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Spin-cluster resonance at 9 GHz in the one-dimensional Ising ferromagnet $[(CH_3)_3NH]\ FeCl_3 \cdot 2H_2O$

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Low-temperature magnetic-resonance spectra at 9.2–9.3 GHz in single crystals of the one-dimensional Ising ferromagnet FeTAC, $[(CH_3)_3NH]\ FeCl_3 \cdot 2H_2O$, were strongly anisotropic with minima in the field occurring for H parallel to the easy axis. A "strong" signal in this orientation with a g value of 8.8 at 5.5 K (after correction for internal demagnetization and exchange fields) is identified with transitions between neighboring spin-cluster resonances. Possible origins of broad and weak lines, with maximum corrected g values of 13 and 3.7 are discussed. Spectra from samples of different shape are consistent with sample-dependent demagnetization fields.

The compound $[(CH_3)_3NH]\ FeCl_3 \cdot 2H_2O$, known as FeTAC, behaves as a quasi-one-dimensional (1D) Ising ferromagnet, with an exchange constant $J/k_B = 17.4$ K in the $S=\frac{1}{2}$ representation.[1] The ratio of the interchain to intrachain exchange-constant J'/J is -1.2×10^{-3}.[2] Such 1D systems have the interesting feature that the ordering temperature T_c is significantly lower than J/k_B. Consequently, intrachain phenomena can be studied at temperatures well above T_c. The purpose of this paper is to present 9.2–9.3 GHz electron paramagnetic resonance (EPR) data obtained from single crystals of FeTAC between 4 and 10 K, and to show how some of the observed signals can be explained in terms of spin-cluster resonance (SCR).[3]

The FeTAC structure contains chains of bichloride-bridged Fe^{2+} ions extending along the b axis of the orthorhombic unit cell. The chains are linked in a two-dimensional (2D) network in the bc plane by hydrogen bonding in the c direction.[1] The planes are well separated in the a direction by the organic parts of the molecules. The b axis is the easy magnetic axis and also the needle axis of the single crystals. The weak exchange interaction between the chains produces a transition to an antiferromagnetic state at 3.1 K. The phase diagram is metamagnetic, with a critical field $H_c(0)$ of 90 Oe.[1]

The effects of the spin-orbit coupling and the orthorhombic components of the crystal field on the free ion ground state of Fe^{2+} ($3d^6$, $S=2$) may be represented by the fine-structure spin Hamiltonian[4]

$$\mathcal{H}_{\rm fs} = DS_z^2 + E(S_x^2 - S_y^2) \ . \tag{1}$$

The condition $|E| \ll |D|$ with D negative gives an $M_S = \pm 2$ pseudo-doublet ground state separated by approximately 3D from the $M_S = \pm 1$ pseudo-doublet. If this splitting is at least of the same order as the exchange splitting $2J$ (in the $S=\frac{1}{2}$ representation), the system will behave as a 1D spin-$\frac{1}{2}$ Ising ferromagnet at low temperatures.[5] Thus a lower limit for $|D|/k_B$ of about 10 K may be set for FeTAC. The spin canting in the a and c directions, measured in FeTAC,[1] causes deviations from pure Ising exchange.[5] In the first approximation, the z axis for the fine-structure term is assumed to be in the b direction.

The $S=\frac{1}{2}$ Hamiltonian, which includes the Ising exchange, the Zeeman interaction for $H \parallel b$, and the zero-field splitting of the single-ion ground pseudo-doublet, may be written[5]

$$\mathcal{H} = -2J \sum_{i=1}^{N} S_i^z S_{i+1}^z - g_z \mu_B H_{\rm eff} \sum_{i=1}^{N} S_i^z + \Delta \sum_{i=1}^{N} S_i^x \ , \tag{2}$$

where $\Delta = 3E^2/|D|$ for the $M_S = \pm 2$ pseudo-doublet. The effective field $H_{\rm eff}$ is given by

$$H_{\rm eff} = H - H_{\rm ex} - H_d \ , \tag{3}$$

where H is the external field, $H_{\rm ex}$ is the exchange field due to neighboring chains, and H_d is the demagnetizing field. At temperature sufficiently low for the population of the ferromagnetic ground state to greatly exceed that of all other states, $H_{\rm ex}$ would be expected to equal the metamagnetic critical field $H_c(0) = 90$ Oe. The demagnetizing field may be calculated for a particular sample from the expression $H_d = DM/V_m$, where D is the demagnetizing factor, V_m is the molar volume of the sample, and M is the total magnetization per mole.

