ESRF	Experiment title: Determination of spin and orbital moments of Re(I) in the molecular nanomagnet [Er($ReCp_2$)$_3$] and its Gd analog	**Experiment number**: CH-6414
Beamline: ID12	**Date of experiment**: from: 12.09.2022 to: 19.09.2022	**Date of report**:
Shifts: 15	**Local contact(s)**: Andrei Rogalev	*Received at ESRF:*

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Abstract:

The design strategy for the synthesis of high performance molecular nanomagnets (MNMs) based on metal ions surrrounded by p-electron donor ligands is reaching its limits as exemplified by the organometalic MNM [(Cp^{iPr5})Dy(Cp)]$^+$ (Cp^{iPr5}, penta-iso-propylcyclopentadienyl; Cp**,** pentamethylcyclopentadienyl) retaining magnetic memory effect up to 80 K. The new design ideas go beyond p-electron donors as in the [$Ln^{III}(Re^{I}Cp_2)_3$] (Ln = Gd^{III}, Er^{III}) compound, where three Re^{I} metals act as d-electron donors toward the central lanthanide Ln^{III}. Results of magnetic measurements demonstrate that this compound has the highest energy barrier for magnetization reversal among known Er^{III}-based MNMs (313 K). This might be caused by the nature of the metal-metal bonds in such a system. In this experiment the XMCD spectra of the magnetically isotropic [$Gd^{III}(Re^{I}Cp_2)_3$] analog, where the magnetic moment arises solely from unpaired electrons, were compared with thos recorded for magnetically anisotropic [$Er^{III}(Re^{I}Cp_2)_3$] SMMs, where spin-orbit coupling is responsible for the magnetic properties. Such an experiment enabled the assessment of the magnetic moment delocalization from the central lanthanide center towards the surrounding diamagnetic donor Re^{I} atoms. Additionally, Fe_2Re_2 sample with Fe-Re metal-metal bonds was studied for 3d-5d interactions. This research was only possible thanks to the ESRF and XMCD ID12 beamlinee. This method is selective towards the elements constituting the molecules as it probes their X-ray absorption edges, enabling separate study of magnetic moments localized at different metal ion centers. Moroever, the strength of the XMCD signal is related to the magnetic moment of the targeted metal ion. The list of data collected during the experiment is presented in Table 1:

Table 1. Summary of XANES and XMCD experiments performed over the course of the CH-6414. Comment rely the most important conclusion or that the sample's decomposition rendered interpretation inconclusive.

No.	*Sample*	*Edge*	*Transition*	*Temp*	*Fields / T*	*Comment*
1	$ErRe_3$	Er	L_2, L_3	3 K	−17, +17	Hysteresis
2	$ErRe_3$	Er	L_2, L_3	3 K	+10, −10	XMCD at Er
3	$ErRe_3$	Re	L_2	3 K	+ 5, − 5	Thermal damage/undulator artifact
4	$ErRe_3$	Re	L_2, L_3	3 K	+10, −10	Thermal damage/undulator artifact
5	Fe_2Re_2	Re	L_2, L_3	3 K	−17, +17	Thermal damage/undulator artifact
6	GdRe3	Re	L_2, L_3	3 K	−17, +17	XMCD at the Re or undulator artifact
	Supporting samples					
8	$Er(btmsm)_3$	Er	L_2, L_3	RT	-	XANES
9	$ErCl_3$	Er	L_2, L_3	RT	-	XANES
10	$Gd(btmsm)_3$	Gd	L_2, L_3	RT	-	XANES
11	Cp_2ReH	Re	L_2, L_3	RT	-	XANES

Experimental details:

Measurements were conducted on powder samples immersed in parafin oil and covered by kapton tape which were prepared using a state-of-the-art gloveboxe available at the ESRF Chemistry Laboratory managed by Harald Müller.

Results and conclusions (bold text):

Experiments started with $ErRe_3$ sample at the Erbium L_2 and L_3-edges where XANES and XMCD spectra were collected (Figure 1). Clear XMCD signal could be observed. The magnetic field dependence of the XMCD signal at both edges were then measured to compare with the magnetization vs field curves obtained beforehand by SQUID magnetometry. The overlap was observed for $M(H)$ curves recoreded using SQUID magneotmeter at 5K, which indicates the actual temperature during the measurements at the ESRF ID12 beamline.

