Probing the magnetic moments of $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ single-molecule magnets—A cross comparison of XMCD and spin-resolved electron spectroscopy

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A B S T R A C T

Single-molecule magnets (SMM) of the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ structural type prepared on Si and gold-coated glass substrates have been investigated by spin-resolved electron spectroscopy (SPES) and X-ray magnetic circular dichroism (XMCD) at the Mn $L_{3,2}$ edge and in addition by XMCD at the Cr $L_{3,2}$ edge using synchrotron radiation. Differences between the two methods are discussed. Despite its severe limitations for 3d transition metals, a spin sum rule evaluation is nevertheless performed for the Mn^{III} centres in the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM to provide a simple means of comparing XMCD and spin-resolved electron spectroscopy results.

Keywords:

Spin-resolved

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1. Introduction

The annual amount of data being produced worldwide has reached the Exabyte (10^{18} byte) range and is increasing rapidly [1]. While data storage mainly relies on hard disc drives, fundamental limitations [2–4] of the magnetic recording principle define a maximum recording density of approx 1 Tbit/inch² [2,5]. Beyond this critical density, thermal fluctuations are able to overcome the energy barrier against magnetization reversal, leading to a loss of stored information [2,3,6]. Efforts are being made to replace bulk magnetic and semiconductor devices by single molecules, which can perform as memory cells, transistors or even logical

devices [7–9]. A comprehensive review of this field is given in [10]. Single-molecule magnets (abbrev. SMM) [11–13] represent a promising approach with regard to quantum computing and information storage [14–17]. Single-molecule magnets require individual addressing to retrieve the stored information—therefore first successful attempts to deposit SMM on surfaces with a preferential orientation [18] or in periodic 3D arrays [19] represent important steps towards future applications.

A ‘serendipitous approach’ [20] resulted in the discovery of the first single-molecule magnet **Mn₁₂ac** [21–23]. However, a different method involving rational bottom-up molecular design was chosen to obtain the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ single-molecule magnet [24–26]. It is representative of the general $[\text{M}^{\text{I}}_6\text{M}^{\text{C}}]^{n+}$ structure type that has been studied thoroughly in the past years [24–31].

The stability of the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM deposited on various substrates against soft X-ray irradiation was investigated in earlier work [32], indicating the important role of the anions associated with the SMM core for the radiation stability. First spin-resolved

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electron spectroscopy (SPES) experiments on SMM were performed [33] using the most stable $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ type with perchlorate anions. With the controlled deposition of the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM on surfaces being a central question for future applications, the deposition behaviour on surfaces was studied as well by AFM and STM [34,35]. Within the work presented here, SPES measurements were performed at the $L_{3,2}$ edge of the Mn ions in the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM, using circularly polarized synchrotron radiation for the excitation step. XMCD measurements at the Mn and Cr $L_{3,2}$ edges were carried out as well in order to cross compare them with the electron spin polarization spectra.

2. Scientific background

The availability of high-quality synchrotron radiation sources with variable polarization was the key factor for the XMCD method to become a versatile, widely used tool for the investigation of the magnetic properties of solids [36–38]. However, the technique requires the samples to exhibit a magnetic orientation—usually this condition is achieved by strong external magnetic fields and low sample temperatures.

The wide practical applicability of the XMCD method is based on the discovery of the so-called sum rules for the orbital (Thole et al. [39]) and the spin magnetic moment (Carra et al. [40]), relating the measured helicity-dependent difference in absorption to the local spin and orbital magnetic moments of the absorbing atom [41,42]. This approach allows the element-specific determination of the local magnetic moments present in the sample. However, the approximations used to obtain the sum rules limit the accuracy of the derived spin and orbital magnetic moments, see [43–47]. Especially in the case of 3d transition metals, corrections to the sum rule results are required, either by applying correction factors (Teramura et al. [48]) or by comparing the XMCD data to the results from multiplet calculations as shown by Piamonteze et al. [49]. The latter method has been applied successfully to Mn^{III} systems by Kuepper et al. [50].

The application of external magnetic fields in the XMCD experiment represents an influence on the investigated systems that has the potential to change the condition of the samples with respect to the undisturbed state without external fields. For the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM investigated within this work, the application of the external magnetic field causes distinct changes in the spectral shape of the Mn $L_{3,2}$ edge absorption, confirming the existence of such influences.

