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^{39}K NMR and EPR study of multiferroic $K_3Fe_5F_{15}$

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Abstract

^{39}K NMR spectra and relaxation times of polycrystalline $K_3Fe_5F_{15}$ have been used as a microscopic detector of the local magnetic fields at the magnetic transition at $T_N = 123$ K. The NMR lineshape widens abruptly upon crossing T_N due to the onset of internal magnetic fields, while we find no significant lineshift. The paraelectric to ferroelectric transition at $T_c = 490$ K and the magnetic transition at T_N have also been studied using X-band EPR (electron paramagnetic resonance). An increase and subsequent decrease in the EPR susceptibilities is observed on approaching T_N from above. There is also a significant increase in the linewidth. At the same time the g-factor first decreases and then increases with decreasing temperature. The local magnetic field is different at different K sites and is much smaller than the magnetic field around the Fe sites. This seems to be consistent with the behaviour of a weak ferrimagnet. The ferrimagnetism does not seem to be due to spin canting as the lattice is disordered, but may arise from thermal blocking of superparamagnetic percolation clusters. The ferroelectric transition at T_c shows no electronic anomaly, demonstrating that we are dealing with a classical phonon anomaly as found in conventional oxides rather than an electronic transition.

(Some figures in this article are in colour only in the electronic version)

A great majority of all known ferroelectrics are oxides [1]. The same is true for multiferroics, i.e. for systems where the electric polarization, the stress, and the magnetization coexist. The interaction between the polarization and the magnetization can be linear or quadratic. The coupling between the polarization and the magnetization may be so strong that the spontaneous polarization can be switched by a magnetic field [2–4] and the spontaneous magnetization by an electric field [2–4]. The microscopic mechanism of the coupling is however still open and the object of intensive research [3, 4]. Recently it has been suggested that in multiferroics the ferroelectric transition is of electronic rather than of phonon origin [5]. To understand this mechanism it is important to find new families of ferroelectrics other than oxides.

Here we present the ^{39}K NMR and X-band EPR spectra of a ferroelectric fluoride $K_3Fe_5F_{15}$, which we have recently shown to be a magnetic multiferroic system [6] below $T_N = 123$ K. The $K_3Fe_5F_{15}$ turns out to be a weak ferrimagnet below T_N with a slim hysteresis loop and two different magnetic sublattices at low temperatures. We present here our extension of the work in [6] with ^{39}K NMR around T_N and with X-band EPR T-dependences above the para to ferroelectric transition at $T_c = 490$ K.

At room temperature, $K_3Fe_5F_{15}$ [7, 8] is ferroelectric and belongs to the polar space group Pba2 with two formula units per unit cell. The system crystallizes in an orthorhombically deformed tungsten bronze structure with a small deviation from tetragonality [9]. On heating through the ferroelectric–paraelectric transition temperature $T_c = 490$ K, the point group changes from $mm2$ to $4/mmm$. The most probable space group in the high temperature paraelectric phase is $P4/mbm$ [7]. In the ferroelectric phase, there are 10 Fe cations and 6 K cations in the unit cell. Electrical neutrality of the molecule requires 4 Fe^{3+} ions (each with a spin 5/2) and 6 non-magnetic Fe^{2+} ions each with a spin 2. Fe cations are distributed among three inequivalent sites Fe(1), Fe(2) and

