PHYSICAL REVIEW B VOLUME 42, NUMBER 13 1 NOVEMBER 1990

^{19}F NMR studies in ABF$_4$-type layered antiferromagnets

K. Ghoshray, A. Ghoshray, and N. Chatterjee
Saha Institute of Nuclear Physics, 92, Acharya Prafulla Chandra Road, Calcutta 700 009, India

(Received 26 January 1990)

^{19}F NMR studies of polycrystalline NH_4FeF_4, $RbFeF_4$, and $KFeF_4$ in the paramagnetic phase reveal the existence of two distinct types of fluorine sites. From the line-shift measurements together with the available magnetic susceptibility data, the value for the transferred hyperfine coupling between the fluorine nuclear spin and the neighboring iron electron spin has been derived. The values of the hyperfine tensor components indicate the almost isotropic nature of the Fe—F bond in the three compounds. Furthermore, the hyperfine fields at both types of fluorine sites are found to be almost temperature independent in the paramagnetic phase, which is in agreement with the susceptibility behavior of these compounds. Thus apparently no difference is reflected in the behavior of the time-averaged local properties as a function of temperature among the three compounds. However, an essentially different behavior of the linewidth with temperature of the fluorine atoms [(F(1)] bonded with one iron neighbor and fluorine atoms [F(2)] bonded with two iron neighbors is observed. In all the compounds the resonance lines for both types of fluorines are broadened anomalously below certain temperatures and finally both the lines disappear at T_N. Although the transition temperatures (T_N) of the three compounds are very close among themselves (T_N lie in the range 133.5–136 K), the anomalous line broadening appears in widely different temperature regions. These results are compared with those reported earlier for $CsFeF_4$. Moreover, an attempt has been made to correlate the temperature-dependent linewidth of the F(1) line with the effect of a critical slowing down of the fluctuations of the electronic spins of the Fe^{3+} ion with a lowering of the temperature. The temperature-dependent linewidth $\delta H_1(T)$ is found to fit well with the relation $\delta H_1(T) \propto \epsilon^{-w}$ in the critical regions, where $\epsilon=(T-T_N)/T_N$ is the reduced temperature. The exponent w involves, besides two static exponents γ and ν, the dynamic exponent z and is related by $w=-\gamma+\nu(d-z)$. A comparison of the values of w with that predicted by the current theory of critical dynamics indicates that the magnetic interactions in NH_4FeF_4, $RbFeF_4$, and $CsFeF_4$ are three dimensional in nature, whereas in $KFeF_4$ the two-dimensional (2D) interactions are predominant. Nevertheless, the presence of a broad critical region even in each of the first three systems as observed from the linewidth data indicates that the 2D interactions are still present there.

I. INTRODUCTION

The magnetic properties of a system of paramagnetic ions coupled in a linear chain ($1d$) or within a plane ($2d$), d being the effective lattice dimensionality, have been studied[1] both theoretically and experimentally over the past few years due to great simplifications which one obtains with respect to the three-dimensional (3D) systems. The topological restrictions alter dramatically the spin dynamics. In these systems, even at higher temperatures, i.e., comparable to the exchange interaction within the plane ($2d$) or in the chain ($1d$), short-range order tends to develop and one can observe phenomena associated to fluctuation of the local order over a relatively large temperature range.

Recently, we have studied using nuclear magnetic resonance (NMR) the paramagnetic phase of some members of the ABF$_4$ series of compounds, where A=NH_4, Rb, K, and Cs and B=Fe, V, etc. These compounds are isomorphous with $TlAlF_4$,[2] and are known to be layered antiferromagnets.[3-5] In particular, ^{19}F cw NMR studies[6] in $CsFeF_4$ and ^{1}H-pulsed NMR studies[6] in NH_4FeF_4 provide much useful information regarding the spin dynamics. In the present paper we shall report the detailed results of ^{19}F cw NMR studies (temperature range 100–300 K) of polycrystalline $KFeF_4$, $RbFeF_4$, and NH_4FeF_4 systems (with antiferromagnetic transition temperatures T_N of 136, 133.5, and 135 K, respectively);[3-5] particular emphasis will be placed on the differences of the spin correlations among the various members including $CsFeF_4$ of this isomorphous series.

In these compounds, the fluorine ions being covalently bonded with the Fe^3 ions, the fluorine nuclear spin would then experience a strong local magnetic field via transferred hyperfine interaction $\mathbf{I}\cdot\mathsf{A}\cdot\mathbf{S}$ with the magnetic moments of the Fe^{3+} ions, where A is the hyperfine coupling tensor and $\mathbf{I}$ and $\mathbf{S}$ are the nuclear and electronic, spin respectively. Moreover, the crystal structure of this system offers the opportunity of probing the effect of magnetic fluctuation at two types of fluorine sites: axial fluorine atoms F(1) having one magnetic ion neighbor with the Fe—F(1) bond directed along the c axis (the transferred hyperfine interaction will then be written as $H_{IS}=\mathbf{S}\cdot\mathsf{A}_I\cdot\mathbf{I}$) and planar fluorine atoms F(2) having two equidistant magnetic ion neighbors within the magnetic planes $[H_{IS}=(\mathbf{S}_1+\mathbf{S}_2)\cdot\mathsf{A}_{II}\cdot\mathbf{I}]$. Thus the two classes of nuclear spins should give rise to two distinct resonance lines. Interestingly in the present case the resonance lines for the two types of fluorine atoms even in the polycrystalline samples are well resolved and thus one can obtain reasonably accurate hyperfine interaction parameters using usual powder pattern analysis.

