X-ray magnetic circular dichroism investigation of magnetic contributions from Mn(III) and Mn(IV) ions in Mn12-ac

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We present the results of an x-ray magnetic circular dichroism (XMCD) investigation of the molecular superparamagnet Mn12-ac. Thanks to an approach based on chemical synthesis of model compounds, the contributions of Mn(III) and Mn(IV) ions to the absorption spectrum and the dichroic signal of Mn12-ac have been separated. The two contributions have been analyzed by simulating the XMCD spectra of Mn12-ac by means of crystal-field multiplet calculations. The ferrimagnetic structure of Mn12-ac has been confirmed, and the individual magnetic moments of Mn(III) and Mn(IV) ions are in good agreement with the values obtained by means of first-principles calculations and polarized neutron diffraction experiments. The orbital and spin contributions to the magnetic moment have been evaluated for each manganese ion, providing the evidence of negligible orbital magnetic moments for both Mn(III) and Mn(IV) ions.

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I. INTRODUCTION

Knowledge of the internal magnetic structure of molecular nanomagnets is of great importance for the comprehension of the magnetic properties of these new magnetic materials.¹ The experimental determination of the role of the transition-metal and rare-earth ions making up the magnetic core of the molecule and, in particular, of the spin and orbital contributions to the overall magnetic moment poses several problems.

Magnetic diffraction techniques, such as polarized neutron diffraction and resonant x-ray magnetic scattering, directly give the magnetic structure of the molecule. Local magnetic properties can also be investigated by means of x-ray magnetic circular dichroism (XMCD). In particular, the strong dichroism at the $L_{2,3}$ edges of transition-metal ions and $M_{4,5}$ edges of rare-earth ions provides information about their ground-state magnetic properties. At variance with diffraction techniques, which need large single crystals, the advantage of XMCD is the possibility of performing measurements on powders or polycrystalline samples. Moreover, by exploiting the chemical sensitivity of x-ray absorption edges, contributions from different transition-metal and rare-earth ions within the molecule can be easily separated.

In this paper, we present the results of an XMCD investigation of the molecular superparamagnet $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_{24}] \cdot 2CH_3COOH \cdot 4H_2O$ (in short Mn12-ac).² In a simple ionic picture, the magnetic core of Mn12-ac consists of an external ring of eight Mn(III) ions and an internal tetrahedron of four Mn(IV) ions. The magnetic moments of the four Mn(IV) ions are aligned antiparallel to those of the eight Mn(III) ions, resulting in a ferrimagnetic internal magnetic structure, first assumed to

account for the ground-state magnetic moment of the molecule³ and later demonstrated by polarized neutron diffraction experiments.⁴

Although the internal magnetic structure of Mn12-ac is now well established, direct determination of the groundstate magnetic properties of the Mn ions and, in particular, of the spin and orbital contributions to their magnetic moment is still lacking. In a recent experiment, magnetic circular dichroism at the manganese $L_{2,3}$ edges of Mn12-ac was measured.⁵ Usually, XMCD spectra can be powerfully analyzed by means of sum rules which allow the determination of the orbital and spin magnetic moments of the constituent atoms.^{6,7} In the case of Mn12-ac, due to the copresence of Mn ions in different oxidation states (and therefore with different occupation numbers for the 3d shell), this method is not valid since, in order to obtain information about the ground-state magnetic properties of Mn(III) and Mn(IV) ions, their respective contributions to the XMCD spectra of Mn12-ac must be separated. The impossibility of using XMCD sum rules in a straightforward manner hampered the determination of the orbital and spin magnetic moments of each Mn ion in the above-mentioned experiment.⁵

At least in principle, the Mn(III) and Mn(IV) contributions can be separated by exploiting the sensitivity to oxidation state of the $2p^{6}3d^n \rightarrow 2p^{5}3d^{n+1}$ transitions responsible for x-ray absorption at the manganese $L_{2,3}$ edges. Here, we combine crystal-field multiplet calculations^{8,9} with the measurement of reference XMCD spectra for Mn(III) and Mn(IV) to determine their ground-state magnetic properties in Mn12-ac. The reference XMCD spectra, obtained from molecular paramagnetic compounds, are reported in Sec. II. Through simulation of the reference spectra by means of crystal-field multiplet calculations, the atomic and crystalfield parameters entering the calculations have been determined (Secs. III A and III B). This set of parameters has been used as a starting point to simulate the XMCD spectra of Mn12-ac. This approach, where the synthesis of model molecular compounds is combined with crystal-field multiplet calculations, allowed the separation of the contributions from Mn(III) and Mn(IV) ions and the extraction of information about their respective ground-state electronic and magnetic properties (Sec. III C). In particular, the orbital and spin magnetic moments of each Mn ion have been determined. Concluding remarks follow in Sec. IV.