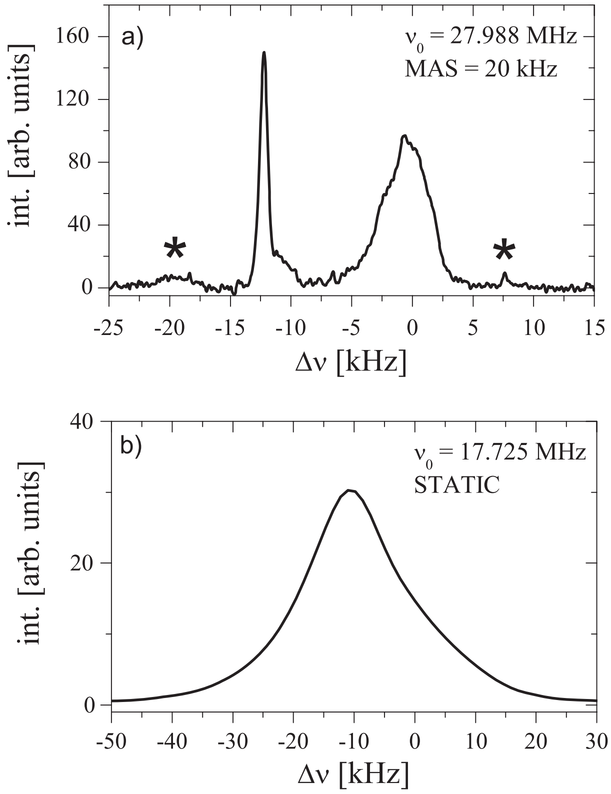

Figure 1. ^{39}K NMR spectrum of polycrystalline $K_3Fe_5F_{15}$ at room temperature: (a) with MAS (peaks marked by stars are the sidebands of the main peaks) and (b) static.

Fe(3) with 2 Fe(1), 4 Fe(2) and 4 Fe(3) sites in the unit cell. Similarly, K cations are distributed among two inequivalent sites K(1) and K(2) with 4 K(1) and 2 K(2) sites per unit cell.

To check on the number of inequivalent K sites in the crystal structure we measured the ^{39}K MAS spectrum at room temperature, at a Larmor frequency of $\omega_L/2\pi = 27.988$ MHz and rotor speed of 20 kHz. The spectra are shown in figure 1(a). Two ^{39}K lines are seen: a narrow line at -12 kHz and a broader line at 1 kHz with respect to a 0.1 mol KCl solution. In a crystal with perfect order, chemically inequivalent ^{39}K sites would appear in a MAS spectrum as separate lines with resolved shoulders and singularities characteristic of residual second order quadrupolar broadening [10]. This is not the case here: the two lines exhibit a featureless, Gaussian-like broadening, reminiscent of disordered crystal structure. The intensities of the two lines are in the ratio of 1:3, in reasonable agreement with the $K_3Fe_5F_{15}$ structure [7, 8]. We can attribute the line at 1 kHz to site K(2) and the line at -12 kHz to site K(1). The difference in their linewidths can be explained as follows. In the $K_xFe_5F_{15}$ family with $2 < x < 3$ the site K(2) becomes partially occupied in a disordered manner when $x < 3$, while the K(1) site remains 100% occupied [8]. We believe that although in our sample ($x = 3$) the two sites should be 100% occupied this disorder lies at the origin of the linewidth difference of the two lines observed with the MAS NMR.

A static ^{39}K NMR spectrum at room temperature and Larmor frequency of $\omega_L/2\pi = 17.725$ MHz is shown in figure 1(b). Here the spectrum consists of a single slightly asymmetric line ~23 kHz wide. This is not unexpected because ^{39}K is a quadrupolar nucleus with a central component as well as two satellite transitions. The central transition is less sensitive to crystallite orientations than the satellites. In a polycrystalline sample this results in a broad spectrum where the three lines are unresolved. Here the two ^{39}K lines corresponding to K(1) and K(2) sites are unresolved too, because the static linewidth (~23 kHz) is larger than the offset difference (~10 kHz). The broadening of the K(1) and K(2) static lines at room temperature is most probably due to chemical shift anisotropy and first order quadrupolar interaction, additionally smeared by local disorder.

