphasize that the trial solution does not contain satellite lines and we have not introduced the answer into the problem. It is difficult to estimate how close our solution will be to the solution of the full self-consistent treatment. Inspection of the results for the normal EPR linewidth, for which a better treatment is available,[8] indicates that the trial-solution method gives very satisfactory results.

If we want to solve Eqs. (19) self-consistently, we have to solve them in the frequency domain. This complicates the calculation considerably because we have to deal with convolution integrals. Our trial solutions imply that in that case we put lorentzians, centered at zero frequency, into the problem as trial distributions (the Zeeman propagator has been taken out of the propagator). The next step would necessarily have to be done numerically.

Calculating the damping constants as indicated yields

$$\Gamma^{+} = i\Gamma^{+}(k=0, \omega_0)$$
$$= a\{\tfrac{1}{3}S(S+1)\}^{1}\hbar^{-2}(2D)^{-1/2}[\tfrac{9}{2}A(0)^2(\Gamma^0+\Gamma^+)^{-1/2} + 8B(0)^2(i\omega_0)^{-1/2} + 12B(0)^2(-i\omega_0)^{-1/2} + 8C(0)^2(-2i\omega_0)^{-1/2}] \qquad (25a)$$

and

$$\Gamma^0 = i\Gamma^0(k=0, 0) = a\{\tfrac{1}{3}S(S+1)\}\hbar^{-2}(2D)^{-1/2}[4B(0)^2(i\omega_0)^{-1/2} + 16C(0)^2(2i\omega_0)^{-1/2} + \text{c.c.}], \qquad (25b)$$

where a is the lattice constant. The factor i between Γ^{α} and $\Gamma^{\alpha}(z)$ is due to the fact that we found it simpler from a notational point of view to define the frequency-dependent self-energies in terms of $(z-L)^{-1}$ rather than $i(z-L)^{-1}$.[4] The frequency dependent damping constants of a three-dimensional system are of the order of ω_D^2/ω_{ex}, and their widths are of the order of ω_{ex}. This can be verified readily with the help of Eqs. (12). The frequency dependent damping constants of a one-dimensional system are much larger whereas their widths are much smaller compared to the three dimensional case. A quantitative confirmation of this statement will be given later on, but now we will give an order-of-magnitude estimate. Eqs. (25) show that Γ^+ and Γ^0 are of the order of $\omega_D^2(\omega_{ex}\omega_0)^{-1/2}$ and Eqs. (19) show that their widths are of the same order. Since $\omega_{ex} \gg \omega_D, \omega_0$ we see indeed that $\Gamma^{\alpha}(k=0, z)_{1\,\text{dim}} \gg \Gamma^{\alpha}(\vec{k}=0, z)_{3\,\text{dim}}$ and $\Gamma^{\alpha}(k=0, z)_{1\text{dim}} \ll \omega_{ex}$. These small widths indicate that the self-energies $\Gamma^{\alpha}(k=0, z)$ do have several resonances which are separated by more than their widths. Inspection of Eqs. (14), which are exact relations, points out that these resonances can manifest themselves in the EPR spectrum. However, for $I^{+}(\omega)$ in the case of a one-dimensional paramagnet these resonances are suppressed by the highly allowed transition at the Larmor frequency. In a magnetic field-swept resonance experiment with the microwave parallel to the static magnetic field [that is observing $I^0(H)$, H being the static magnetic field], the disturbing resonance at zero frequency is mapped towards infinite field. Bearing this in mind, we see that one should expect two extra resonances to occur in the "relaxation configuration," at ω_0 and $2\omega_0$. As will be explained in the experimental section (Sec. III), it is very difficult to do meaningful experiments at the Larmor frequency ω_0 in the relaxation configuration, and so we will focus our attention on the resonance at half-field (at $2\omega_0$). Expression (14b) gives the spectral function $I^0(\omega)$. This expression can be simplified considerably when ω differs much from zero. The fundamental resonance of $I^0(\omega)$ is at $\omega = 0$, but when ω differs much from zero, expression (14b) can be simplified considerably. The self-energy $\Gamma^{\alpha}(k=0, z)$ is of the order of Γ^{α}. When $2\omega_0 \approx \omega$, $\Gamma^{\alpha}(k=0, \omega)$ is always much less than ω. The denominator of expression (14b) can be simplified and the result reads:

$$I^0(2\omega_0 \approx \omega) \approx -2\,Im\,\Gamma^0(k=0, \omega)/\omega^2. \qquad (26)$$

