Spin resolved photoelectron spectroscopy of $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ single-molecule magnets and of manganese compounds as reference layers

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Abstract

Properties of the manganese-based single-molecule magnet $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ are studied. It contains six Mn^{III} ions arranged in two bowl-shaped trinuclear triplesalen building blocks linked by a hexacyanochromate and exhibits a large spin ground state of $S_1 = 21/2$. The dominant structures in the electron emission spectra of $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ resonantly excited at the L_3 -edge are the $L_3\text{M}_{2,3}\text{M}_{2,3}$, $L_3\text{M}_{2,3}\text{V}$ and $L_3\text{VV}$ Auger emission groups following the decay of the primary $p_{3/2}$ core hole state. Significant differences of the Auger spectra from intact and degraded $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ show up. First measurements of the electron spin polarization in the $L_3\text{M}_{2,3}\text{V}$ and $L_3\text{VV}$ Auger emission peaks from the manganese constituents in $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ resonantly excited at the L_3 -edge near 640 eV by circularly polarized synchrotron radiation are reported. In addition spin resolved Auger electron spectra of the reference substances MnO , Mn_2O_3 and $\text{Mn}^{\text{II}}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$ are given. The applicability of spin resolved electron spectroscopy for characterizing magnetic states of constituent atoms compared to magnetic circular dichroism (MCD) is verified: the spin polarization obtained from $\text{Mn}^{\text{II}}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$ at room temperature in the paramagnetic state compares to the MCD asymmetry revealed for a star-shaped molecule with a $\text{Mn}_4^{\text{II}}\text{O}_6$ core at 5 K in an external magnetic field of 5 T.

1. Introduction

As technology develops toward smaller devices and structures, more and more efforts are made to assign specific tasks to single molecules. So-called single-molecule magnets (SMM) represent a promising approach (Bogani and Wernsdorfer 2008). Single-molecule magnets are a class of coordination compounds which exhibit a magnetic bistability (Sessoli *et al*

1993a, 1993b, Christou *et al* 2000). At low temperatures the existence of an energy barrier for spin reversal leads to a slow relaxation of the magnetization (Gatteschi and Sessoli 2003, Gatteschi *et al* 2006). Recently Mannini *et al* (2009) have shown that single-molecule magnets deposited on surfaces do not lose their magnetic properties. In addition, for Fe_4 complexes they have demonstrated that a preferential orientation on Au surfaces could be achieved using chemical methods (Mannini *et al* 2010). Also 3D nanostructures

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built up by single-molecule magnets have been prepared and investigated (Rogez *et al* 2009). These are important steps toward practical applications of SMM.

We have developed the single-molecule magnet $[(\text{talen}^{\text{t-Bu2}}\text{Mn}_3^{\text{III}})_2\{\text{Cr}^{\text{III}}(\text{CN})_6\}]^{3+}$ ($[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$) with $\text{H}_6\text{talen}^{\text{t-Bu2}} = 2,4,6\text{-tris(1-(2-(3,5-di-tert-butylsalicylaldimino)-2-methylpropylimino)-ethyl)-1,3,5-trihydroxybenzene}$ (Glaser *et al* 2006, Glaser 2011). This molecule contains six Mn^{III} ions arranged in two bowl-shaped trinuclear triplesalen building blocks which are linked by a hexacyanochromate. The $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ complex can be isolated with different counterions (e.g. perchlorate (ClO_4^-)) which compensate for its triply positive charge. The strongest interaction within $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ is the antiferromagnetic coupling of the central Cr^{III} ion with the six terminal Mn^{III} ions, leading to a large spin ground state of $S_t = 21/2$ for the molecule. This high-spin ground state in combination with a strong easy-axis magnetic anisotropy and a C_3 symmetry results in an energy barrier for spin reversal and thus in a slow relaxation of the magnetization at low temperatures. $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ has a blocking temperature around 2 K (Glaser *et al* 2006, Glaser 2011). However, to study the spin state and the orbital state of the atomic constituents it is not necessary to use magnetic circular dichroism (MCD) at low temperatures in high magnetic fields, spin resolved photoelectron spectroscopy following the excitation by circularly polarized radiation can be applied as well: atomic theory in the electric dipole approximation has shown that the MCD in photoabsorption and the MCD in the photoelectron angular distribution for free polarized individual atoms both are directly correlated to the spin polarization of photoelectrons from unpolarized paramagnetic atoms excited by circularly polarized radiation (Cherepkov and Kuznetsov 1989). This result of theory has been successfully proven at the $4d \rightarrow 4f$ resonance in Gd in condensed matter (Müller *et al* 2001): MCD asymmetries measured at magnetically ordered Gd layers compare with the spin polarization of electrons emitted from paramagnetic Gd after resonant excitation by circularly polarized radiation.

