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Intracluster interactions in “butterfly” $\{Fe_3LnO_2\}$ molecules

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ABSTRACT

The magnetization contributions of the Fe_3 and Ln subcluster in the “butterfly” molecule $[Fe_3Ln(\mu_3\text{-}O)_2(CCl_3COO)_8(H_2O)(THF)_3]$, in brief $\{Fe_3LnO_2\}$, with Ln=Lu, Gd, Tb, Dy and Ho, have been determined by a combination of vibrating sample magnetometry and x-ray circular magnetic dichroism at low temperature and magnetic field up to 14 T. These contributions have been explained in terms of an effective spin model where the Fe_3 is described by a $S_{Fe_3} = 5/2$ spin, Gd by an isotropic $J=7/2$, Dy by a Kramers doublet, and non-Kramers ions Tb and Ho by a ligand field split doublet. The intracluster interactions J_{FeLn} have been found to amount to a few K.

1. Introduction

The search for new polynuclear coordination compounds that behave as single molecule magnets (SMMs) has attracted special attention in the past decade, due to the possibility to use them as magnetic storage or quantum computing elements. Besides, they provide a variety of new chemical–physical properties, such as the possibility to chemically induce magnetic anisotropy and to exploit intramolecular exchange interactions. In the last decade the “butterfly” molecules $\{Fe_3LnO_2\}$ have become a paradigmatic example of such type of polynuclear molecules, where the Ln(III) may be substituted by ions with very different anisotropies [1].

The present paper deals with the microscopic characterization of the magnetic behavior of the $\{Fe_3LnO_2\}$ compounds. The main objective is to study the interaction between the Fe_3 subcluster and the Ln within the $\{Fe_3LnO_2\}$ cluster, by applying a competing external field at low temperatures to provoke the polarization of the Fe and Ln magnetization within the molecule.

A major problem in this type of compounds is that their magnetic properties are complicated by the large spin–orbit coupling effects of the Ln(III) ions, hampering the quantitative determination of the magnitude of the exchange parameters within these molecules, and the description of the resulting ground state [2].

Therefore, new techniques which explore these molecules at an element selective level are needed to provide information about the microscopic arrangement of magnetic moments and the mechanisms of relative spin orientation within a molecule [3]. An example of these element sensitive probes is the x-ray magnetic circular dichroism (XMCD) technique, which provides element specific magnetization curves that may be compared to cluster magnetization acquired by VSM magnetometry. The combination of XMCD and VSM is able to resolve very small magnetic coupling values in 3d–4f clusters. A detailed magnetic study involving XMCD and VSM magnetometry was carried out to characterize the exchange coupling and magnetic anisotropies of the present “butterfly” molecules. In particular, the evolution of the local magnetization from the 4f states with the magnetic field was explored experimentally by means of XMCD measurements as a function of the applied field at the Ln $L_{2,3}$ edges, and theoretically, by simulation of the Ln and Fe_3 subcluster magnetization dependence on applied field and temperature separately.

In this work we review and compare the results obtained with the methods developed in [3] on Ln substitutions: Lu, non-magnetic ion; Gd, isotropic Kramers ion; Dy, anisotropic Kramers ion, and Tb and Ho as anisotropic non-Kramers ions.

2. Structure and experimental details

The molecule $[Fe_3Ln(\mu_3\text{-}O)_2(CCl_3COO)_8(H_2O)(THF)_3]$ [1], in brief $\{Fe_3LnO_2\}$ has a “butterfly” type structure, with two $Fe_2Ln(\mu_3\text{-}O)$

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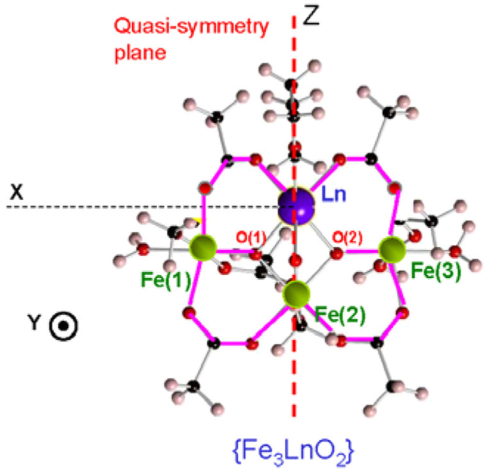

Fig. 1. Structure of the {Fe_3LnO_2} complex. The initial reference system of the Fe_3 subcluster is named as *XYZ*, with *Z* parallel to the quasi-symmetry plane of the molecule.

triangular wings sharing a Ln–Fe body and a dihedral angle between the wings of approximately 146.5° (see Fig. 1). The magnetic core of the molecule can be considered as a triangular pyramid where the basis is an obtuse isosceles triangle with three Fe(III) ions located at the vertices, and the Ln ions located at the pyramid apex.

The total magnetization measurements $M\,(H)$ were performed on randomly oriented powder samples mixed with daphne oil in a vibrating sample magnetometer at low temperature ($T \approx 2.5$ K) and a magnetic field up to 14 T.

The x-ray circular magnetic dichroism measurements were carried out in the ID12 beamline at the ESRF, at identical temperature as the M(H) isotherms and magnetic field up to 17 T, on pellets formed by the compressed powder.

3. Experimental results

The $M\,(H)$ isotherms of {Fe_3LnO_2} Ln=Lu, Gd, Dy, Tb and Ho at low temperature, measured with the VSM technique are shown in Fig. 2a. From direct comparison with the $M\,(H)$ for the non-magnetic Lu ion {Fe_3LuO_2} it is evident that the magnetic Ln ions give an extra contribution to $M\,(H)$. The determination of this contribution $M_{Ln}\,(H)$ at low fields has been the experimental keypoint of this work.

