^{19}F NMR studies in KMnFeF$_6$ systems

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Abstract: ^{19}F NMR spectra of polycrystalline KMnFeF$_6$ at 294 K reveal two types of fluorine sites, viz. F$_I$ and F$_{II}$ (with respect to magnetic hyperfine interaction and the intrinsic line width). The appreciable decreament of K$_{iso}$ for F$_I$ and the increament for F$_{II}$ below $\sim$ 200 K, results from the possible occupancy of fluorine sites within the typical magnetic environment as predicted from neutron diffraction study. The disappearance of both the lines near 148 K corresponds to the ferrimagnetic ordering reported from susceptibility data.

1. Introduction

The fluoride KMnFeF$_6$ exhibits usual tetragonal tungsten bronze type super structure with $a = 12.765$ Å; $c = 8.002$ Å [1] and the space group is P4$_2$bc. The structure may be described essentially as a sequence of layers of corner sharing [FeF$_6$]$^{3-}$ and [MnF$_6$]$^{4-}$ octahedra [Fig. 1]. The high field dc susceptibility data [2] showed that the system exhibits a ferrimagnetic ordering at 148 K with a large value of negative Curie constant (θ), indicating the strong antiferromagnetic exchange interactions. From neutron diffraction studies in KMnFeF$_6$, Lacorre *et al.* [3] showed that the spins belonging to the triangular platelets adopt a star arrangement close to 120° configuration whereas, in square platelets they are exactly antiparallel. They pointed out that the canted spin configuration is due to the competition between antiferromagnetic superexchange interactions in the triangular cycles in contrast to the spins connected by unfrustrated interactions in the square platelets order antiferromagnetically. Our recent low field ac susceptibility and dc magnetisation data

in this compound [4], reveal a ferrimagnetic transition at T_N (onset) $\sim$ 148 K followed by a low temperature spin-glass like transition at 108 K with no evidence of long range magnetic order in the ferrimagnetic region.
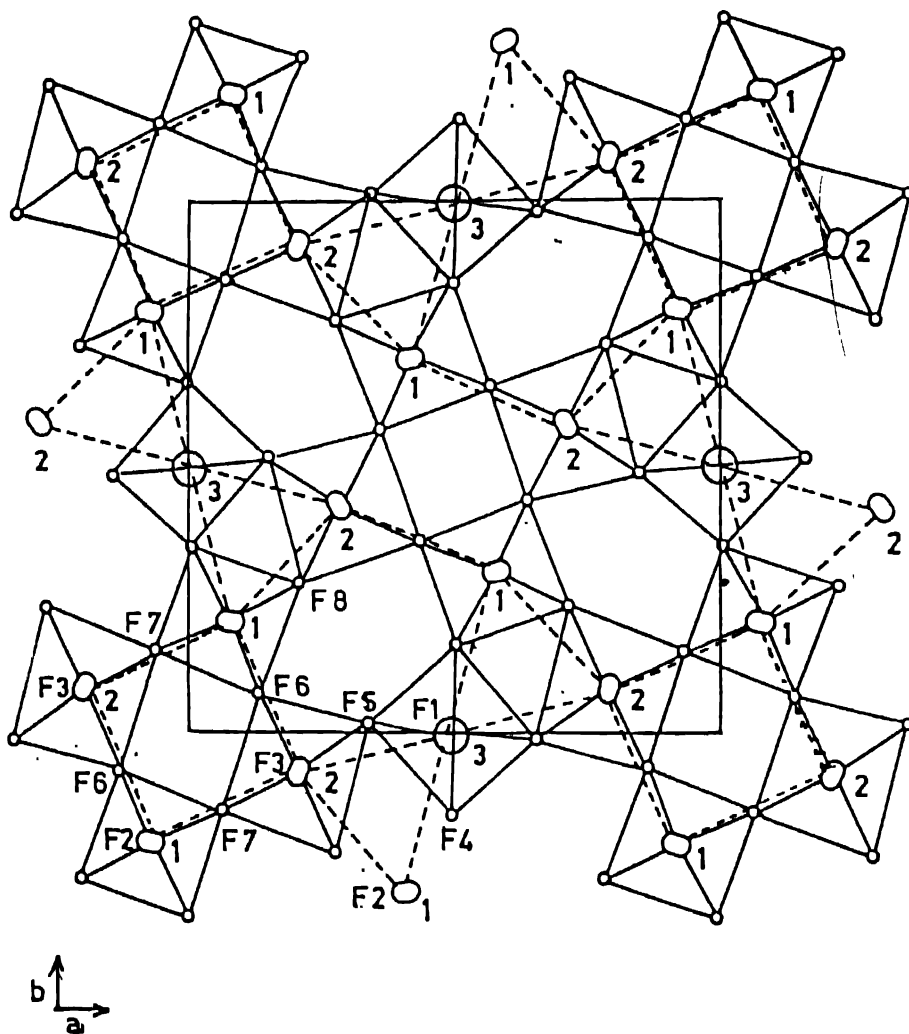

