

## Experimental study of high-temperature spin dynamics in one-dimensional Heisenberg paramagnets

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(Received 6 June 1973)

From room-temperature measurements of proton spin-lattice relaxation rate in  $(\text{CH}_3)_4\text{NMnCl}_3$  (TMMC) and  $\text{CsMnCl}_3 \cdot 2\text{H}_2\text{O}$  (CMC) as a function of magnetic field  $\vec{H}$  the shape of the low-frequency spectral density of the spin fluctuations is directly obtained. For  $\vec{H}$  parallel to the chain axis the spectral density contains a diffusive term which diverges as  $\omega^{-1/2}$ . The experimental results for  $\vec{H} \parallel \vec{c}$  are in good agreement with a theoretical calculation in TMMC in which the two-spin correlation function is assumed to decay at long times as  $t^{-1/2}$ . The lack of frequency dependence of  $\vec{H}$  perpendicular to the chain axis indicates a difference in the "cutoff" time of the two-spin correlation function for the spin components parallel and perpendicular with respect to the external magnetic field.

### INTRODUCTION

The role of dimensionality in the high-temperature spin dynamics of exchange-coupled Heisenberg paramagnets has been experimentally demonstrated by the EPR study<sup>1</sup> in the one-dimensional<sup>2</sup> antiferromagnet  $(\text{CH}_3)_4\text{NMnCl}_3$  (TMMC). In particular, it has been shown that in order to explain the EPR line shape and linewidth one has to take in proper account the long-time persistence of spin correlations due to the slow rate of diffusion in one dimension.

Contrary to the EPR measurements which allow only an indirect determination of the form of the four-spin correlation function at long times the NMR spin-lattice relaxation rate directly gives<sup>3</sup> the shape of the spectral density of the low-frequency local spin fluctuations which is the Fourier transform of the two-spin correlation function.

In fact, the high-temperature relaxation rate in a single crystal can be written, in general, as<sup>4</sup>

$$\frac{1}{T_1} = \sum_j [A_j(\theta, \varphi) f_j^e(\omega_n) + B_j(\theta, \varphi) f_j^s(\omega_s)] \quad (1)$$

where

$$f_j(\omega) = \int_{-\infty}^{\infty} \frac{3 dt}{S(S+1)} \langle S_i^e(t) S_{i+j}^e(0) \rangle e^{-i\omega t} \quad (2)$$

is the spectral density of the electronic-spin auto-correlation ( $j=0$ ) and pair correlation functions and  $\omega_n, \omega_s$  are the nuclear and electronic Larmor frequencies, respectively. An expression identical to Eq. (2) holds also for the spectral density  $f_j^s(\omega)$  of the transverse components (with respect to the external magnetic field) of the electronic spin. The coupling coefficients  $A_j(\theta, \varphi)$  and  $B_j(\theta, \varphi)$  depend on the nuclear-electron interaction which in the case of a dipolar interaction is a function of the angles  $\theta$  and  $\varphi$  defining the direction of

the vectors  $\vec{r}$  joining the nucleus with the electrons and the external magnetic field  $\vec{H}$  (see Appendix).

In this work we report room-temperature measurements of proton spin-lattice relaxation rate in TMMC and  $\text{CsMnCl}_3 \cdot 2\text{H}_2\text{O}$  (CMC)<sup>5</sup> as a function of the external magnetic field. It appears that the spectral density of the spin fluctuations diverges at low frequencies as  $\omega^{-1/2}$  in agreement with the theoretical prediction valid for a spin correlation function which behaves diffusively at long times.

### RESULTS

The measurements of  $T_1$  were performed with a Bruker B-KR306 pulse spectrometer by using a  $180^\circ$ - $90^\circ$  or  $90^\circ$ - $90^\circ$  pulse sequence. The recovery of the magnetization was exponential in all cases over more than a decade. The measurements at 2 MHz were performed with a Varian wide-line spectrometer by using a saturation technique. The rf-field calibration and the other unknown constants entering in the formula for the saturation were determined by comparing the results obtained at 4 MHz by the saturation technique with the one obtained directly by the pulse technique. The single crystals of TMMC and CMC were grown from aqueous solutions by slow evaporation.