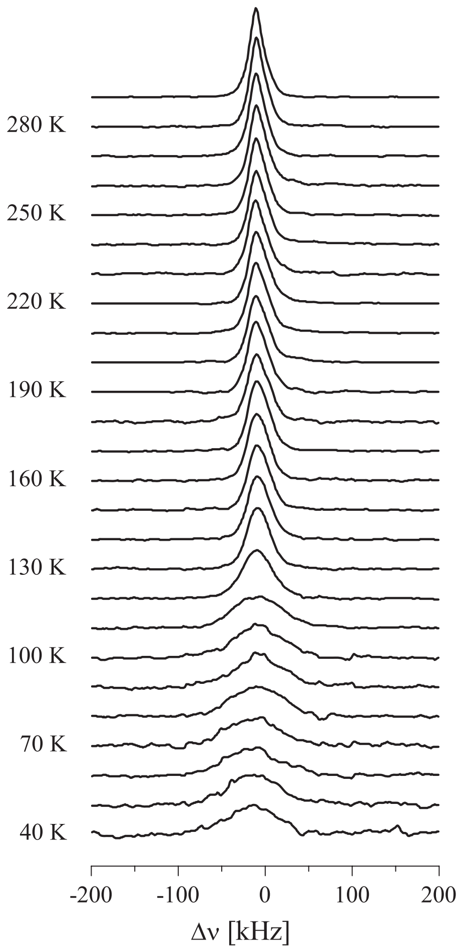

Figure 2. Temperature dependence of the static ^{39}K NMR spectrum of the polycrystalline $K_3Fe_5F_{15}$.

The temperature dependence of the static ^{39}K NMR spectrum from 290 down to 40 K is shown in figure 2. With decreasing temperature the linewidth slightly increases for $T > T_N$. Then, below the Néel temperature $T_N = 123$ K, the second moment M_2 of the whole NMR spectrum (figure 3) abruptly increases from ~200 (kHz)^2 just above T_N to nearly 800 (kHz)^2 just below T_N, i.e. by about a factor of four. Here only the total second moment is extracted as the two individual K(1) and K(2) lines are not resolved. Because the spectrum retains its single peak shape even at the lowest temperatures, the total M_2 is a

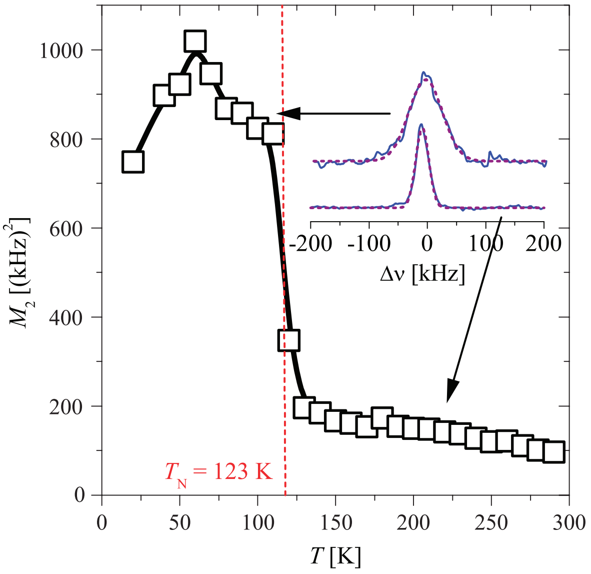

Figure 3. T-dependence of the second moment M_2 of the static ^{39}K NMR spectrum in polycrystalline $K_3Fe_5F_{15}$. The individual second moments corresponding to K(1) and K(2) lines cannot be extracted because the lines overlap. The inset shows the NMR line at 220 K and at 100 K.

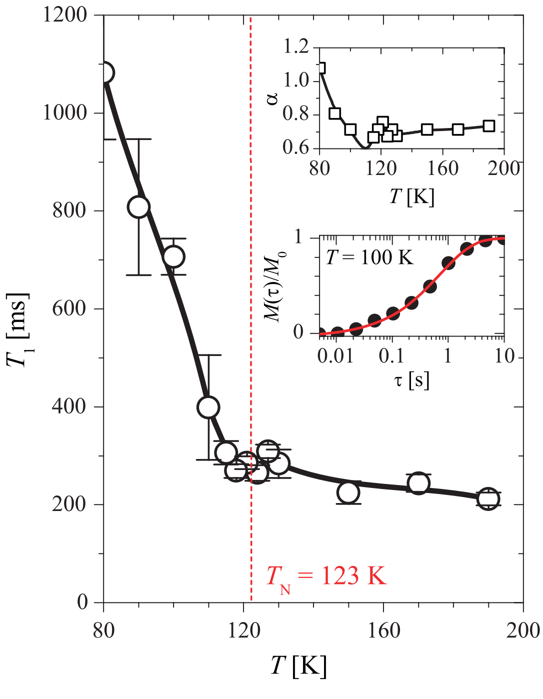

Figure 4. T-dependence of the ^{39}K NMR spin–lattice relaxation time of polycrystalline $K_3Fe_5F_{15}$. The inset shows the magnetization recovery and the T-dependence of the 'stretched' exponent α.

