ESRF	**Experiment title:** Investigation of spin cross-over reversible transition in a mononuclear Cobalt(II) complex using *K*-edge XAS and XMCD (Part I)	**Experiment number**: HC-1788
Beamline: ID12	**Date of experiment**: from: 23 July 2015 to: 27 July 2015	**Date of report**: 10 Sept 2015
Shifts: 12	**Local contact(s)**: Dr. François Guillou	*Received at ESRF:*

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Report:

The goal of the experiment was to investigate the thermally induced hysteretic transition between the high-spin (HS) and low-spin (LS) states of cobalt(II) in the mononuclear complex $Co^{II}(dpzca)_2$ [1]. To do so, we have performed XAS and XMCD measurements at the Co *K*-edge. As a reference system, measurements were also performed on the pyrazine-pyridine analogue, $Co^{II}(pypzca)_2$, which was reported to remain HS down to 4K.

Both samples were mounted in the form of pressed pellets in the 17 Tesla cryomagnet. XMCD and XAS spectra were collected for $Co(dpzca)_2$ and $Co(pypzca)_2$ first at T=295K, then at T=100K, where the spin conversion is expected to be complete according to standard magnetometric techniques [1], and at T=2K. While the XAS spectrum of the reference sample $Co(pypzca)_2$ does not change with temperature, there are significant differences in the XAS spectral signature of $Co(dpzca)_2$ at high temperature (T=295K) and at low temperature (T=100K and T=2K). Although the agreement between theory and experiment can still be improved in the future, the measured variations are actually as significant as those predicted by our preliminary Ligand Field Calculations, which were shown in the submitted proposal. XMCD is detected in the pre-edge region and is associated to electric quadrupole transitions towards unoccupied 3d states. The effect is very small (a few 10^{-4}) at ambient temperature in both samples. As expected, it grows significantly at low temperature in $Co(pypzca)_2$. On the other hand, the XMCD of $Co(dpzca)_2$ remains very small at 100K, which is also consistent with a transition from HS to LS states of the Co^{II} ion. The very good-quality XMCD at 2.2K allows a fine comparison between the $Co(pypzca)_2$ (HS) and the $Co^{II}(dpzca)_2$ (LS) spectra. The XAS and XMCD spectra will be further interpreted by the means of more advanced Ligand Field Multiplet calculations for the pre-edge region and of relativistic DFT calculations for the edge region.

Taking advantage of the significant differences observed in the XAS spectrum of $Co^{II}(dpzca)_2$ between 295K and 100K, we further investigated the SCO transition by following the spectral changes as a function of temperature. In the absence of magnetic field, we recorded XAS at 100K, 120K and every 5K between 140K and 200K. Then after increasing the temperature up to 250K we decreased it back, down to 100K. We investigated the progressive changes in the spectra by fitting the spectrum measured at a given temperature as a linear combination of the HS spectrum (200K) and the LS spectrum (100K). The coefficients obtained this way are reported as a function of temperature in Figure 1. It shows that the transition is abrupt and hysteretic. The opening of the hysteresis is almost 3K, which is smaller by 11K

than what had been obtained from susceptibility measurement with a sweep rate of 5K.min^{-1} [Ref. 1, shown in Figure 2] SQUID measurements are now in progress on the sample that was measured during the beamtime, with the same dynamics in the change of temperature. The aim is to compare the local temperature dependency of the transition (probed by XAS on Co K-edge) to the macroscopic one.

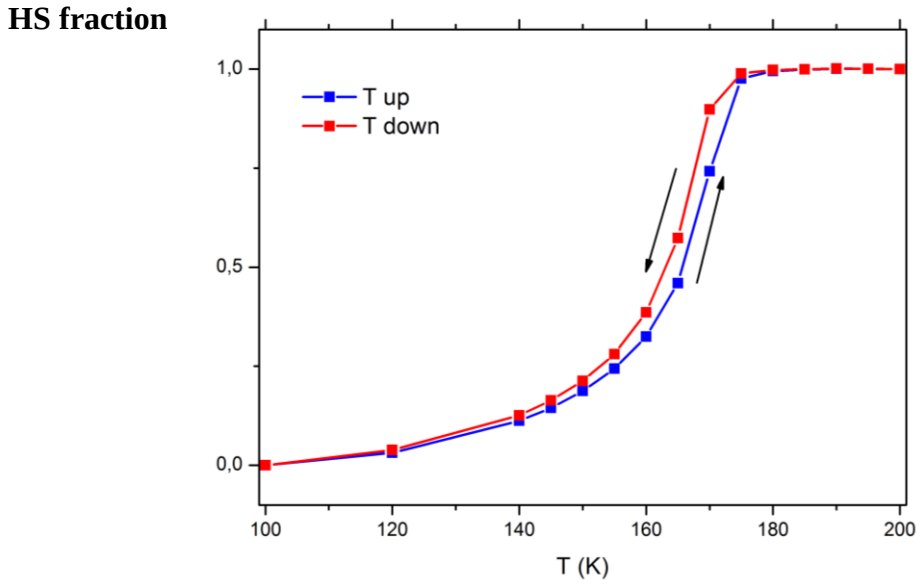

Figure 1. Temperature dependence of the HS fraction, which is obtained by fitting the XAS spectra recorded upon heating and cooling as a linear combination of the spectrum measured at 200K and the spectrum measured at 100K.

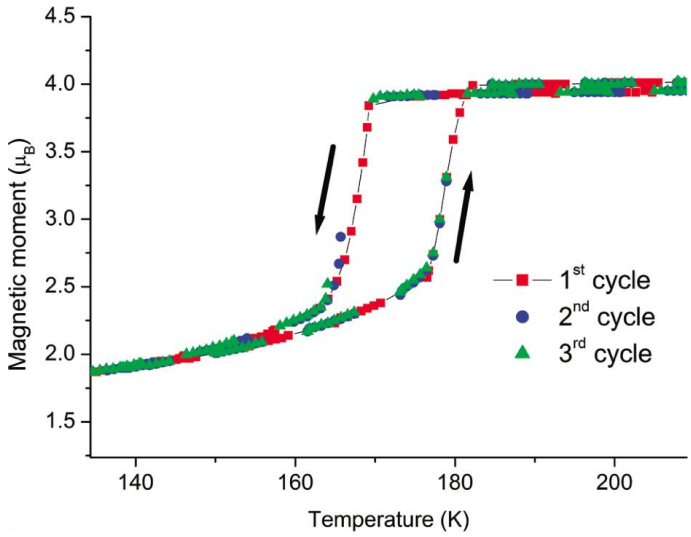

Figure2. Temperature dependence of the effective magnetic moment obtained from susceptibility measurements in Co^{II}-dpzca$_2$. [1]

References

[1]. M. Cowan, J. Olguin, S. Narayanaswamy, J. Tallon and S. Brooker, Journal of the Americal Chemical Society 2012, 134, 2892-2894.