II. EXPERIMENT

XMCD spectra at the manganese $L_{2,3}$ edges of Mn12-ac and of the two reference compounds have been collected at the SU23 beamline of the Super-ACO storage ring at LURE (Orsay, France).⁹ Mn12-ac XMCD spectra, which were already presented by Ghigna *et al.*,⁵ have been measured in order to get all the spectra in the same experimental conditions (degree of x-ray polarization and energy resolution).

Two molecular compounds, containing exclusively Mn(III) or Mn(IV) ions, have been used in order to obtain reference XMCD spectra. The model compounds were chosen so that the coordination environments of the Mn ions are similar to their respective ones in Mn12-ac. Molecular compounds have been preferred to manganese oxides [e.g., Mn_2O_3 for Mn(III) and MnO_2 for Mn(IV)] in order to prevent effects induced by the sensitivity of the total electron yield detection mode, used to measure the absorption spectra, to the surface of grains, where metal ions in different oxidation states or coordination sites might be found.^{10,11}

 $Mn^{III}(dbm)_3$ where Hdbm=1,3-diphenyl-1,3-propanedione (hereafter complex 1) was used as reference compound for Mn(III). X-ray structure analysis shows deviations of the coordination polyhedron of the Mn(III) ion from the idealized tetragonal (D_{4h}) symmetry expected as a result of Jahn-Teller distortion. In spite of such deviations, no evidence of symmetry lower than axial was found in the electronic spectra.¹² Moreover, its anisotropic magnetic properties, obtained by high-frequency and high-field electron paramagnetic resonance (HF-EPR) measurements, can be accounted for at a very satisfactory extent in D_{4h} symmetry and the estimation of the zero-field splitting parameter changes of less than 1% by lowering the symmetry.

As a reference compound for Mn(IV), $[L_2Mn_2^{IV}(O)$ (PhBO₂)₂](ClO₄)₂·2(CH₃)₂CO where L=1,4,7- trimethyl-1,4,7-triazocyclononane (hereafter complex 2) was used. In this molecule, the two Mn(IV) ions are in equivalent octahedral (O_h) sites as revealed by x-ray crystal structure analysis.¹³ Magnetic susceptibility measurements give for the two Mn(IV) ions a spin equal to 3/2 and a zero-field splitting parameter close to zero.

The x-ray source used for the XMCD experiments is an asymmetric wiggler delivering a high flux of elliptically polarized photons. The x-ray beam is monochromatized by a plane grating and focused on the sample with a spot size of $1 \times 1 \text{ mm}^2$. At the manganese $L_{2,3}$ edges, the circular polarization rate is estimated to be about 60% and the energy



FIG. 1. Experimental and calculated XMCD spectra of complex 1. Absorption cross sections and dichroic signals are shown in the upper and lower panels, respectively.

resolution about 0.25 eV.⁹ X-ray absorption spectra were recorded in the total electron yield (TEY) detection mode. The samples were grounded into fine-grained powder in an agate mortar to obtain an isotropic orientation distribution of the crystallites. In order to prevent sample charging and ensure excellent cooling, the powder samples have been pasted on a grid directly carved into the copper sample holder.

During the measurements, the samples have been cooled down to 1.5 K and magnetized by a 4 T magnetic field generated by superconducting coils. Such a low-temperature and high-magnetic-field condition is essential to induce a net magnetic moment in the paramagnetic model compounds and to magnetize at saturation the Mn12-ac molecule. The XMCD spectra of complexes 1 and 2 do not show any detectable degradation of the sample when subjected to the x-ray beam. Mn12-ac, which already showed in previous experiments⁵ its sensitivity to x-ray beams under the high flux of third-generation synchrotron x-ray sources, does not show any sign of degradation during the time required to collect a complete set of XMCD spectra (four spectra, about 150 min) at Super-ACO. The corrections necessary to convert the raw TEY signals into normalized absorption cross sections have been performed.¹⁴

The average absorption cross section $\sigma_m = 1/2(\sigma_+ + \sigma_-)$ and the dichroic signal $\sigma_d = (\sigma_+ - \sigma_-)/\tau = \sigma_l - \sigma_r$ were derived by the absorption cross sections measured with the magnetic field parallel (σ_+) and antiparallel (σ_-) to the x-ray propagation vector. The factor $\tau = 0.6$ takes the incomplete light polarization into account.