The experimental results are shown in Figs. 1 and 2. When the external magnetic field  $\vec{H}$  is parallel to the magnetic chains, a remarkable field dependence of the relaxation rate is observed which can be fitted by an expression of the form

$$1/T_1 = P H^{-1/2} + Q \quad (3)$$

with  $P = 6.0 \times 10^4 \text{ G}^{1/2} \text{ sec}^{-1}$  and  $Q = 3.5 \times 10^2 \text{ sec}^{-1}$  for TMMC and  $P = 3.6 \times 10^5 \text{ G}^{1/2} \text{ sec}^{-1}$  and  $Q = 4.3 \times 10^3 \text{ sec}^{-1}$  for CMC.

We believe that this result represents a direct evidence of the diffusive behavior of the two-spin

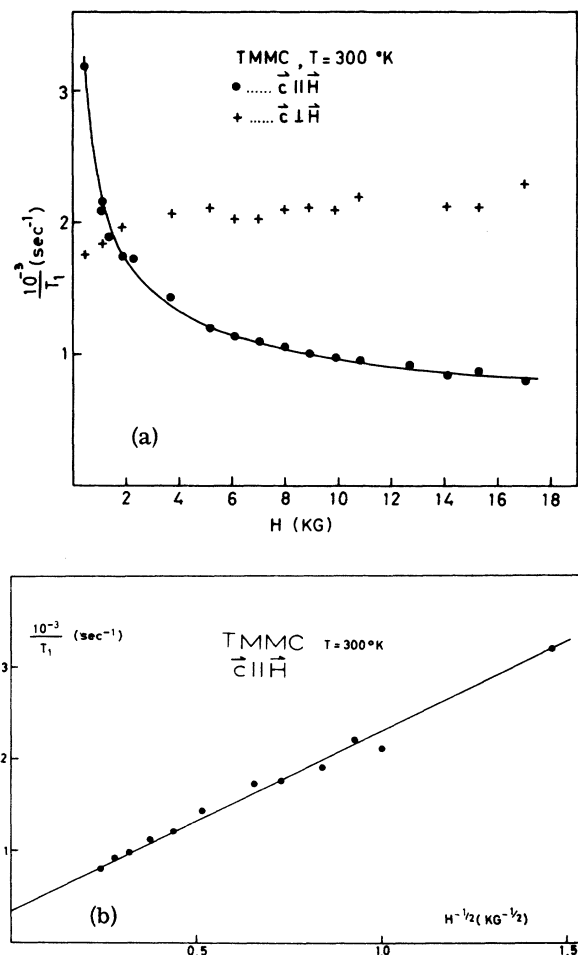


FIG. 1. Proton spin-lattice relaxation rate in TMMC: (a) as a function of applied magnetic field; (b) as a function of  $H^{-1/2}$ . The magnetic chain axis is the  $\vec{c}$  axis. The full curves are the curves of best fit given by Eq. (3) of the text.

correlation function for long times. In fact, in this case  $\langle S_i(t)S_j(0) \rangle$  decays<sup>6</sup> in time as  $t^{-1/2}$  when  $t \rightarrow \infty$  and its Fourier transform diverges for low frequencies as  $\omega^{-1/2}$ . The diffusive behavior becomes important in the spectral density only for frequencies well below the exchange frequency  $\omega_x$  which is of the order of the intrachain exchange constant  $J$ . On the other hand for frequencies below a "cutoff" frequency  $\omega_c$ , the spectral density should become practically frequency independent. The cutoff frequency  $\omega_c$  is related to the interactions which limit the one-dimensional diffusive behavior.<sup>7,8</sup>

From the estimate of  $\omega_c$  one finds that for both TMMC and CMC,  $\omega_c > \omega_n$  for the range of nuclear Larmor frequencies investigated so that any frequency dependence of  $T_1^{-1}$  must arise from the term  $f_j^*(\omega_s)$  in Eq. (1). Therefore one can convert the

abscissa of Figs. 1 and 2 into a frequency scale by multiplying  $H$  by the electronic gyromagnetic ratio.