Experiments performed on paramagnetic Gd in 2001 by Müller et al. [51] indicate that spin-resolved electron spectroscopy of samples in the paramagnetic regime above the Curie temperature yields the same information as XMCD data without the need to apply external magnetic fields: The primary excitation step involving circularly polarized radiation is governed by the relativistic dipole selection rules [52,53] for paramagnetic samples as well as for magnetically oriented materials. As a result, the excitation in both cases generates oriented core holes in the sample. The core hole orientation originating from the primary excitation step can be investigated by analyzing the spin polarization of Auger electrons following the decay of the primary core hole. The $L_{2,3}M_{2,3}V$ Auger decay of the Mn constituents in the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM was used to retrieve the orientation of the primary core holes for the results presented here, see [33].

An XMCD experiment performed with circularly polarized light leads to two different absorption yields [39] Y_+ and Y_- depending on the light helicity (the photon angular momentum) being parallel or antiparallel to the preferential magnetic direction $\mathbf{M}$ present in the sample, respectively. While in magnetically ordered solids $\mathbf{M}$ is defined by the magnetization, for assemblies of non-interacting localized magnetic moments, e.g. for SMM, an external

magnetic field of sufficient strength $\mathbf{B}$ is necessary to define $\mathbf{M}$. As the majority spin orientation of a magnetized sample is antiparallel to $\mathbf{M}$, the availability of empty 3d valence states leads to $Y_+ > Y_-$ for the L_3 edge of a 3d transition metal as investigated within this work. The XMCD asymmetry $A_{\text{XMCD}} = (Y_+ - Y_-)/(Y_+ + Y_-)$ resulting from the XMCD experiment is closely connected to the core hole orientation created in a magnetically non-ordered sample by an excitation step using circularly polarized radiation. The existence of this close relationship between MCD effects in photoexcitation as well as in the angular distribution of photoelectrons and the spin polarization of electrons emitted from paramagnetic samples has been described within the framework of the electric dipole approximation, see [54]. The equivalency of both approaches is restricted to situations in which the exchange splitting is not resolved in the MCD experiment [55]. Also, core level splitting and other effects caused by core–valence interaction in magnetic samples [56] need to be considered.

3. Experimental approach

3.1. Sample preparation

The $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM investigated here were synthesized according to the procedure described in earlier works [26,32]. Methanolic solutions of the SMM with a concentration of $9 \cdot 10^{-5}$ mol/l were prepared. Based on the results of an earlier XAS study on the radiation sensitivity of the investigated SMM [32], the most stable $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ SMM with perchlorate anions was chosen for the spin-resolved electron spectroscopy measurements.

An airbrush process using a commercially available airbrush gun (Grafo T1, see [57]) and high-purity nitrogen as working gas was developed for the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ sample preparation: 200 μl of the methanolic SMM solution were used to coat a square substrate of approx. 11 mm edge length by repeatedly moving the airbrush nozzle across the substrate in a regular pattern. This method allowed the deposition of homogeneous SMM deposits with an area of up to 100 mm^2 . For the results presented within this work, Si(1 1 0) and gold-coated glass substrates (see [58]) were used. The large homogeneous sample area allowed the use of sample scanning during the spin polarization measurements: Data obtained from a large number of sample positions are merged into one spin polarization datapoint, thereby overcoming the limitation of the measuring time due to the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM radiation sensitivity.

Although optical microscopy of the deposited $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ reveals labyrinth-like, irregular structures on small scales below 0.2 mm (see Fig. 1 right), these irregularities are averaged out due to the spot size of approx. 1 mm^2 used for the synchrotron radiation experiments. The homogeneity of the deposition process as well as the condition of the deposited $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM have been checked by Mn $L_{3,2}$ edge XAS characterization. All XAS results presented within this work have been obtained in the total electron yield (TEY) mode i.e. by measuring the sample current and therefore the total number of photo- and secondary electrons leaving the sample.

