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Experiment Report Form

ESRF	**Experiment title:** XMCD study of unusual magnetism in molecular systems with orbitally degenerate transition metal ions	**Experiment number**: CH-5016
Beamline: ID22	**Date of experiment**: from: 17.05.2017 to: 23.05.2017	**Date of report**: 08.09.2017 *Received at ESRF:*
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In the experiment we have examined two groups of molecular magnetic compounds based on $[Re^{IV}(CN)_7]^{3-}$ and $[W(CN)_8]^{3-}$ complex. The 1st group involves $(Bu_4N)_3[Re(CN)_7]$ (**1**) and $(Bu_4N)_3[W(CN)_8]$ (**2**) mononuclear precursors. The 2nd group includes 5d-3d heterometallic coordination polymers of various dimensionality: 1D polymer $[Mn^{III}(SB^{2+})Re(CN)_7]^{2+}{}_n$, 2D layered compounds, $[(Mn^{III}(SB))_2Re(CN)_7]^{+}{}_n$ and $[(Mn^{III}(SB))_2W(CN)_8]^{+}{}_n$, and a 3D compound $[(Mn^{III}(SB))_3Re(CN)_7]_n$; here SB is a quadridentate Schiff base ligand. This study is motivated by presence of unquenched orbital momentum *L* in orbitally-degenerate cyanometallates $[Os(CN)_7]^{3-}$ [1], $[Mo(CN)_7]^{4-}$ [2], $[Re(CN)_7]^{3-}$ [3], which produces highly anisotropic spin coupling with high-spin metal ions tied by cyanides[1]. In contrast to other techniques (magnetic, optical, EPR and INS measurements), XMCD provides direct info on the spin and orbital components of the magnetic moment induced by Re, using the sum rules. One more important goal was to inspect manifestations of the interplay of anisotropic Re-CN-Mn spin coupling and single-ion ZFS anisotropy of Mn^{III} ions. It was done by a comparative XMCD study of a series of 0D (**1** and **2**), 1D÷3D compounds at the Re L_2/L_3 and K_{Mn} edges and T=2.7 K. The XANES spectra for Re/W ions are collected in Figure 1. Determined from the experiment data the orbital (μ_L) and spin (μ_S) magnetic moments treated in terms of the magneto-optical sum rules are summarized in Table 1. The XMCD spectra of Mn_nRe and Mn_2W/2D *vs* **1** and **2** are presented in Figure 2. The field variations of the XMCD signal for **1** and **2** and for the heterometallic compounds as well as magnetization curves and XANES *vs* XMCD spectra for all samples measured on K_{Mn} edge at ~2.7 K are shown in Figure 3. These results clearly show a distinct orbital momentum $\langle L_z \rangle$ on Re and very unusual variation of the μ_L/μ_S ratio across the 1D-2D-3D series. XMCD spectra reveal a hysteresis loop for 2D and 3D Re compounds and some signature of metamagnetic transitions at low field. From these data, we can say that the CH-5016 experiment has provided a very rich and highly intriguing information on the magnetic behavior of Re-based molecular magnets. A theoretical study based on a microscopic model and quantum chemical calculations is underway.

[1] J. Dreiser, K.S. Pedersen, A. Schnegg, K. Holldack, J. Nehrkorn, M. Sigrist, P. Tregenna-Piggott, H. Mutka, H. Weihe, V.S. Mironov, J. Bendix,; Waldmann, O. *Chem. Eur. J.* **2013**, 19, 3693. [2] V.S. Mironov, *Inorg. Chem.* **2015**, 54, 11339. [3] D.G. Samsonenko, C. Paulsen, E. Lhotel, V.S. Mironov, K.E. Vostrikova *Inorg. Chem.* **2014**, *53*, 10217.

Table 1. The data obtained for the samples applying the magneto-optical sum-rules.

