^{1}H NMR study of the layered antiferromagnet NH_4FeF_4

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Abstract. ¹H NMR studies of the polycrystalline NH_4FeF_4 system in the temperature range 110–300 K reveal an anomalous increase in the line-width as well as the spin–lattice relaxation rate, T_1^{-1} near the antiferromagnetic transition temperature 135 K. In the critical region, T_1^{-1} diverges as $\varepsilon^{-0.50}$, where $\varepsilon = (T - T_N)/T_N$. The exponent indicates pronounced 3D magnetic interaction near the transition point. However, the broad critical region (135 K < T < 160 K) observed from the temperature dependence of T_1^{-1} is an indication of the presence of 2D magnetic interaction.

1. Introduction

NH_4FeF_4 belongs to the orthorhombic space group Pnma [1] with $a = 7.559$ Å, $b = 7.575$ Å and $c = 12.754$ Å. The structure may be described essentially as a sequence of layers of $[FeF_6]^{3+}$ octahedra with the ammonium ions in between. The ammonium ions are linked with the $[FeF_6]^{3+}$ octahedra by strong N–H—F hydrogen bonds. The two-dimensional (2D) magnetic properties are manifested in the susceptibility data of poly-crystalline NH_4FeF_4 [2]. At about 200 K, the χ^{-1} versus T curve shows a flat minimum typical of a 2D magnetic system. A calculation [2] of the exchange integral using the high temperature series expansion technique leads to $J/k = -26$ K. Neutron scattering data are not available for this compound. However, 2D magnetic behaviour is expected because of the similarity between NH_4FeF_4 and $RbFeF_4$ for which neutron scattering studies have shown a pronounced 2D behaviour [3]. The Néel temperature, T_N (135 K) was determined from Mössbauer studies of the variation of the hyperfine field with temperature [2]. However, the critical exponent, β, estimated from these measurements in the antiferromagnetic state was found to be 0.26 which is closer to those found for 3D magnetic systems than that obtained from the theoretical calculation using the 2D Ising model. This suggests the presence of simultaneous two- and three-dimensional magnetic correlations above T_N in NH_4FeF_4. Thus, it appears that the nature of the magnetic interactions of Fe^{3+} ions in NH_4FeF_4 even in the paramagnetic phase is not well understood. It may be pointed out that ¹⁹F NMR investigation [4] of the isomorphous $CsFeF_4$ system reveals the presence of simultaneous two- and three-dimensional magnetic correlations above T_N.

So far, experimental information regarding the static critical behaviour of this compound near T_N has been obtained. These parameters can be related to the equal-time or instantaneous spin correlation function. On the other hand, measurements of the

dynamic parameters provide information about the time dependent correlation function. Nuclear spin–lattice relaxation time, T_1, measurement is particularly suitable for investigating the long time behaviour of the correlation function which is important in the process of slowing down of the fluctuations occurring around the transition point. In the case of non-magnetic solids, coupling of nuclear spins with lattice vibrations provides the main source of relaxation rate and it proceeds at a very slow rate at low temperatures. The additional hyperfine interaction in a magnetic material can produce a relaxation rate that is orders of magnitude larger than that caused by lattice vibration. Hence, the ^{1}H spin–lattice relaxation time T_1, may be directly related to the spin dynamics of the electronic spins.

2. Experimental details

NH_4FeF_4 was obtained by co-precipitation from an equimolecular solution of the constituents, i.e. NH_4F and FeF_3 in hydrofluoric acid. Ferric fluoride was prepared by dissolving pure (99.9%) iron powder in 48% hydrofluoric acid with subsequent oxidation of the product via hydrogen peroxide in a strong acid medium. NH_4FeF_4 crystals thus obtained were washed with alcohol, then dried and heated at 300 °C in an argon atmosphere and subsequently sealed for NMR studies. The compound was characterised by room temperature x-ray powder diffraction and magnetic susceptibility measurement in the temperature range 110–300 K.