3.2. Spin-resolved electron spectroscopy

The spin-resolved electron spectroscopy (SPES) measurements presented here have been performed at the beamlines UE52-SGM and UE56/2-PGM2 of the BESSY-II storage ring at the Helmholtz-Zentrum Berlin (HZB). Both beamlines use the synchrotron radiation of permanent magnet undulators of the APPLE-II type and provide a range of photon energies that extend from approx. 90 eV to 1300 eV, covering the 640 eV region of the Mn $L_{3,2}$ edge. For detailed information concerning the specifications

Fig. 1. Left: XAS characterization of a $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ SMM sample prepared by the described airbrush method. Mn $L_{3,2}$ edge absorption spectra recorded at different sample positions across the full 11 mm by 11 mm sample area are shown. Right: Microscopy image of the SMM sample—the irregularities of the SMM deposition visible at this magnification are averaged out due to the synchrotron radiation spot size used in the experiment (black square).

of both beamlines see [59–61]. An off-focus sample position was chosen to reduce the synchrotron radiation flux at the sample to 10^{11} photons/s/100 mA with respect to the radiation sensitivity of the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM [32].

The experimental setup used for the spin-resolved electron spectroscopy experiments consisted of a UHV apparatus equipped with a 90° spherical field electron spectrometer in normal incidence, normal emission geometry. After energy analysis the collected electrons were transferred to a spherical Mott polarimeter of the Rice type [62], using a scattering energy of up to 45 keV. The polarization sensitivity (Sherman function) of the Mott polarimeter at 25 keV (45 keV) was $S_{\text{eff}} = -0.17 \pm 0.02$ ($S_{\text{eff}} = -0.23 \pm 0.02$). Note that the uncertainty of the polarization sensitivity as a scale factor is not included in the error bars of the SPES results given in Figs. 3 and 4. Detection of the scattered and retarded electrons was performed by channel electron multipliers [63] with a circular entry funnel (diameter 25 mm) to maximize detection efficiency. The electron spectrometer as well as the Mott polarimeter has been used successfully before [33,51,53,64,65] and has been described in more detail elsewhere, see [53,65]. The UHV setup was completed by an electrically isolated sample stage in order to perform total-electron-yield mode XAS measurements, a sample transfer and preparation system providing UHV storage for up to 6 samples and a load-lock with a pump-down time of less than 1 h, allowing frequent sample changes made necessary by the limited sample lifetime under soft X-ray exposure [32].

3.3. XMCD measurements

Comparative XMCD investigations of $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ SMM have been performed at the SIM beamline of the SLS storage ring at the Paul-Scherrer institute in Villigen, Switzerland. The SIM beamline is based on a double undulator comparable to the UE56 undulators at the BESSY-II storage ring. Both undulators are slightly tilted against each other and can be operated with opposite helicity. However, only one undulator was used for the measurements presented within this work. The available energy range of 90–2000 eV [66] covers the Mn and Cr $L_{3,2}$ edges which were studied in our experiment. The photon flux at the sample position was reduced by tuning the beamline monochromator to a fix-focus constant of approx. 20 instead of the usual value of 2.25 and adding an aluminium filter in order to take into account the radiation sensitivity of the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM. The low temperature XMCD setup of the IPCMS Strasbourg [66] providing sample temperatures of approx.

2 K and a magnetic field of up to 6.9 T was used to obtain the XMCD data presented here. All XMCD measurements were done in TEY mode by measuring the sample current.

4. Results and discussion

4.1. XAS sample characterization

Prior to the spin-resolved electron spectroscopy measurements, the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ samples were characterized by X-ray absorption spectroscopy. The spectral shape of the Mn $L_{3,2}$ absorption edge is very sensitive to changes in the oxidation state of the Mn ions, thereby making XAS a useful tool to monitor the sample condition. Reference data obtained from bulk Mn^{II} and Mn^{III} oxides provide a means to determine the $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$ ratio present in the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ sample [32]. The intact $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ molecule contains solely Mn^{III} , therefore this ratio serves as an indicator of changes to the molecule condition due to preparation or radiation exposure.

The samples prepared by the airbrush method described before were checked by XAS with regard to the homogeneity of the deposition process: The homogeneity of the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ sample with respect to the molecule condition is crucial as the spin polarization data from different sample positions are merged to reduce the statistical error of the results.

