

Magnetic dipolar effects in the spin-cluster resonance spectra of $[(\text{CH}_3)_3\text{NH}]\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$

R. S. Rubins, A. Sohn,* and T. D. Black

Department of Physics, PO Box 19059, University of Texas at Arlington, Arlington, Texas 76019

John E. Drumheller

Department of Physics, Montana State University, Bozeman, Montana 59717

(Received 18 October 1999; revised manuscript received 13 January 2000)

Electron magnetic-resonance (EMR) spectra observed at liquid-helium temperatures in the one-dimensional Ising ferromagnet $[(\text{CH}_3)_3\text{NH}]\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ result from transitions within the first excited set of cluster states. Improved fits of the EMR data in the range 10–35 GHz are presented both with and without the inclusion of the magnetic dipolar interaction within a ferrous chain. In the absence of spin canting, an expression independent of the chain length is derived for the matrix elements of the dipolar interaction. Justification for the omission of spin canting is obtained from the rotational behavior of the 17-GHz spectrum, which supports a canting angle of less than 10° .

I. INTRODUCTION

The compound $[(\text{CH}_3)_3\text{NH}]\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ (known as FeTAC) is, below 20 K, a good example of a one-dimensional Ising ferromagnet.¹ The well-separated chains of ferrous ions extend in the b direction of the crystal, which is the easy axis of magnetization. Weak interchain exchange causes a transition to a higher dimensional state at 3.1 K.^{1,2} The metamagnetic phase diagram has a critical field of 90 Oe, which is well below the fields at which electron magnetic resonance (EMR) occurs in this material in the microwave range. The Ising form of the exchange coupling within a chain is a consequence of the isolation of the ground $M_s = \pm 2$ pseudodoublet of each single ferrous ion. In an effective $S = \frac{1}{2}$ representation, the Ising exchange Hamiltonian may be written

$$\mathcal{H}_{\text{ex}} = -\sum 2JS_i^z S_{i+1}^z. \quad (1)$$

The elementary excitations of an Ising spin system are localized spin reversals, known as spin clusters.^{3,4} For a closed ring of N spins, the first set of excited cluster states lies at an energy $2J$ above the ferromagnetic ground state. A member of this set contains n neighboring reversed spins, and is known as an n fold spin cluster, with $0 < n < N$. The second cluster set, containing two separated clusters, has excitation $4J$; the third, containing three separated clusters, has excitation $6J$, and so on. For a linear chain with end effects, low degeneracy intermediate states of excitations J , $3J$, etc., are also present.⁵

EMR in FeTAC at liquid-helium temperatures has been interpreted in terms of transitions between adjacent cluster levels of the first excited set.^{6–8} A simple model, containing only Ising exchange and Zeeman terms, would lead to a single EMR line. However, the observed spectra are more complicated, showing four inequivalent magnetic sites, each of which gives a spectrum of many lines. The EMR spectra of the four inequivalent sites coincide in the b direction, where a sharp resonance line is observed below 20 K on the high-field side of a satellite structure, which is unresolved below 10 GHz. As the frequency is increased from 10 to 40 GHz, the satellite spectra are characterized by a decrease in

the number of lines and increases in both their intensities relative to the high-field line and their mean separations. These features are illustrated in Fig. 1, which is taken from Rubins *et al.*⁹ An additional weak satellite line, appearing above the high-field line (see spectra b and d), was not explained.

The spectra of Fig. 1 were explained quantitatively by including the following phenomena:

- (i) an internal magnetic field, which lowers the resonance field of each satellite line by a fixed amount independent of both frequency and line position;
- (ii) a zero-field splitting of the $M_s = \pm 2$ pseudodoublet by

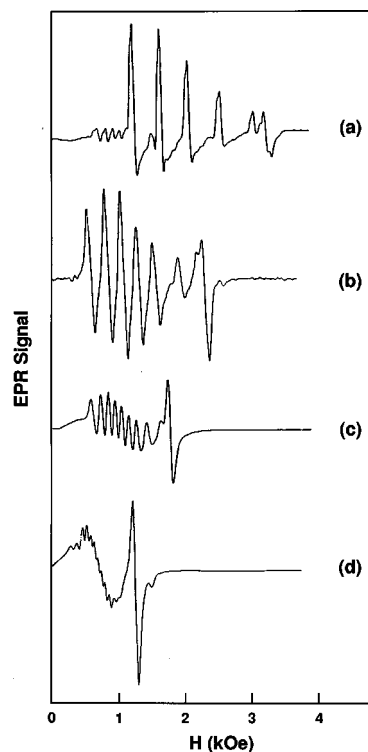


FIG. 1. EMR spectra at 3.6 K with H parallel to the chain axis and microwave frequencies of (a) 35.6 GHz, (b) 25.0 GHz, (c) 17.6 GHz, and (d) 12.4 GHz (taken from Rubins *et al.*, Ref. 9).

the low-symmetry components of the crystal field, which leads to the satellite structure.