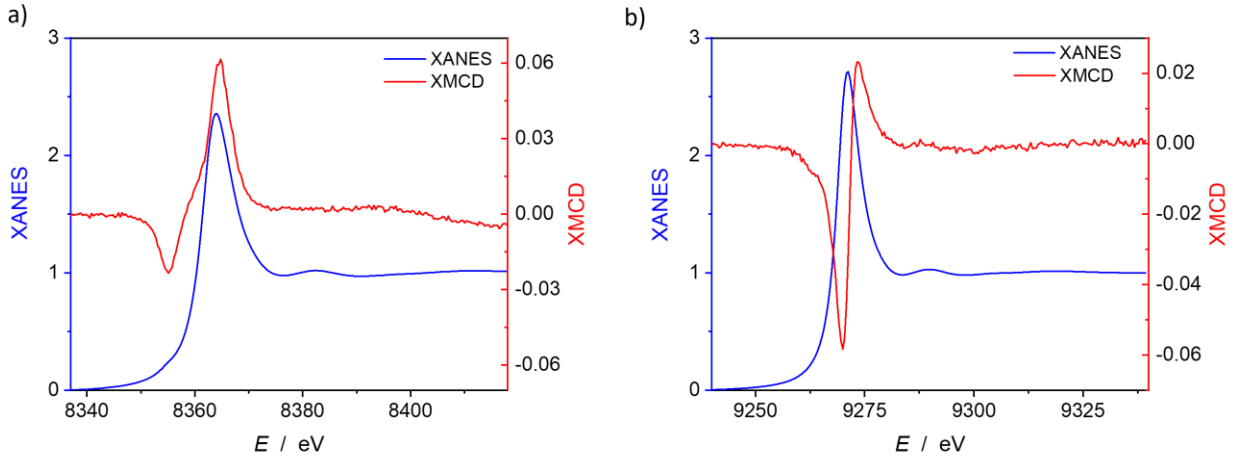

Figure 1. XMCD and XANES spectra of $ErRe_3$ at Er L_3-edge a) and L_2-edge b).

Then, the focus was shifted towards the Re $L_{2,3}$ – absorption edges in order to detect the possible magnetic moment transfer from Er^{III} to the diamagnetic Re^{I} (Table 1 rows no. 3 and 4), where the XMCD spectra were measured at ±5 T and ±10 T. Data analysis could not prove significant magnetic moment transfer to Re^{I} in $ErRe_3$ due to the weakness of the XMCD signal and impact of other overlapping effects like thermal decomposition of the sample and issues with the undulator generating some artifact signal. **To summarize, no appreciable XMCD signal was detected at the Re absorption edges for $ErRe_3$.**

Measuremens of Fe_2Re_2 sample containing Fe-Re 3d-5d metal-metal bonds were performed to assess the delocalization of magnetic moment towards the diamagnetic Re^{I} in this system with supposedly more accessible 3d orbitals of the Fe centers as compared to 4f orbitals of the Er. Similarly to $ErRe_3$, the results obtained for Fe_2Re_2 compound were inconclusive suggesting undetectable magnetic moment transfer from Fe to Re.

Similar set of XANES/XMCD measuremnts on the $GdRe_3$ were more interesting. **$GdRe_3$ system exhibited weak but clear XMCD signal at the Re $L_{2,3}$-edges** suggesting the presence of significant magnetic moment at the formally diamagnetic Re^{I} ions (Figure 2) transferred from the central Gd^{III}. **However, due to the possible problems with the undulator during the beamtime, the experiements should be repeated and extended to include $DyRe_3$ analog. This would confirm the possible observation of the magnetic momet transfer and help us understand its mechanism.**

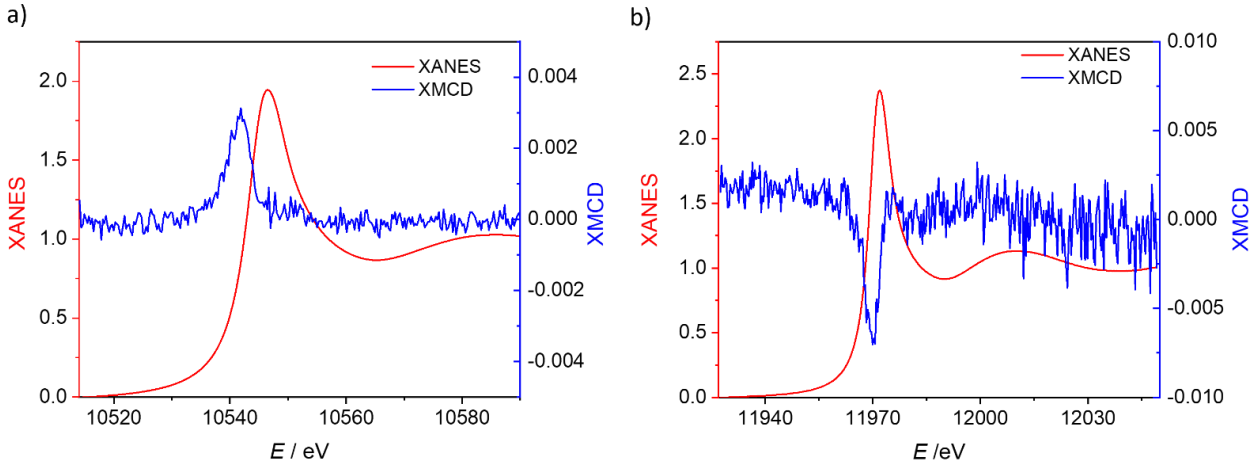

Figure 2. XMCD and XANES spectra of $GdRe_3$ at Re L_3-edge a) and Re L_2-edge b).