^{1}H continuous-wave (CW) NMR measurements were performed in a Varion WL210 spectrometer with a V7400 electromagnet. The temperature variation study was performed with a V4540 temperature controller. The instrument used for pulsed NMR measurements was a Bruker MSL100 spectrometer combined with the same field regulated electromagnet. The ^{1}H resonance spectra were obtained by Fourier transform (FT) of the free induction decay (FID) signal observed after an $\approx 90°$ pulse. The ^{1}H spin–lattice relaxation time T_1, was measured in the temperature range 120–297 K and frequency range 16–43 MHz using the inversion-recovery ($180°–\tau–90°$) and/or saturation-recovery ($n \times 90°–\tau–90°$) technique, where n is the number of 90° pulses. In the case of broad lines, a solid echo sequence ($90°–\tau–90°$) was used as the monitoring pulse and thus the complete pulse sequence for the inversion-recovery was $180°–\tau–90°–\tau_1–90°–\tau_2–$echo. The change in magnetisation with the delay time τ was obtained from the peak values of the amplitude of the Fourier transformed signals taken at different values of τ and was found to be exponential with a time constant T_1. During measurements of T_1, the temperature of the sample was controlled within ± 1 °C of the set temperature by using a Bruker BVT 1000 temperature controller. The temperature was measured with a Cu–constantan thermocouple kept close to the sample.

3. Results and discussion

3.1. Behaviour of line-width with temperature

Variation of ^{1}H NMR line-width, δH (peak to peak separation of the absorption derivative), of the polycrystalline NH_4FeF_4 system in the temperature range 110–300 K at the
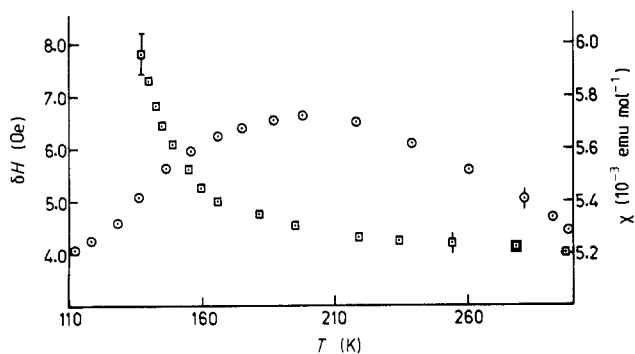
Figure 1. Plot of the ^{1}H NMR line-width, δH (peak to peak separation of the absorption derivative), measured at the resonance frequency 15.0 MHz (□) and the magnetic susceptibility, χ (○) of the NH_4FeF_4 system as a function of temperature, T.
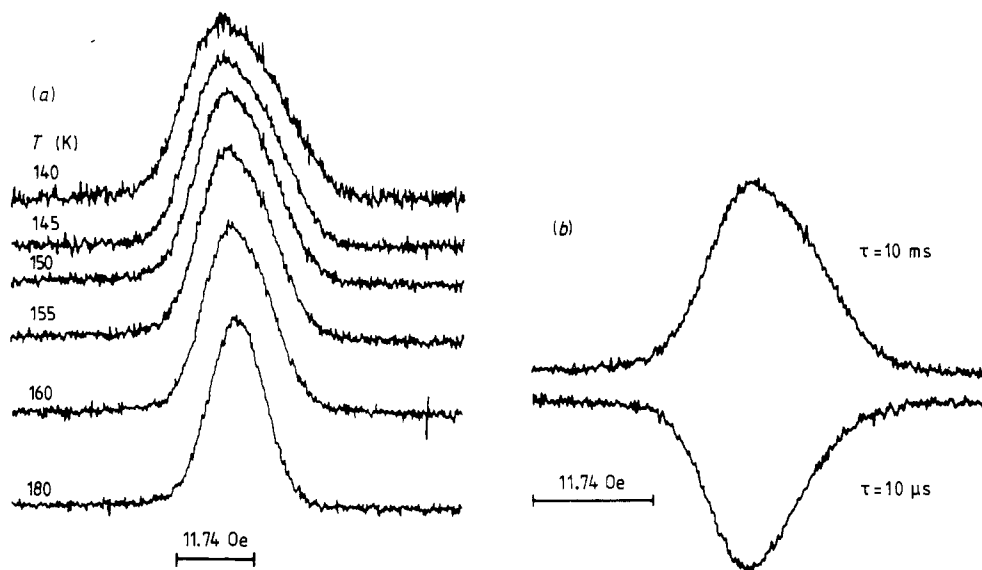

Figure 2. ^{1}H FT NMR spectra of NH_4FeF_4 at the resonance frequency 33.5 MHz: (a) variation of line-shape in the temperature range 140–180 K; and (b) spectra at 155 K corresponding to two extreme delay times, τ, used in the inversion-recovery ($180°–\tau–90°$) pulse sequence.

resonance frequency of 15 MHz is shown in figure 1. On lowering the temperature, δH is found to increase very slowly up to 170 K. However, below this temperature, δH is found to increase sharply. Figure 2 shows some typical ^{1}H FT NMR spectra in the range 140–180 K. Near $T_N = 135 \pm 1$ K, the s/N ratio falls drastically and thus inhibits the measurement of the line-width. As is evident from figure 2(a), the ^{1}H NMR spectra are asymmetrically broadened as is usually found in the case of a polycrystalline specimen. Thus, we could not derive anything quantitatively from the line-width. Nevertheless, we shall consider the various contributions to the line-width in a qualitative fashion.