In addition, the temperature dependence of the 25 GHz spectrum between 3.0 and 4.3 K has been explained by a random distribution of chain lengths.¹⁰

While the agreement between experiment and theory has been satisfactory, there remain other factors which should be taken into account. Two such factors are spin canting, which according to Greeney *et al.*¹ should be appreciable, and the magnetic dipolar interaction between neighboring ferrous ions, resulting from the high effective g value in the z direction and the proximity of the neighboring ferrous ions on a chain. Consideration of these two factors is the main purpose of this paper. Following a review of the theory of Rubins *et al.*,⁹ a theoretical derivation of the dipolar contributions is presented in Sec. II, and the fit of the data is reanalyzed. In Sec. III, the omission of spin canting in the earlier sections is justified on the basis of a recent experimental study of the angular behavior of the EMR spectrum of FeTAC.

II. THEORY

Exchange in FeTAC is dominated by the indirect interactions between neighboring ferrous ions on a chain. In an effective spin- $\frac{1}{2}$ representation, the exchange interaction is of the Ising form given in Eq. (1), where the summation is over a single chain and the exchange constant $2J/k_B \approx +35$ K.¹ If not too short, each chain produces the same spectrum.⁹

For a hypothetical chain in the form of a closed ring, the eigenstates of Eq. (1) are highly degenerate sets of spin-cluster states with excitations $2mJ$ relative to the ferromagnetic ground state, where m is the number of separated clusters on the ring. Each member of the first excited cluster set ($m=1$) contains a single n fold spin cluster with $0 < n < N$, where N is the number ferrous ions on the chain. Since the spin positions on a ring are distinguishable, there is an N fold degeneracy associated with each value of n . Members of the second excited cluster set ($m=2$) contain p fold and q fold spin clusters, which are separated from each other. In the practical case of finite linear chains, intermediate levels of excitation $(2m+1)J$ occur if there is a reversed spin at one end of a chain.⁵ However, the lower lying cluster sets of this type have very low degeneracies, and so may be ignored. Restricting our considerations to long chains containing few reversed spins, which is the practical situation encountered in the interpretation of the EMR spectra of FeTAC,¹⁰ we may assume the m th excited cluster set to have a degeneracy of the order N^m .

Each cluster set is split by an external magnetic field. If we neglect spin canting (see Sec. IV), the crystallographic b axis is the z axis for each ferrous ion, so that the Zeeman interaction for a single chain may be written¹²

$$\mathcal{H}_{ze} = g_z \mu_B H_{\text{eff}} \sum S_1^z, \quad (2)$$

where $g_z \approx 8$ in the spin- $\frac{1}{2}$ representation, and

$$H_{\text{eff}} = H - H_{\text{int}}, \quad (3)$$

where H_{int} is an internal field of several hundred oersted. Relative to the Zeeman energy of the ferromagnetic ground state, those of the cluster states are proportional to the total

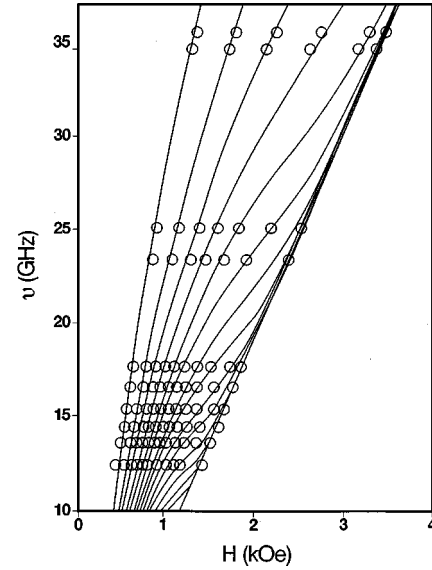


FIG. 2. A plot of resonance field against microwave frequency is shown for the FeTAC data at liquid-helium temperatures for H parallel to the chain axis. The experimental data, given by the circles, were taken at 3.6 K, except for the 10-GHz point, which was obtained at 4.2 K. The solid lines represent the theoretical fit of the data for chain sizes N between 30 and 60 obtained by Sohn (Ref. 11).

number of reversed spins on the chain. $\Delta M = \pm 1$ transitions are allowed between states belonging to the neighboring Zeeman levels of a given cluster set. In this approximation, a single EMR line would occur at a resonance field H_o given by

$$h\nu = g_z \mu_B (H_o - H_{\text{int}}), \quad (4)$$

where ν is the microwave frequency. Equation (4) gives the resonance field of the high-field line of the FeTAC spectrum,^{7,8} which is the strongest line in spectra (c) and (d) of Fig. 1.