The results of the XAS characterization reveal a very good homogeneity of the absorption yield measured at different sample positions, see Fig. 1. Furthermore, the oxidation state of the Mn ions in the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ SMM, indicated by the spectral shape of the Mn $L_{3,2}$ absorption, is the same over the whole sample area, fulfilling the requirements for the application of the sample scanning during the spin polarization measurements.

4.2. Monitoring of radiation-induced reduction

Besides the characterization of SMM samples upon preparation, XAS was also used to monitor radiation-induced changes to the molecule condition. Previous investigations revealed that the oxidation state of the Mn ions in $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM changes from Mn^{III} to Mn^{II} under exposure to soft X-rays, with the rate of the reduction process being strongly correlated to the choice of anions [32].

Mn $L_{3,2}$ edge absorption spectra were recorded before and after the acquisition of one SPES datapoint to investigate the

Fig. 2. Radiation-induced change of the Mn oxidation state in $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ SMM. The initial Mn^{III} content of 0.93 is reduced to 0.78 by the reduction process occurring upon soft X-ray exposure. The radiation damage shown corresponds to the acquisition of a single SPES datapoint at a photon energy of 642 eV, clearly demonstrating the necessity of sample scanning.

radiation damage caused by the measurement, see Fig. 2. The $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ sample showed an initial Mn^{III} content of 0.93, indicating that the majority of the deposited SMM were in their intended original state. The Mn^{III} content was reduced to 0.78 by a soft X-ray exposure of approx. 60 s, corresponding to the acquisition of a single SPES datapoint. The SPES measurement was performed at the Mn^{III} absorption maximum at 642 eV, leading to the creation of a maximum number of secondary electrons in the SMM sample. Therefore the extent of radiation-induced reduction shown in Fig. 2 can be regarded as a worst-case estimate. For excitation energies with a lower absorption cross section (off-resonance), less radiation damage was observed.

4.3. SPES of manganese(II)acetate

SPES measurements of manganese(II)acetate were performed in order to demonstrate that SPES and XMCD results correspond also for Mn ions in a chemical environment resembling the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM more closely than MnO and Mn_2O_3 . Based on the results of previous spin-resolved electron spectroscopy investigations of Mn bulk oxides and manganese(II)acetate (see [33]), the spin polarization of the electrons ejected from a manganese(II)acetate reference sample as a result of the $\text{Mn } L_{2,3}M_{2,3}V$ Auger transition has been measured for different excitation energies covering the whole $\text{Mn } L_{3,2}$ region. Due to singlet coupling being predominant in the investigated Auger transition, the spin polarization of the Auger electrons equals the spin polarization of the oriented core holes from the primary excitation process with the opposite sign.

Instead of recording full spin-resolved Auger spectra as shown in [33], a different approach was chosen here: After locating the appropriate Auger line in an overview spectrum, the spin-resolved measurements were performed with a fixed electron energy corresponding to the selected Auger transition. The results obtained from manganese(II)acetate are given in Fig. 3, the bottom panel shows the corresponding absorption spectrum with the excitation energies marked. The integration time of the SPES measurement was set to 300 s per helicity and datapoint. The bandwidth of the excitation was chosen individually for each datapoint, representing a compromise between resolution and the required count rates depending on the varying electron yield. The selected bandwidth is given by the horizontal error bars of the spin polarization

Fig. 3. SPES results of manganese(II)acetate. Top panel: The spin polarization of the Auger electrons resulting from the $\text{Mn } L_{2,3}M_{2,3}V$ Auger transition is shown. The horizontal error bars represent the bandwidth of the circularly polarized radiation used in the excitation step. The vertical error bars correspond to the statistical error of the measurements. The solid line represents XMCD data obtained from manganese(II)acetate (7 T, approx. 15 K) for comparison. Bottom panel: A corresponding $\text{Mn } L_{3,2}$ edge absorption spectrum of manganese(II)acetate is shown.

datapoints in Fig. 3, while the vertical error bars represent the statistical error of the measurements.