#### COMPARISON OF THEORY AND EXPERIMENTS

A quantitative comparison of theory and experiments is complicated by the long-range character of the dipolar interaction which drives the proton spin-lattice relaxation and by the large number of protons contained in the unit cell of both compounds studied. We present here the results of a theoretical calculation of the nuclear relaxation rate in TMMC. In this material the manganese ions are surrounded by a distorted octahedron of chloride ions<sup>9</sup> as shown in Fig. 3. Long chains of  $\text{MnCl}_6$  octahedra lie parallel to the  $\vec{c}$  axis and are linked by sharing [111] faces. The distance between  $\text{Mn}^{2+}$  ions within the chain is  $\frac{1}{2}c = 3.247 \text{ \AA}$ , while the distance between chains is  $a = 9.151 \text{ \AA}$ . The most probable structure regarding the  $(\text{CH}_3)_4\text{N}^+$  ions is a centrosymmetric structure with the  $(\text{CH}_3)_4\text{N}^+$  ions along the threefold axis  $(\frac{1}{3}, \frac{2}{3}, z)$ , with the nitrogen atoms located on the mirror plane, and with the carbon atoms situated above and below the mirror in a statistically disordered manner. As a consequence there are two nonequivalent carbons which are labeled C(1) and C(2). The protons of the methyl group H(1) and H(2) are also nonequivalent and have weights of  $\frac{1}{4}$  and  $\frac{3}{4}$ , respectively.

We have divided the terms in Eq. (1) into terms involving the spin autocorrelation functions ( $j=0$ ) and into terms involving pair correlation functions ( $j \neq 0$ ). The nuclear-electron interaction has been assumed to be only dipolar and since the  $\text{CH}_3$

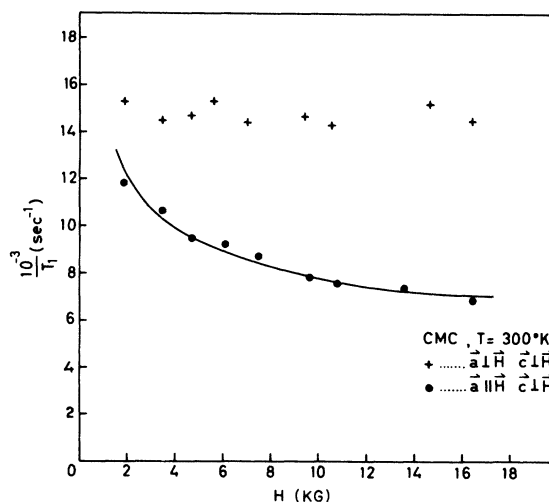


FIG. 2. Proton spin-lattice relaxation rate in CMC as a function of applied field. The  $\vec{a}$  axis is the magnetic chain axis. The full curve is the curve of best fit given by Eq. (3) of the text.

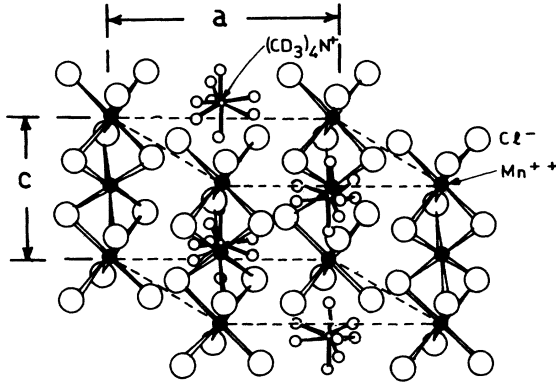


FIG. 3. Crystal structure of  $(\text{CH}_3)_4\text{NMnCl}_3$  from Refs. 2 and 9. The structure is based on the space group  $P6_3/m$  with the  $(\text{CH}_3)_4\text{N}^+$  ions statistically disordered. Both possible orientations of these ions have been drawn. Note that the protons surrounding the carbon atoms are not explicitly shown.