Here we report on first spin resolved fixed kinetic energy measurements of electrons emitted from $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ following resonant $2p_{3/2} \rightarrow 3d$ excitation. The signature of Mn^{II} and Mn^{III} constituents in these spin resolved data is demonstrated by comparing them with spin resolved electron emission spectra from the resonantly excited stable manganese oxides MnO and Mn_2O_3 .

The feasibility of applying spin resolved spectroscopy as a method to probe the magnetic properties of Mn constituents in a chemical complex in a mode equivalent to MCD studies is proven by comparing data from spin resolved $2p_{3/2} \rightarrow 3d$ resonant electron emission from magnetically non-ordered $\text{Mn}^{\text{II}}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$ with MCD data from a star-shaped molecule with a $\text{Mn}_4^{\text{II}}\text{O}_6$ core. These MCD reference data are measured in x-ray absorption at the manganese L-edge at a temperature of 5 K in a magnetic field of 5 T (Khanra *et al* 2008). Both substances contain Mn^{II} ions as constituents but, although a different impact of the surrounding atoms will be present, a first proof of the correspondence between MCD and spin polarization measurements is given.

2. Experimental details

Crystalline batches of $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ were checked by x-ray diffraction (XRD) and infrared spectroscopy with regard to their desired chemical and physical properties. Solutions of $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ with a concentration of $4.5 \times 10^{-4} \text{ mol l}^{-1}$ were prepared by dissolving the compound in methanol⁶. For the measurements presented here, an amount of 10 μl of the methanolic solution of $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ was dripped on horizontally oriented square substrates with a size of 5 mm. Microcrystallites began to form in the liquid phase during solvent evaporation and form a deposit (microcrystals of about 500 nm height) on the substrate surface. The substrates used for our investigations were commercially available borosilicate glass plates coated with $2.5 \pm 1.5 \text{ nm Cr}$ and $250 \pm 50 \text{ nm Au}$ on top⁷.

The MnO and Mn_2O_3 reference samples were prepared by pressing the powders into an adhesive carbon tape. MnO requires sputtering after the transfer to the vacuum system, because under atmospheric conditions the Mn^{II} in the surface of the MnO crystallites changes to the Mn^{III} oxidation state. $\text{Mn}^{\text{II}}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$ was prepared by dissolving the powder in methanol and dripping onto a gold substrate as described before. All samples were transferred into the UHV system via load lock and transfer systems. The measurements shown in this work were all performed at room temperature, i.e. above any ordering or blocking temperature.

Non-spin-resolved electron emission spectra were taken at the MAX-lab beamline D1011 using a MAX-lab end station equipped with a Scienta SES-200 electron energy analyzer and a sample transfer system.

The spin resolved photoemission experiments were performed at the helical undulator beamline UE52-SGM at BESSY II using the apparatus schematically shown in figure 1. The essential parts for spin resolved photoelectron spectroscopy have been used in previous experiments (David *et al* 1994, Müller *et al* 2001). The apparatus used here is supplemented by a load lock and sample transfer system.

In the apparatus the incoming circularly polarized radiation from the undulator beamline hits the target in normal incidence. Electrons emitted antiparallel to the direction of the incoming radiation are energy analyzed by a 90° spherical-field spectrometer (mean radius 84 mm) followed by a spherical-field Mott polarimeter for electron spin analysis of the Rice type (Gray *et al* 1984). The spectrometer is operated at a path energy of 140 eV resulting in an energy resolution below 1 eV. Non-spin-resolved intensity spectra are measured by means of a flat ceramic channel electron multiplier⁸ behind a second exit slit near to the central trajectory of the electrons. In the Mott polarimeter the electrons are accelerated to 25 keV, scattered by a thorium sheet, decelerated to discriminate against electrons having lost more than about 700 eV along

⁶ It must be noted that perchlorate salts of metal-organic compounds exhibit potentially shock sensitive or explosive properties. Appropriate measures have to be taken during handling and preparation of the investigated compounds.