$\Gamma^0(k=0,\omega)$ can be calculated with the help of Eqs. (19), (21), and (25). Retaining the largest, resonating term at $2\omega_0 \approx \omega$ gives:

$$I^0(\omega)(2\omega_0 \approx \omega) \approx \tfrac{32}{3}\hbar^{-2}S(S+1)(2D)^{-1/2}C(0)^2\omega^{-2} \times \mathrm{Re}(i\omega - \epsilon - 2i\omega_0 - 2\Gamma^+)^{-1/2}, \qquad (27)$$

which resonates at $2\omega_0 \approx \omega$. Eqs. (26) and (27) have been derived under the implicit assumption that ω_0 rather than ω is varied (that is sweeping of the magnetic field.) From Eq. (27) we conclude that the resonance should be observable, because its linewidth is of the order of the EPR linewidth in the normal resonance configuration, viz. Γ^+. The intensity factor $C(0)^2 \propto \sin^4\theta$ indicates that the intensity should be highly anisotropic, with a maximum when the magnetic field is perpendicular to the chain axis ($\theta = 90°$). Actually, the intensity of the derivative of the absorption (that is the peak-height of the derivative spectrum) should be proportional to the factor

$$C(0)^2(\Gamma^+)^{-3/2}.$$

An interesting and important feature of Eq. (27) is also that it shows that the linewidth of the half-field transition should roughly have the same angular dependence as the normal EPR line. In other words, a maximum in the linewidth when $\theta = 90°$ and a minimum when $\theta = 54.76°$.[1] The maximum linewidth at $\theta = 0°$ can, of course, not be checked experimentally because the intensity is zero then. The peak-to-peak derivative linewidth of the resonance Eq. (27), ΔH_{pp}, is

$$\Delta H_{pp} = 3.13\Gamma^+, \qquad (28)$$

if one neglects the small imaginary part of Γ^+. To conclude this section we would like to say that we have shown that in one-dimensional paramagnets which are exchange-coupled we expect, as a result of their one-dimensionality, a half-field transition in the relaxation configuration. The angular dependence of both linewidth and line-intensity of this transition is very important because both should show one-dimensional behavior. An observation of such an angular dependence would, on the one hand, prove that we are observing an intrinsic, one-dimensional, effect and on the other hand strongly support present ideas of high-temperature spin-dynamics in one-dimensional systems.[1-3,8,10]

III. EXPERIMENTAL

Single crystals of TMMC were grown as has been described previously.[11] The crystals used in this study had dimensions of about $7\times2\times2$ mm^3, the first number referring to the chain direction.

The EPR experiments were performed with a commercial Varian E 12 spectrometer operating at X-band. Low-frequency field modulation (270 Hz) was achieved with the help of two home-built coils which were secured onto the poles of the magnet. Using an audio amplifier, modulation amplitudes of about 100 G peak-to-peak were obtained.

The cavity, needed to perform experiments in the relaxation configuration, should have a very homogeneous microwave field and should allow rotation of the sample. These two requirements cannot be optimized independently. However, the previous section has shown that the detection of angular variations is essential. Bearing this in mind the following high Q (~9 000) cavity has been constructed. The brass cylindrical cavity operates in the TE_{011} mode. The degenerate TM_{111} mode is suppressed by electrically insulating one of the base plates. A hole is drilled in the middle of the cylindrical cavity wall 90° away from the coupling hole. This hole supports a quartz sample rod onto which the sample was glued. The homogeneity of the microwave field is very good, although not enough to eliminate completely the strongly allowed transition of the resonance configuration. The known methods to improve this, usually do not permit rotation of the sample, which we think is the most important aspect of the present experiment. Of course, in all experiments we have minimized this effect by careful rotation of the magnet with respect to the cavity.

IV. RESULTS

A. Relaxation configuration

In Fig. 1, we present the first derivative EPR spectrum observed in the relaxation configuration with the magnetic field perpendicular to the chain axis of TMMC at room temperature. The fact that there is indeed a new resonance is beyond all doubt. In Fig. 2, the peak-to-peak linewidth is displayed as a function of the orientation of the applied magnetic field. In Fig. 3, we present the intensity (that is peak-to-peak height of the derivative) as a function of the direction of the static magnetic field. No attempt was made to analyze the results obtained in the neighborhood of the Larmor frequency. The off-axis components of the microwave field were still not small enough to completely eliminate the strongly allowed ω_0 transition of the resonance configuration. All that can be said is that there are indications that the ω_0 resonance of the relaxation configuration is present at $\theta \approx 45°$. The intensity of the half-