Fig. 1. Ionic ordering in $KMnFeF_6$ system in the a-b plane. M(1), M(2) and M(3) are occupied by Mn^{2+}, Fe^{3+} and Mn^{2+}/Fe^{3+} statistically. The positions of crystallographically eight types of fluorines viz. F1 to F8 are shown.

Since in this type of compound the flourine ions are covalently bonded with the Fe^{3+}/Mn^{2+} ions, the fluorine nuclear spin would experience a strong local magnetic field via transferred hyperfine interaction with the magnetic moments

of Fe^{3+} and Mn^{2+} ions. It is expected that ^{19}F NMR study on $KMnFeF_6$ would be a very sensitive probe for studying the effect of temperature variation of the local magnetic field at different fluorine sites.

2.. Theory

On the assumption that the hyperfine and dipolar tensors are coincident, the resonance position in a single crystal for measurements made at a constant resonance frequency ν is given by [5]

$$H = H_R \pm \alpha(3cos^2\theta - 1) \qquad (1)$$

Where $H_R = (1 + K_{iso})H_S$ and $\alpha = K_{ax}H_S$; θ is the angle between the magnetic field and the symmetry axis of crystal. H_S is the field position corresponding to the ^{19}F NMR line in diamagnetic analogue. K_{iso} and K_{ax} are the isotropic and axial components of the shift tensor. The dipolar field yields no contribution to the isotropic shift, but the anisotropic part is sufficient in many cases. The projection of the dipolar field along the external field H_o may be written as

$$H_d = \sum_j \frac{3cos^2\theta_j - 1}{r^3_{ij}} < \mu_j > \qquad (2)$$

The geometrical factor can be evaluated by lattice summation and $< \mu_j > = \chi H_o/N$. where χ is the molar susceptibility. In a polycrystalline sample the shape of the resonance line will be [5]

$$f(H') = \int_{H_R-2\alpha}^{H_R+\alpha} p(\Delta H)exp[-\frac{(H' - H)^2}{2\beta^2}]dH \qquad (3)$$

where β^2 is the second moment of the component Gaussian and

$$p(H - H_R) \propto (-(H - H_R)/\alpha + 1)^{-1/2}, -2\alpha < (H - H_R) \leq \alpha \qquad (4)$$

The intrinsic line width can be written as $\delta H = 2\beta$ [$\delta H \sim T_2''^{-1}$]. As it is well understood that the shape and width of the fluorine resonance absorption line in single crystal of this type of compounds consists of two contributions 1) due to interaction between ^{19}F nuclear spins and Mn^{2+}/Fe^{3+} electron spins [$T_2'^{-1}(T)$] and 2) due to interaction between ^{19}F nuclear spins and ^{19}F nuclear

spin with other unlike nuclear spins $[T_2^{-1}]$. Therefore, the total line width $[T_2''^{-1}]$ in a single crystal is given by

$$T_2''^{-1} = T_2^{-1} + T_2'^{-1}(T) \tag{5}$$

The line width for the iron-fluorine interaction follows from an expression for $1/T_2'^{-1}(T)$ given by [6]

$$T_2'^{-1}(T) = \sqrt{\pi/2}[nS(S+1)]/[6\hbar^2\omega(T)]\sum(1+\cos^2\theta_i)A_i^2 \tag{6}$$

$\omega(T)$, in the high temperature limit, is the exchange frequency $\omega_e = \omega(\infty)$, n is the number of nearest neighbour magnetic ions. The summation is over the three principal axes of the hyperfine interaction tensor. θ_i is the angle between the ith axis and the direction of the external magnetic field. The orientation dependent part is averaged out in a polycrystalline sample.