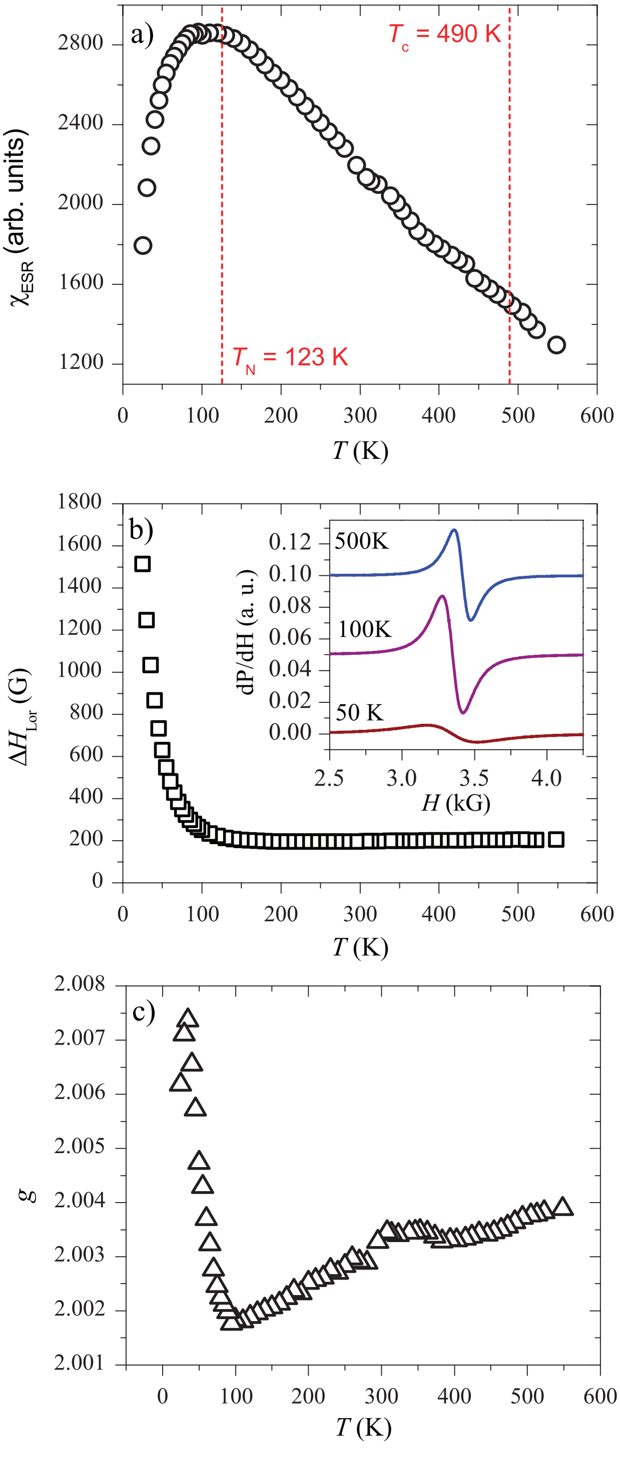

Figure 5. X-band EPR (a) susceptibility χ_{ESR}, (b) Lorentzian linewidth ΔH_{Lor}, and (c) g-factor of polycrystalline $K_3Fe_5F_{15}$. The inset in (b) shows the EPR spectra at three representative temperatures.

good indicator of the K(1) and K(2) individual moments. This increase of the linewidth is attributed to the coupling of the nuclear spin with the two sublattice magnetizations. The corresponding internal magnetic field at the K sites ($B_K \sim B_0 \Delta\nu/\nu_L = 330$ G at $T = 40$ K) is small compared to the internal fields $B(1)$ and $B(2)$ at the Fe sites in the two magnetic sublattices. Mössbauer spectra [6] show that $B(1) = 585$ kG and $B(2) = 263$ kG at low temperatures. These values suggest that we deal with a large cancellation of the internal field. The 'weak' magnetization seen by the 'squid' measurements [6] seems to be due to the inequivalence of the two sublattices. Throughout the temperature range investigated we have found no significant shift of the NMR lines, which is usually observed in ferrimagnetic systems.