The shape and width of the ^1H resonance absorption lines in the single crystal of this class of compound will be governed by two different contributions. The nuclear dipolar interaction between the ^1H nuclear spins and also between ^1H and ^{19}F nuclear spins gives rise to a line-width with a Gaussian line-shape. This part is always field independent and normally temperature independent, except in cases where the nuclei belong to atoms/ ions that undergo some kind of rapid (with respect to NMR frequency) motion in solids. In the isomorphous compound NH_4AlF_4, NH_4^+ ions undergo fast reorientational motion at room temperature as observed from ^1H NMR line-width measurements [5]. In the present case, the NH_4^+ ions in NH_4FeF_4 may be supposed to reorient at room temperature and, as such, the contribution to the line-width may be temperature dependent.

The most important contribution to the line-width is due to the interaction of the ^1H nuclear spin with the unpaired iron (Fe^{3+}) electron spin. However, the resulting line-widths for both effects are of the same order of magnitude because the proton–iron line-width is strongly narrowed by the very fast fluctuation frequency of the exchange-coupled iron spins (of the order of J/h at $T \gg T_N$). A temperature dependent line-width generally corresponds to a decrease of this exchange fluctuation frequency (increasing degree of short range order).

In a polycrystalline specimen an inhomogeneous distribution of the homogeneous line-width which arises due to the two contributions mentioned above is obtained due to the interaction *IAS*. The hyperfine coupling tensor **A** includes both non-classical contact and dipolar interactions. For protons, the contact part is negligible compared with the dipolar contribution, of which only the anisotropic part is to be considered. Thus, the strength of this anisotropic interaction in comparison with the homogeneous line-width determines the line-shape of the powder pattern. In the present case, the line-width of the powder pattern should be a complex function of homogeneous line-width and the degree of anisotropy. Furthermore, the spread of the line due to anisotropic interaction is proportional to the average static component of the magnetic moment, μ, and thus in a normal paramagnetic system, the line (for the powder system) follows the magnetic susceptibility directly.

Thus, in order to compare the behaviour of ^1H line-width with that of the magnetic susceptibility, we have measured the susceptibility of NH_4FeF_4 in the same temperature range and the results are shown in figure 1. The susceptibility, x shows a broad maximum around 200 K which corroborates the results of Menil *et al* [2]. It may be seen that from around 170 K, where the ^1H NMR line-width increases sharply with the lowering of temperature, the susceptibility starts to decrease slowly. Therefore, the anomalous increase in the line-width could not be related to the behaviour of the magnetic susceptibility of NH_4FeF_4. So, the significant increase in the line-width in the temperature range 135 K $< T <$ 170 K could be associated either with the process of slowing down of the exchange fluctuation frequency or the effect of slowing down of reorientational motion of NH_4^+ ions with the lowering of temperature. The latter effect is manifested in the case of NH_4AlF_4 through the marginal increment of the ^1H line-width from 6.0 Oe to 7.3 Oe when the temperature is lowered to 77 K from 297 K [5]. Thus, the behaviour of the line-width in the NH_4FeF_4 system could be related to the dynamics of the Fe^{3+} electronic spin fluctuation.