groups rotate at high temperature<sup>10</sup> we take the average position of the protons to be at the carbon site.<sup>9</sup> We have included the contribution of four  $\text{Mn}^{2+}$  ions for each of the three-nearest-neighbor chains. The results for the coefficients in Eq. (1) for the two proton sites H(1) and H(2) are nearly identical. Furthermore, the results obtained by assuming static or dynamic disorder of  $(\text{CH}_3)_4\text{N}^+$  ions are also similar. In the comparison with the experiments we will use the values of the coefficients obtained for H(2) protons and assuming static disorder. The coefficients for  $\text{H}\parallel\vec{c}$  are

$$\begin{aligned} A_0 &= 102 \times 10^{-6} \text{ \AA}^{-6} \\ A_P &= \sum_{j=1,2,3} A_j = 175 \times 10^{-6} \text{ \AA}^{-6} ; \\ B_0 &= 26.2 \times 10^{-6} \text{ \AA}^{-6} \\ B_P &= \sum_{j=1,2,3} B_j = -25.7 \times 10^{-6} \text{ \AA}^{-6} . \end{aligned} \quad (4)$$

Regarding the spin correlation functions one can use different methods to obtain the time dependence over the entire time interval.<sup>6,11,12</sup> Since the results of the different theories are similar we have used the simplest approach which consists of matching the short-time expansion to the long-time diffusive behavior in the same way as done by Gulley *et al.*<sup>11</sup> in three-dimensional systems. The results of the matching are shown in Fig. 4. From the short-time expansion, valid for  $0 \leq t/\tau_x \leq 1$ , one finds for the normalized correlation function of the  $\alpha$  component of the electronic spin:

$$\Psi_A^1(t) = \frac{3 \langle S_i^\alpha(t) S_i^\alpha(0) \rangle}{S(S+1)} = 1 - \frac{1}{2} \left( \frac{t}{\tau_x} \right)^2$$

$$\begin{aligned} &+ 0.1336 \left( \frac{t}{\tau_x} \right)^4 + \dots , \\ \Psi_P^1(t) &= \frac{3 \langle S_i^\alpha(t) S_{i+j}^\alpha(0) \rangle}{S(S+1)} = \frac{1}{4} \left( \frac{t}{\tau_x} \right)^2 \\ &- \frac{1}{2} \left( \frac{t}{\tau_x} \right)^4 + \dots , \end{aligned} \quad (5)$$

where the exchange frequency  $\omega_x = \tau_x^{-1}$  for nearest-neighbors exchange interaction only is defined

$$\omega_x^2 = \frac{8}{3} z S(S+1) J^2 / \hbar^2 \quad (6)$$

( $z$  is the number of nearest neighbors).

For TMMC,  $z = 2$  and  $J = 6.5^\circ\text{K}$  so that  $\omega_x = 6 \times 10^{12} \text{ sec}^{-1}$ . For the long-time behavior we have used a diffusive correlation function of the form

$$\Psi_j(t) = (4\pi D a_0^{-2})^{-1/2} t^{-1/2} e^{-R_{ij}^2/4Dt} , \quad (7)$$

where  $D$  is the microscopic diffusion coefficient and  $a_0$  is the  $\text{Mn}^{2+}$ - $\text{Mn}^{2+}$  distance within the chain. By matching Eqs. (5) and (7) one obtains, for  $1.5 \leq t/\tau_x < \infty$ ,

$$\begin{aligned} \Psi_A^3(t) &= 0.285 \left( |t|/\tau_x - 1 \right)^{-1/2} , \\ \Psi_P^3(t) &= 0.285 \left( |t|/\tau_x - 1 \right)^{-1/2} \\ &\times \exp[-0.255 (t/\tau_x - 1)^{-1}] . \end{aligned} \quad (8)$$