The satellite structures observable in Fig. 1 were explained by the addition of a zero-field splitting term⁹

$$\mathcal{H}_{zfs} = \Delta_s \sum S_1^x, \quad (5)$$

which describes the low-symmetry components of the crystal field of a non-Kramers ion in a $S = \frac{1}{2}$ representation.¹³ With basis states within the first excited spin-cluster set given by the cluster size n , the nonzero matrix elements of Eq. (5) are

$$\langle n | \mathcal{H}_{zfs} | n \pm 1 \rangle = \Delta_s / 2. \quad (6)$$

The observed EMR spectra are associated with the transitions ($n \leftrightarrow n+1$) between states associated with adjacent cluster levels. The satellites result from the energy shifts produced by the off-diagonal elements of Eq. (6) between states of lowest and highest n (although the contributions of the latter are negligible, since states of high n are relatively unpopulated). The main line, which occurs at the resonance field H_o , is a composite arising (for large N) from transitions between the many states of intermediate n . By solving the Hamiltonian matrices for values of N up to 60, Sohn¹¹ obtained the excellent fit of the data shown in Fig. 2 with the values

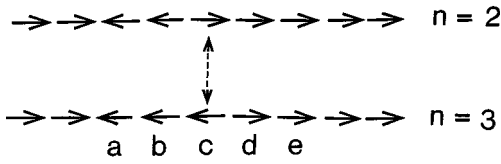


FIG. 3. An $n \leftrightarrow n+1$ spin-cluster transition with $n=2$ is illustrated schematically for the case in which the ferrous spin labeled c is reversed. The two closest spins on either side of c , labeled a , b , d , and e , produce cancelling fields at spin c . Thus the noncancelling contributions to the dipolar field at c begin with its third nearest neighbors, justifying the lower limit of $n+1$ in the summations of Eqs. (9) and (13).

$$H_{\text{int}} = 337 \text{ Oe}, \quad g_z = 8.20, \quad \Delta_s/k_B = 3.43 \text{ K}. \quad (7)$$

These values represent a better fit than the ones quoted in Ref. 9 and shown in Fig. 2 of that paper.¹²

Although an excellent fit of the data has been obtained without its inclusion, a more realistic theory should include the intrachain dipolar contribution because of the proximity of neighboring ferrous ions and the high value of g_z . The procedure we shall follow is to calculate the matrix elements of the dipolar interaction and then redetermine the value of the zero-field parameter Δ_s needed to fit the data. The value $2J/k_B \approx 33 \text{ K}$ was obtained from the intensity dependence of the high-field line on temperature.

We begin by estimating the dipolar field at a site in which a ferrous ion changes its state during the transition ($n \leftrightarrow n+1$). The situation for the hypothetical case of $n=2$ is illustrated in Fig. 3, where arrows pointing to the right represent spins parallel to the external field. If the latter is parallel to the easy axis and spin canting is ignored, then the intrachain dipolar field at the i th spin of an Ising ferromagnet is of the form

$$H_{\text{dip}}^i = \pm \sum_j 2\mu/r_{ij}^3, \quad (8)$$

where $\mu = g_z \mu_B/2$ and the $+$ and $-$ signs refer, respectively, to spins aligned parallel and antiparallel to H . For the k th nearest neighbor, $r_{ij} = kr_o$, where $r_o = 3.68 \text{ \AA}$ is the separation of nearest-neighbor ferrous ions.¹ The quantity $2\mu/r_o^3$ is approximately 1.5 kOe for FeTAC.

In order to evaluate the summation of Eq. (8) for a typical cluster with $n \ll N$, we assume that the cluster is not near the end of a chain. The dipolar field at the site of the spin reorienting during the transition ($n \leftrightarrow n+1$) is then given by

$$H_{\text{dip}}^n = (4\mu/r_o^3) \sum k^{-3}, \quad (9)$$

so that

$$H_{\text{dip}}^n = H_{\text{dip}}^{n+1} + (4\mu/r_o^3)(n+1)^{-3}. \quad (10)$$

Thus the net effect of the dipolar interaction is to move the EMR spectra to lower fields by amounts which decrease with increasing n . The lower limit $k=n+1$ in Eq. (9) occurs because contributions of the n fold spin cluster on one side of the reorienting spin are cancelled by the n nearest spins on the other side (see Fig. 3). The more distant neighbors on both sides of that spin contribute dipolar fields parallel to H , giving an additional factor of 2 in Eq. (9). The upper limit

$k=n'$ may be chosen arbitrarily to ensure that the sum of the contributions for $k>n'$ is negligible.

