

Report on the Experiment: HE-3660

***“Electron Dynamics on 4f shells of Eu ions in valence-fluctuating compounds”***

This experiment has been devoted to XPCS measurements of the valence-fluctuating strongly correlated rare-earth compound  $\text{Eu}(\text{Rh}_{1-x}\text{Ir}_x)_2\text{Si}_2$  with  $x=0.5$  to study dynamics of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ion distribution while following the system behavior across the valence transition and aiming to learn about fundamental coupling mechanisms driving redistribution of electrons on the 4f shells of the Eu ions as a function of temperature. During the experiment several important steps have been accomplished: (1) experimental setup was assembled and characterized; (2) crystallographic measurements were performed for the sample quality characterization; (3) the first speckle was observed and the XPCS measurements were performed showing the slow speckle-fluctuations in vicinity of the valence transition.

The experiment was devoted to investigation of the valence instability of the europium electronic configurations in the  $\text{Eu}(\text{Rh}_{1-x}\text{Ir}_x)_2\text{Si}_2$  ( $x=0.5$ ) valence fluctuating compound as a function of temperature. In particular, we were looking for modification of the time scale of the slow fluctuations ( $\sim 10$ - $100$  second time scale) in the coherent speckle pattern formed by scattering of coherent x-rays on the sample with inhomogeneous distribution of the  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  atoms at different temperatures in vicinity of the  $\text{Eu}^{3+}/\text{Eu}^{2+}$  valence transition. Slow fluctuations should be originally driven by intervalence quantum tunneling between the two valence states. In this material the intervalence fluctuations between the two valence states of Eu ions take place on the timescale of about  $\sim 10$ - $13$  ps [1] and should lead to different statistical weights in the distribution of the  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  ions in the sample at different temperatures.

On the macroscopic scale the mixture of the  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  ions in the sample should lead to the presence of  $\text{Eu}^{3+}$  ( $\text{Eu}^{2+}$ ) islands distributed over the sample and this distribution should be non-static, since the random fluctuations of the electronic configurations of the Eu atoms should result in slow evolution of the system in time. The slightly different radius of  $\text{Eu}^{3+}$  or  $\text{Eu}^{2+}$  ions leads to interplay between the ionic configuration of Eu ions and the crystal lattice dynamics. This, in combination with the variation of the potential barrier between the ionic configuration as a function of temperature, leads to the delicate balance between related energies scales. At the temperatures well below the transition dynamics of the system should be very slow, but it becomes sizable in vicinity of the valence transition. Above the transition the fluctuation is expected to slow down again.

The diffractometer was assembled with scintillation counter or CCD camera as a detector. The sample was mounted on the cryostat. Avalanche photo-diode (APD) was used for the x-ray absorption spectroscopy (XAS) measurements. Beamline was turned up and its parameters were characterized. We analyzed influence of the Be dome on coherence of the x-rays by monitoring the Fraunhofer diffraction pattern. It was learned that the dome does disturb the coherence of the x-ray beam, however the x-ray beam remains sufficiently coherent for the XPCS measurements.

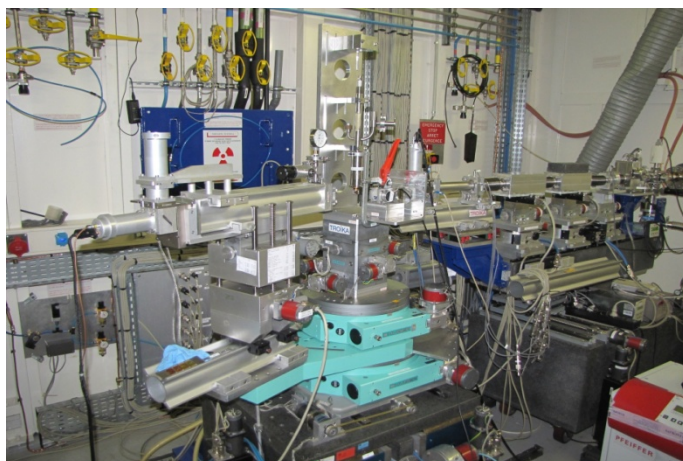


Figure 1. Assembled diffractometer with the cryostat and the detector.

Wide theta-2theta scan confirmed previously calculated positions of the (002) and (004) diffraction peaks.

