ESRF	**Experiment title:** Magnetic circular dichroism on superparamagnetic metal based clusters	**Experiment number:** HE651
Beamline: ID-12b	**Date of experiment:** from: 1-March-2000 to: 6-March-2000	**Date of report:** 1-August-2000
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We have collected the first XMCD spectra on molecular superparamagnets. In particular, the Mn-$L_{III,II}$ edges of $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_{24}]\bullet 2CH_3COOH\bullet 4H_2O$ (in short Mn12) and at the Fe-$L_{III,II}$ edges in $[Fe_8O_2(OH)_{12}(tacn)_6]Br_8\ 9H_2O$ (in short Fe8) have been investigated at different temperatures and in different fields. The above compounds are up to now two of the most accurately investigated systems presenting magnetic properties at molecular scale. The structure of Mn12 can be described as formed by an external ring of 8 Mn(III) ions (S=2) and an internal tetrahedron of four Mn(IV) ions (S=3/2). In the low temparature range, the molecule behaves as a magnetic cluster with a ground state of total spin S=10. This state can be loosely described setting all the Mn(III) ions with spin up (S=2x8=16), and all the Mn(IV) ions with spin down (S=-4x3/2=-6). The Fe8 compounds presents a well known "butterfly" spin structure in which S=5/2 Fe(III) ions are coupled via antiferromagnetic interactions: the total spin in the ground state is again S=10. The ground state multiplet both in Mn12 and Fe8 is split by the crystal field effects to leave the M=±10 components lying lowest; a "superparamagnetic" barrier Δ/k_B (60K in Mn12 and 27K in Fe8) is formed. In our XMCD experiment (exp. no. HE-651) on Mn12 and Fe8, we have found (in the range 5-100 K) a qualitative agreement between the standard magnetization temperature behavior obtained by SQUID measurements and the one found by analyzing the dichroic signal (figures 1 and 2). In particular for Mn12 the Mn(III) and Mn(IV) contributions are clearly distinguishable (figure 3), and evidence the opposite spin arrangement of the two ions, while for Fe8 the typical two peaks structure of Fe(III) compounds is found (figure 4). A quantitative analysis of the dichroic signals yielded for both Mn12 and Fe8 a negligible $\langle L_z \rangle$ (figures 3 and 4), thus giving the first experimental evidence of the quenching of the angular momentum by the crystal field in these systems.

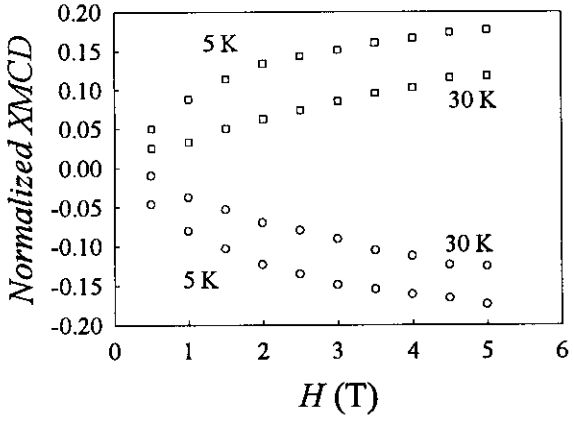

Fig. 1 – Normalized XMCD intensity for the peak at 642 eV (circles) and 643.5 eV (squares) in Mn12 as a function of H and at different temperatures.

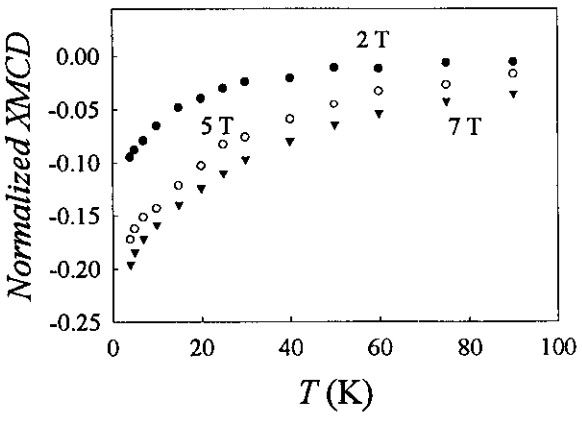

Fig. 2 – Normalized XMCD intensity for the peak at *c.a.* 710 eV in Fe8 as a function of T and at different fields.

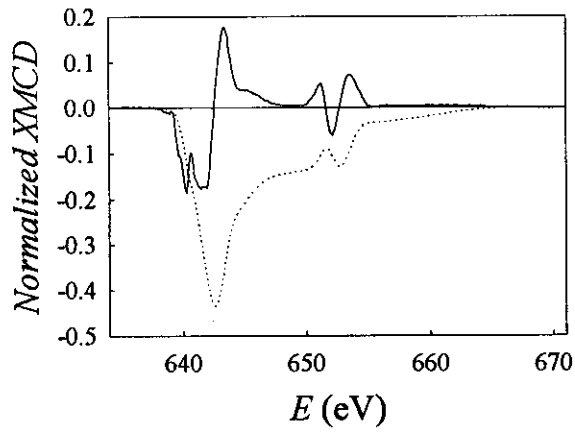

Fig. 3 – XMCD signal, normalized at unit white line intensity at the L-III edge for the Mn12 compound (full line). The field is 5 T and temperature is 5 K. The dotted line is the integrated XMCD. By direct comparison with the XAS spectra of Mn_2O_3 and MnO_2, the peaks between 640 and 642.5 eV are attributed to Mn(III), while the peak at c.a. 643.5 eV is attributed to Mn(IV).

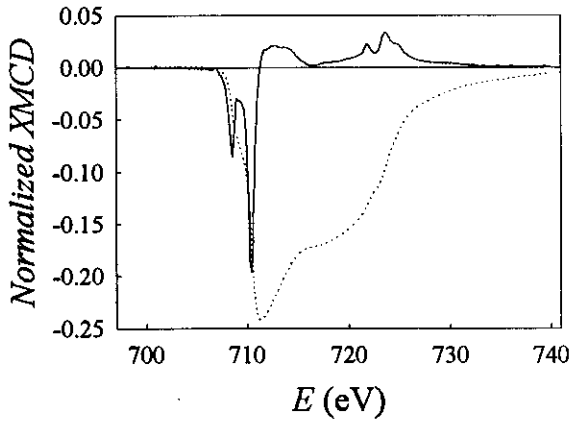

Fig. 4 – XMCD signal, normalized at unit white line intensity at the L-III edge for the Fe8 compound (full line). The field is 7 T and temperature is 4 K. The dotted line is the integrated XMCD.