*Scientific paper*

# The Muon F–μ⁺–F Hydrogen Bond–like Complex

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***Dedicated to Professor Dušan Hadži on the occasion of his 90th birthday***

## Abstract

Muon spin rotation (μSR) and relaxation has been used to study the local magnetic structure of $K_3Fe_5F_{15}$. A collinear F–μ⁺–F ''hydrogen bond-like'' symmetric double minimum type complex with a F···F distance of 2.8 Å and a separation between the two minima of 0.8 Å has been found in the paramagnetic phase. The apparent central position of the muon seems to be the result of fast muon tunneling between two equivalent minima in the F–μ⁺–F bond.

**Keywords:** Multiferroics, multiferroic fluorides, muon spin rotation, hydrogen bond, F–μ⁺–F complex

## 1. Introduction

Muon spin rotation and relaxation uses the implanted positive muons as microscopic probes to determine the magnetic structure of materials. Since the muon mass is only about 1/9 of the mass of the proton, muon tunneling among different equilibrium sites is much faster than proton or deuteron tunneling.

$K_3Fe_5F_{15}$ is a multiferroic fluoride[1,2] which exhibits a ferroelectric transition at $T_C$ = 490 K and a magnetic transition at $T_N$ = 125 K. In the paraelectric phase it belongs to the P4/mbm space group and in the ferroelectric phase to the Pba2 space group with two formula units per unit cell.[1] The structure consists of a framework of corner sharing $FeF_6$ octahedra. There are four $Fe^{3+}$ and six $Fe^{2+}$ ions in the unit cell (Fig. 1).

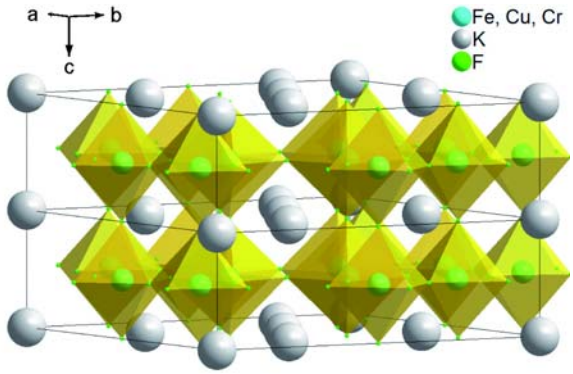


**Figure 1:** Crystal structure of $K_3(Fe,Cr,Cu)Fe_2F_{15}$. The unit cells are marked by the black line.

Positive muons are initially nearly 100% polarized along the beam direction.[3] Muon coupling with local transverse magnetic fields causes a precession of the muon polarization. The frequency of this precession is $\omega_\mu = \gamma_\mu B_L$. Here $\gamma_\mu = 2\pi \times 135.5$ MHz/T is the muon gyromagnetic ratio. When the fields are static, 1/3 of the muons are non-precessing as their polarization is parallel to the local fields in a powdered sample. This is the origin of the characteristic 1/3 tail in zero external magnetic field experiments.

## 2. Experimental

The μSR experiment measures the polarization of the muon ensemble $P_Z(t)$ along the initial muon direction, $z$. In the simplest case the oscillations can be fitted by a damped cosine function

$$P_z(t) = Ae^{-t/T_2}\cos(\omega_\mu t + \phi) + B_g \quad (1)$$

where $A$ is the oscillation amplitude, $T_2$ the relaxation time, $\omega_\mu$ the oscillation frequency, $\phi$ the phase and $B_g$ the background due to the 1/3 tail.

The oscillations of the $\mu^+$ asymmetry above $T_N$ (Fig. 2) result from the muon-fluorine dipolar interactions[4,5]

$$\mathcal{H}_{d-d} = \Sigma_{i<j}\mu_0\frac{\gamma_i\gamma_j}{4\pi\left(r_{ij}^3\right)}\left[\boldsymbol{S}_i\boldsymbol{S}_j - 3\left(\boldsymbol{S}_i\frac{\boldsymbol{r}_{ij}}{|\boldsymbol{r}_{ij}|}\right)\left(\boldsymbol{S}_j\frac{\boldsymbol{r}_{ij}}{|\boldsymbol{r}_{ij}|}\right)\right] \quad (2)$$

where $\gamma_i$ and $\gamma_j$ are gyromagnetic ratios of either the fluorine or the muon, $\boldsymbol{r}_{ij}$ is the inter-nuclear dipolar vector, and $\boldsymbol{S}_i$ and $\boldsymbol{S}_j$ are the corresponding spins. The only free parameters are the spatial coordinates of the nuclei and the muon.

The muon precession frequency has been estimated as 2.6 MHz from the first minimum of the $\mu^+$ polarization asymmetry oscillation (Fig. 2). This yields a local field $B_L$ = 31 Gauss at the muon site and a F···F distance of 2.4 Å for a central position of the muon. This is however much less than predicted from the crystal structure.