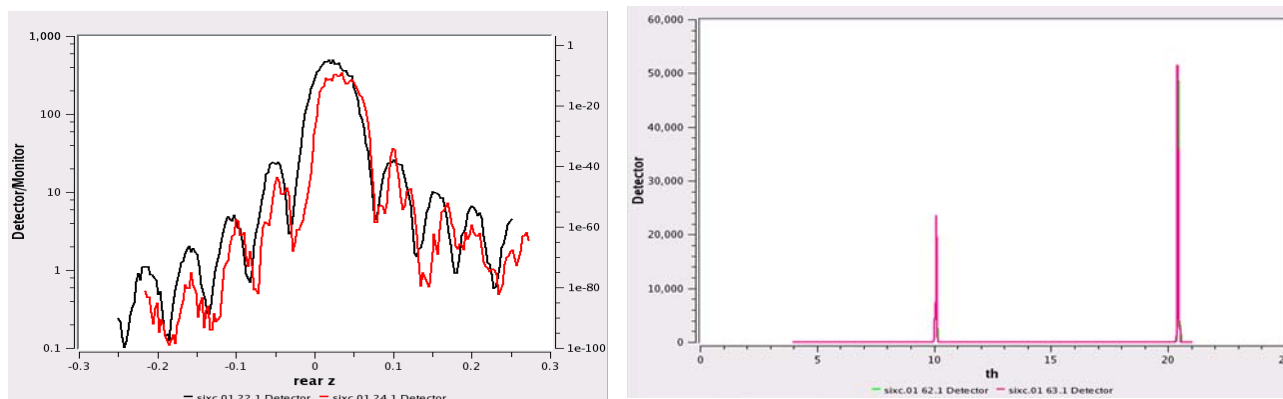


Figure 2. Influence of the Be dome on the Fraunhofer diffraction pattern. Wide theta-2theta scan showing positions of (002) and (004) diffraction peaks.

Theta-2theta and theta scans were performed to characterize the lattice spacing and mosaicity of the sample at  $T=90$  K, direct beam profile was recorded to estimate resolution of the beamline.

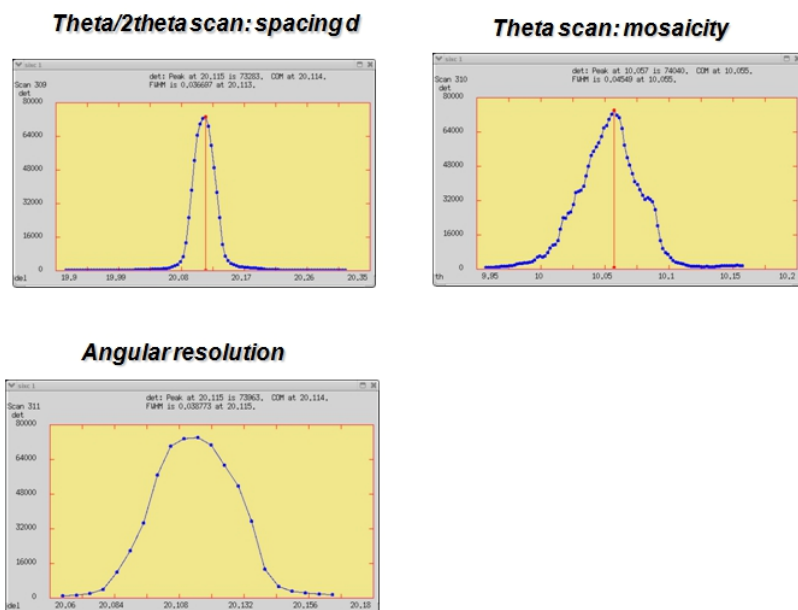


Figure 3. Theta-2theta and theta scans at T=90 K, direct beam profile used to estimate resolution of the beamline.

XAS spectra were taken at T=90 K and T=40 K clearly showing the phase transition between  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ionic configuration as a function of temperature. XAS-intensity maps of the sample taken at the  $\text{Eu}^{2+}$   $L_3$ -edge photon energy shows Rh/Ir segregation within the sample, based on these data good spot on the sample was chosen for the measurements.

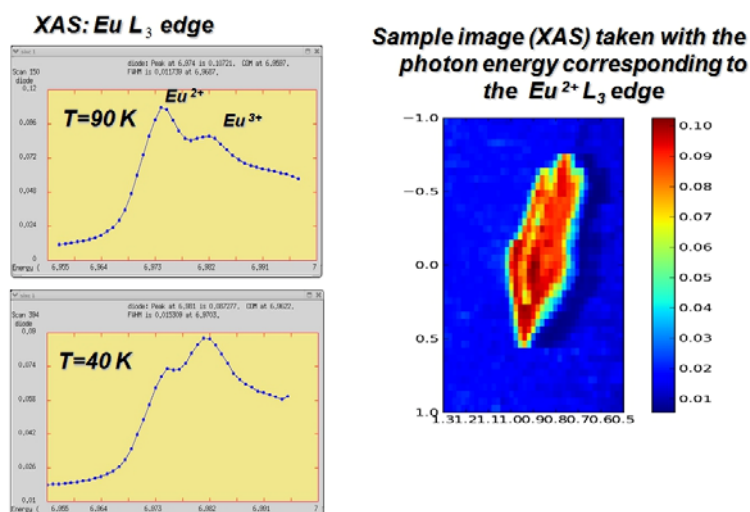


Figure 4. XAS spectra taken at T=90 K and 40 K. XAS-intensity maps of the sample taken at the  $\text{Eu}^{2+}$   $L_3$ -edge photon energy.