⁷ Delivered by Arrandee, Dr D Schröer, Schlossstrasse 94, 33824 Werther, Germany.

⁸ KBL210, sensitive entrance 2 mm $\times$ 10 mm, Dr Sjuts Optotechnik GmbH, 37007 Göttingen, Germany.

Figure 1. Scheme of the experimental setup used for spin polarization measurements. Note that in the drawing the Mott polarimeter is rotated by 90° around the incoming electron beam.

the multiple scattering path in the thorium target, and then counted by a pair of channel electron multipliers with an entrance cone of 25 mm diameter⁹. With this setup the spin polarization component parallel to the helicity of the incoming radiation is measured. The polarization sensitivity has been determined by spin resolved LEED (low-energy electron diffraction) measurements on Pt(111) with reference to data from Bauer *et al* (1980) to be $S_{\text{eff}} = -0.16 \pm 0.02$. Apparatus related asymmetries are eliminated by combining runs with reversed helicity.

Circularly polarized radiation in the region of the L_3 -edge of Mn (photon energy 637–644 eV) was delivered by the helical undulator UE 52 in the second harmonic. Here the circular degree of polarization (Stokes parameter S_3) was 0.90 ± 0.01 . The bandwidth of the spherical mirror monochromator was set to ~ 0.8 eV.

3. Results and discussion

3.1. Electron emission spectra from resonantly excited $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$

Resonantly excited electron emission spectra from non-degraded $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ are displayed in figure 2, together with x-ray absorption spectroscopy (XAS) data for sample characterization recorded before the electron spectra. Comparative XAS studies on $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ salts with different counterions have shown that perchlorate counterions give the highest stability of the SMM against x-ray exposure (Helmstedt *et al* 2011). The XAS spectrum clearly shows the multiplet structure significant for Mn^{III} , confirming the predominance of the essential Mn^{III} oxidation state of the non-reduced $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ molecules. The vertical lines A and B mark the two photon energies 640.1 eV and 642 eV corresponding to the peak resonance (L_3 white line) for $2p_{3/2} \rightarrow 3d$ transitions in Mn^{II} and Mn^{III} ions, respectively. These two excitation energies are used for measuring the

Figure 2. Top: electron spectra obtained from $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ with excitation in the Mn^{II} (A) and Mn^{III} (B) resonance. The identification of the different main Auger groups is given for manganese by Kikas *et al* (1995) and Vayrynen (1981). Bottom: corresponding XAS spectrum taken before the photoelectron spectroscopy measurements. The absorption spectrum clearly shows signatures characteristic for Mn^{III} .

electron emission spectra. In the electron emission spectra the dominant structures result from the resonant Auger decay processes $L_3M_{2,3}M_{2,3}$, $L_3M_{2,3}V$ and L_3VV of the primarily excited $2p_{3/2}$ core hole state. The striking double line structure at about 85 eV below the valence band maximum (VBM) is due to emission out of the spin-orbit split 4f core states of the Au substrate. Comparing both spectra, a lower intensity is found in the spectrum excited at the photon energy corresponding to the Mn^{II} excitation. This is related to the different x-ray absorption yields at the Mn^{II} and Mn^{III} resonances marked A and B, respectively, in the lower panel of figure 2.

In figure 3 corresponding XAS and electron emission spectra are shown for a $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ target reduced by exposure to soft x-rays. In the XAS spectrum the increased absorption at the photon energy 640.1 eV marked by the line A, i.e. the energy of the main L_3 absorption line of Mn^{II} , is obvious. Accordingly, the increased intensity in the spectrum excited at the photon energy corresponding to the Mn^{II} excitation indicates the presence of Mn^{II} constituents. For the excitation at the Mn^{III} resonance all three Auger groups appear to be diminished, especially in the $L_3M_{2,3}M_{2,3}$ group

⁹ KBL25RS/90, Dr Sjuts Optotechnik GmbH, 37007 Göttingen, Germany.

