EUROPEAN SYNCHROTRON RADIATION FACILITY

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Experiment Report Form

ESRF	**Experiment title:** Study of magnetic, elastic and charge order in the multiferroic $K_3Fe_5F_{15}$ compound	**Experiment number**: HE2904
Beamline: ID20	**Date of experiment**: from: 16/11/08 to: 26/11/08	**Date of report**:
Shifts: 18	**Local contact(s)**: Claudio Mazzoli	*Received at ESRF:*

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Report:

The formula $K_{3-x}Fe^{+2}{}_{3-x}Fe^{+3}{}_{2+x}F_{15}$ (0<x<1) identifies a family of multiferroic materials presenting tetragonal tungsten bronze structure. Below the magnetic ordering temperature (120-150 K, depending on stoichiometry) they are ferroelectric, ferroelastic and ferrimagnetic; in addition, charge ordering involving Fe^{2+} and Fe^{3+} ions is observed. As a consequence these compounds are complete multiferroics and they may be considered as model systems for the study of ferroic phenomena and for the comprehension of their interplay [1]. For high potassium content (x<0.25), the crystal lattice is distorted to orthorhombic; this phase has been widely studied and the crystal structure associated to the different ferroic properties is known, allowing the accurate determination of the phase diagram as a function of temperature [2]. A similar study on the potassium-poor compound (1<x<0.75) is in progress [3].
In a previous experiment carried out at ESRF on ID20 beamline (HE2586) we have performed preliminary measures on a $K_3Fe_5F_{15}$ crystal (orthorhombic structure), detecting peculiar behavior of both energy scans and reflection intensities as a function of temperature. The structure of the resonant energy scans relative to several reflections showed dramatic changes between RT and 150 K, well above the magnetic ordering temperature. On the other hand the intensity of some ferroelastic reflections showed a maximum at T_N,

suggesting a possible coupling of the ferroic orders. Nevertheless the complex structure generated by the coexistence of the different phenomena strongly limits the possibility of the computational simulations required for the interpretation of the data. For this reason in our following proposal we suggested the study of the simpler tetragonal system $K_2Fe_5F_{15}$.

During the present experiment (HE2904) we have concentrated our efforts mainly on searching for pure magnetic reflections with the aim to explain the main characteristics of the frustrated ferrimagnetic structure and the nature of its interaction with charge degrees of freedom. A crystal previously characterized by laboratory x-ray diffraction was mounted with the *c* axis in the scattering plane on the four circles diffractometer provided of displex cooling system. The incident beam energy was tuned at the Fe K-edge (7.112 keV) and an MgO (111) crystal was used as a polarisation analyser.

At room temperature (RT) we collected fluorescence data which reveal a complex electronic structure probably due to the simultaneous presence of Fe^{II} and Fe^{III} ions and to multipolar contributions, in analogy with $K_3Fe_5F_{15}$ compound. Then a large number of reflections characteristic of fundamental, charge ordering and ferroelastic structures were studied by means of azimuth and energy scans in σ–σ and σ–π configuration. The structure of the energy resonant data appears complex and characterized by the presence of several features at different energies. Azimuth scans were performed on selected reflections at different energies (Fig. 1). The peculiar behavior observed evidences an oscillation with periodicity equal to 90°, on both channels, with a π/4 phase shift of the σ–σ and σ–π signals. The origin of this behavior is likely connected to the local distortions around Fe ions induced by ferroelectric and ferroelastic structures. Energy and azimuth scans performed at 250 K (above the magnetic ordering temperature) do not show any change with respect to the data collected at RT.

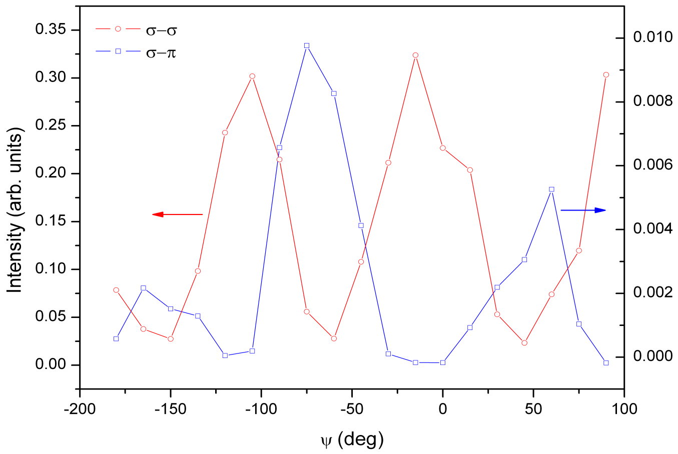

Fig. 1: azimuth scans of the (003) reflection collected at RT in the σ (red) and π (blue) channels, with incident beam energy 7.129 keV.

The sample temperature was then moved to 50 K, in the magnetically ordered phase, where we attempted to identify purely magnetic reflections. No purely magnetic signal could be detected since charge reflections that should be forbidden by symmetry showed a small but measurable off-resonant contribution. This may be originated by the complexity of the system, in which the real structure is the result of the superimposition of different structures related to charge, ferroelectric and ferroelastic orders. Moreover the quality of the crystal sample, essential for the extintion rules to be fulfilled, could be affected by the disorder induced by compositional variations, that in bronze-like structures cannot be excluded.

In order to compare the behavior of the examined sample with that of $K_3Fe_5F_{15}$, the intensity and q-vector of some reflections indicative of fundamental, charge ordering and ferroelastic structures were followed in the range 50-200 K through an explorative data collection. The intensity effects observed crossing the magnetic ordering temperature appear to be much smaller here than in the potassium rich compound, we hence conclude that the system $K_3Fe_5F_{15}$ is more suitable for measures devoted to the study of ferroic coupling.

References:

[1] Fabbrici S., Montanari E., Righi L., Calestani G., Migliori A.; *Chem. Mater*. **16,** 307 (2004)

[2] Mezzadri F., Fabbrici S., Montanari E., Righi L., Calestani G., Gilioli E., Bolzoni F., Migliori A.; *Phys Rev. B*. **78,** 064111 (2008)

[3] Sezzi C.; *Crescita, proprietà strutturali e diagramma di fase del sistema multiferroico $K_xFe_5F_{15}$ per 2<x<2.25* (2008)