The Auger electron spin polarization observed in manganese(II)acetate reveals negative values in the $\text{Mn } L_3$ region. Towards higher photon energies, a sign change occurs at the upper edge of the $\text{Mn } L_3$ multiplet. The highest positive values of the spin polarization are observed around the satellite structure at 641.5 eV which is a characteristic spectral feature of Mn^{II} [32]. The sign change occurring between the main absorption and the satellite structure has been observed in XMCD investigations of other molecular Mn^{II} compounds [32,67]. While no significant spin polarization is found for the photon energy range in between the L_3 and L_2 multiplet structures, a small positive spin polarization with absolute values below 5% has been measured for the higher excitation energies of the L_2 multiplet.

The measured spin polarization strongly depends on the excitation bandwidth in the proximity of sharp polarization features: At an excitation energy of 641.6 eV, two measurements were performed with different excitation bandwidths of 250 meV and 750 meV. While the measured spin polarization is close to zero for the larger excitation bandwidth, a polarization of +12% corresponding to the sign change in XMCD observed by Khanra et al. [67] is obtained for the smaller excitation bandwidth.

XMCD measurements of manganese(II)acetate have been performed in cooperation with the group of E. Goering at the MPI for Intelligent Systems located in Stuttgart for comparison (see Fig. 3 top panel, solid line). The XMCD samples have been prepared by a drop-casting process on gold coated glass substrates. The measurements were carried out using a magnetic field of 7 T and cooling the sample to a temperature of approx. 15 K at the BESSY-II storage ring facility of the HZB (beamline PM3). The difference in absorption yields obtained from the XMCD experiment has been normalized to the sum of the helicity-dependent yields to derive A_{XMCD} as described in the theoretical background. The XMCD asymmetry and the detected spin polarization of the Auger electrons exhibit opposite signs as seen in previous experiments [33], which has been taken into consideration by changing the direction of the vertical axis.

A good qualitative agreement between the spin polarization of the Auger electrons and the XMCD asymmetry is found for the energy range of the whole L_3 region up to the onset of the L_2 multiplet at 649.5 eV. Within the L_2 edge region, some differences occur between the two physical quantities. It has to be noted that despite

Fig. 4. SPES results of $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ SMM. Top panel: Spin polarization results obtained from $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ SMM using the described method are presented. The meaning of the horizontal and vertical error bars is given in the caption of Fig. 3. Comparative XMCD data are given by the solid line, see main text for details. Bottom panel: Mn $L_{3,2}$ edge absorption spectrum of $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$, the excitation energies used for the SPES measurements are marked by circles (diameter equals excitation bandwidth).

the satisfactory qualitative agreement found here, the absolute values of the XMCD asymmetry are approximately 3 times lower than the corresponding spin polarization data: Note the different scaling of the left and right vertical axis of Fig. 3; we expect this difference to be correlated to an insufficient magnetic ordering of the manganese(II)acetate sample in the external magnetic field during the XMCD measurement.

4.4. SPES of $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM

Due to the radiation sensitivity of the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM [32], the above approach had to be modified, as the occurrence of radiation damage limited the measuring time. Therefore, a sample scanning method was introduced: A new, previously unexposed sample position was selected after each measurement of approx. 60 s. A large number of measurements was combined into one spin polarization datapoint. Variations of the SMM layer thickness cancelled out, as only the asymmetry of the count rates of the two detectors was evaluated. Instrument related asymmetries were cancelled out by combining measurements with different helicity of the circularly polarized light used for the excitation. The $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ SMM with the perchlorate anion was chosen for the SPES measurements, as previous investigations revealed its higher radiation stability compared to the SMM types with tetraphenylborate and lactate anions [32].

Spin polarization results obtained from $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ samples are shown in the upper panel of Fig. 4. The result of a comparative XMCD study at $B = -6.9$ T and approx. 2 K is given by the solid line in the top panel. Again, the lower panel of the figure represents the corresponding absorption spectrum with the excitation energies for the SPES measurements marked. For $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ a negative spin polarization with absolute values up to 20% is predominant in the Mn L_3 edge region. In strong contrast to the results obtained from manganese(II)acetate the spin polarization remains negative right to the onset of the L_2 absorption multiplet—the distinct change of sign observed in Mn^{II} systems is not found here. A positive spin polarization of up to +8% was detected in the first peak structure of the L_2 multiplet.