In order to redetermine Δ_s , we calculate the matrix elements of the dipolar Hamiltonian \mathcal{H}_{dip} within the first excited cluster set. The dipolar energy may be written

$$W_{\text{dip}} = -\mu \cdot H_{\text{dip}} = \pm D_d \sum \sum k^{-3}, \quad (11)$$

where

$$D_d = (g_z \mu_B)^2 / 2r_o^3. \quad (12)$$

The positive and negative signs are used in Eq. (11) when the i th and j th spins are, respectively, parallel and antiparallel. The value of D_d/k_B for FeTAC is 0.42 K.

In general, the dipolar energy for a given value of n depends on both the chain size N and the position of the cluster on the chain. However, the fact that the satellite lines are clearly delineated indicates that neither of these factors is important for the cluster states of lowest N . We seek a result independent of N by calculating the dipolar energies relative to the ferromagnetic ground-state ($n=0$) for an arbitrary value of N .

As illustrated in Fig. 3, the difference in energies between the cluster states n and $n+1$ results from the reversal of a single spin. Denoting the dipolar energies of the two states W_n and W_{n+1} , Eq. (11) gives

$$W_{n+1} = W_n - 4D_d \sum k^{-3}. \quad (13)$$

The factor 4 in Eq. (13) arises both from the energy increase in reversing a spin and from the fact that the summation of Eq. (11) is performed in both directions along the chain. Since the transition fields involve energy differences only, the ground-state energy W_0 may be chosen to be zero. Then, using Eqs. (11) and (13), we may write the nonzero matrix elements of \mathcal{H}_{dip} as

$$\langle n | \mathcal{H}_{\text{dip}} | n \rangle = W_n. \quad (14)$$

If just the leading term in the summation of Eq. (15) is retained, then the approximate result $W_n = 4D_d/(n+1)^3$ again shows the relative importance of the dipolar interaction for transitions involving the cluster states of lowest n .

The matrix elements shown in Eqs. (6) and (14) give rise to a tridiagonal Hamiltonian matrix,⁹ which was solved by Sohn¹¹ for values of N of up to 60. Using the calculated value

$$D_d/k_B = 0.42 \text{ K}. \quad (15)$$

He obtained a fit of the EMR data essentially indistinguishable from that shown in Fig. 2, for the values

$$g_z = 8.20, \quad H_{\text{int}} = 337 \text{ Oe}, \quad \Delta_s/k_B = 3.32 \text{ K}. \quad (16)$$

Comparison with Eq. (7) shows that Δ_s is reduced by just 3% when dipolar coupling is included. The very small effect of the dipolar term in obtaining the fit is basically a consequence of the fact that $D_d \ll \Delta_s$. Both perturbations have their largest effects on the outermost transition (for which $n=1$).

III. DISCUSSION

Although found to occur in FeTAC,¹ spin canting has been ignored in the preceding calculations. In FeTAC, the z axes of the ferrous ions on a chain alternate in direction, each axis making an angle θ_c (the canting angle) with the easy axis (the chain direction). In the absence of canting, the effects of the intrachain dipolar interaction on the EMR spectra are given by the diagonal matrix elements of Eq. (14). With spin canting, nonzero off-diagonal matrix elements of the dipolar interaction would be introduced, while the magnitudes of the diagonal elements would be reduced. For canting angles of appreciably less than 10° , their effects on the EMR spectrum should be unimportant. On the other hand, if the 30° canting angle deduced from Mossbauer data by Greeney *et al.*¹ is correct, the calculations of the preceding sections would require appreciable modification.

We have estimated the maximum magnitude of the canting angle by investigating orientational dependence of the EMR spectra at 4 K, since each distinct ferrous site would in general give rise to a separate spectrum. For reasons of symmetry, one would expect the different spectra to have the same principal g values but different principal axes, with each individual z axis making an angle of magnitude θ_c with the chain axis (or crystallographic b axis).

Ravindran's original 9 GHz study showed a movement to higher fields, but no splitting of the high-field line into components, on rotation of the magnetic field away from the chain axis.⁶ In our measurements at 17 and 36 GHz, movements of both the high field and satellite lines to higher fields, as well as line-splittings were observed on rotation. At all frequencies, the EMR spectra moved rapidly above the 12-kOe limit of our magnet as the crystallographic ac plane was approached.