Method of sample preparation and the experimental arrangement have been described earlier.[6] For the sake of clarity and self-explanation, we shall mention only that the shifts have been measured with respect to the reference field, H_R corresponding to the ^{19}F NMR line in NH_4F solution.

II. EXPERIMENTAL RESULTS

A. Behavior of the shift parameters

At room temperature in all the three compounds, two distinct resonance lines appear (similar to that of $CsFeF_4$)[6], which are shifted to the low-field side with respect to the position of H_R (Fig. 1). As discussed in Ref. 6, the line that suffers the smaller shift is attributable to the axial fluorine atoms F(1) having one magnetic ion neighbor with the Fe—F bond directed along the c axis. As in these compounds the lattice parameters a and b are almost equal; the symmetry of the F(1) site may be fully axial. However, the almost symmetric nature of the line reveals that the anisotropic shift $K_{\text{ax}} < 2\beta$, the intrinsic width. Thus the shift ΔH from H_R has been measured from the zero crossing of the derivative of the absorption spectrum. The values of ΔH are found to be linear with H_R. This supports the assumption that the anisotropic magnetic interaction is negligible for this site. Nevertheless, the dipolar contribution to the total shift has been computed using the magnetic susceptibility data, for the cases when the Fe-F(1) bond is parallel to the magnetic field and when it is perpendicular to the magnetic field. It has been found that consideration of up to 20 nearest iron lattice sites is sufficient for the calculation of the dipole sum. Although the values (Table I) correspond to axial symmetry ($\Delta H_{d\parallel} = -2\Delta H_{d\perp}$), the anisotropy is not large enough to be discernible in the powder pattern of the F(1) line. Thus, only the isotropic component A_s of the hyperfine coupling tensor has been obtained from the value of isotropic shift K_{iso} and is given in Table I.

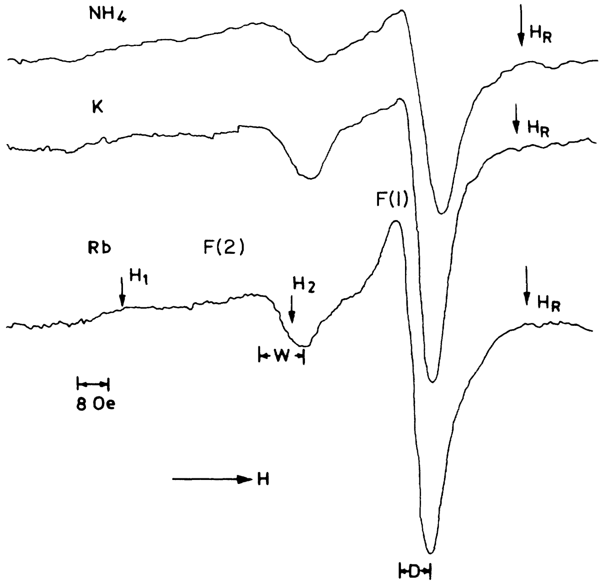

FIG. 1. ^{19}F NMR spectra (using 12 scans) of polycrystalline NH_4FeF_4, $RbFeF_4$, and $KFeF_4$ at $T = 297$ K and $\nu_R = 15$ MHz, showing the various features as mentioned in the text.

The highly asymmetric line (Fig. 1), which has a step (H_1) at the down-field side with the intensity maximum at H_2 and appearing at a lower field than the F(1) line does, corresponds to the planar fluorine atoms F(2) having two distinct magnetic ion neighbors. According to the site symmetry of the F(2) site, even if $a = b$, there must be a departure from the axial symmetry. Thus ideally, the F(2) line should correspond to a powder pattern having two steps interposed about the intensity maximum[7] in contrast to the situation for cylindrical symmetry where only a single step appears as well as the maximum. In the present case the step corresponding to the high-field side of the maximum may overlap the F(1) line. Thus only the step at the low-field side can be located in the derivative spectra in the whole frequency range studied. As the field changes, the position of the step H_1 (Fig. 1) and the intensity maximum H_2 with respect to H_R change linearly with the field. From this variation the values of the isotropic shift K_{iso} and the anisotropic shift K_{ax} are determined.[6] The fractional shifts $\Delta H / H_R$ for the cases when Fe—F(2) bond axis is parallel ($\mathbf{H}_0 \parallel \mathbf{a}$) and perpendicular ($\mathbf{H}_0 \perp \mathbf{a}$) to the magnetic field have been obtained by the method used in the case of $CsFeF_4$ (Table I). The dipolar contribution to the total shift is computed as discussed earlier. It is seen from Table I that the F(1) site departs (not very appreciably) from axial symmetry. Nevertheless, the contribution due to the hyperfine field H_{hf} has been separated out by subtracting the average value for $\Delta H_{d\perp} / H_R$ in order to comply with the assumption of axial formulation of the shift tensor. The hyperfine interaction constants A_s and A_p thus determined are given in Table I. The A_s values determined directly from K_{iso} are also given in Table I for comparison.