	$[Re(CN)_7]^{3-}$	$[W(CN)_8]^{3-}$	Mn_1Re/1D	Mn_3Re/3D	Mn_2Re/2D	Mn_2W/2D	Remarks
number of holes	7	7	7	7	7	7	n_h, fixed
branching ratio	0.708	0.682	0.710	0.703	0.703	0.677	$B=IL_3/(IL_3+IL_2)$
$N_{5/2}$	1.450	1.673	1.437	1.496	1.493	1.713	
$N_{3/2}$	1.550	1.327	1.563	1.504	1.507	1.287	
$\mu_L = -\langle L_z \rangle$	0.286	0.018	-0.075	-0.200	-0.231	-0.004	μ_B
$\langle S_{eff} \rangle = \langle S_z \rangle + (7/2)\langle T_z \rangle$	-0.029	-0.234	-0.050	0.024	-0.015	0.262	
$\langle S_z \rangle$	-0.407	-0.241	-0.050	0.024	-0.015	0.262	
$\mu_S = -2\langle S_z \rangle$	0.814	0.482	0.100	-0.048	0.030	-0.525	μ_B
$-\mu_L/\mu_S$	-0.037	-0.037	0.754	-4.149	7.747	-0.007	
J	0.5	0.5					magnetization fit
g	2.2	1					magnetization fit
$\mu_{Tot} = g*J$	1.1	0.5					μ_B
$\mu_S = \mu_{Tot} - \mu_L$	0.814	0.482					μ_B
$\langle S_z \rangle = -\mu_S/2$	-0.407	-0.241	Mn_1Re/1D = $[Mn^{III}(SB^{2+})Re(CN)_7]^{2+}{}_n$; Mn_2Re/2D = $[(Mn^{III}(SB))_2Re(CN)_7]^{+}{}_n$ Mn_2W/2D = $[(Mn^{III}(SB))_2W(CN)_8]^{+}{}_n$, Mn_3Re/3D = $[(Mn^{III}(SB))_3Re(CN)_7]_n$				
$\langle T_z \rangle$	0.108	0.002					
$\langle T_z \rangle / \langle S_z \rangle$	-0.265	-0.009					

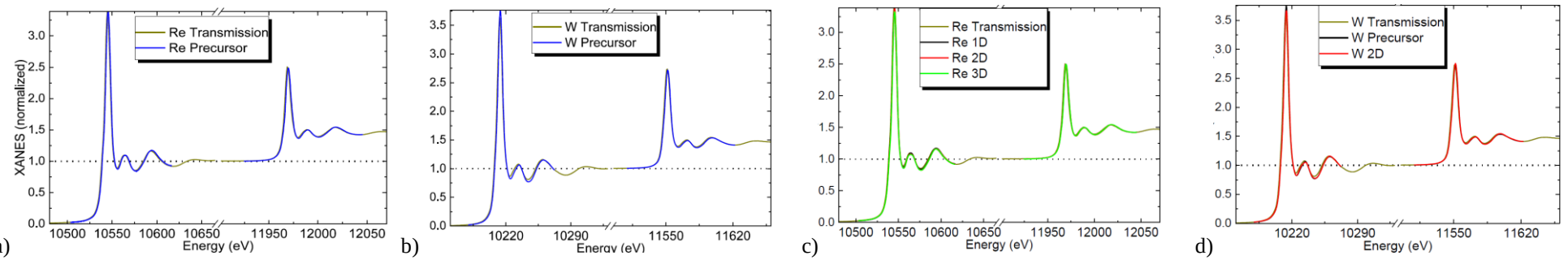

Figure 1. Corrected for self-absorption normalized XANES spectra for **1** (a), **2** (b), Mn_nRe (c) and Mn_2W/2D (d) *vs* transmission data of **1** and **2**; All data were collected at 2.7 K and H=17 T.