Figures 1 and 2 show the average absorption cross section



FIG. 2. Experimental and calculated XMCD spectra of complex 2. Absorption cross sections and dichroic signals are shown in the upper and lower panels, respectively.

 σ_m and the dichroic signal σ_d at the manganese $L_{2,3}$ edges of complexes 1 and 2, respectively. Figure 3 shows σ_m and σ_d at the manganese $L_{2,3}$ edges of Mn12-ac.

III. DISCUSSION

In order to extract information about the electronic ground-state configurations of Mn(III) and Mn(IV) ions in Mn12-ac, the experimental XMCD spectra of the two reference compounds were simulated by performing crystal-field multiplet calculations.⁸ This approach, which is by now generally familiar thanks to the seminal work of Thole et al., takes exactly into account the spin-orbit coupling and describes the effect of chemical environment on the 3d states of the absorbing atom through the crystal-field parameters. Besides them, the parameters used to fit the experimental spectra are the reduction factors of the Slater integrals and the ξ_{2n} and ξ_{3d} spin-orbit parameters. Hybridization effects were included by reducing the Slater integrals and no configuration interaction was implemented in the calculations presented in this paper. Different reduction factors were used for the Slater integrals which describe 2p-3d and 3d-3dCoulomb and exchange interactions (κ_{pd} and κ_{dd} , respectively). In particular, since hybridization effects expand the wave function of 3d electrons without affecting the 2p core hole, the interactions between 3d electrons are more influenced by hybridization than the ones between 2p and 3delectrons. The correctness of this approach is a posteriori



FIG. 3. Experimental and calculated XMCD spectra of Mn12ac. Absorption cross sections and dichroic signals are shown in the upper and lower panels, respectively.

confirmed by the good agreement between calculations and experimental results and by the absence in the measured spectra of additional satellites not reproduced by calculations, usually induced by hybridization effects.¹⁵

In the calculations, a 4 T magnetic field was assumed and the effect of temperature was included by statistically populating the low-energy states. In fact, at variance with ferromagnetic or ferrimagnetic materials where the strong exchange field is responsible for the Zeeman splitting and, as long as the sample is fully magnetized, XMCD spectra do not depend much on temperature, for paramagnetic compounds, as complexes 1 and 2, the interplay of temperature and the intensity of the magnetic field is essential for the magnetization and must be taken explicitly into account in the calculations ($\mu_B B/k_B = 0.67$ K for an induction B= 1 T).

The experimental spectra σ_l and σ_r were measured on powder samples with the external magnetic field **B** parallel and antiparallel to the photon propagation vector. In order to calculate σ_l and σ_r , the absorption cross sections for all possible orientations of the molecules should be averaged. An approximate method of integration by Ayant *et al.*¹⁶ allows one to obtain the powder spectrum as a weighted sum of the spectra calculated for some particular orientations of the molecule. By expanding on spherical harmonics the spectrum as a function of the relative orientation of the magnetic field and the molecule and by truncating it to fourth order, the powder spectra can be approximated by

	κ_{pd} (%)	κ_{dd} (%)	ξ_{2p} (eV)	ξ_{3d} (eV)	Dq~(eV)	Ds (eV)	Dt (eV)
Mn(III) in 1	65	50	7.1	0.035	0.22	0.2	0.05
Mn(IV) in 2	35	30	7.45	0.026	0.23		
Mn(III) in Mn12-ac	65	50	7.1	0.035	0.21	0.15	0.035
Mn(IV) in Mn12-ac	35	30	7.45	0.026	0.25		

TABLE I. Atomic and crystal-field parameters extracted by the fit of the experimental XMCD spectra.

$$\sigma_{l(r)}^{\text{powder}} = \frac{1}{15} \left(\sum_{i} \sigma_{l(r)}^{i} + 2\sum_{k} \sigma_{l(r)}^{k} \right), \quad (1)$$

where $i \in \{[100] \| \mathbf{B}, [010] \| \mathbf{B}, [001] \| \mathbf{B}\}$ and $k \in \{[110] \| \mathbf{B}, [110] \| \mathbf{B}, [101] \| \mathbf{B}, [101] \| \mathbf{B}, [011] \| \mathbf{B}, [011] \| \mathbf{B}\}$. This method assumes no preferential orientation of the molecule within the powder which, in the case of the Mn12-ac sample, is confirmed by comparing x-ray diffraction from powder and single-crystal samples.