Figure 3. Top: electron spectra of a degraded $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ sample taken with excitation in the Mn^{II} (A) and Mn^{III} (B) resonances. The assignment for the Auger lines is given in accordance with data obtained from iron (Kucherenko *et al* 2000). Iron and manganese both have an identical Ar-like core structure. Bottom: corresponding XAS spectrum taken before the photoelectron spectroscopy measurements. Compared to figure 2, the effects of reduction are visible, the absorption features of Mn^{II} (A) are predominant.

the $3\text{P}_{0,1,2}$ part is significantly reduced compared to the 1S_0 and 1D_2 components, while for the resonant Mn^{II} excitation all three Auger groups are clearly present.

3.2. Spin resolved reference measurements for manganese oxides

Spin resolved measurements require long integration times and therefore an enlarged exposure of the target to the radiation, as the detection efficiency of the Mott polarimeter is reduced by about two orders of magnitude against the efficiency of counting directly behind the electron spectrometer exit slit. To demonstrate the essential properties of spin resolved electron emission spectra from resonantly excited Mn^{II} and Mn^{III} ions, measurements obtained from the radiation-stable reference materials MnO (Mn^{II}) and Mn_2O_3 (Mn^{III}) are presented. Figure 4 shows spin resolved electron emission data from MnO resonantly excited by circularly polarized radiation with a photon energy of 640.1 eV, figure 5 contains the corresponding spectra measured at Mn_2O_3 excited by radiation with a photon

Figure 4. Spin resolved electron spectra obtained from MnO following excitation in the Mn^{II} resonance at 640.1 eV. Shown are the partial intensities I_+ and I_- with spin parallel and antiparallel to the light helicity, derived as described in the text. The upper panel gives the spin polarizations averaged over the peak region corresponding to the horizontal bar. Vertical error bars indicate the statistical errors of the measurements; the uncertainty of the polarization sensitivity $\Delta S_{\text{eff}}/S_{\text{eff}} = \pm 0.13$ is not included.

Figure 5. Spin resolved electron spectra obtained from Mn_2O_3 following excitation in the Mn^{III} resonance at 642 eV. Shown are the partial intensities and averaged spin polarizations as in figure 4.

energy of 642.0 eV. Both excitation energies correspond to the related L_3 absorption peak maximum determined by XAS.

In the main panels of figures 4 and 5 the spin resolved spectra are displayed by the partial intensities I_+ and I_- of the electrons with spin parallel and antiparallel to the photon spin, respectively. I_+ and I_- are connected with the total intensity I and the spin polarization P by $I_{\pm} = 1/2 \times I(1 \pm P)$. In all the partial intensity spectra shown in this work the inelastic background, which originates from the inelastic scattering connected with each electron emission process, is removed by applying the Tougaard formalism (Tougaard 1989). In the maximum of the L_3 VV as well as of the $\text{L}_3\text{M}_{2,3}\text{V}$ Auger emission peak the two electrons involved in the Auger decay are predominantly coupled to a singlet. Therefore the spin polarization of the emitted electrons reflects the orientation of the primary $2\text{p}_{3/2}$ core hole state with the preferential spin

direction antiparallel to the core hole orientation. As in both peaks I_- is the dominant partial intensity, the primary core hole state is oriented parallel to the helicity. In the top panels of figures 4 and 5 the spin polarizations of the L_3VV and $L_3M_{2,3}V$ emission peaks are given. They are evaluated from the raw data using the counting rates for all energy steps inside the half width of the peaks, and they are corrected for the degree of circular polarization of the radiation. The spin polarization determined for each energy interval step scatters around the indicated mean value according to the statistical uncertainty.

The significant difference of the spin polarizations measured for MnO and Mn_2O_3 is remarkable. For MnO the resulting spin polarizations are $P = -0.29 \pm 0.02$ (L_3MV) and $P = -0.41 \pm 0.03$ (L_3VV), and for Mn_2O_3 $P = -0.11 \pm 0.02$ ($L_3M_{2,3}V$) and $P = -0.17 \pm 0.04$ (L_3VV). The degrees of polarization measured for Mn_2O_3 are clearly smaller than the ones measured for MnO.