During measurement of shifts at low temperature it is observed that the resonance lines of both types of fluorines in all the compounds are appreciably broadened below certain temperatures. Thus in Table I the values of the shift parameters of the three compounds are given at those temperatures whereupon, decreasing further, the lines begin to overlap and also the step at the low-field side of the F(2) line is not discernible. A detailed discussion regarding the behavior of the linewidth will be given in Sec. II B. The almost unchanged values of the shift parameters of the F(1) and F(2) lines in the paramagnetic phase resemble the susceptibility behavior of the compounds in those particular temperature ranges. Thus there is no apparent difference in the behavior of the time-averaged local properties as a function of temperature among the three compounds as T_N is approached.

B. Behavior of linewidth with temperature

The NMR linewidth is an important parameter in the phase transition problem since it yields direct information regarding the fluctuation of the electronic spins. Information on the short-range magnetic ordering above T_N may be obtained from the observed temperature dependence of the fluorine resonance linewidth. The best result could be obtained from the linewidth data in a single-crystal specimen. However, in certain favorable cases, it is also possible to have reasonably good information from the powder pattern analysis. In the present case for the resonance line shape of F(1) which is nearly symmetric, the distance D (Fig. 1) is taken to be a measure of the linewidth, where $K_{\text{ax}} < 2\beta$. However, this straightforward definition does not apply to the asymmetric line of F(2). Nevertheless, the distance W, as shown in Fig. 1, is considered to be a measure of the linewidth for comparison purpose. In fact, W is a function of 2β and K_{ax}. For general description, henceforth we shall use δH for linewidth measurement instead of D and W. Figures 2(a)–2(c) show the behavior of the linewidths of the F(1) and F(2) lines with temperature in NH$_4$FeF$_4$, RbFeF$_4$, and KFeF$_4$, respectively. It is interesting to see that though the shift parameters of both types of fluorines do not change significantly, even at temperatures close to T_N, the linewidths show anomalous broadening, which starts at certain temperatures and continues down to T_N. At T_N both the lines disappear. Attempts to detect the ^{19}F NMR lines at temperatures below T_N (up to 100 K) under the same experimental conditions failed in all the compounds. Furthermore, the behavior of linewidths with temperature are not the same for the three compounds and also with respect to that observed earlier[6] in the case of CsFeF$_4$. For example, the feature of line narrowing of the F(2) line in the three compounds with the lowering of temperature is the same as that in CsFeF$_4$. However, in CsFeF$_4$ ($T_N = 160$ K) the anomalous broadening of the F(2) line has been observed in a small temperature interval $\Delta T = T - T_N \sim 5$ K, whereas ΔT in NH$_4$FeF$_4$ and KFeF$_4$ as observed here is ~ 35 K, which is comparatively large. For RbFeF$_4$ the value of ΔT is ~ 15 K. Moreover, as the transition temperatures in the three compounds are very close among themselves, i.e., they lie within a temperature interval of

TABLE I. Shift parameters of ^{19}F NMR in NH$_4$FeF$_4$, RbFeF$_4$, and KFeF$_4$ at two different temperatures. θ is the angle between the direction of the external magnetic field H_0 and the bond axis.

System	Fluorine	T (K)	K_{iso} (%)	Field direction	θ (deg)	$\Delta H / H_R$	$\Delta H_d / H_R$	A_s and $A_p \times 10^4$ (cm^{-1})
NH$_4$FeF$_4$	F(1)	297	0.80±0.03	$\mathbf{H}_0 \parallel \mathbf{c}$	0		0.003 02	$A_s = 19.12 \pm 1.0$[a]
				$\mathbf{H}_0 \perp \mathbf{c}$	90		−0.001 51	
							−0.001 51	
	F(1)	144	0.75±0.05					$A_s = 17.08 \pm 1.0$[a]
	F(2)	297	2.16±0.05	$\mathbf{H}_0 \parallel \mathbf{a}$	0	0.0307	0.005 93	$A_s = 25.6 \pm 1.0$[a]
				$\mathbf{H}_0 \perp \mathbf{a}$	90	0.0171	−0.002 63	$A_s = 25.6 \pm 1.0$
							−0.003 29	$A_p = 1.86 \pm 0.5$
	F(2)	144	2.03±0.07	$\mathbf{H}_0 \parallel \mathbf{a}$	0	0.0371	0.006 71	$A_s = 23.2 \pm 1.0$[a]
				$\mathbf{H}_0 \perp \mathbf{a}$	90	0.0152	−0.002 74	$A_s = 23.2$
							−0.003 43	$A_p = 2.37$
RbFeF$_4$	F(1)	297	0.80±0.03	$\mathbf{H}_0 \parallel \mathbf{c}$	0		0.003 17	$A_s = 18.5 \pm 1.0$[a]
				$\mathbf{H}_0 \perp \mathbf{c}$	90		−0.001 58	
							−0.001 59	
	F(1)	144	0.78±0.05					$A_s = 18.04 \pm 1.0$[a]
	F(2)	297	2.08±0.05	$\mathbf{H}_0 \parallel \mathbf{a}$	0	0.0295	0.005 87	$A_s = 24.17 \pm 1.0$[a]
				$\mathbf{H}_0 \perp \mathbf{a}$	90	0.0168	−0.002 64	$A_s = 24.35$
							−0.003 23	$A_p = 1.49 \pm 0.5$
	F(2)	144	2.03	$\mathbf{H}_0 \parallel \mathbf{a}$	0	0.0309	0.005 68	$A_s = 24.22 \pm 1.0$[a]
				$\mathbf{H}_0 \perp \mathbf{a}$	90	0.0149	−0.002 55	$A_s = 24.22$
							−0.003 13	$A_p = 2.97$
KFeF$_4$	F(1)	297	0.74±0.003	$\mathbf{H}_0 \parallel \mathbf{c}$	0		0.003 19	$A_s = 17.12 \pm 1.0$[a]
				$\mathbf{H}_0 \perp \mathbf{c}$	90		−0.001 59	
							−0.001 60	
	F(1)	150	no F(1) line					
	F(2)	297	1.98	$\mathbf{H}_0 \parallel \mathbf{a}$	0	0.0274	0.005 96	$A_s = 22.97 \pm 1.0$[a]
				$\mathbf{H}_0 \perp \mathbf{a}$	90	0.0157	−0.002 69	$A_s = 22.7$
							−0.003 27	$A_p = 1.03 \pm 0.05$
	F(2)	150	1.81	$\mathbf{H}_0 \parallel \mathbf{a}$	0	0.0287	0.005 87	$A_s = 21.27$[a]
				$\mathbf{H}_0 \perp \mathbf{a}$	90	0.0128	−0.002 65	$A_s = 21.27$
							−0.003 22	$A_p = 2.78$