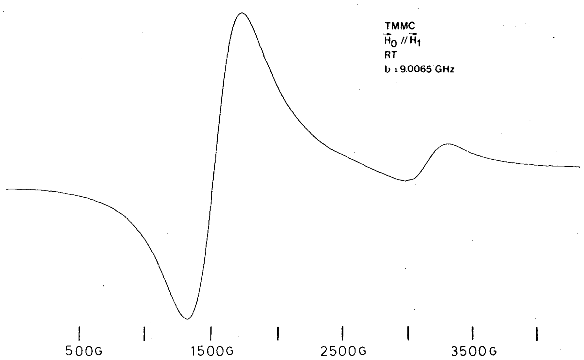

FIG. 1. EPR spectrum of TMMC at room temperature with the microwave field polarized parallel to the static field. The angle θ between H_0 and the chain axis is 90°.

field resonance is roughly 300 times smaller than the intensity of the normal resonance.

B. Resonance configuration

No satellite lines have been observed in the normal EPR spectra, not even at the magic angle $\theta = 54.76°$, where the allowed transition has the smallest linewidth.

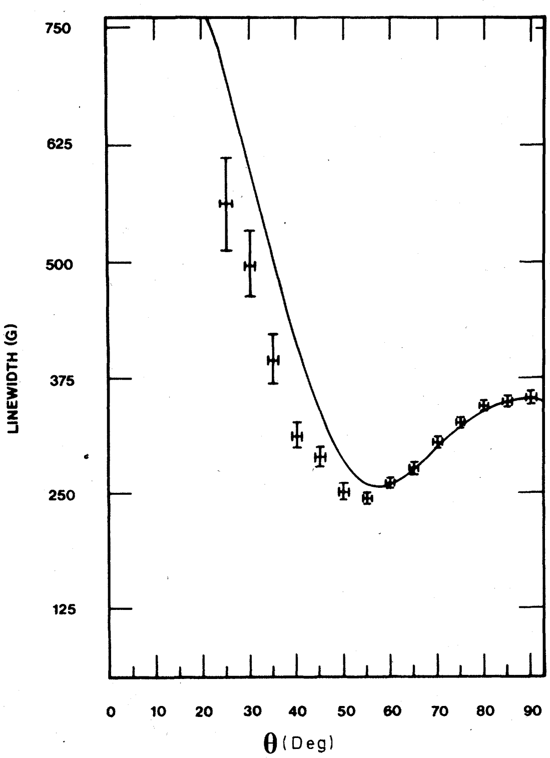

FIG. 2. Angular dependence of the peak-to-peak linewidth of the half-field transition in TMMC. Solid line: theory.

V. DISCUSSION

The qualitative features of the half-field transition, predicted in the theoretical section, are extremely well obeyed. The line intensity is at a maximum when $\theta = 90°$ and decreases very rapidly when the magnetic field is rotated away from this direction. The linewidth does indeed scale with the normal linewidth. It shows a maximum at the orientation $\theta = 90°$ and a minimum when the magnetic field makes the magic angle with the chain axis.

We will now compare the results from Sec. II quantitatively with experiment. In the first place, we will compare using Eq. (27), the experimental $\Delta H_{pp}(\theta = 90°)$ with the calculated value. The calculated $\Delta H_{pp}(\theta = 90°)$ is 515 G. One should be careful in converting frequency units in magnetic field units because $g = 4$ at half field. The experimental $\Delta H_{pp}(\theta = 90°)$ is 355 G which means that the theoretical value is about 1.5 times larger than the experimental value. This is not surprising. All calculations done so far for TMMC yield linewidths which are larger than the experimental ones by factors of about 1.6–1.9.[1–3,8] Two explanations for this discrepancy have been put forward so far. A first explanation is sought in the inadequacy of the mode coupling theory. One fact favor-

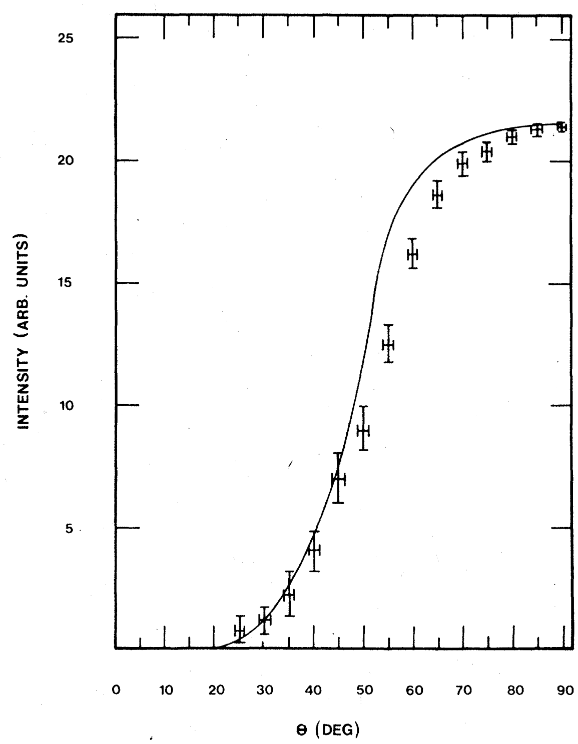

FIG. 3. Angular dependence of the peak-to-peak height of the half-field transition in TMMC. Solid line: theory.