A. XMCD of Mn(III) ions

Mn(III) site in complex 1 has tetragonal (D_{4h}) symmetry and three parameters (usually named Dq, Ds, and Dt) describe the effect of crystal field on 3d states.

Powder spectra were calculated by means of Eq. (1) which, in D_{4h} symmetry, reads

$$\sigma_{l(r)}^{\text{powder}} = \frac{1}{15} (2 \sigma_{l(r)}^{[010] \| \mathbf{B}} + \sigma_{l(r)}^{[001] \| \mathbf{B}} + 4 \sigma_{l(r)}^{[110] \| \mathbf{B}} + 8 \sigma_{l(r)}^{[101] \| \mathbf{B}}),$$
(2)

where the [001] direction is parallel to the tetragonal C_4 axis.

The reduction factors of the Slater integrals and the spinorbit and crystal-field parameters were varied in order to obtain the best agreement of the calculated average absorption cross section and dichroic signal with the experimental spectra. The parameters corresponding to the best fit shown in Fig. 1 are reported in Table I. The crystal-field parameters are in good agreement with those obtained by means of HF-EPR spectroscopy¹² while the 3*d* spin-orbit parameter was reduced to 75% of the value calculated for the free ion.

In Fig. 4, the results of the calculations of the average absorption cross section σ_m and the dichroic signal σ_d for the different orientations of the molecule used to evaluate the powder spectra are shown as solid and dashed lines, respectively. Besides σ_m and σ_d , we calculated the isotropic absorption cross section $\sigma_{
m iso}$ (dotted lines in Fig. 4) defined as $1/3(\sigma_0 + \sigma_l + \sigma_r)$ where σ_0 corresponds to the absorption of x rays linearly polarized along **B**. The isotropic cross sections for the different orientations of molecule are almost identical since the Zeeman term in the Hamiltonian is a small perturbation $(1 \mu_B B = 5.79 \times 10^{-5} \text{ eV}$ for an induction B =1 T) which does not play a role when the absorption selection rules, based on the polarization of light, are irrelevant. On the contrary, the calculated σ_m and σ_d show large differences which are induced by the different degeneracy lift and allowed electric-dipole transitions in which magnetic anisotropy plays a major role. In fact, due to the large uniaxial magnetic anisotropy of Mn(III) in D_{4h} symmetry, if the 4 T magnetic field used in experiments and calculations is parallel to the hard xy plane ([010]]|**B** and [110]||**B** in Fig. 4), it is not able to force the magnetic moment parallel to it and the dichroic signal is about one order of magnitude smaller than the one calculated along the easy z axis ([001]]|**B** in Fig. 4).¹⁷ This finding is confirmed by the ground-state expectation values of the projections of the spin and orbital angular moment along the quantization axis defined by the magnetic field ($\langle S_z \rangle$ and $\langle L_z \rangle$, respectively) reported in Table II.

In spite of the highly anisotropic character of Mn(III) ion in complex 1, the correctness of the approximated average obtained by means of Eq. (2) is confirmed by the comparison of σ_m^{powder} with the powder isotropic cross section $\sigma_{\text{iso}}^{\text{powder}}$ evaluated analogously to the other powder spectra and for which $\sigma_{\text{iso}}^{\text{powder}} \simeq \sigma_m^{\text{powder}}$ holds.^{15,17} The differences between



FIG. 4. Calculated σ_m (solid line, left axis), σ_d (dashed line, right axis), and σ_{iso} (dotted line, left axis) for Mn(III) ion in complex 1. The different sets of XMCD spectra correspond to calculations performed for different orientations of the molecule.

	$\langle S_z \rangle / \langle L_z \rangle$ with B $\ $ [010]	$\langle S_z \rangle / \langle L_z \rangle$ with B [001]	$\langle S_z \rangle / \langle L_z \rangle$ with B [110]	$\langle S_z \rangle / \langle L_z \rangle$ with B [101]					
Mn(III) in 1	$0.21/<1\times10^{-2}$	1.97 / -0.04	$0.2/<1\times10^{-2}$	1.48/-0.03					
Mn(IV) in 2	1.5/-	1.5 / -0.05		1.5 / -0.05					

TABLE II. Ground-state expectation values of spin and orbital angular moment projections along the quantization axis defined by the applied magnetic field.