[a] A_s is calculated from $K_{\text{iso}} = z' A_s \langle S_z \rangle / \gamma_N \hbar H_0$, where z' is the number of nearest magnetic neighbors.

133.5–136 K, the anomalous line broadening may be expected to start from nearly the same temperature region, and this is more or less observed in the linewidth behavior of the planar fluorines. However, by probing the F(1) site, it is observed that there is a drastic difference in the behavior of the linewidth with temperature in the three compounds [Figs. 2(a)–2(c)]. In $KFeF_4$ the broadening of the F(1) line starts from a considerably higher temperature of 220 K and the line disappears near 170 K; in contrast, the broadening of the F(1) lines in NH_4FeF_4 and $RbFeF_4$ starts from 170 K. It may be pointed out that this difference in the behavior of the linewidth with temperature in $KFeF_4$ compared to those in NH_4FeF_4 and $RbFeF_4$ could not be observed by probing the linewidth of the planar fluorine [F(2)].

C. Theory of linewidth

The shape and width of the fluorine resonance absorption lines in single crystals of this type of compounds will be governed by the two different contributions: (1) interaction between ^{19}F nuclear spins and Fe^{3+} electron spins resulting in a Lorentzian line shape with temperature-dependent width and (2) interaction between ^{19}F nuclear spins and other ^{19}F nuclear spins giving a Gaussian line shape of temperature-independent width. The linewidth for the iron-fluorine interaction follows from an expression for $1/T_2$ given by[8]

$$T_2^{-1} = (\sqrt{\pi/2})[nS(S+1)]/[6\hbar^2\omega(T)]\sum_i (1+\cos^2\theta_i)A_i^2 \ , \tag{1}$$

where $\omega(T)$, in the high-temperature limit, is the exchange frequency $\omega_e = \omega(\infty)$, n is the number of Fe^{3+} neighbors. 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. $A_i = A_s + 2A_p$ along the Fe—F bond axis and $A_i = A_s - A_p$ perpendicular to this direction. Although the interactions of the ^{19}F nuclear spins with the Fe^{3+} electron spins are much stronger than those with the other ^{19}F nuclear spins, the resulting linewidths are of the same order of magnitude, because Fe—F linewidth is strongly narrowed by the very high fluctuation frequency of the exchange-coupled iron spins (of the order of J/h at $T \gg T_N$). A temperature-dependent linewidth 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 linewidth (governed by the above two interactions) is obtained due to the interaction $\mathbf{I}\cdot\mathbf{A}\cdot\mathbf{S}$. The hyperfine coupling tensor includes both nonclassical contact and dipolar interactions. Thus the strength of the anisotropic interaction in comparison with the homogeneous linewidth determines the line shape of a powder pattern. In the present case, the linewidth of the powder pattern should be a complex function of homogeneous linewidth and the degree of anisotropy as mentioned earlier. Furthermore, the spread of the line due to anisotropic interaction is proportional to the average static component of the magnetic moment $\langle \mu \rangle$ (which is proportional to the applied magnetic field) and thus in a normal paramagnetic system, the linewidth for the powder system follows directly the magnetic susceptibility and is also proportional to the applied magnetic field. Therefore, in a polycrystalline sample, the total width (δH) is given by

$$\delta H = \delta H_0 + \delta H_1(T) + \delta H_2(\chi, H) \ , \tag{2}$$

where δH_1 and δH_0 are the two contributions mentioned above (in case of a single crystal) with the orientation-dependent part being averaged out in powder system. δH_2 is the contribution due to anisotropic magnetic interaction. Thus, in a polycrystalline system, the observed temperature-dependent linewidth could not be directly associated to the effect of slowing down of $\omega(T)$ with temperature as in Eq. (1) and may also arise from the magnetic susceptibility $\chi(T)$. Interestingly, as in the compounds NH_4FeF_4, $RbFeF_4$, and $KFeF_4$ the variation of $\chi(T)$ with temperature in the range $T_N < T < 297$ K is very small, there is an opportunity to relate the observed anomalous increase in δH to the effect of slowing down of exchange fluctuation frequency with temperature, as given by Eq. (1), i.e., the dynamics of electron spin fluctuation.