The temperature dependence of the ^{39}K spin–lattice relaxation time T_1 is shown in figure 4 between 200 and 80 K. T_1 is relatively long and varies between 250 ms above T_N to 1000 ms below T_N. The magnetization decay is of the 'stretched' exponential type, where the 'stretched' exponent α varies between 0.5 and 1. The above data together with the data presented in figure 3 show that the linewidth is inhomogeneously broadened, and supports our conclusion that the ^{39}K static NMR broadening below T_N is of a magnetic origin. The long T_1 shows that the $Fe^{3+} \leftrightarrow Fe^{2+}$ exchange must be rather fast so that the spectral density of the fluctuating field component at the ^{39}K Larmor frequency is rather small.

To check on the nature of the para to ferroelectric transition of polycrystalline $K_3Fe_5F_{15}$ at $T_c = 490$ K we have measured the T-dependence of the g-factor and the X-band EPR linewidth around T_c. The data are shown in figures 5(b) and (c), respectively. The EPR susceptibility is also shown in figure 5(a). There is no EPR anomaly at the paraelectric–ferroelectric transition at T_c which can be seen by X-band EPR. Near the magnetic transition at T_N, on the other hand, there are significant changes. The EPR susceptibility χ_{EPR} first increases with decreasing temperature, exhibits a maximum and then decreases with decreasing T. The broad maximum in χ_{EPR} occurs around 100 K, i.e. 20 K below T_N. The position of the centre of the line, given by the g-factor, on the other hand, shows at first a large monotonic increase with decreasing T below T_N and then an increase. Such a downshift of the EPR signal is due to the development of the large internal magnetic fields below T_N. The Lorentzian linewidth ΔH_{Lor} shows a significant monotonic increase from 100 to 700 G between 270 and 25 K. There is no critical broadening of the EPR linewidth as T_N is approached from above as usually observed at the phase transition of anisotropic antiferromagnets like MnF_2 [11]. The linewidth behaviour is rather characteristic of a cubic magnetic system like $KMnF_3$ [12]. The small internal field at the two K sites cannot be due to spin canting of the two sublattices [13] which are disordered.

The above EPR data around T_c are now discussed in relation to the two recently proposed models of magnetoelectric behaviour [2–4]. The common feature of both models is that ferroelectricity and magnetoelectric coupling can be understood in terms of electron physics rather than lattice dynamics which is the key to the understanding of conventional ferroelectricity. The lack of any anomaly in the EPR data suggests that the transition is not electronic in origin but rather of the phonon type [13, 14].

The magnetic field at ^{39}K sites in polycrystalline $K_3Fe_5F_{15}$ has been probed by ^{39}K NMR below the magnetic transition T_N and found to be small compared to the magnetic field of the two Fe magnetic sublattices [6]. In addition the two Fe magnetic sublattices are not equivalent. This suggests a large cancellation of the two magnetizations, which may be due to the inequivalence of the two sublattices. It supports our previous conclusion that $K_3Fe_5F_{15}$ is a 'weak' but disordered ferrimagnet. The later statement is also supported by our X-band EPR measurements, where the susceptibility χ_{EPR} has a peak below T_N. It should be also pointed out that any electronic contributions to ferroelectric transition should result in a deviation from the Curie–Weiss-like $\chi_{EPR}(T)$ close to T_c. Since this was not observed, our data contradict models [2–4] suggesting an electronic origin of the ferroelectric transition. They seem to prove that we rather deal with a classical phonon transition as found in other conventional oxides [13, 14]. The above data also suggest that we do not deal with classical spin canting but rather with thermal blocking of superparamagnetic percolation clusters [15].

Acknowledgment

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