Quasielastic and inelastic neutron-scattering studies of $[(CD_3)_3ND]FeCl_3 \cdot 2D_2O$: A one-dimensional Ising ferromagnet

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Ferrous trimethylammonium chloride (FeTAC) is a member of a family of compounds that consist of chains of bihalide-bridged metal ions aligned along the *b* axis of the orthorhombic unit cell. The chains are connected in (*bc*) planes by hydrogen bonding of the waters of hydration; these planes are isolated along the *a* axis by the large trimethylammonium groups. FeTAC orders three dimensionally below $T_N=3.16$ K, with the moments, which are canted from the *b* axis by ~20°, coupled ferromagnetically along the *b* axis and staggered along the [101] direction. The order parameter follows the exact Onsager solution for a rectangular 2D Ising lattice below $T/T_N \approx 0.95$, with ratio for the two in-plane magnetic exchange constants of 1.3×10^{-3}. However, quasielastic scattering measurements in the vicinity of T_N show that the correlations do not evolve as do those of the 2D Ising antiferromagnets $ErBa_2Cu_3O_7$ and K_2CoF_4. Above T_N, magnetic excitations along the *b* axis that follow the dispersion relation of a 1D ferromagnet with a gap of 3.7 meV have been observed.

Recently, much attention has been focused on synthesizing organic-based magnets with various desirable properties.[1] Initially, this work focused on tailoring magnets to have reduced magnetic exchange along one or two dimensions, as model low-dimensional systems.[2,3] The series of compounds $[(CH_3)_3NH]MX_3 \cdot 2H_2O$, where X=Cl or Br and M=Mn, Fe, Co, Ni, or Cu (hereafter referred to as MTAX) is characterized by 1D anisotropic Heisenberg magnetic behavior. All of these compounds, with the exception of MnTAB and CuTAC, are orthorhombic, of space group *Pnma*. The transition-metal ions are at the center of distorted octahedra of four halides and two oxygens, with the X^- ions bibridging the M^{2+} ions into chains along the *b* axis, and the waters of hydration providing *c*-axis hydrogen bonding of the chains into planes. The large trimethylammonium groups isolate the planes along the *a* axis.

Extensive bulk susceptibility measurements of single crystals of undeuterated FeTAC ($[(CH_3)_3NH]FeCl_3 \cdot 2H_2O$)[4] indicate that the Fe moments point along the *b* axis with a strong ferromagnetic interchain exchange, with an excellent fit of the data above T_N to a 1D Ising model. Molecular-field corrections to the simple 1D model indicate that the interchain exchange is quite small and opposite in sign to the interchain exchange. Detailed analysis of the susceptibility measurements suggest that the ferromagnetic chains are antiferromagnetically aligned both within the planes and along the *a* axis. This magnetic structure gives rise to a cancellation of near-neighbor interplane interactions along the *a* axis, and thereby leads to an ordering like that of a rectangular 2D Ising antiferromagnet. An analysis of the magnetic specific heat, C_{mag}, over the temperature range $1<T<25$ K,[5] shows that C_{mag} in the vicinity of T_N is extremely well described by the exact expression for the rectangular 2D Ising model, with parameters that are entirely determined by the high-temperature, one-dimensional behavior of C_{mag} and the bulk ordering temperature. These results imply that FeTAC should behave like a 1D ferromagnet at temperatures well above T_N, and cross over to 2D behavior in the vicinity of T_N. Below T_N, FeTAC would be expected to exhibit 3D order, with an order parameter that is determined by two-dimensional ordering of the planes (as in the case of K_2CoF_4 and $ErBa_2Cu_3O_7$, below).

Neutron-diffraction measurements[6] on deuterated powder and single-crystal FeTAC indicate that $T_N=3.16(2)$ K. The spin structure, however, is not that suggested by susceptibility and specific-heat measurements. Rather, the ferromagnetic chains within a plane are aligned ferromagnetically, and the spins are staggered along the [101] direction. As suggested by the susceptibility measurements, the spin structure is noncollinear with the Fe moments canted from the *b* axis by about 20°C. The order parameter, however, does follow the exact Onsager solution for a rectangular 2D Ising lattice for $T/T_N<0.95$, with a ratio for the two in-plane magnetic exchange constants of 1.3×10^{-3}, in agreement with the analysis of both susceptibility and C_{mag} data.