D. Discussion

The narrowing of the F(2) line in all three compounds up to a certain temperature, as seen from Fig. 2, could be explained by the position of this site half-way between two iron sites. For short-range ordering, the spins of two magnetic ion neighbors become mutually antiparallel, which evidently will influence the linewidth of the fluorine atoms in between. This result is in conformity with that reported earlier in $CsFeF_4$ (Ref. 6) and K_2NiF_4-type[9] compounds from ^{19}F NMR studies. However, observation of the broadening of the F(2) line over a large temperature interval in NH_4FeF_4, $RbFeF_4$, and $KFeF_4$ is not only in contrast to that of isomorphous $CsFeF_4$ but also with the F(2) linewidth data reported in the literature for the K_2NiF_4-type 2D antiferromagnets. One may ascribe the broadening of the F(2) line to the magnetic susceptibility behavior since the contribution $\delta H_2(\chi, H)$ of Eq. (2) to the total width is appreciable for the F(2) line, as has been discussed earlier. However, in the present case, increase in the F(2) linewidth appears in a temperature region where there is a decreasing trend in the magnetic susceptibility with a lowering of the temperature.[3–5] Thus, the anomalous broadening of the F(2) line could not be associated with the susceptibility behavior. However, the reason for divergence in the F(2) linewidth, despite the cancellation of the hyperfine field due to antiferromagnetic coupling, is not clearly understood.

In order to study the critical behavior from the ^{19}F linewidth data in the present case, we have to first separate out the contribution δH_1 arising from the electronic spin fluctuation from the total width δH by using Eq. (2). For this purpose we have chosen the F(1) line which is nearly symmetric, so that one can expect a comparatively smaller contribution to the total width arising from the susceptibility-dependent and/or magnetic-field–dependent part (δH_2). Nevertheless, in order to estimate δH_2 we have studied the magnetic-field dependence of the F(1) linewidth for the three compounds at 297 K. It may be seen from Fig. 3 that though there is a field-dependent part to the total width of the F(1) line, this part is not significantly large. The zero-field extrapolated value $\delta H'$ (Fig. 3) of the total width contains the two contributions δH_0 and δH_1, as may be seen from Eq. (2). We have also computed δH_0, the contribution due to the nuclear-nuclear dipolar interaction and it lies in the range 4–5 Oe for the four compounds including CsFeF$_4$. Moreover, in order to check whether the zero-field extrapolated value of δH agrees well with the sum of δH_0 and δH_1 we have also computed the contribution δH_1 to the linewidth due to electronic spin fluctuation in the case of NH$_4$FeF$_4$ for which the J/k value (-26 K) is known from the magnetic susceptibility data.[5] Then estimating the exchange frequency from the relation[9] $\hbar^2\omega_e^2=\frac{8}{3}J^2nS(S+1)$ with $S=\frac{5}{2}$, we obtain $\omega_e=3.3\times10^{13}$ sec^{-1}. $\delta H_1(T)$ is then determined from the relation $\delta H_1(T)=2/(\sqrt{3}\gamma_N T_2)$ by using Eq. (1) for T_2^{-1} with the θ-dependent part being averaged out for all possible orientations of the crystallites in the polycrystalline specimen. The calculated value of δH_1 for the F(1) line in NH$_4$FeF$_4$ is found to be 2.7 Oe and that of δH_0 is 5.0 Oe. So the value of $\delta H_0+\delta H_1$ in this case is $\sim$7.7 Oe, which is in close agreement with the zero-field extrapolated value ($\delta H'$) of the F(1) linewidth in NH$_4$FeF$_4$ at 297 K. Thus by subtracting $\delta H'$ from the total width δH, we have estimated the susceptibility-dependent contribution δH_2 to the total width at room temperature for the three compounds. Since the variation of χ with temperature in the range $T_N<T<297$ K is very small, one can assume that the contribution δH_2 to δH remains the same in the whole temperature range. Thus by subtracting the room-temperature value of $\delta H_2+\delta H_0$ from the total width of the F(1) in the whole temperature range $T_N<T<297$ K, we have estimated the contribution $\delta H_1(T)$ to the F(1) linewidth arising from the electronic spin fluctuations of the Fe^{3+} ion.

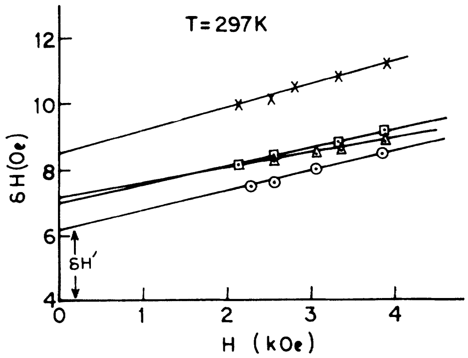

FIG. 3. Variation of the linewidth, $\delta H(=D)$ of F(1): ⊙, CsFeF$_4$; △, KFeF$_4$; □ RbFeF$_4$; ×, NH$_4$FeF$_4$; with the external magnetic field (H_0) at $T=297$ K. $\delta H'$ is the zero-field extrapolated value, shown in the case of CsFeF$_4$.