3.2. Temperature dependence of the spin–lattice relaxation time

Figure 3 shows the temperature dependence (120–300 K) of the ^1H spin–lattice relaxation time, T_1, at different resonance frequencies for the polycrystalline NH_4FeF_4
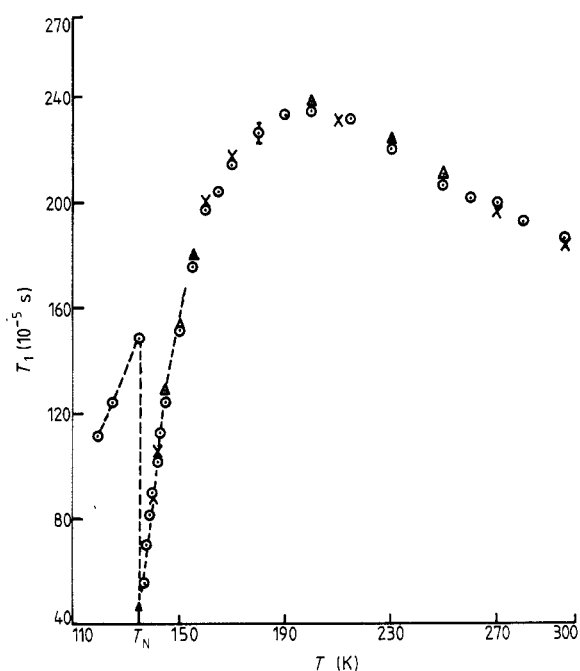
Figure 3. Plot of the ¹H spin–lattice relaxation time, T_1, against temperature at different resonance frequencies: (×) 16.0 MHz; (○) 33.5 MHz; and (▣) 43.0 MHz. The broken curve is drawn as a visual aid.

system. Starting at 300 K, as we cool the sample, T_1 increases linearly with temperature down to around 210 K. In the range 190–210 K, the value of T_1 does not change significantly. Below 190 K, it starts to decrease slowly. A broad peak can be seen at around 200 K, where the maximum in the χ versus T curve (figure 1) was observed. Interestingly, below 170 K, the rate of decrease of T_1 with the lowering of temperature increases sharply. At around T_N (135 ± 1 K), T_1 increases drastically. It may be pointed out that in the region 135 K < T < 170 K, although the resonance line is considerably broadened, there was no problem in inverting the magnetisation by applying a 180° pulse of width 2.75 μs. The intensity of the FT spectra corresponding to the longest τ (time delay) and that for the shortest τ are found to be almost the same as shown in figure 2(b). Thus, the sharp fall in T_1 below 170 K could not be due to some experimental artifact. Below T_N, where the S/N ratio is too poor, the measurement of T_1 has been performed by accumulating the FID of ¹H resonance by repeating the acquisition more than two hundred times for each value of τ. It is observed that in the antiferromagnetic phase, T_1 decreases almost linearly with temperature. The measurements could not be performed below 120 K due to instrumental limitations.

In this system, the relaxation rate at any temperature is given by

$$T_1^{-1} = T_{1d}^{-1} + T_{1hf}^{-1}$$

where T_{1d}^{-1} represents the contribution due to the modulation of the dipolar interaction between ¹H nuclear spins as well as ¹H and ¹⁹F nuclear spins as a result of the motion of NH_4^+ ions. T_{1hf}^{-1} contains the contribution from the fluctuating part of the dipolar field originating from Fe^{3+} electron spins.
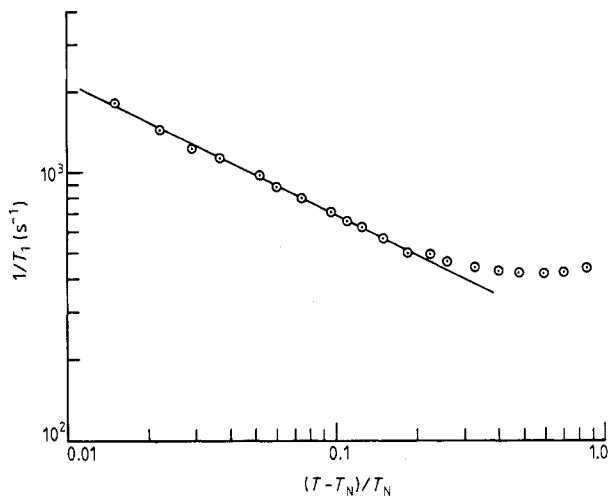
Figure 4. The critical behaviour of the ^1H spin–lattice relaxation time, T_1, as a function of reduced temperature $(T - T_N)/T_N$.

The variation of T_{1d}^{-1} with temperature in the NH_4FeF_4 system should be close to that obtained for the NH_4AlF_4 system, where T_{1d}^{-1} is the only contribution to the spin–lattice relaxation rate, T_1^{-1} [5]. In the latter case, the slowing down effect of the NH_4^+ ion reorientational motion (with decrease in temperature) is manifested in the variation of T_1 which, starting at 0.6 s at 297 K, decreases continuously and attains the value of 0.04 s at 147 K and then increases continuously again. In contrast, the maximum value of T_1 found in the case of NH_4FeF_4 is 2.45 ms.