Finally, the two functions  $\Psi_{A,P}^1(t)$  and  $\Psi_{A,P}^3(t)$  can be connected in the small-time interval  $1 < t/\tau_x < 1.5$  by a straight line. It should be observed that for all practical purposes we can approximate  $\Psi_P(t) \approx 0$  for  $t < \tau_x$  and  $\Psi_A(t) \approx \Psi_P(t)$  for  $t \gg \tau_x$ . The pair correlation function in Eq. (7) refers to nearest-

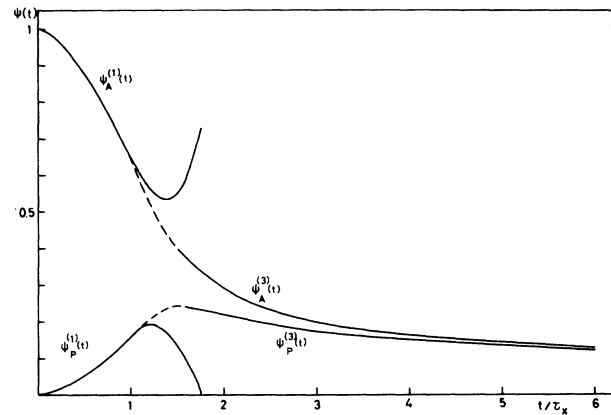


FIG. 4. Time dependence of the reduced autocorrelation  $[\Psi_A(t)]$  and pair  $[\Psi_P(t)]$  correlation functions for a one-dimensional magnetic chain. The full curves are the functions described by Eqs. (5) and (8) in the text. The dashed curves represent the interpolation between the short- and long-time behavior, i. e.,  $\Psi_{A,P}^2(t)$ . The total correlation function is obtained as the sum of the three parts  $\Psi_{A,P}(t) = \Psi_{A,P}^1(t) + \Psi_{A,P}^2(t) + \Psi_{A,P}^3(t)$ .

neighbor pairs ( $j=1$ ). For next-nearest-neighbor ( $j=2$ ) and next-to-next pairs ( $j=3$ ) the short-time behavior would be different. However, since for  $t \rightarrow \infty$ , where most of the contribution comes, they all join together, we have approximately taken the  $j=2$  and  $j=3$  pair correlation functions equal to the  $j=1$ .

It should be pointed out that the present matching procedure leads to a diffusion coefficient  $Da_0^2 \approx 5.87 \times 10^{12} \text{ sec}^{-1}$  if  $\tau_x = 0.167 \times 10^{-12} \text{ sec}$ . This value is somewhat larger than the value that can be obtained from the theory of spin diffusion,<sup>12</sup> i. e.,

$$Da_0^2 = \left(\frac{2}{3}\pi\right)^{1/2} (J/\hbar) [S(S+1)]^{1/2} \approx 4 \times 10^{12} \text{ sec}^{-1}$$

The final result for the proton spin-lattice relaxation rate obtained from Eqs. (1), (2), (4), (5), and (8) is for  $\vec{H} \parallel \vec{c}$ :

$$1/T_1 = 195 + 0.2(\omega_x/\omega_c)^{1/2} + 7.8 \times 10^4 H^{-1/2} \text{ sec}^{-1} \quad (9)$$

The coefficient in front of the term  $(\omega_x/\omega_c)^{1/2}$  is small because of the cancellation<sup>13</sup> of the coefficients  $A_j$  in Eq. (1) when  $\vec{H} \parallel \vec{c}$ . This is an important feature which should be emphasized since it makes the field-independent term in Eq. (1) small with respect to the field-dependent one and makes the result for  $1/T_1$  practically independent from the choice of the cutoff frequency  $\omega_c$  ( $\omega_c$  is the frequency at which the divergency in the spectral density is truncated).

The agreement between Eqs. (3) and (9) is satisfactory considering the approximations involved and considering that no adjustable parameter was used in the calculation. Most of the uncertainty comes from the fact that the exact position of the protons is not known. The fact that the field-dependent term in Eq. (9) is too large reflects in part the fact that the contribution of the  $j=2, 3$  correlation functions has been overestimated by assuming it to be equal to the one for nearest-neighbor ( $j=1$ ) pairs.