In other systems that undergo 2D Ising ordering, such as $ErBa_2Cu_3O_7$ (Ref. 7) and K_2CoF_4,[8] there are no correlations between planes above T_N. There are, however, extensive correlations within the planes, and as a result, "rods" of scattering are observed. Bragg "rods" are observed, rather than points, since there is no restriction on the momentum transfer required for scattering to occur in the direction normal to the uncorrelated planes. Below T_N, the "rods" develop into the 3D Bragg points with the behavior of the order parameter controlled by the 2D behavior of the ordered moment.[9]

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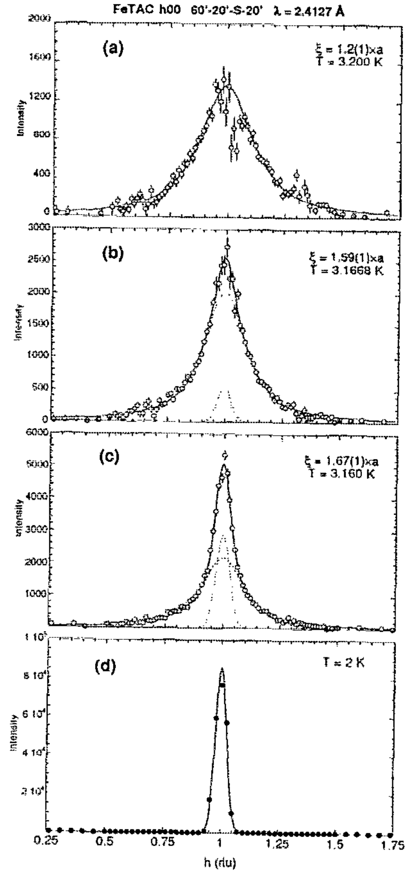

FIG. 1. Evolution of longitudinal scans around the (100) magnetic reflection in the vicinity of the ordering temperature: (a) $T=3.2$ K, above T_N; (b) and (c) $T=3.1668$ and 3.160 K, very close to T_N; (d) $T=2$ K, well below T_N. The dotted lines indicate the Lorentzian and resolution-limited Gaussian components to the fits of the scans below T_N. The width of the Lorentzian component is inversely related to the length of the interplanar correlations.

In an effort to understand the apparent two-dimensional behavior of the magnetic ordering of FeTAC, we have measured the quasielastic scattering along several directions in reciprocal space. All measurements were made on a ≈ 200 mg single crystal mounted in a ^{3}He cryostat at BT-2, a triple-axis spectrometer located at the NIST research reactor. For the quasielastic measurements, the collimation was typically 60′-20′-*S*-20′, before and after the monochromator and between the sample and detector, respectively. The neutron wavelength $\lambda=2.4127$ Å was chosen to minimize multiple Bragg scattering; the remainder of the multiple Bragg scattering was removed by subtracting a background scan taken at $T=6$ K. No analyzer crystal was employed for these measurements. The crystal was initially mounted so that (h0*l*) reflections were in the scattering plane.

The widths of longitudinal scans about the (100) magnetic reflection are inversely related to the correlation length perpendicular to the planes, i.e., along the *a* axis. The evolution of these scans from well below T_N to just above T_N is shown in Fig. 1. At $T=2$ K, well below T_N, the Bragg peak was a resolution-limited Gaussian. The intensity of the resolution-limited Gaussian decreased as T increased, while the quasielastic scattering became observable. This quasielastic scattering increased in intensity and width as the temperature increased to T_N, which indicates that the length of the correlations between the planes is decreasing. Transverse scans, which show the correlations along the *c* axis, that is, perpendicular to the chains but within the planes, show similar behavior. Just above T_N, at $T=3.5$ K, the quasielastic scattering is gone. The fact that we have not been able to observe 2D Bragg "rods" in FeTAC, despite the other indications of 2D Ising behavior from measurements of the order parameter, the susceptibility, and C_{mag}, is a puzzle which requires further work.