To explain the method an example is given in Fig. 3, namely the Ln=Dy case. The XMCD spectra at the $L_{2,3}$ edges of Dy were measured at 17 T Fig. 3a, where the photon energy of the maximum (minimum) at the $L_3(L_2)$ edges is determined with high precision. At the selected incoming photon energy, the XMCD maximum intensity was followed as a function of applied field up to 17 T in this case (Fig. 3b). Since the saturation magnetization of the Fe_3 sublattice M_{Fe_3} (H=14 T) is known from the VSM experiment (see Fig. 2a), its value was subtracted to the total M_{tot} (H=14 T), thus determining the value of M_{Dy} (H=14 T). The resulting value was used to scale the curve obtained from the field dependent XMCD, i.e. $I_{XMCD}(H)$, obtaining the $M_{Dy}\,(H)$ curve shown in Fig. 3c. In a subsequent step, $M_{Fe_3}\,(H)$ is obtained by the difference $M_{Fe_3}\,(H)=M_{tot}\,(H)-M_{Dy}\,(H)$, shown in Fig. 3c. The resulting $M_{Ln}\,(H)$ and $M_{Fe_3}\,(H)$ for the {Fe_3LnO_2} compounds are collected in Fig. 2b and c, respectively.

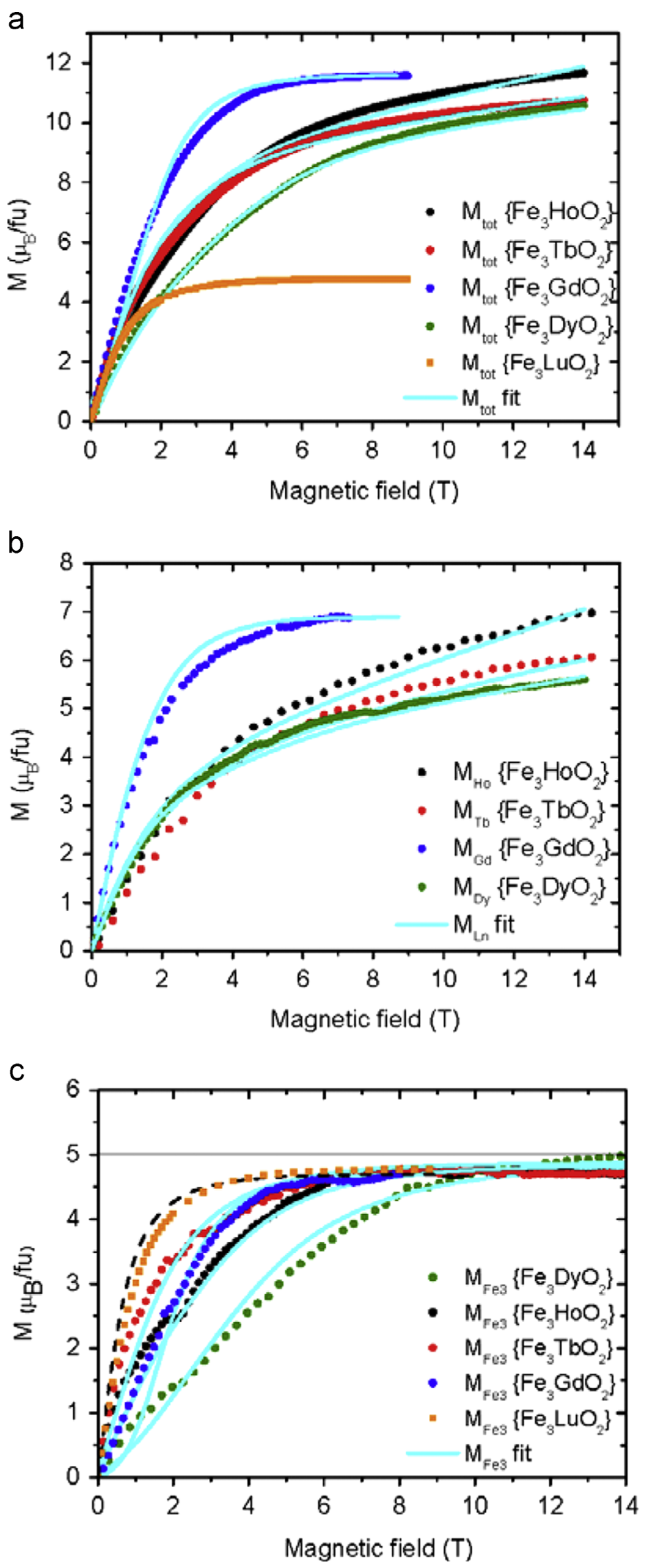

Fig. 2. (a) $M_{tot}\,(H)$ isotherms of {Fe_3LnO_2} for Ln=Lu (1.8 K), Gd and Ho (2.2 K), Dy, Tb (2.7 K). (b) $M_{Ln}\,(H)$ contribution of the Ln ion, (c) $M_{Fe_3}\,(H)$ of the Fe_3 subcluster. (Dashed line) Brillouin function for a single S=5/2 moment.

4. Discussion

For {Fe_3LuO_2} $M_{tot}\,(H)=M_{Fe_3}\,(H)$, since Lu is not magnetic. This corresponds to the contribution of the three Fe(III) S=5/2