Analysis of the data using the intensity intensity time autocorrelation  $g_2$  function [2] shows (see Figure 5 and 6) that the fluctuations do increase at  $T=80$  K compared to the temperature above and below the transition. This coincides with the 1st order phase transition in the compound. This is the promising result, however further experimental work is required to obtain data with smaller temperature step around the transition region.

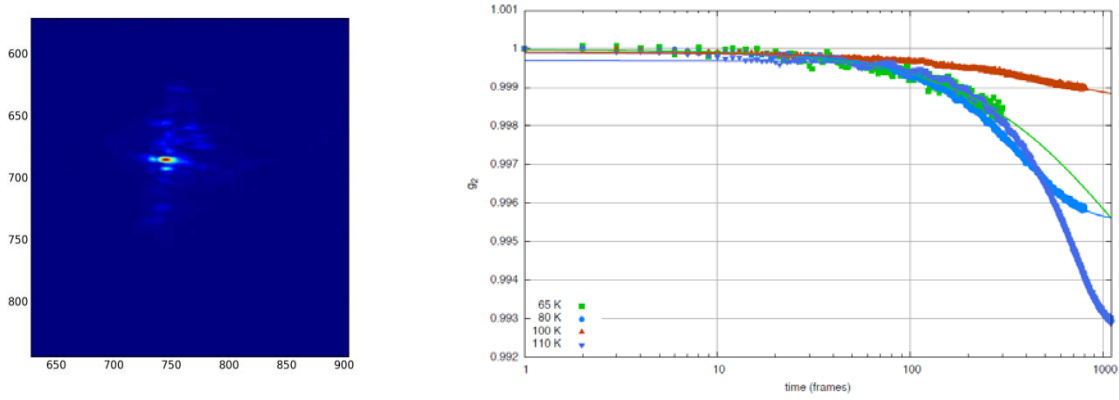


Figure 5. Observed speckle image and XPCS measurements for the 10x10 pixels region that has the largest intensity. The length of the all XPCS scans is approximately 1800 frames. The fits to the data are shown by the lines.

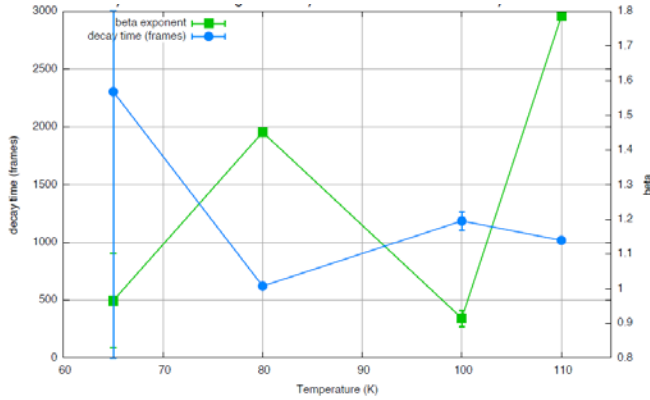


Figure 6. Fit of the XPCS correlation curves using the Equation 1. The decay time reaches a minimum at 80K, meaning the system is speeding up there and slowing down above and below 80K. At 80K the exponent is 1.5, which is indicative of collective motion. On either side of 80K the exponent is  $\sim 1$ , meaning that the system is not moving collectively and the fluctuations are really random.

Fit of the XPCS correlation curves using the following equation:

$$f(x) = a + b \exp(- (t/t_f)^\beta)^2 \quad (1)$$

is presented on Fig. 6. Two important parameters are exponent and decay time. The decay time reaches a minimum at 80K, meaning the system is speeding up there and slowing down above and below 80K. At  $T=80$ K the exponent is 1.5, which is indicative of collective motion. On either side of 80K the exponent is  $\sim 1$ , meaning that the system is not moving collectively and the fluctuations are really random.

Summing up, we obtained the first XPCS data on the  $\text{Eu}(\text{Rh}_{1-x}\text{Ir}_x)_2\text{Si}_2$  ( $x=0.5$ ) valence-fluctuating strongly correlated rare-earth compound aiming to study dynamics of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ions distribution in vicinity of the valence transition region. Results look promising showing change of the time scale of the speckle fluctuations, that was confirmed by correlation analysis.

**References:**

- [1] F. Lu, N. Stoffel, R. A. Neifeld, S. Gunapala, M. Croft and M. L. den Boer, *Phys. Rev. B* **38**, 1508 (1988)
- [2] D. Lumma, L. B. Lurio, S. G. J. Mochrie, and M. Sutton, *Rev. Sci. Instrum.* **71** 3274