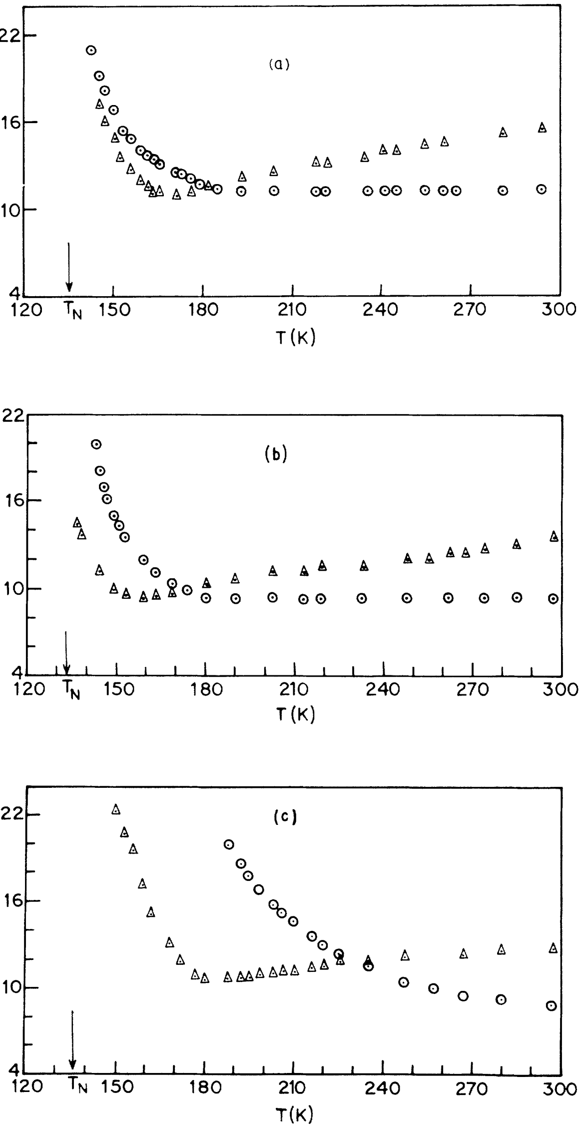

FIG. 2. Plots of the linewidths (δH) of F(1) ($\delta H=D$): (⊙) and F(2) ($\delta H=W$): (△) of (a) NH$_4$FeF$_4$, (b) RbFeF$_4$, and (c) KFeF$_4$ (as defined in the text) as a function of temperature at $\nu_R=15$ MHz.

In Figs. 4(a)–4(c), the log-log plots of $\delta H_1(T)$ versus the reduced temperature $\epsilon=(T-T_N)/T_N$ are shown for the F(1) lines in NH$_4$FeF$_4$, RbFeF$_4$, and KFeF$_4$. In Fig. 4(d) we have also shown the same plot in the case of CsFeF$_4$ using the F(1) linewidth data reported earlier.[6] The two curves in each figure correspond to the cases where (1) $\delta H_1(T)$ is calculated by subtracting from the total width (δH) the sum of the values of δH_0 and δH_2 and (2) the contribution of δH_2 is neglected so that $\delta H_1(T)=\delta H-\delta H_0$. It is seen that in all compounds, the values of $\delta H_1(T)$ are well described by straight lines within certain temperature intervals obeying the power law $\delta H_1(T)\propto\epsilon^{-w}$. From the slopes of the linear region the values of the exponent w are determined (Table II) for the two cases mentioned above and are found not to differ significantly if the contribution δH_2 (due to anisotropic interaction) to the total width is neglected. It may be pointed out that in a 3D magnetic system, the anomalous increase in the linewidth takes place in a very narrow temperature range $\lesssim 1$ K.[10] Close to the transition temperature, where the fluctuation $q = q_c$ dominate (q_c being the critical wave vector) $\delta H_1(T)$ is related by[11] $\delta H_1(T) \propto \epsilon^{-\gamma+\nu(d-z)}$ where d denotes the lattice dimensionality, $\gamma = (2-\eta)\nu$ (η being the critical exponent introduced by Fisher[12] as a correction to the behavior of the static pair correlation function) ν are the static critical exponents, and z is the dynamic exponent. Thus, in this case, w is given by $w = -\gamma + \nu(d-z)$.

The value of the exponent w in the case of NH_4FeF_4 is very close to that reported from our ^1H spin-lattice relaxation studies.[6] In the case of $RbFeF_4$ the value of w is found to agree well with that reported by Keller and Savic[13] from the study of characteristic line broadening of ^{57}Fe Mössbauer line due to critical spin fluctuations observed within a very narrow temperature interval of $10^{-4} < \epsilon < 10^{-2}$ using a single-crystal specimen. Though in the present case the ^{19}F NMR experiments cannot be done as close to T_N as it was done in Mössbauer experiments, due to excessive line broadening, yet the close agreement of the value of w from both the measurements seems to indicate that there is not much error involved in the present ^{19}F NMR results obtained for $RbFeF_4$ in polycrystalline form. For $CsFeF_4$, the exponent has not been previously determined from any other experiment. The values of the exponent in NH_4FeF_4, $RbFeF_4$, and $CsFeF_4$, when compared to those predicted by the current theory of critical dynamics,[14] indicate that as T_N

TABLE II. Values of the critical exponent w of the F(1) fluorine in $NHFeF_4$, $RbFeF_4$, and $KFeF_4$ as estimated from linewidth measurements.