Besides the qualitative agreement between the spin polarization data in Fig. 4 and the XMCD result shown for comparison, a number of distinct differences are visible: The absolute value of the XMCD asymmetry is approximately twice the absolute value of the spin

Fig. 5. Mn $L_{3,2}$ edge XMCD data obtained from $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ SMM at $B = -6.9$ T and 2 K. The helicity dependent absorption spectra (top panel) are shown together with the resulting XMCD difference (bottom panel).

polarization in the L_3 region, though the overall structure within the L_3 multiplet is comparable. The large positive excursion of the XMCD asymmetry at the high energy side of the L_3 multiplet is not reproduced in the spin polarization data. A comparable difference is also found at the high energy side of the L_2 multiplet. A more detailed discussion of the differences is given later following the XMCD results.

4.5. XMCD results of $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$

XMCD measurements at an external field of -6.9 T and a temperature of approx. 2 K were performed at the SIM beamline of the SLS storage ring (Villigen, Switzerland) on $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ samples for comparison. As indicated by magnetization measurements with varied temperature and external field (VTVH), saturation is reached for $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ with external fields of approx. 7 T, see reference [29].

A series of eight consecutive XAS scans was performed to estimate the radiation damage caused by the XMCD measurement. No discernible radiation damage effects were found in this series. Using the continuous mode of the beamline monochromator, a set of three absorption spectra was recorded for each helicity and magnetic field orientation. The averaged helicity-dependent XAS spectra as well as the resulting XMCD difference are shown in Fig. 5.

Despite the very low signal-to-noise ratio, XMCD measurements were successfully performed also at the Cr $L_{3,2}$ edge. Using the same setup as before, series of 5 XAS scans were averaged to obtain the results shown in Fig. 6. A distinct difference in the sign of the XMCD effect is visible in the Cr $L_{3,2}$ XMCD data compared to the results obtained at the Mn $L_{3,2}$ edge (see Fig. 5), indicating that the antiferromagnetic coupling between the terminal Mn^{III} ions and the central Cr^{III} [24] is still effective at an external field of 6.9 T.

4.6. Sum rule evaluation of SPES data

According to the approach described in the theoretical background, information equivalent to XMCD data should be obtainable from the SPES measurement. Therefore a sum rule analysis (see [39–42]) was performed for both methods.

It has to be noted that the applicability of the sum rule approach to $3d^4$ systems like the Mn^{III} ions in the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM is severely limited by a number of physical constraints, see [49] for a detailed discussion. However, these constraints apply to both experimental methods, therefore the sum rule approach remains

Fig. 6. Cr $L_{3,2}$ edge XMCD data obtained from $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ SMM at $B = -6.9\text{ T}$ and 2 K . Top panel: Helicity dependent absorption spectra. Bottom panel: Resulting XMCD difference. Note the difference in the sign of the XMCD effect compared to Fig. 5, indicating an antiferromagnetic orientation of the Mn and Cr magnetic moments.

a useful tool for the comparison between XMCD and spin-resolved electron spectroscopy data. Charge-transfer multiplet calculations as described in references [49,50] are required to derive absolute values for the local magnetic moments without the limited accuracy of the sum rule formalism.

The linearly interpolated SPES data were multiplied point-wise with absorption data recorded in connection with the SPES measurements without an external magnetic field as the measured electron spin polarization corresponds to the asymmetry of the helicity dependent absorption intensities. The multiplication accounts for the fact that the difference of the two absorption yields Y_+ and Y_- instead of the asymmetry A_{XMCD} is required for the usual formulation of the XMCD sum rules. Additionally the sign of the SPES data was inverted in this step to account for the sign change introduced into the SPES measurements by the Auger process involved [33].

It is well known that the full separation of the L_2 and L_3 contributions is difficult for $3d^4$ systems as Mn^{III} . Due to the complex structure of the L_2 and L_3 multiplets, an attempt to fit the absorption data with theoretical models was not performed. Instead, the following simplified approach was chosen: The XMCD difference nearly vanishes between 650 eV and 652 eV , creating a region in which the value of the p integral changes only slightly with photon energy. The upper limit of the p integration was chosen in this region for both XMCD and spin-resolved electron spectroscopy data. With this choice, the resulting error due to the inaccurate separation of the edges is expected to be small compared to the other contributions to the sum rule error described in [49].