3. Results and discussions

^{19}F NMR studies of polycrystalline $KMnFeF_6$ have been performed in the temperature range 100 - 294 K and in the frequency range 7 - 15 MHz. The composite spectrum of two superimposed lines at 294 K [Fig. 2] is observed which is shifted to the low field side with respect to the ^{19}F NMR line in
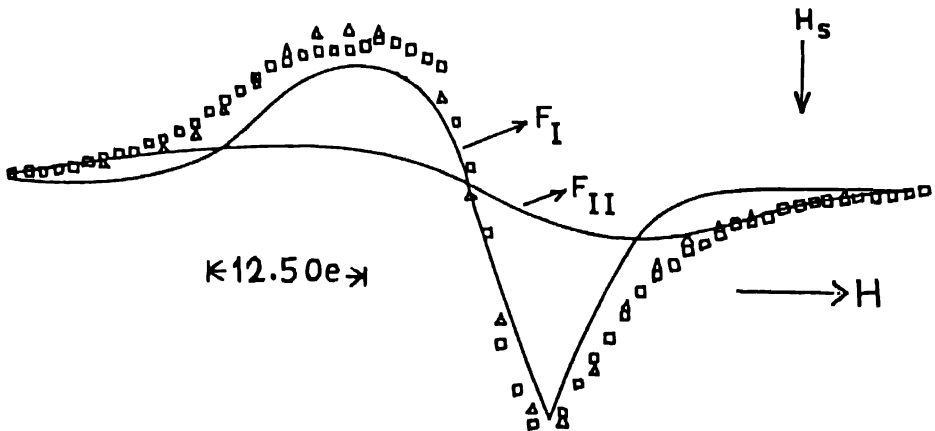

Fig. 2. ^{19}F NMR spectra ($\square$) of polycrystalline $KMnFeF_6$ at 294 K; at 7 MHz and theoretically fitted spectra ($\triangle$). The continuous lines are F_I and F_{II} lines from theoretical fitting.

NH$_4$F solution (H$_s$). In order to extract the shift parameters and the intrinsic line width from this line, we have fitted this with the derivative of f(H′) [eq. 3]. The fitted spectra reveals the existence of two types of fluorine sites, viz. F$_I$ and F$_{II}$ [Fig. 2]. The shift parameters (K$_{iso}$ and K$_{ax}$) and intrinsic line width (δH) for different fluorine sites are shown in table 1. Further, It is well understood from the available crystal structure data [1] that there are

Table 1: Shift parameters and intrinsic line width of ^{19}F NMR in KMnFeF$_6$ at 294 K

Fluorine	Magnetic neighbour	Groups of fluorine	T_2^{-1} Oe	δH Oe	K_{ax} %	K_{iso} %	Field direction	$\Delta H_d/H_R$ %
F(1)	M(3)/M(3)						H$_o$ ⊥ c	-.494
								-.493
							H$_o$ ∥ c	.987
F(4)	M(1)/M(3)						H$_o$ ⊥ c	-.246
		F$_I$	7.94	20.25	0.48	1.56		-.563
							H$_o$ ∥ c	.809
F(5)	M(2)/M(3)						H$_o$ ∥ c	.934
							H$_o$ ⊥ c	-.34
								-.6
F(2)	M(1)/M(2)						H$_o$ ⊥ c	-.539
								-.453
							H$_o$ ∥	.992
F(3)	M(1)/M(2)						H$_o$ ⊥ c	-.534
								-.448
							H$_o$ ∥ c	.983
F(6)	M(1)/M(2)	F$_{II}$	5.9	9.75	0.31	1.53	H$_o$ ⊥ c	-.227
								-.546
							H$_o$ ∥ c	.772
F(7)	M(1)/M(2)						H$_o$ ∥ c	.773
							H$_o$ ⊥ c	-.217
								-.556
F(8)	M(1)/M(2)						H$_o$ ∥ c	.213
								.336
							H$_o$ ⊥ c	-.549

eight types of fluorine sites in the unit cell. A comparison of the NMR results with the x-ray data therefore indicates that the eight types of fluorines in the unit cell are divided into two groups according to the magnetic environment. The nearest neighbour magnetic environment of these eight types of fluorines are shown in table 1 which is also focussed in Fig. 1. The calculated nuclear-nuclear dipolar contribution to the intrinsic line width are listed in table 1. The

calculated values show that there are two groups of fluorine atoms, supporting the results of theoretical fitting. The dipolar contribution to the total shift is computed from eq. 2, using susceptibility data [4] for the cases when the F-Fe^{3+}/Mn^{2+} bond is parallel to the magnetic field and when it is perpendicular to the magnetic field. It is observed [table 1] that the dipolar contribution to the total shift are axial for F(1), F(2), F(3) fluorine sites and values for F(4), F(5), F(6), F(7), F(8) fluorine sites depart from axial symmetry.