	Critical exponent w estimated from	
System	$\delta H_1(T) = (\delta H - \delta H_0 - \delta H_2)$ vs ϵ curve	$\delta H_1(T) = (\delta H - \delta H_0)$ vs ϵ curve
NH_4FeF_4[a]	0.6	0.5
$RbFeF_4$	0.8	0.7
$KFeF_4$	1.5	1.4
$CsFeF_4$[b]	0.9	0.8

[a] $w = 0.5$, from ^1H spin-lattice relaxation data (Ref. 6).

[b] w in $CsFeF_4$ is estimated using the earlier linewidth data (Ref. 6).

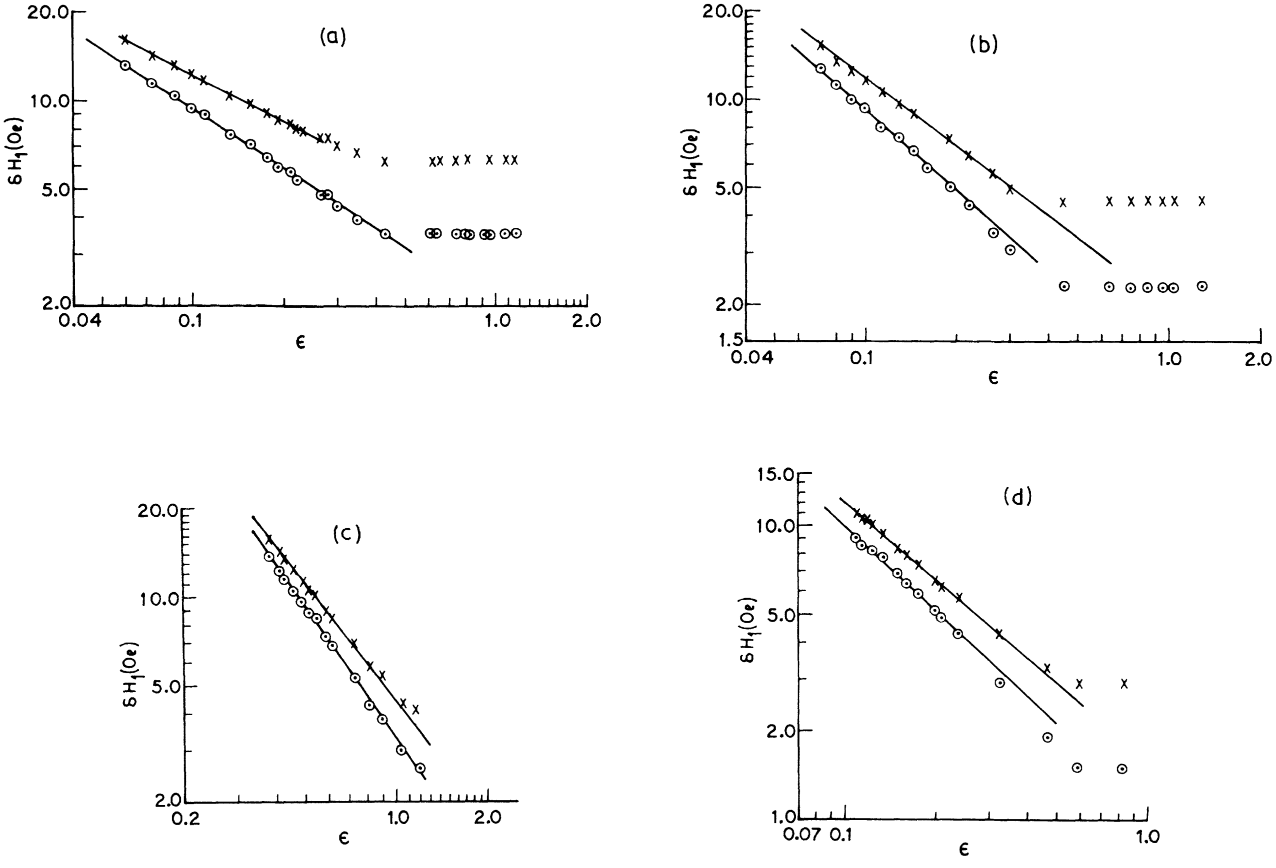

FIG. 4. The critical behavior of the contribution δH_1 to the total linewidth (δH) of the axial fluorine F(1) as a function of reduced temperature ϵ. (a) NH_4FeF_4, (b) $RbFeF_4$, (c) $KFeF_4$, and (d) $CsFeF_4$. The two curves in each figure correspond to the following: ×, $\delta H_1 = \delta H - \delta H_0$; ⊙, $\delta H_1 = \delta H - \delta H_0 - \delta H_2$, as discussed in the text.

is approached in the paramagnetic phase, each of them behaves more like a 3D system rather than a 2D system. This means that the ratio of interplanar exchange and intraplanar exchange is not sufficiently small to allow 2D magnetic ordering. Nevertheless, the existence of a broad critical region as observed from the behavior of the linewidth in these compounds indicates the presence of 2D magnetic interactions.