Assuming a free ion behavior of the Mn constituents and neglecting crystal-field effects, the different spin polarizations measured for MnO and Mn_2O_3 result from changes in the empty 3d states. In the Mn^{II} ions present in MnO the five 3d electrons form a half-filled shell with total spin $S = 5/2$ (configuration 6S_0) and all empty 3d states have identical spin. For Mn^{III} in Mn_2O_3 , there are only four 3d electrons which couple to a total spin of $S = 4/2$ (configurations 5D_J , $J = 0, 1 \dots 4$). Within the now six empty 3d states, one exhibits antiparallel spin with respect to the others.

If crystal-field effects are taken into account, detailed molecular orbital calculations (Sherman 1984) carried out for MnO (Mn_2O_3) exhibit a crystal-field splitting of 1.4 eV (2.4 eV) between the resulting $3e_g$ and $2t_{2g}$ orbitals and an additional exchange splitting of 4.5 eV (3.4 eV) between spin up and spin down states (Kurata and Colliex 1993). The structure of Mn_2O_3 shows a measurable Jahn–Teller distortion (Norrestam 1967). However, only $3e_g$ and $2t_{2g}$ states with identical spin orientation are occupied in MnO as well as in Mn_2O_3 (high-spin configuration), in agreement with the simplified free ion consideration above. In the case of Mn_2O_3 , the lowest unoccupied spin up and spin down states are separated by 1 eV (Kurata and Colliex 1993). In our measurements, this separation is not resolved in the excitation step and in the obtained Auger spectra. Therefore the lower degree of measured spin polarization for Mn_2O_3 corresponds to the empty spin states being different for MnO and Mn_2O_3 .

3.3. Spin polarization measurements for $[Mn_6Cr]^{3+}$

As the $[Mn_6^{III}Cr^{III}](ClO_4)_3$ degrades with exposure to radiation, at first spin resolved measurements of the SMM samples are performed at fixed electron energies only. In the electron emission spectra measured from $[Mn_6^{III}Cr^{III}](ClO_4)_3$ as well as from MnO and Mn_2O_3 the $L_3M_{2,3}V$ and L_3VV Auger peaks are clearly separated from the background. Therefore the intensity maxima of these two peaks at 60 eV and 8 eV below the VBM, respectively, are chosen for two fixed energy settings of the electron spectrometer.

The results of the spin resolved measurements for $[Mn_6^{III}Cr^{III}](ClO_4)_3$ are displayed in table 1. These data

Table 1. Spin polarizations obtained from $[Mn_6^{III}Cr^{III}](ClO_4)_3$ samples at fixed electron energies corresponding to the energetic positions of the manganese $L_3M_{2,3}V$ and L_3VV Auger peaks.

Excitation	640.1 eV (A)		642 eV (B)	
Peak	$L_3M_{2,3}V$	L_3VV	$L_3M_{2,3}V$	L_3VV
Spin polarization	-0.27 ± 0.02	-0.26 ± 0.01	-0.11 ± 0.05	—

are obtained by exciting the resonant $2p_{3/2} \rightarrow 3d$ transition of Mn^{II} and Mn^{III} in the SMM by radiation with photon energies of 640.1 eV and 642 eV, respectively, and setting the electron spectrometer to the two fixed electron energies derived above. It has to be noted that the spin polarization given for the $L_3M_{2,3}V$ emission peak includes a contribution from the spin polarized inelastic background originating from the L_3VV emission process.

A comparison with the results from the Mn oxide references displayed in figures 4 and 5 shows that by selecting the appropriate excitation energy Mn constituents in the oxidation state Mn^{III} and accordingly Mn^{II} are selectively excited. The measured spin polarizations compare well to the corresponding values measured for the reference materials.

3.4. Spin resolved electron spectroscopy of $Mn^{II}(acetate)_2 \cdot 4H_2O$ and comparison with magnetic circular dichroism

In the case of magnetic materials, the specific magnetic properties, i.e. the spin and orbital momenta of the atomic constituents, are of special interest. These data can be obtained from MCD data using the sum rules. For the $4d \rightarrow 4f$ excitation in Gd it has already been proved that MCD investigations of a magnetically ordered system and spin polarization measurements of the system in a magnetically non-ordered state yield corresponding results (Müller *et al* 2001).