The elementary excitations of an Ising ferromagnet are localized spin reversals, known as spin clusters or magnon bound states.[5] Ignoring the zero-field splitting parameter Δ in the first approximation and assuming $J \gg g_z \mu_B H_{\rm eff}$, the first set of excited states consists of chains in which a single group of n neighboring spins is reversed. The energy of such an n-fold spin cluster is given by

$$E_n = E_0 + 2J + n g_z \mu_B H_{\rm eff} \ , \tag{4}$$

where E_0 is the ground-state energy in a field $H_{\rm eff}$. The

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second group of excited states consists of chains with two separated spin clusters and a zero-field excitation of $4J$. SCR at microwave frequencies was first reported in $CoCl_2{\cdot}2H_2O$ by Date and Motokawa[3,6] and later in ferrous compounds.[5,7]

In the present work, single crystals of FeTAC were investigated at microwave frequencies near 9.2 GHz with a Varian *E* 109 series electron paramagnetic resonance (EPR) spectrometer and at temperatures down to 4 K using an Oxford "flowthrough" cryostat.

Three distinct resonance signals were observed below about 10 K.[8] These were highly anisotropic, with low field extrema occurring for $H\|b$. Figure 1 shows the anisotropies of the signals at 5.5 K, with the angle $\theta=0°$ corresponding to the orientation $H\|b$. A typical spectrum in the latter orientation, taken at 5.5 K, is shown in Fig. 2. In addition to a strong signal centered at approximately 1050 Oe, a weak signal at 2160 Oe and a broad one near 760 Oe may be seen. For convenience, these signals will be referred to as "strong," "weak," and "broad," respectively. The weak signal had an intensity about two orders of magnitude smaller than the strong signal and was not observed in most samples.

The variations of the FeTAC spectra with temperature have been studied in numerous samples.[8-10] Rubins *et al.*[10] have reported 14.7 GHz measurements of the temperature variations of the line intensity, linewidth, and resonance field for the strong signal between 2.5 and 12 K. In the sample used to obtain the data shown in Figs. 1 and 2, the intensity of the weak signal was found to vary as $\exp(-\Delta E/k_B T)$, with $\Delta E/k_B \sim 45$ K.[8]

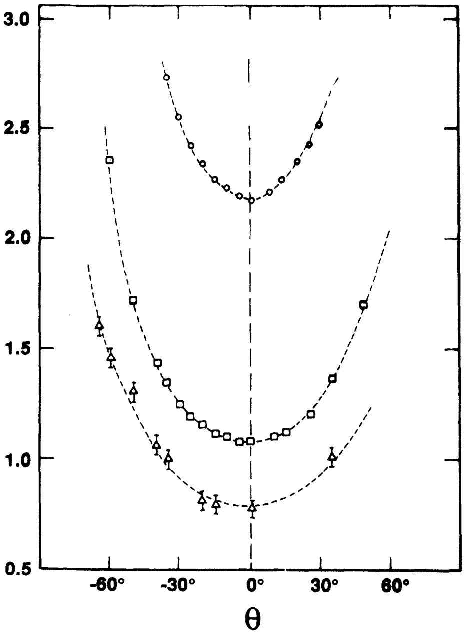

FIG. 1. The angular dependence of the 9.24 GHz EPR spectrum of FeTAC at 5.5 K. The angle $\theta=90°$ corresponds to $H\|b$ (the easy axis) and the symbols ○, □, and △ denote the weak, strong, and broad signals, respectively. The broken lines are guides to the eye.

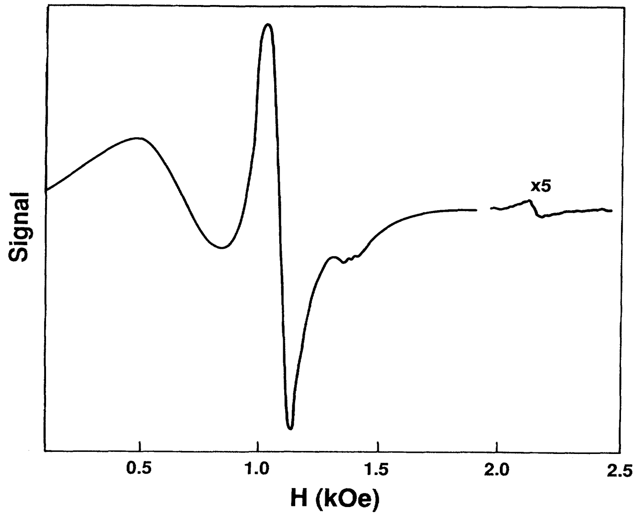

FIG. 2. The EPR spectrum of a FeTAC crystal at 9.24 GHz and 5.5 K with $H\|b$ (the easy axis). The weak, strong, and broad signals occur at 2.16, 1.05, and approximately 0.76 kOe, respectively. In order to show the weak signal, the sensitivity of the detector was increased by the factor 5.