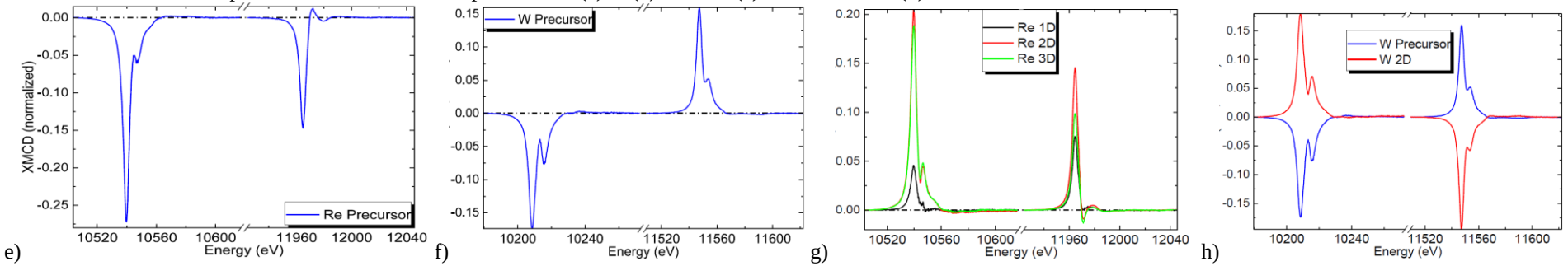

Figure 2. Normalized XMCD spectra of Mn_nRe (e) and Mn_2W/2D (f) *vs* **1** and **2**; All data were collected at 2.7 K and H=17 T.

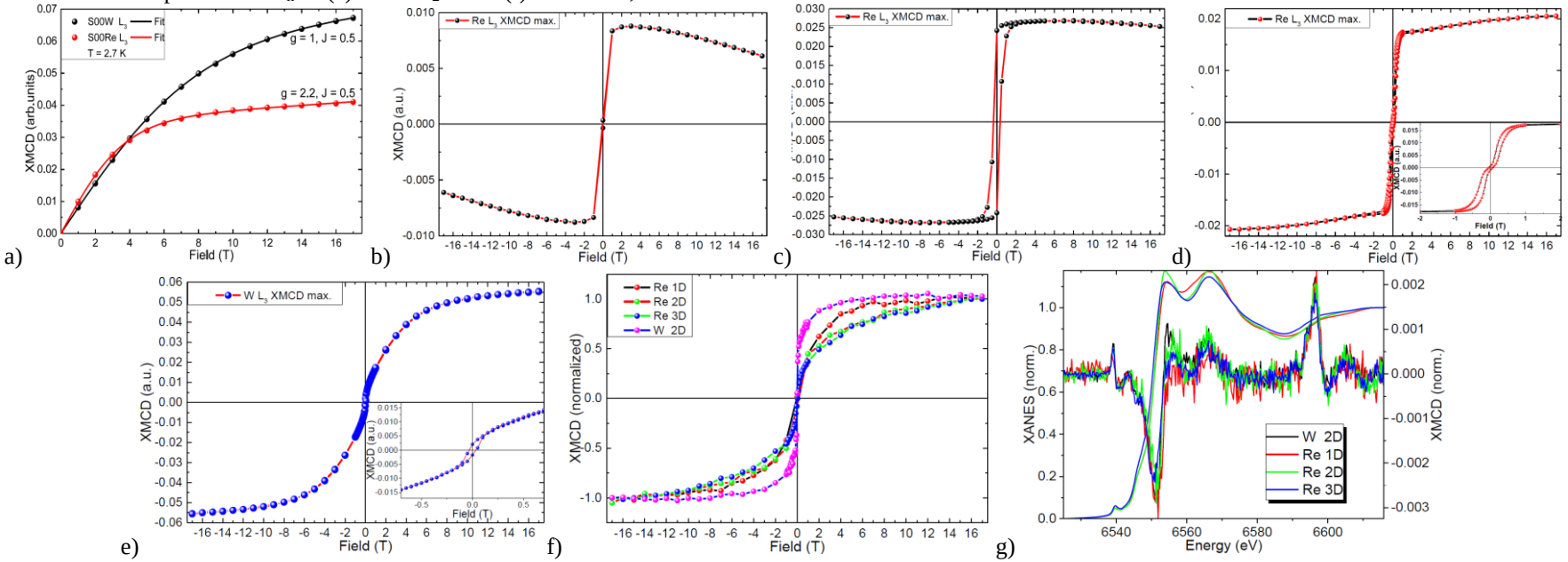

Figure 3. XMCD/H plots (dots) measured on Re/W L_3 edges for **1** (red) and **2** (black) and their fits to a sum of Brillouin and Van-Vleck functions (a). Magnetization curves measured on Re/W L_3 edge for Mn_1Re/1D (b), Mn_2Re/2D (c), Mn_3Re/3D (d), Mn_2W/2D (e). Magnetization curves (f) and XANES *vs* XMCD spectra (g) for all samples measured on K_{Mn} absorption edge at ~2.7 K.