An identical calculation performed for  $\vec{H} \perp \vec{c}$  leads to the following theoretical expression:

$$1/T_1 = 159 + 38(\omega_x/\omega_c)^{1/2} + 3.75 \times 10^4 H^{-1/2} \text{ sec}^{-1} \quad (10)$$

This result is more approximate than the one for  $\vec{H} \parallel \vec{c}$  because for  $\vec{H} \perp \vec{c}$  the value of the geometrical coefficients in Eq. (1) is more sensitive to the exact location of the protons. As it can be seen from Fig. 1 the relaxation rate for  $\vec{H} \perp \vec{c}$  has an almost field-independent value, i. e.,  $T_1^{-1} = 2.1 \times 10^3 \text{ sec}^{-1}$  with a tendency to decrease at the lowest field values. This experimental behavior is in contrast with Eq. (10) which predicts a divergent behavior of  $T_1^{-1}$  at small fields which, even if smaller than the one predicted for  $\vec{H} \parallel \vec{c}$ , should still be observable experimentally. One could ar-

gue that a qualitative agreement with the experiment can be obtained if the "cutoff" frequency were field dependent,<sup>14</sup> in such a way that the contributions from the second and third term in Eq. (10) go in the opposite way. However, even in this case no quantitative agreement for the field dependence of  $T_1^{-1}$  can be obtained by using Eq. (10) since the coefficient in front of the term  $(\omega_x/\omega_c)^{1/2}$  is too small with respect to the one multiplying  $H^{-1/2}$ . As a matter of fact since one has to work on the balance of two large terms one cannot hope to make this argument quantitative unless one finds a way to calculate exactly the coefficients in Eq. (1).

It was pointed out by Richards<sup>15</sup> that a field-dependent cutoff frequency  $\omega_c^*$  for the two-spin correlation function  $\langle S_i^z(t) S_{i+j}^z(0) \rangle$  is possible since  $\omega_c^*$  should be of the order of the electronic spin-lattice relaxation rate. This rate can be less than the spin-spin relaxation rate and can be field dependent through the nonsecular terms. At the maximum field used in our experiments,  $H = 17 \text{ kG}$ , one should choose  $\omega_x/\omega_c^* \approx 1.600$  in order to have agreement between Eq. (10) and the experimental value of  $T_1^{-1}$  for  $\vec{H} \perp \vec{c}$ . Since  $\omega_x = 6 \times 10^{12} \text{ sec}^{-1}$ , one obtains  $\omega_c^* \approx 3.7 \times 10^9 \text{ sec}^{-1}$ . On the other hand for  $\vec{H} \parallel \vec{c}$ , the NMR  $T_1^{-1}$  depends on the correlation function of the transverse spin components  $\langle S_{i,j}^+(t) S_{i,j}^+(0) \rangle$ . The cutoff frequency  $\omega_c^*$  for this function should be of the order of the EPR linewidth expressed in frequency units. In fact if  $\omega_c^*$  were greater than  $\gamma_e \Delta H_{\text{EPR}}$  then one should not see the non-Lorentzian shapes observed in TMMC.<sup>1</sup>

Therefore, one can deduce from the EPR measurements<sup>1</sup> that  $\omega_c^* \approx 10^{10} \text{ sec}^{-1}$ . From our measurements one deduces that since no leveling off of  $T_1^{-1}$  is observed down to  $H = 500 \text{ G}$  it must be  $\omega_c^* < 9 \times 10^9 \text{ sec}^{-1}$ . One can conclude that the above set of values is of the right order of magnitude but not entirely consistent with each other. Therefore, it cannot be completely ruled out that the spin correlation function be different for the spin components parallel and perpendicular to the chain axis even if this anisotropy would be very unlikely for a Heisenberg magnet at high temperature.