Using the most common sum rule expression [41,42] and calculating the required integrals p (L_3 edge XMCD difference), q ($L_{3,2}$ edge XMCD difference) and r ($L_{3,2}$ edge helicity averaged absorption), the following results were derived from SPES data:

$$\mu_{\text{spin}} = -\frac{(3p - 2q) \times (10 - n_{3d})}{r \times k_{\text{corr}}} = -1.8 \pm 0.4 \mu_{\text{Bohr}}$$

$$\mu_{\text{orbit}} = -\frac{2 \times q \times (10 - n_{3d})}{3r} = -0.60 \pm 0.12 \mu_{\text{Bohr}}$$

A possible magnetic dipole contribution ($\langle T_z \rangle$) to the spin magnetic moment has been ignored given the fact that this effect is small for $3d$ transition metals [48]. Due to the nature of the Mn^{III} -ligand bond present in the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM the system can be regarded as being purely $3d^4$. An additional correction factor k_{corr}

Fig. 7. Comparison of XMCD and spin polarization data obtained from $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ SMM. Note that the sign of the spin polarization has been inverted. The spin polarization raw data were multiplied with a helicity-independent absorption spectrum derived from the XMCD measurements to account for the differences in the intensity normalization used by the SPES and XMCD method.

has been applied to the result, following the approach suggested by Piamonteze et al. [49]. The correction factor successfully derived for Mn^{III} ions by Kuepper et al. [50] was used, although it has to be considered that the Mn^{III} ions in $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ are embedded in a different chemical environment.

The error given in the spin and orbital magnetic moment results was derived using the following method: Each spin polarization data point was varied with a normal distribution within its uncertainty limits (see error bars in Fig. 4), leading to a new asymmetry curve. The result was evaluated using the sum rules as before to obtain new values for μ_{spin} and μ_{orbit} . After 500 runs, the standard deviation of the calculated values was derived to estimate the error of the results.

Results for the local spin and orbital magnetic moments were derived accordingly from the XMCD data given in Fig. 5. Note that the correction factor for the spin magnetic moment was applied as before and the magnetic dipole contribution was neglected:

$$\mu_{\text{spin}} = -\frac{(3p - 2q) \times (10 - n_{3d})}{r \times k_{\text{corr}}} = -1.9 \pm 0.2 \mu_{\text{Bohr}}$$

$$\mu_{\text{orbit}} = -\frac{2 \times q \times (10 - n_{3d})}{3r} = -0.30 \pm 0.03 \mu_{\text{Bohr}}$$

The error of the derived spin and orbital magnetic moments has been estimated following the same approach as used for the SPES results—the uncertainty of each XMCD difference datapoint was derived from the averaging of the original spectra. Afterwards, the variation method described before was applied.

4.7. Discussion of differences between XMCD and spin-resolved electron spectroscopy

Despite the reasonable agreement between the spin magnetic moment obtained via the sum rule method from SPES and XMCD data, significant differences between the two datasets exist. A direct comparison of the XMCD difference signal and the measured spin polarization is shown in Fig. 7. Note that the sign of the spin polarization has been inverted and the spin polarization data have been multiplied with a spin-integrated absorption spectrum to account for the different intensity normalization of both methods.

It is striking that in the whole Mn L_3 edge region, the XMCD signal reveals larger absolute values with respect to the spin

Fig. 8. XAS spectra of $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ SMM obtained under different experimental conditions: Measurement at room temperature (black solid line) and at 2 K without external field (dark yellow solid line). Spectra recorded at 2 K and -6.9 T with opposite light helicity (dotted lines) have been averaged to obtain the spin independent absorption spectrum (red solid line). Inset: A shift of approx. 300 meV occurs for the main Mn^{III} absorption feature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

polarization data. Nevertheless, the structure of the multiplet with its three peaks at approx 640 eV, 641 eV and slightly above 642 eV is reproduced reasonably well in both methods. The sign change and the large negative excursion of the XMCD signal at energies above the L_3 multiplet is not reproduced in the spin polarization data. The measured spin polarization retains its sign up to the onset of the L_2 peak structure. Here, the XMCD signal reveals again relatively large negative values which are not reproduced in the (sign-corrected) spin polarization. Due to these characteristic differences, the integral-based sum rule evaluation leads to comparable results for the spin magnetic moment: The larger positive swing of the XMCD signal in the $\text{Mn } L_3$ region and the negative excursion in between the L_3 and L_2 multiplet region cancel out, resulting in comparable values for the L_3 and $L_{3,2}$ integrals.