As the temperature lowers, it is interestingly observed that the value of K_{iso} remains unaltered for F_{II} upto ~ 200 K, but starts to increase appreciably below this temperature, whereas the value of K_{iso} for F_I decreases slowly upto ~ 200 K and then decreases considerably below this temperature [inset of Fig. 3], though the value of bulk susceptibility starts to increase appreciably below
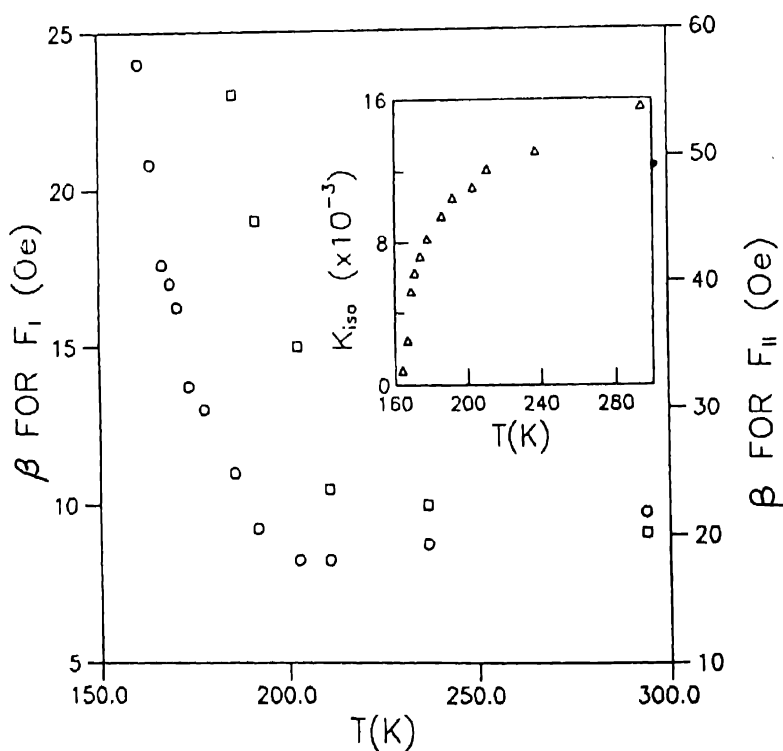
Fig. 3. Plots of temperature variation of line widths of F_I (o) and F_{II} (□) in the range 160-294 K at 7 MHz. The inset shows the temperature dependence of K_{iso} (Δ) of F_I.

~ 200 K. The decrease in K_{iso} for F_I line may be due to the fact that the nearest neighbour spins on both sides are exactly antiparallel in such a way that the nearest neighbour time averaged local moments cancell each other as the system approaches ferrimagnetic ordering temperature. But in case of F_{II}, the nearest neighbouring spins on both sides exhibit canted spin arrangements such that the time averaged local moment begin to increase below 200 K, resulting in an increament of K_{iso} value below this temperature. A comparison of this result with those predicted from neutron diffraction reveal that the F_I fluorines are occupied within the square platelets where nearest neighbour spin configurations are exactly antiparallel and the F_{II} fluorines are occupied within the triangular platelets where the nearest neighbour spin arrangements exhibit canted spin configuration. Our ^{19}F NMR results therefore support the magnetic structure predicted by Lacorre *et al.*. Focussing on the temperature variation of line width [Fig. 3], it is observed that the temperature variation of intrinsic line width are very slow upto ~ 200 K and then increases sharply below this temperature for both the F_I and F_{II} lines. The large enhancement of β below 200 K indicates the effect of critical slowing down of electron spin fluctuations on the line width. Detailed analysis of these results are in progress.

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