EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

ESRF	**Experiment title:** Study of magnetic, elastic and charge order in the multiferroic $K_3Fe_5F_{15}$ compound	**Experiment number**: HE2586
Beamline: ID20	**Date of experiment**: from: 12/09/07 to: 18/09/07	**Date of report**: 29/02/08
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Report:

$K_3Fe_3^{+2}Fe_2^{+3}F_{15}$ is an interesting material with TTB structure which may be considered as a model system for multiferroism. Below the magnetic ordering temperature it is ferroelectric, ferroelastic and ferrimagnetic; in addition it presents charge ordering involving Fe^{2+} and Fe^{3+} ions. The origin of the different properties has been widely studied and the crystal structure associated to each of them is actually known. Charge ordering superstructure (COS), which appears below 490K, leads to the doubling of the *c* axis with respect to the TTB cell. Ferroelasticity, initialy produced by a tetragonal-orthorhombic transition occurring at 570K, becomes connected to a cooperative tilt modulation of FeF_6 octahedra along the *c* axis below 300K. This phenomenon is described by a larger cell (FES superstructure) whose *a* and *b* axes are directed along the COS cell diagonals in *ab* plane. The magnetic behavior is ferrimagnetic with T_c=120 K and is related to a frustrated antiferromagnetic spin interaction. The magnetic structure has been determined through neutron diffraction data leading to the definition of a cell coincident with the COS one.

The aim of the experiment carried out at the ID20 beamline of ESRF was to collect data relative to charge and magnetic order and to give proof of possible coupling between the different ferroic parameters. In particular the electronic structure of iron ions and their local distortions were investigated at RT. Below 120K magnetic reflections were studied in order to define geometry and weight of the magnetic interactions and to determine the multipolar ordering contributions. The crystal 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).

At room temperature 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. Then a large number of reflections characteristic of both TTB and COS structures were studied through θ–2θ scans and energy scans in σ–σ and σ–π configuration. For this purpose an Au crystal was mounted in (222) direction as polarization analyzer. It should be pointed out that often E-scans were affected by the presence of very broad multiple scattering peaks, making their interpretation quite difficult.
Some of the reflections analyzed at RT were studied in the same conditions at 150 and 20K and data were collected at these temperatures also for some satellites reflections related to the FES modulation. Whereas no sensible change was detected between 150 at 20 K, the structure of the resonant energy scans relative to numerous COS reflections changes dramatically between RT and 150 K (Fig. 1), making clear that a deep modification of the electronic structure takes place well above T_N. This fact is quite surprising, since no phase transition is known to occur in this range of temperature. However it could be related to the appearing of short range magnetic order, in agreement an increase of the magnetic background previously observed around 200K in the neutron diffraction measurements.

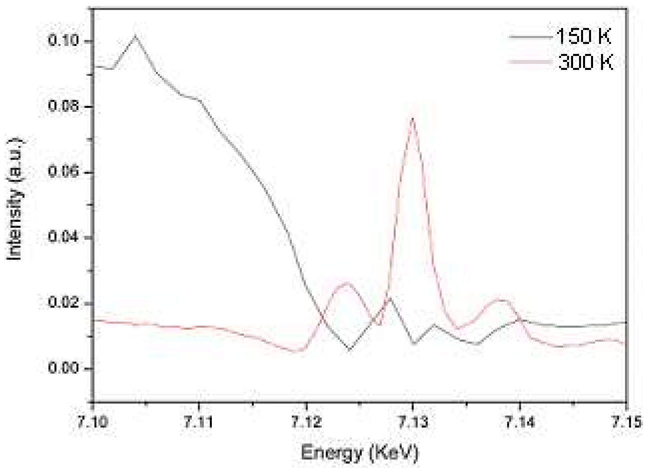

Fig. 1 Energy scan of the 430 reflection at 20 and 300K

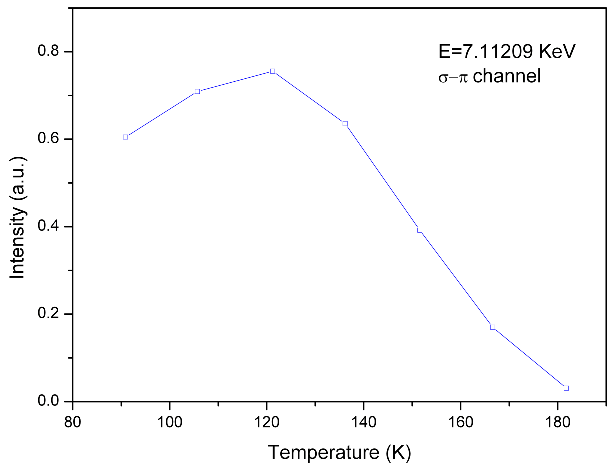

Fig. 2 Intensity variation of the 331 reflection measured in σ–π configuration

This was confirmed by measuring in σ–π configuration, as a function of the temperature, the intensity of the 331 COS reflection, whose contributions show only magnetic nature (Fig. 2). The intensity is close to zero at RT, increases at 200K and shows a maximum at T_N. In order to obtain additional information, we performed azimuth scans relative to this reflection in σ–σ and σ–π channels for different energies of the incident beam. Unfortunately the sample orientation for this particular reflection did not allow us to reach a wide range of azimuth angles, making the successive data analysis prohibitive, also in virtue of the complex multipolar structure of the reflection. These measurements should be repeated by changing the crystal orientation.
Without polarization analyzer and off-resonance we followed the evolution in temperature of the wave vector of the FES modulation, by measuring the peak position of two ferroelastic satellites symmetrical with respect a central COS reflection. FES modulation start as incommensurate at RT and become commensurate at about 200K. This confirm that importance of the electronic transition occurring at this temperature and the necessity to investigate its nature.
We couldn’t perform part of the data collection planned because of beam failure in the last day of measurements.