Thus, the observed behaviour of T_1 in NH_4FeF_4 over the whole temperature range could not be related to the effect of the slowing down of the NH_4^+ ion motion with temperature—rather it may be associated with the characteristic of the electron spin dynamics in this 2D antiferromagnet as T_{1hf}^{-1} is the dominant contribution to the relaxation rate of protons in NH_4FeF_4. The anomalous increase of T_1^{-1} and the line-width close to T_N could therefore be related to the effect of slowing down of a certain part of the electron spin fluctuation as suggested by Moriya [6] for Heisenberg paramagnets with localised moments.

From figure 3 it may be seen that T_1 in NH_4FeF_4 is almost independent of the resonance frequency over the whole temperature range. Even very close to the transition temperature no frequency dependence of T_1 is observed. This indicates that the decay rate of the fluctuation is much greater than the resonance frequency, ω_0 and exchange frequency ω_e.

Figure 4 shows the critical behaviour of T_1^{-1}—both T_1^{-1} and the reduced temperature, $\varepsilon = (T - T_N)/T_N$, being plotted on a logarithmic scale. The result is reasonably well described by a straight line in the temperature range 135 K < T < 160 K. The slope of the line gives the exponent of $(T - T_N)/T_N$. Surprisingly the exponent, 0.50, is very close to the value predicted by Moriya for the critical behaviour of a 3D cubic antiferromagnet [6]. However, it may be pointed out that in a 3D magnetic system, the anomalous increase of the relaxation rate takes place in a very narrow temperature range. For an antiferromagnet with $T_N \simeq 100$ K, the anomalous increase in the relaxation rate is generally expected to be seen at $T - T_N \simeq 1$ K [6]. Close to the transition temperature,

where the fluctuation for $q = q_c$ dominates (q_c being the critical wave vector) T_1 is related via [7]

$$1/T_1 \propto \varepsilon^{-\gamma + \nu(d-z)}$$

where d denotes the lattice dimensionality, $\gamma = 2 - \eta$ and ν are the static exponents introduced by Fisher [8], and z is the dynamic exponent. Again, it has been shown [9] that near the critical point the characteristic broadening of the Mössbauer line due to the critical spin fluctuation diverges as $\varepsilon^{-\omega}$ where $\omega = \gamma - \nu(d - z)$. A detailed Mössbauer measurement for $RbFeF_4$ and $KFeF_4$ systems [10] reveals the feature of characteristic broadening near T_N in both cases. The exponent, ω was found to take the values 0.81 and 0.91 respectively. Thus ^1H spin–lattice relaxation measurements for NH_4FeF_4 and Mössbauer studies [10] for $RbFeF_4$ and $KFeF_4$ systems reveal that the values of the exponent, ω, are close to the 3D antiferromagnetic system as predicted by theory [11]. However, this conclusion is to be judged taking into consideration the fact that the NMR measurement has been made for a polycrystalline specimen.

4. Conclusion

^1H NMR studies of the polycrystalline NH_4FeF_4 system indicate the effect of Fe^{3+} electron spin fluctuation on the line-width and spin–lattice relaxation time near the transition region. The enhancement of the line-width and the relaxation rate near T_N is very similar to what is found for 3D magnetic system. However, the broad critical region (135 K $< T <$ 160 K) observed in the temperature dependence of the relaxation rate is an indication of the presence of 2D magnetic interactions.

References

[1] Leblanc M, Ferry G and De Pape R 1985 *Acta. Crystallogr.* C **41** 657
[2] Menil F, Tressaud A, Sabatier R and Le Flem G 1977 *Mater. Res. Bull.* **12** 983
[3] Eibschutz M, Davidson G R, Guggenheim H J and Cox D E 1971 *AIP Conf. Proc.* **5** 670
[4] Ghoshray K, Ghoshray A and Chatterjee N 1988 *J. Phys. C: Solid State Phys.* **21** 2247
[5] Mackowiak M and Brown R J C 1984 *Mater. Res. Bull.* **19** 249
[6] Moriya T 1962 *Prog. Theor. Phys.* **28** 371
[7] Borsa F and Rigamonti A 1979 *Magnetic Resonance of Phase Transitions* ed. F J Owen, C P Poole Jr and H A Farach (New York: Academic) p 79
[8] Fisher M E 1967 *Rep. Prog. Phys.* **30** 615
[9] Hohenemser C, Chow L and Suler R M 1982 *Phys. Rev.* B **26** 5056
[10] Keller H and Savic I M 1983 *Phys. Rev.* B **28** 2638
[11] Hohenberg P C and Halperin B I 1977 *Rev. Mod. Phys.* **49** 435 and references therein