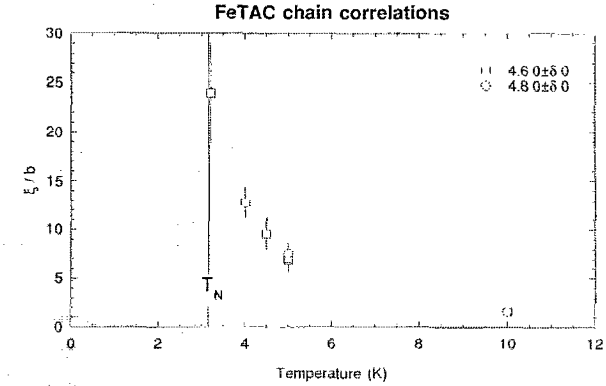

FIG. 2. Temperature dependence of the correlation length along the *b* axis above T_N, as determined by scans along b^* around (4.6 0 0) and (4.8 0 0). The 1 D short-range order increases from four chain sites at 10 K to ≈ 50 chain sites just above T_N at 3.2 K. Note that there are two Fe moments per unit cell along the *b* axis; thus, the correlation length in chains sites is twice that shown in the figure.

To examine the chain order, we changed the crystal orientation so that (*hk*0) reflections were in the scattering plane. In the ideal case of chain ordering, there are no correlations perpendicular to the chains and so the momentum transfer required for the Bragg condition is restricted only in the direction parallel to the chains. As a result, we observed planes of magnetic scattering normal to b^* (which is parallel to *b* in this orthorhombic system). The measured correlation lengths, which increased as T decreased from 10 K to T_N, are shown in Fig. 2. The location of the quasielastic scattering provides additional information about the character of the chain order. The intensity of this scattering is proportional to the component of the fluctuations that is perpendicular to the scattering vector **Q**. As the moments point along the *b* axis, the quasielastic scattering would be strongest for scattering vectors nearly pointing along b^* if the fluctuations were nearly isotropic. However, we could not observe quasielastic scattering around (0*k*0) points, whereas it was strong around (*h*00) points. This suggests that the spin fluctuations occur only along the moment direction and that the moments are very Ising-like.

Perhaps the greatest interest in linear ferromagnets involves the spin excitations of the chain. Since the exchange along the chain is ~ 17 K for FeTAC, whereas the interchain exchange is a factor of 10^3 smaller, we expect to

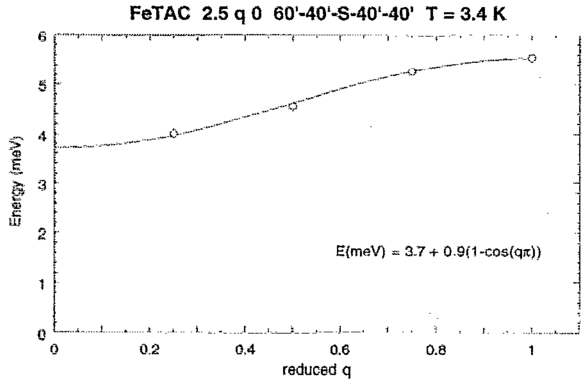

FIG. 3. Measured dispersion of the chain inelastic magnetic scattering at $T=3.4$ K. The solid line is a fit to a spin-energy gap and a 1D ferromagnetic dispersion curve as described by Eq. (1).

observe only the excitations along the ferromagnetic chains. We observed magnetic excitations along the chain with the crystal mounted in the $(hk0)$ scattering plane. The collimation was 60′-40′-S-40′-40′, where the final collimation is that between the analyzer and the detector. Figure 3 shows the measured dispersion relation along with a fit to the expected dispersion relation for a 1D ferromagnet spin wave,[10]

$$E(\text{meV})=3.7+0.9\left[1-\cos\left(q\frac{2\pi}{b}\frac{b}{2}\right)\right], \qquad (1)$$

where the $b/2$ term arises from the fact that there are two Fe moments along the chain in each structural unit cell. The measured spin-gap energy of 3.7 meV indicates, in agreement with the quasielastic intensity results, that there is a very strong anisotropy. Our survey measurements all point to the fact that FeTAC is indeed a very good 1D Ising ferromagnet and worthy of further study.

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