In the approximation of Eq. (4), the resonance condition for a transition between single cluster states in which $\Delta n=1$ is

$$h\nu=g_z\mu_B H_{\rm eff} \ . \qquad (5)$$

In order to evaluate $H_{\rm eff}$ for the various spectra observed from sample used to obtain Figs. 1 and 2, estimates of H_d were made from the sample dimensions, which were approximately 1.93 mm×0.95 mm×0.64 mm (with the b dimension given first). Assuming the sample to be a prolate spheroid of similar dimensions and volume, the factor D/V_m was estimated to be 0.016 cm^{-3}/mol,[8] using the method given by Haines.[11] Isothermal ac susceptibility measurements at 2.4 K were used to calculate an upper limit for this factor of 0.02 cm^{-3}/mol.[8] From the measured values for $M(H,T)$ in this sample, demagnetization fields of 283, 210, and 160 Oe were obtained for the weak, strong, and broad lines, respectively, at 5.5 K. With $H_{\rm ex}=90$ Oe and H_d both included in calculating $H_{\rm eff}$ [see Eq. (3)], g_z values of 3.7, 8.8, and 13, respectively, were obtained for the three signals. We propose that the strong line is produced by transitions between neighboring spin-cluster states; i.e., SCR with $\Delta n=\pm 1$ [see Eq. (5)], as first suggested by Ravindran.[8] This assignment is based primarily on the proximity of the g value to 8 in the $S=\frac{1}{2}$ representation, which is consistent with a $\Delta M_S=\pm 4$ transition in Fe^{2+} (in the $S=2$ representation). While such a result would be obtained for an isolated Fe^{2+} spectrum,[12] only the spin-cluster interpretation is consistent with the clearly Ising-like behavior exhibited in the magnetic susceptibility data.[1] Additional evidence in support of this conclusion has been obtained by Rubins *et al.*[10] through both the characteristic temperature dependence of the line intensity below 6 K and the linear dependence of the resonance field on the microwave frequency observed at 4.2 K in the range 12–36 GHz, from which the value $g_z = 8.3$ was obtained.

Two possible reasons for the difference between the above value of g_z for the strong line and the value of 8.8 obtained in this work are errors in the estimated value of H_d and the effect of a non-negligible zero-field splitting parameter Δ [see Eq. (2)]. Work at higher frequencies on different samples by Rubins *et al.*[10,13] has allowed direct experimental determinations of H_d. The effect of the Δ term on the SCR spectra is currently under investigation.[13]

The decrease of the demagnetization and exchange fields with increasing temperature may be inferred from Fig. 3, which shows the movement to lower fields of the spectrum from one needle-shaped FeTAC sample as the temperature was raised above 4 K. This is consistent with the higher-frequency data reported by Rubins *et al.*[10]

Noticeable in Fig. 3 is the splitting of the strong line at the lowest temperature into an irregular distribution of components. This breakup of the single line is probably associated with microwave heating of the sample caused by the relative inefficiency of the gas-flow cooling system to maintain thermal equilibrium, since it was not observed at 10 GHz for samples placed in contact with a liquid helium bath.[13] This effect is illustrated in Fig. 4, which shows spectra in the range 4.4–4.9 K with $H \| b$ for three samples. Spectrum (c), taken on a sample cut so that the smallest dimension was parallel to the b axis, shows much larger demagnetization fields than the needle-shaped samples used to obtain spectra (a) and (b).

While the main features of the strong line can be explained in terms of SCR with $\Delta n = 1$, the weak and broad lines remain unexplained, although possible explanations of the latter have been suggested.[8,10] Ravindran[8] attributed the broad line to an unresolved spectrum of SCR transitions with $\Delta n = 2, 3$ or more. Resolved SCR lines with Δn up to 6 have been reported in the ferromagnetic phase of the 1D Ising antiferromagnet $RbFeCl_3 \cdot 2H_2O$.[5] Doubt on this interpretation was cast by the observation that at microwave frequencies above 14 GHz the "broad" line appeared as a satellite structure of roughly equally spaced lines,[10] whereas, according to Eq. (4), the lines would get closer as Δn increased. Alternative suggestions for the satellite structure have been given elsewhere,[10] but a convincing explanation is still lacking.