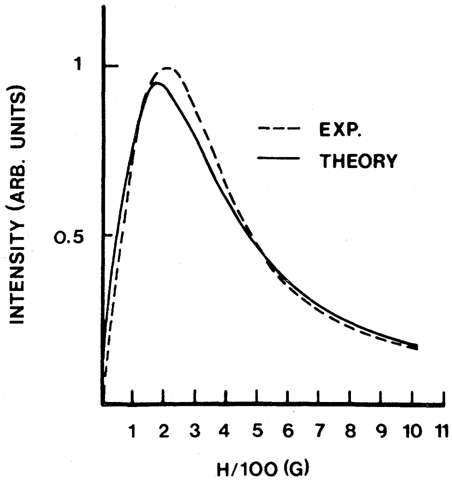

FIG. 4. Comparison of experimental lineshape with theory (least-square fit). The figure shows the high-field portion of the half-field resonance for $\theta = 90°$. The origin corresponds to the center of the half-field line (see Fig. 1).

ing this explanation is that diffusion coefficients calculated with this theory are wrong by ~50%.[12] The experiments of Ref. 3 do not support this explanation. These experiments sample pure four-spin correlation functions. No projection operators are involved. The discrepancy found could be attributed solely to the decoupling.[13] However, it is hard to accept that the simple decoupling would be that wrong. A second explanation put forward is that TMMC could have a sizable single-ion anisotropy, DS_z^2. In one-dimensional systems the sign of this interaction determines whether an additional narrowing or an additional broadening takes place.[13] The interplay of dipole-dipole interaction and single-ion anisotropy is possible because the $k \approx 0$ modes are dominant. In three-dimensional systems no interplay is possible and as a result single-ion anisotropy is always an additional broadening mechanism. The susceptibility data seem to indicate that there is no single-ion anisotropy in TMMC.[14] Anyway, we think that the fact that theoretical and experimental linewidth differ by a factor of 1.5 is reassuring rather than alarming and indicates that our simple approach is not far from a full mode-coupling treatment. In Fig. 2, a theoretical curve is drawn showing the angular dependence of the linewidth scaled at the $\Delta H_{pp}(\theta = 90°)$ value. The agreement is quite satisfactory. In Fig. 3, a theoretical line is drawn representing $\sin^4\theta(\Delta H_{pp})^{-3/2}$ scaled to the maximum intensity. We have used ΔH_{pp} rather than Γ^+ because we would like to test linewidth and intensity independently. The agreement is very gratifying. From (27) the intensity of the half-field resonance is estimated to be smaller than the normal resonance by two orders of magnitude. This is confirmed by the experiments. In Fig. 4, we present the experimental line shape at $\theta = 90°$ together with a least-square fit to the first derivative of the lineshape function (27). Realizing that this is essentially a two-parameter fit it is clear that the agreement is satisfactory. Both a fit to a gaussian and a lorentzian were worse.

EPR experiments on three-dimensional paramagnets in the parallel configuration have been performed.[15] In the strongly exchange coupled systems no resonances were detected. This proves that the resonance we have observed is a pure one-dimensional effect.

VI. CONCLUSIONS

We have reported the observation of a half-field transition in TMMC using EPR with the microwave field polarized along the static magnetic field. The transition has highly anisotropic features. A simple theory has been presented which indicates that the half-field transition is due to the one-dimensionality of the magnetic interactions in TMMC. The theory accounts in a very satisfactory way for the anisotropic features. The only discrepancy is that the absolute magnitude of the linewidth is about 1.5 times smaller than the calculated one. However, all resonance linewidths calculated so far for TMMC show this,[3,8,10,13] and this type of disagreement is not surprising.

It is important to point out that the half-field transition of one-dimensional systems can serve as a quantitative measure of the one-dimensionality. Another interesting question is to what extent impurities (para- or diamagnetic) can influence the half-field transition.[16] The study of this effect has already been started in our laboratory.

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