 σ_m^{powder} and $\sigma_{\text{iso}}^{\text{powder}}$ are smaller than 1%, indicating the validity of Ayant's development.

B. XMCD of Mn(IV) ions

Mn(IV) sites in complex 2 have octahedral (O_h) symmetry and the crystal-field strength is determined by only one parameter (usually named 10Dq). At variance with the above reported case of Mn(III) ion in complex 1, the absorption cross sections at $L_{2,3}$ edges of Mn(IV) ions in O_h symmetry are highly isotropic. Figure 5 shows the results of the calculation of the average absorption cross section and the dichroic signal for the two symmetry-inequivalent orientations correspond to the magnetic field and the photon propagation vector parallel to the C_4 and C_2 axes of the Mn(IV) site. For the two orientations, the differences in σ_m are about 5% while those in σ_d are smaller than 1%. The differences are extremely small because of the isotropic character of the magnetization of Mn(IV) ions in O_h symmetry.¹⁸

In O_h symmetry, Eq. (1) reads

$$\sigma_{l(r)}^{\text{powder}} = \frac{1}{15} (3 \sigma_{l(r)}^{[001] \| \mathbf{B}} + 12 \sigma_{l(r)}^{[101] \| \mathbf{B}}), \qquad (3)$$

where the [001] direction is parallel to one of the octahedral C_4 axes.



FIG. 5. Calculated σ_m (solid line, left axis), σ_d (dashed line, right axis), and σ_{iso} (dotted line, left axis) for Mn(IV) ions in complex 2. The different sets of XMCD spectra correspond to calculations performed for different orientations of the molecule. For both orientations σ_m and σ_{iso} are indistinguishable.

The set of parameters which allow one to obtain the best agreement between the calculated and experimental cross sections (shown in Fig. 2) is reported in Table I. The 3d spin-orbit parameter is reduced to 50% of the value calculated for the free ion and the Slater integrals must be strongly reduced in order to obtain a reasonable agreement with the experimental spectra. A reduction of about 50% of the Slater integrals describing 3d-3d interactions was found by means of UV-Vis spectroscopy in MnCl^{2–}₆ and a larger reduction is expected for the more covalent bond between tetravalent manganese and oxygen.¹⁹

The strong reduction of the Slater integrals from their Hartree-Fock values is induced by the strong covalent character of the bond which is in contrast with the ionic bond assumed in the crystal-field theory. On the other hand, any attempt to improve the simulation by including hybridization effects through the inclusion of configuration interactions with low-energy excited configurations was ineffective. The impossibility of improving the simulation by including configuration interaction and the good agreement between the calculated and experimental cross sections indicate that, in this particular case, the covalent character of the bond can be taken into account by simply reducing the Slater integrals.

C. XMCD of Mn12-ac

In Mn12-ac, the 12 manganese ions are in three symmetry-inequivalent sites, the first of which are located in the tetrahedral core of the molecule and the other two form the external ring of eight Mn ions. In a simple ionic picture, the four manganese ions, which form the inner tetrahedron, are in the Mn(IV) state (S=3/2) while the eight manganese ions in the external ring are in the Mn(III) state (S=2). Magnetization measurements give a total spin equal to 10 in the ground state, which can be accounted for by assuming an antiparallel alignment of the magnetic moments of Mn(III) and Mn(IV) ions.

Each manganese ion is coordinated to six oxygen ions belonging to the μ -oxo bridges and the acetate ligands which complete the Mn12-ac molecule. In order to simulate the XMCD spectra by means of crystal-field multiplet calculations, the coordination polyhedra of the Mn(III) and Mn(IV) ions were, respectively, assumed to have idealized tetragonal and octahedral symmetry. No distinction was made between the two sites in the external ring.