A similar comparison of theory and experiments can be done also for CMC which is a much less perfect one-dimensional paramagnet with a three-dimensional ordering temperature  $T_N = 4.89 \text{ }^\circ\text{K}$ <sup>16</sup> to be compared with  $T_N = 0.8 \text{ }^\circ\text{K}$ <sup>17</sup> for TMMC. The main feature is that for  $\vec{H} \parallel \vec{c}$  there appears to be a cancellation of autocorrelation and pair correlation terms in the  $A_j$  coefficients of Eq. (1) like for TMMC. The cancellation is related to the fact that the protons lie close to a mirror plane perpendicular to the chain axis. From the experimental results for  $\vec{H} \parallel \vec{c}$  shown in Fig. 2 one can deduce an upper limit for the cutoff frequency which is given by the electronic Larmor frequency

$\omega_s$  at the lowest field for which measurements were possible. One finds  $\omega_c \lesssim \omega_s = 3.5 \times 10^{10} \text{ sec}^{-1}$ . This upper limit is perfectly consistent with the cutoff frequency estimated in CMC from theoretical arguments and EPR-line-shape analysis<sup>8</sup> which ranges from  $10^9$  to  $10^{10} \text{ sec}^{-1}$  according to the theoretical model used. Unfortunately, the measurements could not be extended to very low fields because the nuclear spin-lattice and spin-spin relaxation rates are too short. A detailed analysis of the data will be attempted if it will be possible to perform more low-field measurements in CMC together with measurements in the isostructural compound  $\text{CsCoCl}_3 \cdot 2\text{H}_2\text{O}$  which should behave more as an Ising linear chain.

In conclusion we have shown in a direct way the diffusive character of the high-temperature two-spin correlation function at long times in one-dimensional  $S = \frac{5}{2}$  Heisenberg paramagnets. It was also found a very different behavior of  $T_1^{-1}$  for  $\vec{H} \parallel \vec{c}$  and  $\vec{H} \perp \vec{c}$  which could be ascribed to a different cutoff mechanism for the correlation function of the longitudinal and transverse components, with respect to  $\vec{H}$ , of the electronic spin.

#### ACKNOWLEDGMENTS

It is a pleasure to acknowledge helpful conversations with G. Bonera, J. P. Boucher, D. Hone,

M. Nechtschein, P. M. Richards, A. Rigamonti, and C. Scherer, and help in computation by M. Bosco.

#### APPENDIX

In this appendix we give the explicit expression for the coefficients appearing in Eq. (1) for the case of interest here in which the interaction between the nuclear spin system  $\vec{I}$  and the electronic spin system  $\vec{S}$  is only dipolar. The coefficients are

$$A_j(\theta, \varphi) = \sum_i 2\gamma_N^2 \gamma_e^2 \hbar^2 S(S+1) \alpha_{i,i+j},$$

$$B_j(\theta, \varphi) = \sum_i 2\gamma_N^2 \gamma_e^2 \hbar^2 S(S+1) \beta_{i,i+j},$$

where  $i$  and  $j$  refer to the electronic-spin operator  $S_i$  and  $S_{i+j}$  and  $\gamma_N$  and  $\gamma_e$  are the nuclear and electronic gyromagnetic ratios and

$$\begin{aligned} \alpha_{i,i+j} &= \frac{3}{4} \cos(\varphi_i - \varphi_{i+j}) \\ &\quad \times \frac{\sin\theta_i \cos\theta_i \sin\theta_{i+j} \cos\theta_{i+j}}{r_i^3 r_{i+j}^3}, \\ \beta_{i,i+j} &= \frac{1}{24} \frac{(1 - 3 \cos^2\theta_i)(1 - 3 \cos^2\theta_{i+j})}{r_i^3 r_{i+j}^3} \\ &\quad + \frac{3}{8} \cos 2(\varphi_i - \varphi_{i+j}) \frac{\sin^2\theta_i \sin^2\theta_{i+j}}{r_i^3 r_{i+j}^3}. \end{aligned}$$

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