For star-shaped molecules with a $Mn_4^{II}O_6$ core, MCD/XAS measurements at a temperature of 5 K and a magnetic field of 5 T have been performed and magnetic moments have been determined (Khanra *et al* 2008). The MCD asymmetry shows a change of sign when the excitation energy changes from the main peak at 640.1 eV to a smaller absorption peak at 641.5 eV (see figure 8). To compare with this finding, spin resolved electron spectra on the radiation-stable, magnetically non-ordered Mn compound $Mn^{II}(acetate)_2 \cdot 4H_2O$ were measured at these energies at room temperature. Thereby the orientation of the primarily excited core hole states is determined by measuring the spin dependent (resonant) Auger decay of these states.

The results of these measurements are presented again as partial intensities I_+ and I_- with spin parallel and antiparallel to the light helicity in figures 6 and 7. As mentioned before, the two peaks visible in both spectra are due to the L_3VV and $L_3M_{2,3}V$ (resonant) Auger decay of the oriented primary $2p_{3/2}$ core hole state. A significant change in the spin polarization depending on the choice of the excitation energy is observed for both Auger peaks. Averaging the polarizations given in

Figure 6. Spin resolved electron spectra obtained from $\text{Mn}^{\text{II}}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$ after excitation in the Mn^{II} resonance at 640.1 eV. Shown are the partial intensities and averaged spin polarizations as in figure 4.

Figure 7. Spin resolved spectra of $\text{Mn}^{\text{II}}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$ following excitation at 641.5 eV. Shown are the partial intensities and averaged spin polarizations as in figure 4.

the upper panels of figures 6 and 7 from both peaks for the two different excitations leads to $P(640.1 \text{ eV}) = -0.36 \pm 0.07$ and $P(641.5 \text{ eV}) = -0.05 \pm 0.03$. The given errors include the error ΔS_{eff} of the polarization sensitivity S_{eff} of the Mott polarimeter and the uncertainty in the degree of circular polarization P_{circ} of the synchrotron radiation.

In the lower panel of figure 8 the resulting polarizations are compared to the MCD asymmetry revealed from the helicity dependent absorption data of Khanra *et al* (2008). The upper panel of figure 8 shows an L_3 x-ray absorption total-yield spectrum (pink) measured for paramagnetic $\text{Mn}^{\text{II}}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$ in the $2p_{3/2} \rightarrow 3d$ excitation region using circularly polarized radiation, and a corresponding total-yield spectrum (blue) derived by averaging the helicity dependent total-yield spectra from Khanra *et al* (2008) for Mn^{II} ions in the Mn_4O_6 star magnetically aligned by the external field. The photon-energy scale of the spectrum shown in blue is fitted to the energy scale of our spectrum (pink).

In correspondence with the MCD asymmetry data, the averaged spin polarization changes significantly between the

Figure 8. Comparison between MCD data measured at 5 T and 5 K for a Mn_4O_6 star-shaped molecule (Khanra *et al* 2008) and spin polarization data obtained by spin resolved photoemission from $\text{Mn}^{\text{II}}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$ in a magnetically unordered state. Top panel: absorption spectra of the Mn_4O_6 star-shaped molecule (blue curve) and of $\text{Mn}^{\text{II}}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$ (pink curve). Bottom panel: MCD asymmetry (blue) measured for the Mn_4O_6 star-shaped molecules compared to the spin polarization (pink) obtained from $\text{Mn}^{\text{II}}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$ (see figures 6 and 7).

two excitations. It has to be taken into account that a bandwidth of about 800 meV was used for the spin resolved measurements. The data presented in figure 8 already take into account that the MCD asymmetry and the spin polarization determined in the $L_3\text{M}_{2,3}\text{V}$ and $L_3\text{VV}$ Auger peaks are of opposite sign: a positive MCD asymmetry in the $2p_{3/2} \rightarrow 3d$ transition means that positively oriented primary $2p_{3/2}$ -hole states are generated if the helicity and magnetic field are parallel. As mentioned before, the two electrons involved in the resonant $L_3\text{VV}$ and $L_3\text{M}_{2,3}\text{V}$ Auger decay are predominantly coupled to a singlet, leading to the emission of electrons with spin antiparallel to the orientation of the $2p_{3/2}$ core hole state (see also Müller *et al* 2001).

There is a connection between the MCD data and spin polarization results that follows from correlated local excitation steps.

