| ESRF | **Experiment title:**<br>Temperature induced spin-state transitions in $EuCoO_3$ | **Experiment number**:<br>HE-1917 |
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## Report:

$EuCoO_3$ belongs to a class of *Re*$CoO_3$ (*Re* = rear earth) cobaltites, which show a number of thermally induced magnetic, electronic and structural phase transitions. The exact nature of these transitions remains controversial despite decades of continuing interest [1]. Recently, the spin state properties of cobaltites have gained considerable interest after the proposition of a novel "intermediate" spin (IS) state of the $Co^{3+}$ ions in $LaCoO_3$ [2]. In addition, the discovery of superconductivity in the related hydrated $Na_xCoO_2$ system [3] has boosted the interest on the physics of cobalt oxides. Practical applications of the *Re*$CoO_3$ systems are also starting to surface in the fields of thermoelectronics, oxide fuel cells and gas sensor materials and possibly as specialized catalysts in CO oxidation process. Most of these applications rely heavily on the peculiar spin state properties of cobalt.

The $Co^{3+}$ ions in $EuCoO_3$ have a $3d^6$ valence. According to classical crystal field theory cobalt 3+ ions occupy in the ground state either a low-spin (LS) $t_{2g}^6 e_g^0$; $S = 0$ or a high-spin (HS) $t_{2g}^4 e_g^2$; $S = 2$ configuration, depending on the strength of the octahedral crystal field perturbation. In $LaCoO_3$ the $Co^{3+}$ ions have been, instead, found to occupy a novel "intermediate" spin ground state configuration with $t_{2g}^5 e_g^1$; $S = 1$. At low temperatures the cobalt ions in $LaCoO_3$ are in LS state. The IS state is populated when $LaCoO_3$ is heated trough a transition point at around 90 K [2]. At even higher temperatures around 500 K the system is believed to go into HS state in a second transition. New evidence, however, suggest that the IS state is populated also after the second transition point [4]. For $EuCoO_3$ recent susceptibility data shows that the cobalt ions undergo a first spin transition between 400 K and 800 K [1]. The nature of this spin transition seems to be similar to $LaCoO_3$, with cobalt ions populating the intermediate spin state at elevated temperatures. At even higher temperatures the converging cobalt susceptibilities in $LaCoO_3$ and $EuCoO_3$ point to a common spin state. Orbital ordering phenomena are most likely playing a role in these transitions. Very little experimental data, however, exists on $EuCoO_3$ spin phase transitions.

In this experiment we looked at the spin state of cobalt in $EuCoO_3$ as a function of temperature using cobalt $K\beta$ emission and high resolution cobalt K-edge absorption spectroscopy. These techniques provide a direct probe of the local spin moment and *d* electron states. The experiment was performed at ESRF ID26 beamline. The Rowland circle crystal spectrometer equipped with an avalanche photodiode was used for analyzing the emitted radiation. We utilized Si(444) analyzer crystal with 1m bending radius, yielding 1.8 eV energy resolution. The count rates at the peak cobalt K$\beta$ emission line were in the order of 50 kcps. During the experiment we measured cobalt $K\beta$ emission and high resolution cobalt K-edge absorption spectra in a temperature range of 300-1000K at about 35 temperature points using a resistor heated vacuum oven for controlling the sample temperature.

The Kβ emission spectra revealed an increase in the intensity of a satellite peak of the main line. The intensity of this satellite is proportional to the local spin magnetic moment of the cobalt ions. Thus, the observed increase in the intensity of the satellite indicates an increase in the spin moment of the cobalt ions between 340K and 720K. The reordering of the cobalt 3*d* electrons on $t_{2g}$ and $e_g$ orbitals, responsible for the increased moment, was observed also in the cobalt K-edge absorption spectra. The so called pre-peak in the absorption spectra is partly due to $1s \rightarrow 3d$ transitions and the partial filling of the higher lying $e_g$ orbital at elevated temperatures is reflected in the evolution of the peak structure.

In conclusion, we measured the cobalt Kβ emission spectroscopy and high-resolution cobalt K-edge absorption spectra of $EuCoO_3$. The high technical quality and highly professional operational expertise of the ESRF beamline ID26 enabled the measurements of very high quality data at a large number of temperature points. The data reveals an increase in the local magnetic moment of the cobalt ions when $EuCoO_3$ is heated from room temperature to 1000 K. At room temperature the cobalt ions occupy LS ground state. The increase in the magnetic moment is due likely due to the population of IS ground state configuration of cobalt ions at elevated temperatures. Further effort is on the way to analyze the experimental spectra in more detail.

References:


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