Fluorescence-Detected X-ray Magnetic Circular Dichroism of Well-Defined Mn\textsuperscript{II} and Ni\textsuperscript{II} Doped in MgO Crystals: Credential Evaluation for Measurements on Biological Samples

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ABSTRACT: L\textsubscript{2,3}-edge X-ray magnetic circular dichroism (XMCD) spectra have been measured for the well-defined dilute Ni\textsuperscript{II} and Mn\textsuperscript{II} ions doped into a MgO crystal, with sub-Kelvin dilution refrigerator cooling and 2 T magnetic field magnetization. A 30-element Ge array X-ray detector has been used to measure the XMCD for these dilute ions, whose concentrations are 1400 ppm for Ni\textsuperscript{II} and 10 000 ppm for Mn\textsuperscript{II}. Large XMCD effects have been observed for both Ni\textsuperscript{II} and Mn\textsuperscript{II}, and multiplet simulation described the observed spectra. The fluorescence-detected L-edge absorption spectrum and XMCD of Ni\textsuperscript{II} in MgO are comparable with both theoretical calculations and the total electron yield measured ions in similar chemical environments, at least qualitatively validating the use of the sensitive fluorescence detection technique for studying XMCD for dilute 3d metal ions, such as various metalloproteins. Sum rule analyses on the XMCD spectra are also performed. In addition, these XMCD measurements have also been used to obtain the sample’s magnetization curve and the beamline’s X-ray helicity curve. This study also illustrated that bend magnet beamlines are still useful in examining XMCD on dilute and paramagnetic metal sites.

1. INTRODUCTION

X-ray magnetic circular dichroism (XMCD) measures the X-ray absorption difference between the left and the right circularly polarized X-ray beams in the presence of a magnetic field. It has been developed as a powerful element and site-specific probe of electronic and magnetic structures in various fields.\textsuperscript{1–6} Through ligand field multiplet simulations\textsuperscript{7–11} and the application of X-ray sum rules,\textsuperscript{12,13} predictions can be made about the electronic configuration as well as the orbital and spin angular momentum for a particular element present in the probing sample. XMCD spectroscopy is now a well-established technique for materials sciences\textsuperscript{5,6,14,15} and even for some biological sciences.\textsuperscript{16–18}

Since the first X-ray crystal structure report on iron-containing sperm whale myoglobin in 1950s, the X-ray probe of metalloproteins has attracted chemists, biochemists, as well as other scientists for decades.\textsuperscript{19} Measuring metals inside of biological samples has several practical issues. First, biological metals are dilute in concentration, for example, one myoglobin molecule (17 KDa) has only one iron, leading to 0.33% iron concentration (by weight). Therefore, sensitive fluorescence detection has to be employed to extract the weak metal signal from the dilute samples. Questions have been raised as to the accuracy of fluorescence-detected X-ray absorption spectra.\textsuperscript{20–23} Although some previous theoretical work suggests that the problem is for the rare earth elements and that the X-ray fluorescence detection should be valid for 3d transition-metal complexes,\textsuperscript{24} and X-ray fluorescence detected XAS on biological 3d metals\textsuperscript{17,18,20,21} have been reported, it is still important to evaluate the X-ray fluorescence detect on some well-defined standard systems.

Second, unlike ferromagnetic materials, metal sites in biological samples are paramagnetic. Therefore, an ultrahigh magnetic field (B, in the level of Teslas) and an ultralow cryogenic temperature (T, in the level of Kelvin or sub-Kelvin) have to be employed to effectively align the paramagnetic moments inside of the metalloprotein samples. The magnetic saturation extent is an exponential function of B/T, and B/T = 4 is needed for an almost full magnetization of a spin = 1 paramagnetic moment (the metal centers inside of biological samples). Nevertheless, the dilute samples’ real magnetic saturation level still better be calibrated experimentally with well-defined standard systems.