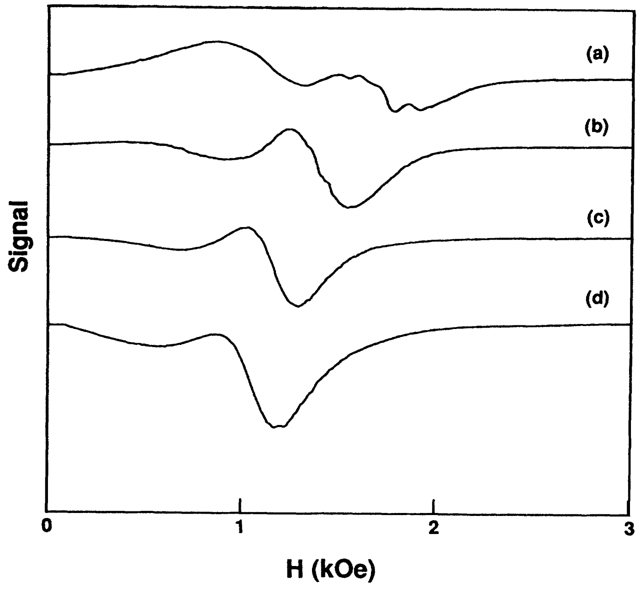

FIG. 3. The EPR spectrum of a FeTAC crystal at 9.32 GHz with $H \| b$ at (a) 4.6 K, (b) 5.8 K, (c) 7.4 K, and (d) 9.5 K.

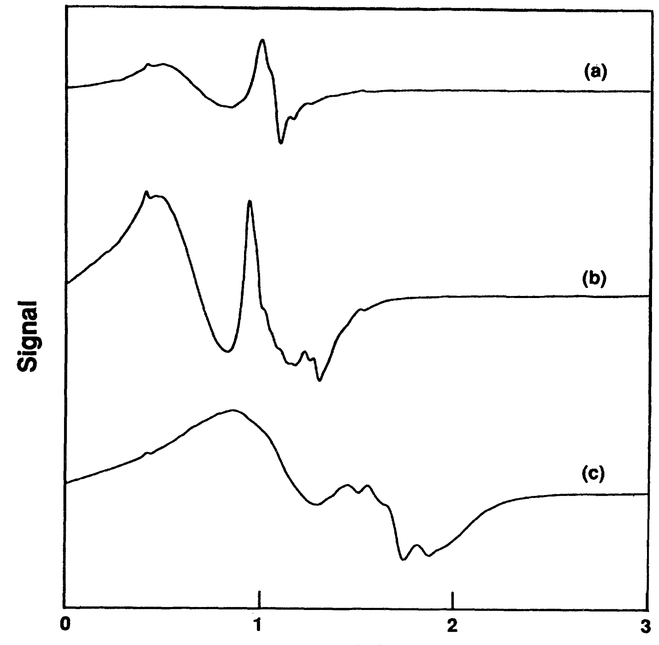

FIG. 4. The EPR spectra of three FeTAC crystals at 9.32 GHz with $H \| b$ near 4.6 K. The temperatures and approximate sizes of the crystals (with the b dimension given first) are (a) 4.9 K, 2.5 mm×1.0 mm×0.5 mm; (b) 4.6 K, 3.0 mm×1.0 mm ×1.0 mm; (c) 4.4 K, 2.0 mm×2.0 mm×(2.5–3.0) mm.

The value $g_z \simeq 4$ observed for the weak line at first sight would appear to be associated with a transition between the $M_S = -1$ and $+1$ states of a single Fe^{2+} ion.[8] However, this interpretation requires that E be very small, since the Hamiltonian of Eq. (1) gives a zero-field splitting for the $M_S = \pm 1$ pseudo-doublet of $6E$. It is possible to associate a $g_z \sim 4$ line with the $M_S = \pm 2$ pseudo-doublet through a double-quantum transition,[4] although it is not clear that the necessary conditions are satisfied in this case. Such a transition would occur at twice the field of a normal ($M_S = -2 \leftrightarrow M_S = +2$) transition and its intensity would vary as the square of the microwave power.[14] Attempts to test this possibility have so far failed, since increasing the microwave power caused sample heating.

Note added in proof. A current EPR study of FeTAC by Rubins *et al.*[13] has established that the broad line, which becomes a resolved satellite structure at higher microwave frequencies,[10] is a result of $\Delta n = 1$ transitions of low n shifted to lower fields by the Δ term in Eq. (2).

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