Our rotational observations were made on the high-field line at 4.2 K and 17.1 GHz, with the crystal mounted on a face containing the b axis. This choice of frequency was a compromise between spectral resolution, which increases with frequency, and the relative intensity of the high-field line, which decreases with increasing frequency (see Fig. 1). At this frequency, a rotation of 15° from the chain axis in either direction caused a fully resolved splitting of the high-field line into two components of similar magnitude. For rotations of over 20° , a further splitting of the upper compo-

nent was observed, which was probably a result of a slight crystal alignment. However, the latter splitting was useful in establishing that at least four inequivalent ferrous sites are present in FeTAC, which is the same as the number of inequivalent cuprous sites observed in the related compound CuTAC.¹³

Since the effective g values of ferrous single-ion ground state in the spin- $\frac{1}{2}$ representation are approximately $g_z=8$ and $g_x, g_y=0$,⁹ the g value for an angular rotation θ from the chain axis is given approximately by $g(\theta)=g_z \cos \theta$. If g_b represents the g value in the chain direction, making an angle θ_c with the true z axis of the ferrous spectrum, then this relationship becomes

$$g_b = g_z \cos \theta_c \quad (17)$$

with $g_b=8.2$. For the canting angles $\theta_c=5, 10, 15, 20,$ and 30° , Eq. (17) gives the values $g_z=8.2, 8.3, 8.5, 8.7,$ and 9.5 , respectively. Only the first two values are realistic, since the value of g_z for the $M_S=\pm 2$ doublet of Fe^{2+} ion should not be very much larger than 8 in a spin- $\frac{1}{2}$ representation. Also, the larger values of θ_c might be expected to lead to extrema in directions sufficiently removed from the chain axis to show resolved field minima.

From the 17-GHz rotational data, the angular rotation θ_m of a resonance field minimum from the chain axis in the plane of measurement has been estimated to be $(4 \pm 1)^\circ$ in either direction. Since this angle leads to a g -value maximum in this plane only 0.24% higher than g_b , its only effect on the observed spectrum is to produce a slight broadening of the line on either side of the chain axis. Further experimental work is needed before θ_c may be calculated from this result. However, if the projections of the z axes of the four ferrous sites onto the ac plane of the crystal are assumed to be the similar to those for Cu^{2+} in CuTAC,¹⁴ then a canting angle of about 6° is obtained. Thus we conclude that our various estimates of the magnitude of θ_c give a value sufficiently small to justify its omission from the calculations of the two preceding sections.

ACKNOWLEDGMENT

This work was supported in part by National Science Foundation Grant No. DMR-99-74273.

*Present address: Precision Engineering Center, North Carolina State University, Box 7918, Raleigh, NC 27695.

¹R. E. Greeney, C. P. Landee, J. H. Zhang, and W. M. Reiff, *Phys. Rev. B* **39**, 12 200 (1989).

²C. P. Landee, R. Kuentzler, and J. J. M. Williams, *J. Appl. Phys.* **67**, 5604 (1990).

³M. Date and M. Motokawa, *Phys. Rev. Lett.* **16**, 1111 (1966).

⁴J. B. Torrance, Jr. and M. Tinkham, *Phys. Rev.* **187**, 587 (1969).

⁵J. D. Johnson and J. C. Bonner, *Phys. Rev. B* **22**, 251 (1980).

⁶K. Ravindran, Ph.D. dissertation, Montana State University, 1991, pp. 50–59.

⁷K. Ravindran, S. Waplak, T. E. Grigereit, J. E. Drumheller, and R. S. Rubins, *Phys. Rev. B* **47**, 14 568 (1993).

⁸R. S. Rubins, T. D. Black, K. Ravindran, T. E. Grigereit, and J. E. Drumheller, *J. Appl. Phys.* **73**, 6977 (1993).

⁹R. S. Rubins, T. D. Black, A. Sohn, and J. E. Drumheller, *Phys. Rev. B* **49**, 15 366 (1994).

¹⁰R. S. Rubins, D. K. Smith, T. D. Black, and J. E. Drumheller, *IEEE Trans. Magn.* **31**, 4148 (1995).

¹¹A. Sohn, M. S. thesis, University of Texas at Arlington, 1994, pp. 13–36.

¹²By error in Ref. 9, the diagonal matrix elements of Eq. (6) were written too small by a factor 2, while the quoted value for Δ was too large by the same factor.

¹³See, for example, A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, 1st ed. (Oxford, 1970), p. 734.

¹⁴R. S. Rubins, K. S. Park, D. K. De, T. D. Black, and J. E. Drumheller, *Bull. Am. Phys. Soc.* **44**, 392 (1999).