In this paper, two well-defined samples, Mn\textsuperscript{II} and Ni\textsuperscript{II} ions doped into single MgO crystals,\textsuperscript{25} were used to examine the fluorescence-detected XMCD and to examine the magnetic saturation. The observed XMCD spectra were simulated with the ligand field multiplet calculations\textsuperscript{20,22} and examined against the XMCD sum rules.\textsuperscript{17} The Ni XMCD spectra obtained here are comparable to the previously reported total electron yield measured ions (TEY) measured XMCD spectra on similar ferromagnetic Ni materials.\textsuperscript{26,27} These XMCD spectra were also used as an indicator to study and calibrate the samples’ magnetic saturation curves and the beamline’s X-ray helicity curves. All of these illustrated well that the X-ray fluorescence-detected XMCD is valid, at least for the later 3d metal ions (e.g. Ni). This is the first report of XMCD on a well-defined, dilute, and paramagnetic metal ion system.
Of course, real metalloproteins have various local symmetries (e.g., $O_h$, $T_d$ square planar, tetragonal, etc.), various ligands (S, N, C, as well as O), and the even more complicated environment beyond the first-layer ligands. All of these aspects affect the details of X-ray absorption spectra or XMCD spectra. The doped Ni and Mn in MgO used in this study have only $O_h$ symmetry and only O ligands and thus cannot represent the real biological metals in every detail. However, these standard samples do have some generalized similarities with the biological metal sites: (1) both have a localized metal–ligand interaction; (2) both have dilute metal ions; and (3) both have paramagnetic metal ions, which are not coupled with the neighboring metal sites. These similarities, along with their simplicity, well-defined properties, and the chemical stability, make them useful standards samples for evaluating and calibrating the XMCD measurements on real biological metals.

2. EXPERIMENTS

A. Samples. Samples of Ni$^{ll}$ and Mn$^{ll}$ doped into a single crystal MgO were obtained from Goodfellow Metals, Inc. and used without further treatment. Both doped crystals were flat plates with a smooth (001) surface. In our XMCD experiments, the crystals were attached to a gold-plated sample holder with silver paint to achieve good thermal conductivity. The incoming X-ray beam made an angle of 55° with respect to the sample’s normal (a $C_a$ or 001 axis). The Ni$^{ll}$ dopant concentration was 0.14% (1400 ppm by weight), while the Mn doped sample contained 1% Mn. These concentration levels resemble the normal (a $C_a$ or 001 axis). The Ni$^{ll}$ dopant has $I_e=1$, while the Mn$^{ll}$ has $S=5/2$ for the ground states. These two well-defined metal models are good "calibration" systems for testing and evaluating the crecence of the fluorescence-detected XMCD of a super high field produced magnetic saturation, as well as of other experimental issues for dilute 3d metal systems in general (e.g., for various metalloprotein molecules).

B. XMCD Instrument. The advanced XMCD apparatus, built in collaboration with Janis Instruments, uses a 76 cm split-coil 2 T superconducting magnet surrounded by a UHV chamber (maintained at $\sim 5 \times 10^{-9}$ Torr), a $^3$He/$^4$He dilution refrigerator insert (Janis Research, MK-400T), and a 30-element Ge fluorescence detector (Canberra Industries, GUL055S). The detector is inserted horizontally between the two coils, perpendicular to the photon beam path under windowless operation.16,17 The overview of the XMCD setup is as shown in Figure 1a. The maximum magnetic field is $B=2$ T in this apparatus; and we did not observe significant "field-induced" degradation of detector performance with the temperature between 50 mK and 4.2 K as well as the apparatus’s other temperature zones were illustrated as shown in Figure 1b. The LHe shields have entrance and exit holes and polypropylene thermal shielding widows for the incoming X-ray beam and for the outgoing fluorescence emission signal. The thermal shielding is critical to reduce the room-temperature thermal load and maintain the samples at sub-Kelvin temperatures.

The temperature on the coldfinger was monitored down to 1.4 K with a Lakeshore DT-470-12A silicon diode. The temperature between 50 mK and 4.2 K was measured using a calibrated Matsushita carbon resistance thermometer. The sample’s real temperature can also be determined (confirmed) by the analysis of sample magnetization curves, as will be described later. The operating temperature in our experiments was about 0.5 K. Periodic magnetic field reversal is required to modulate the sign of the XMCD. To avoid excessive heat impact to the dilution fridge during this procedure (via eddy current heating of the coldfinger), a moderate magnetic field window was selected around the oxygen fluorescence. The oxygen signal was used as a measure of the incident intensity ($I_0$). The raw spectrum was then collected as $<F/I_0>$ versus the excitation energy ($E$). The energy was calibrated with NiF$_2$ and MnF$_2$.

The $^3$He/$^4$He dilution refrigerator insert enters the magnet bore from the top of the chamber, and the sample is attached to the coldfinger at the center of the magnet bore (Figure 1a). The $^3$He/$^4$He dilution refrigerator achieves an ultralow temperature by continuous evacuation and cycling of $^3$He from a $^3$He + $^4$He mixture.30 Around the sample/coldfinger, a 4 K liquid helium (LHe) shielding and a 77 K liquid nitrogen (LN2) shielding were used to minimize the coldfinger’s thermal load. Samples were introduced into the magnet bore through a vacuum load-lock and screwed onto the coldfinger using a removable sample insertion device. Samples with sample holder were precooled to the LN2 temperature inside the UHV load-lock environment prior to being loaded into the XMCD chamber to minimize the thermal impact of the “warm” samples to the coldfinger. The 4 and 77 K as well as the apparatus’s other temperature zones were illustrated as shown in Figure 1b. The LHe shields have entrance and exit holes and polypropylene thermal shielding widows for the incoming X-ray beam and for the outgoing fluorescence emission signal. The thermal shielding is critical to reduce the room-temperature thermal load and maintain the samples at sub-Kelvin temperatures.
sweep rate of 50 g/s was used, and this kept the corresponding temperature rise to less than 100 mK per switch. The temperature recovered to the equilibrium (0.5 K) in five minutes after a field change; at this time, the XMCD measurement could be resumed.