In photoexcitation by circularly polarized radiation in magnetically non-ordered (paramagnetic) materials two reference directions for the coupled spin and angular momentum are introduced by the radiation, the directions parallel and antiparallel to the helicity. The core hole orientation resulting from the excitation is averaged over excitations with the two reference directions with identical weight. Thereby the excitation is controlled by the selection

rules for circularly polarized radiation: $\Delta l = \pm 1$, $\Delta m_j = +1$ and $\Delta l = \pm 1$, $\Delta m_j = -1$ for positive and negative helicity, respectively. In the (resonant) Auger decay of the primary excited core hole state, the orientation of the hole state is transferred to the spin of the emitted Auger electron by spin–spin coupling of the two electrons involved in the decay, the electron filling up the primary hole state and the emitted electron (Klar 1980, Kabachnik and Lee 1989, Stoppmanns *et al* 1992). These two electrons can be coupled to a singlet or to a triplet. With the Auger decay a two hole state is created. Due to the different correlation energies connected with the two-hole state, the two types of coupling result in different energies of the emitted electrons (Cini 1976, Sawatzky 1977) as shown for Fe by Kucherenko *et al* (2000). In the case of singlet coupling, the spin polarization of the emitted electrons is antiparallel to the core hole orientation, whereas in the case of triplet coupling it is parallel to the core hole orientation. In both cases the core hole orientation is retrieved if the spin polarization component parallel to the direction of the helicity of the exciting circularly polarized radiation is measured.

In an MCD experiment recorded by XAS the helicity of the radiation is set parallel or antiparallel to the magnetization **M** (intrinsic or defined by an external magnetic field). Two XAS measurements are performed with reference directions for the coupled spin and angular momentum parallel and antiparallel to **M** resulting in absorption yields Y_+ and Y_- , respectively. As in a magnetized sample the majority spin is antiparallel to **M**, the empty valence states are predominantly spin states parallel to **M**. This results in $Y_+ > Y_-$. The asymmetry of the MCD/XAS intensities Y_+ and Y_- , defined as $A_{\text{MCD}} = (Y_+ - Y_-)/(Y_+ + Y_-)$, directly corresponds to the orientation of the primary hole states created in the magnetically non-ordered material by radiation with positive helicity, as long as the exchange splitting is not resolved spectroscopically in the MCD experiment. In the corresponding spin resolved measurements this core hole orientation is probed via the Auger decay of the hole state.

Hence MCD data and results from the corresponding spin resolved electron spectroscopy are strongly correlated. It should be noted that, as core–valence transitions are local transitions determined by the relativistic dipole selection rules, MCD as well as spin resolved Auger electron spectroscopy both probe directly only local properties (spin and orbital momentum) and not properties of the itinerant electron system.

One restriction for the equivalency exists: in magnetic materials valence states can be shifted and core level splitting can be caused by valence–core interactions (van der Laan and Thole 1995). But for the materials studied here, these splittings can be neglected.

4. Conclusion

Photoelectron spectroscopy of $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ samples shows significant differences between intact $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ and that degraded by exposure to radiation. These differences appear as overall intensity changes connected with a corresponding variation of the excitation energy as well as in the structure of the $\text{L}_3\text{M}_{2,3}\text{M}_{2,3}$ Auger group.

Comparative spin resolved measurements from the stable reference materials MnO and Mn_2O_3 show clear changes of the spin polarization measured in the $\text{L}_3\text{M}_{2,3}\text{V}$ and L_3VV emission peaks if the excitation is correspondingly changed from the Mn^{II} resonance in MnO at 640.1 eV to the Mn^{III} resonance in Mn_2O_3 at 642.0 eV.

Spin polarization measurements of $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ samples at fixed electron energies related to the $\text{L}_3\text{M}_{2,3}\text{V}$ and L_3VV Auger peaks yield results comparable to the values obtained from the MnO and Mn_2O_3 reference substances for the corresponding excitation energies. This indicates a selective resonant excitation of the Mn constituents of the SMM in the oxidation states Mn^{II} and Mn^{III} .

The comparison of MCD asymmetries to the results obtained by spin resolved electron spectroscopy shows again that spin polarization measurements of magnetically non-ordered samples lead to results that are otherwise accessible to MCD/XAS intensity asymmetry measurements of samples magnetically oriented in strong magnetic fields and at the lowest temperatures.

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