The Mn12-ac average absorption cross section was calculated as the sum of the Mn(III) and Mn(IV) contributions weighted by their relative abundance in the molecule. In order to calculate the dichroic signal, the elongated axes of the Mn(III) ions have been considered parallel to each other and

to the easy magnetization axis of the molecule. As for the calculation of the dichroic signal of complex 1, the Mn(III) contribution to the dichroic signal of Mn12-ac was calculated as the average over all possible orientations of the molecule with respect to the direction of the applied magnetic field by using Eq. (2). With regard to Mn(IV) ions, due to the large superexchange coupling which forces their magnetic moments antiparallel to those of Mn(III) ions, their contribution was calculated as the average over all photon propagation vectors while keeping the superexchange field antiparallel to the magnetic moment of Mn(III) ions. In this way, the anisotropic magnetic environment of Mn(IV) ions in Mn12-ac has been taken into account. Due to the isotropic character of Mn(IV) in O_h symmetry figured out by the calculations reported in Sec. III B, their dichroic signal is expected to scale with the modulus of the cosine of the angle between the photon propagation vector and the superexchange field.¹⁸ The contribution of each Mn(IV) ion has been therefore scaled by a factor of -1/2 where the minus sign stands for the antiferromagnetic coupling between the two ions.

In order to fit the experimental XMCD spectra, the parameters obtained for the reference compounds have been used as a starting point. The calculated σ_m and σ_d which best simulate the measured ones are shown in Fig. 3. The parameters used in the calculations are reported in Table I.

The ground-state expectation values of the projection of spin and orbital angular moment along the easy magnetization axis of the molecule were deduced from the crystal-field multiplet calculations. Orbital angular moment projections for the Mn(III) $(|\langle L_z \rangle| < 1 \times 10^{-2})$ and Mn(IV) $(\langle L_z \rangle)$ =0.04) ions are much smaller than spin projections $[\langle S_z \rangle]$ = 1.9 and $\langle S_z \rangle$ = -1.5 for Mn(III) and Mn(IV) ions, respectively] so that the orbital contribution to their magnetic moment is negligibly small. The agreement of the calculated magnetic moment for the Mn(III) ions $(M = 2\mu_B \langle S_z \rangle)$ $+\mu_B \langle L_z \rangle = 3.81 \mu_B$ with the results of polarized neutron diffraction experiments [$M = 3.69 \mu_B$ and $3.79 \mu_B$ for the two inequivalent Mn(III) ions in Ref. 4] and calculation [M = 3.6 μ_B (Ref. 20) and M = 3.52 μ_B and 3.84 μ_B for the two inequivalent Mn(III) ions in Ref. 21] is satisfactory. Concerning the magnetic moment of Mn(IV) ions, a value (M $=2\mu_B \langle S_z \rangle + \mu_B \langle L_z \rangle = -2.96\mu_B$ larger than the one obtained by means of polarized neutron diffraction [M $= -2.34 \mu_{B}$ (Ref. 4)] was found while a good agreement

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with the results of calculations $[M = -2.6\mu_B \text{ (Ref. 20)} \text{ and } M$

 $= -2.92\mu_B$ (Ref. 21)] was obtained. If compared to the results obtained for Mn(III) ions, the larger discrepancy of the magnetic moment of Mn(IV) ions extracted by XMCD data and polarized neutron diffraction might be induced by the inadequacy of the ionic model for describing the electronic properties of tetravalent manganese where stronger hybridization effects are expected.

The magnetic moment of the molecule is smaller than the one obtained by means of magnetization measurements. Such discrepancy might originate from either the above reported overestimation of the magnetic moment of Mn(IV) ions or the ionic model used to simulate the XMCD spectra. In fact, the presence of polarization density on oxygen atoms, which is foreseen by *ab initio* calculations^{20,21} and not included in the ionic model adopted in crystal-field multiplet calculations, cannot be excluded.

IV. SUMMARY AND CONCLUSIONS

XMCD was used to investigate the internal magnetic structure of Mn12-ac and, in particular, to determine the orbital and spin contributions to the magnetic moments of the different manganese ions making up its magnetic core. In order to separate the Mn(III) and Mn(IV) contributions, the synthesis of model compounds to obtain reference XMCD spectra has been combined with crystal-field multiplet calculations.

The magnetic moment of Mn(III) and Mn(IV) ions in Mn12-ac are in good agreement with those found by means of polarized neutron diffraction. The orbital and spin contributions to the magnetic moments of the two ions were also extracted by the XMCD spectra of Mn12-ac and, for both of them, a negligibly small orbital contribution was found. The results of this experiment provide direct evidence of the quenching of the orbital magnetic moment of Mn(III) and Mn(IV) ions in Mn12-ac.

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