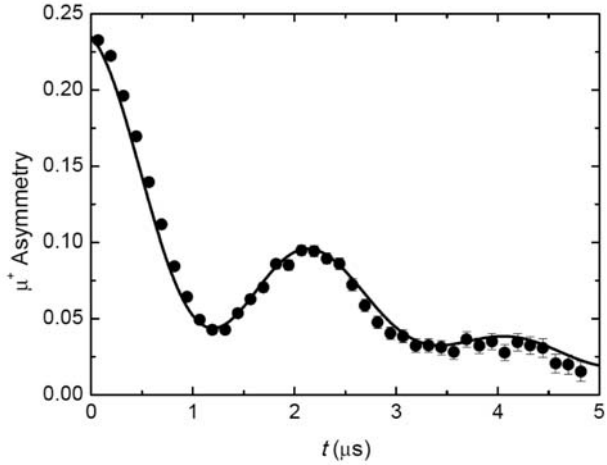


**Figure 2:** Irregular oscillations of the $\mu^+$ asymmetry at zero magnetic field in the paramagnetic phase of $K_3Fe_5F_{15}$ can be described by the entangled linear F–$\mu^+$–F complex.

## 3. Results and Discussion

A simulation (Fig. 3) of the $\mu^+$ asymmetry decay provides the best fit for a collinear symmetric $F^-$–$\mu^+$–$F^-$ bond. An asymmetric location of the $\mu^+$ in the F–$\mu^+$–F bond gives a much worse fit. The same is true for a symmetric but non-collinear F–$\mu^+$–F bond where the muon is located out of the F···F direction.

The discrepancy between the F···F distance obtained from the crystal structure, 2.7–2.9 Å and the value of 2.4 Å obtained from the observed local magnetic field, can be explained as follows:

(i) either the muon significantly distorts the crystal structure, or

(ii) the F···F distance is the same as given by the crystal structure (≈ 2.8 Å on the average) but we have a double minimum F–$\mu^+$–F potential with two equivalent off-center sites and rapid muon tunneling among them so that the potential appears to have a single central minimum on the time average. The effective F–μ dipolar interaction is in this case given by:

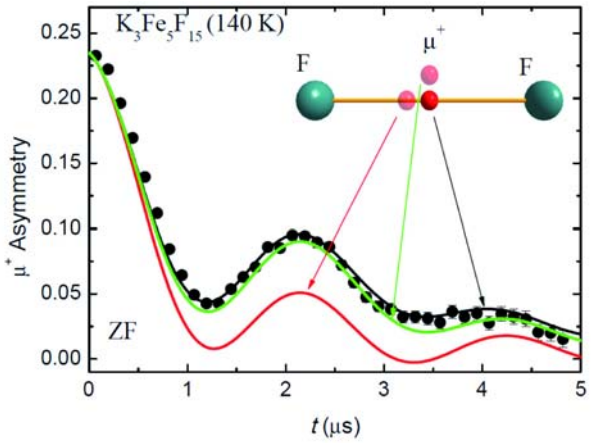


**Figure 3:** Simulation of the $\mu^+$ asymmetry decay for different muon positions between the two $F^-$ ions. The central position of the muon gives the best agreement of the simulated polarization decay with the measured data.

$$\left\langle \frac{1}{R^3} \right\rangle = \frac{1}{2}\left[ \frac{1}{R^3_{F-\mu}} + \frac{1}{R^3_{\mu-F}} \right] \tag{3}$$

Here the local field is determined by the muon positions in the off-center site → $R \approx R_{F-\mu}$ which is of course closer to $R$ = (F···F)/2. This results in a larger local fluorine induced magnetic field at the muon site and an apparent shorter F–$\mu^+$–F bond than predicted from the crystal structure.

Thus the average F···F distance is not distorted and amounts in agreement with the crystallographic data to $R$ = 2.8 Å. The muon is tunneling between two off-center sites in the double minimum potential. Each site is positioned 0.4 Å away from the center (Fig. 4).

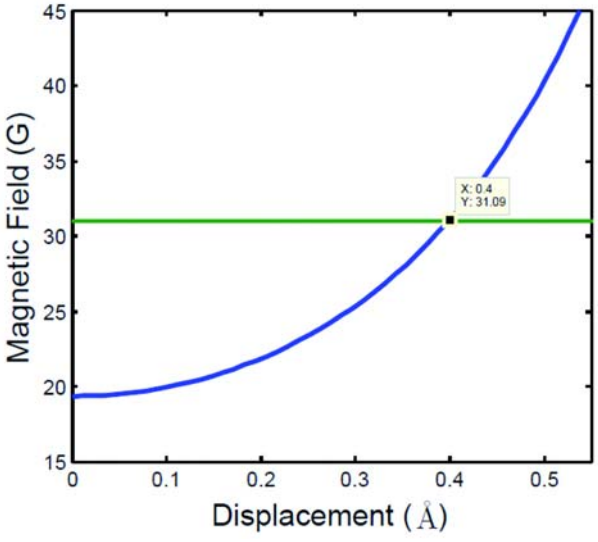


**Figure 4:** Magnetic field at the muon site when the muon is displaced from the central position. The F–$\mu^+$–F distance 2.8 Å is taken from the crystal structure.

# 4. References

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## Povzetek

Mionsko spinsko rotacijo (μSR) in relaksacijo smo uporabili za študij lokalne magnetne strukture $K_3Fe_5F_{15}$. V paramagnetni fazi smo odkrili vodikovi vezi podoben kolinearni kompleks F–$\mu^+$–F s simetričnim dvojnim minimumom z razdaljo F···F = 2,8 Å in razmikom 0,8 Å med minimumoma. Navidezna centralna lega miona v kompleksu je lahko posledica hitrega tuneliranja miona med dvema ekvivalentnima minimumoma v vezi F–$\mu^+$–F.