With respect to the experimental conditions which the sample is subjected to, two major differences exist between the XMCD and SPES method: While the XMCD method required (1) the application of an external magnetic field of -6.9 T and (2) a low sample temperature of approx. 2 K, the SPES measurements were performed at room temperature and with all external magnetic fields compensated to negligible values.

Absorption spectra obtained under different experimental conditions were compared to investigate the influence of these two factors, see Fig. 8. Two spectra obtained at room temperature (MAX-lab beamline D1011, black solid line) and at approx. 2 K (dark yellow solid line, measured at SLS) show a very good agreement and hint at a negligible influence of the sample temperature on the $\text{Mn } L_{3,2}$ absorption. Two spectra recorded at 2 K and -6.9 T with opposite helicity (dotted lines) were averaged to obtain the spin-independent spectrum (red solid line) shown in Fig. 8.

Distinct differences are observed with respect to the experimental situation without external magnetic fields: The Mn^{III} absorption maximum (leftmost arrow) reveals a higher relative absorption. It appears to be shifted towards higher photon energies by approx. 300 meV. The high-energy edge of the L_3 multiplet as well as the whole spectral region between L_3 and L_2 right to the onset of the L_2 multiplet reveal a higher absorption yield than without external fields. It has to be noted that this difference in the Mn absorption coincides with the spectral region in which the largest discrepancy between XMCD and SPES results occurs. A non-negligible influence

of the external magnetic field on the electronic structure of the Mn^{III} ions present in $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}](\text{ClO}_4)_3$ SMM may be assumed to play a major role in the observed differences between the two methods. This may be correlated to the fact that the $S_t = 21/2$ spin ground state of the $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM is energetically not well separated, but several spin states of different spin quantum numbers are within a few wavenumbers [24,26].

Despite the reasonably good agreement of the spin magnetic moment derived via the sum rule approach from XMCD and SPES data, the obtained results are significantly lower than the theoretical value expected for the Mn^{III} and Cr^{III} coupling scheme and previous data from AC and DC magnetometry [26], indicating the physical limitations of the sum rule formalism for $3d^4$ systems as described by various authors [43–50].

5. Summary and conclusion

Comparative XMCD (2 K, 7 T) and spin-resolved electron spectroscopy measurements (room temperature, no external field) at the $\text{Mn } L$ edge have been performed on $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ single-molecule magnets deposited on Au and Si substrates. An influence of the external magnetic field on the absorption spectrum of the SMM samples has been observed. Despite its limited applicability to $3d^4$ systems, a simple sum rule evaluation was performed to provide a means of comparing the two experimental methods. However, the absolute value of the local spin magnetic moment obtained from both methods differs significantly from previous results measured by AC and DC magnetometry. Further investigations are required: The correction factor used in the sum rule evaluation needs to be refined for the investigated SMM system using the charge transfer multiplet approach [49] for comparative calculations of the XMCD and spin polarization effect.

It is unlikely that the distinct differences in the absolute magnitude of the spin polarization and the XMCD effect are caused solely by the observed influences of the magnetic field. The results seem to indicate that the initial assumption of a direct one to one correspondence needs to be refined by theoretical investigations. However the existence of a correspondence is clearly proven by the very good agreement of the energy dependence found for the electron spin polarization and the XMCD including their sign change, which has been shown for Gd as well as for manganese(II)acetate. Despite the observed differences, a qualitative agreement has been confirmed for $[\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}$ SMM as well. It might be possible that there is an energy-independent factor of negative sign, depending upon the angular momenta J , L and S for the ratio of electron spin polarization and XMCD asymmetry. Therefore further theoretical work is required to gain more insight into the nature of the observed correspondence and to derive a quantitative relation between the two physical quantities.

As the magnetization studies [26] probe only the total magnetization of the SMM sample without providing elemental resolution, an investigation of the Cr^{III} contribution is required to provide a deeper understanding.

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