In the case of KFeF$_4$ since the F(1) line disappears near 170 K, which is far away from $T_N = 136$ K, we do not have the linewidth data as close to T_N as we have for NH$_4$FeF$_4$, RbFeF$_4$, and CsFeF$_4$.[6] Even in this case $\delta H_1(T)$ is found to fit well with the relation ϵ^{-w} in the interval $0.3 \le \epsilon \le 0.9$ with $w = 1.4$. The value of this exponent is very close to that predicted by the 2D Ising model ($w = 1.5$), indicating that in case of KFeF$_4$ the intraplanar exchange interaction is much greater than the interplanar exchange interaction. This fact is further supported by the value of the static critical exponent $\beta = 0.151$ for KFeF$_4$ deterimed from the temperature dependence of the hyperfine field at the ^{57}Fe site determined from Mössbauer studies[13] performed in a very narrow region $10^{-4} \le \epsilon \le 10^{-2}$. Thus from the present ^{19}F NMR results it emerges that the three compounds NH$_4$FeF$_4$, RbFeF$_4$, and also CsFeF$_4$ have an essential difference with KFeF$_4$ in respect to the strength of the interaction between the adjacent magnetic planes. This is also in agreement with the results of neutron scattering,[15,16] which shows that in contrast to RbFeF$_4$ the adjacent magnetic layers in KFeF$_4$ are shifted by half a lattice constant with respect to each other, leading to staggered magnetic structure. Since the interaction within the layers is antiferromagnetic, this configuration causes a cancellation of the magnetic interaction between neighboring layers. As a result the interaction can take place only via the next-nearest planes leading to much weaker interlayer interaction.

III. CONCLUSIONS

^{19}F NMR studies in polycrystalline NH$_4$FeF$_4$, RbFeF$_4$, and KFeF$_4$ indicate the existence of two types of fluorine sites, viz., F(1) bonded with a Fe^{3+} ion and F(2), bonded with two Fe^{3+} ions. The time-averaged value of the hyperfine field (as obtained from the shift values) at both sites remain almost unchanged as T_N is approached in the paramagnetic phase in all cases. However, the linewidth, which reflects the behavior of the fluctuating part of the hyperfine field, increases drastically as T_N is approached and interestingly the nature of this change differs significantly in different compounds.

An attempt has been made to correlate the behavior of the linewidth with the effect of critical slowing down of the electronic spin fluctuation of the Fe^{3+} ion as T_N is approached. The values of the critical exponent w determined from the linewidth behavior of the axial fluorine F(1) indicate that the 2D magnetic interactions are predominant in KFeF$_4$, whereas in NH$_4$FeF$_4$, RbFeF$_4$, and CsFeF$_4$ the 3D characters are much stronger. However, the existence of a broad critical region even in each of the last three compounds indicates the presence of the 2D magnetic interactions.

---

[1] L. J. de Jongh and A. R. Miedema, Adv. Phys. **23**, 1 (1974).

[2] R. W. G. Wyckoff, *Crystal Structures 3* (Interscience, New York, 1965), p. 1.

[3] G. Heger and R. Geller, Solid State Commun. **9**, 335 (1971).

[4] M. Eibschutz, H. J. Guggenheim, and L. Holmes, J. Appl. Phys. **42**, 1485 (1971).

[5] F. Menil, A. Tressaud, R. Sabatier, and G. L. Flem, Mater. Res. Bull. **12**, 983 (1977).

[6] K. Ghoshray, A. Ghoshray, and N. Chatterjee, J. Phys. C **21**, 2247 (1987); J. Phys. Condens. Mat. **2**, 1007 (1990).

[7] N. Bloembergen and T. J. Rowland, Acta Metall. **1**, 731 (1953).

[8] T. Moriya, Prog. Theor. Phys. **16**, 641 (1956).

[9] C. Bucci and G. Guidi, in *Local Properties at Phase Transitions,* edited by K. A. Muller and R. Rigamonti (North-Holland, Amsterdam, 1976), p. 624.

[10] T. Moriya, Prog. Theor. Phys. **28**, 371 (1962).

[11] F. Borsa and A. Rigamonti, in *Magnetic Resonance of Phase Transitions,* edited by F. J. Owen, C. P. Poole, Jr., and H. A. Farach (Academic, New York, 1979), p. 108.

[12] M. E. Fisher, Rep. Prog. Phys. **30**, 615 (1967).

[13] H. Keller and I. M. Savic, Phys. Rev. B **28**, 2638 (1983).

[14] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977), and references therein.

[15] M. Eibschutz, G. R. Davidson, J. H. Guggenheim, and D. E. Cox, in *Magnetism and Magnetic Materials—1971 (Chicago),* Proceedings of the 17th Annual Conference on Magnetism and Magnetic Materials, AIP Conf. Proc. No. 5, edited by C. D. Graham and J. J. Rhyne (AIP, New York, 1972), p. 670.

[16] G. Heger and R. Geller, Phys. Status Solidi B **53**, 227 (1972).