C. Data Collection. The XMCD experiments were performed at the SSRL bend magnet beamline 8-2.31,32 using the 1100 L/mm grating. Elliptically polarized X-rays were obtained by moving the first mirror above or below the electron orbit plane. On the basis of previous calibration experiments on polarized ferromagnetic samples, the optimum XMCD signal was obtained at a beam takeoff angle corresponding to a circular polarization of 80 ± 5%. At this takeoff angle, the beam intensity is about 25% of its maximum intensity. As described below, this value was later checked by comparison of theoretical and experimental polarization estimated on the NiII doped MgO sample. The entrance and exit slits were both set to 50 μm, and the energy resolution was estimated to be 1.2 eV at the Ni L-edge and 0.8 eV at the Mn L-edge for the circularly polarized beam. The oxygen fluorescence measured Io signal was checked to be proportional to the incident flux (measured with a gold mess) to a good approximation.

Individual scans were taken over the metal L-edges using 0.2 eV steps at 5 s per point integration time. One set of 16 scans was taken with right circular polarization. Every two scans, the magnetic field was switched between −2 and +2 T. A second set of 16 scans was then taken with left circular polarization, again alternating the sign of the magnetic field. The apparent XMCD effect did reverse with opposite beam polarization. For measurement of the magnetization curves, a similar procedure was followed, collecting only the L2,3-edge region using a magnetic field between 0.1 and 2.0 T. For the polarization curves, the XMCD measurements were done (again, the L1-edge only at a fixed field of 2 T) at different mirror positions, corresponding to different takeoff angles above and below the ring orbital plane. As a convention, the mirror position reading (mm to cm steps) was first converted to the observation angle ψ (in mili-radians) and then converted to αααα by measuring αααα by a factor of γ = electron energy/rest energy = 3 GeV/0.511 MeV = 5870.84 (which is a SSRL parameter).

The model compound NiIFe was measured at ALS beamline 4.0.2 using a published regular procedure with a channeltron. For comparison, the regular L-edge XAS NiII/MgO was also measured at ALS beamline 4.0.2 at 4 K with a 30-element X-ray fluorescence detector (Canberra Industries, GUL005S). The NiII/MgO L-edge XAS such measured was very similar to the averaged XMCD spectrum (I↑↑ + I↑↓)/2 measured at SSRL BLS-2 (as described above).

D. Data Analysis. L-edge excitation spectra (F/I0) taken with the X-ray photon angular momentum either parallel (I↑↑) or antiparallel (I↑↓) to the angular momentum of the metal ion were first added together (16 scans each side). Then, each spectrum was normalized to the edge jump between the pre-L3- and post-L3-edge and then corrected for the small energy offset between spectra recorded on opposite sides of the orbital plane. A double step curve was then fit to the raw data (F/I0) in the pre-L3- and post-L3 regions to simulate and remove the two-step nonresonant background of the spectra. Finally, the parallel and antiparallel absorption spectra were corrected for the fact that the illuminating X-rays were only 80% polarized by

\[ I↑↑ = \frac{(α + 1)I↑↑ + (α - 1)I↑↓}{2α} \]  

\[ I↑↓ = \frac{(α + 1)I↑↓ + (α - 1)I↑↓}{2α} \]  

\[ \text{XMCD} = \frac{(I↑↑ - I↑↓)/(I↑↑ + I↑↓)}{I↑↑ + I↑↓} = \frac{[I↑↑ - I↑↓]}{I↑↑ + I↑↓} \]  

where the I↑↑ and I↑↓ represent the observed spectra while the I↑↑, I↑↓, and XMCD are the polarization-corrected intensities, α is the beam’s polarization.

The multiplet simulations7−11 for the observed XAS spectra were performed by published methods. For NiII, the calculation involves electronic transitions from the 3d6 ground state to the 2p3d5 excited state, where 2p3 stands for the 2p core hole. For MnII, the calculation simulates electronic transitions from a 3d5 ground state to a 2p3d6 excited state. Coulomb, exchange, and spin–orbital interactions for both initial and final states were first calculated. The atomic multiplet approximation was used to calculate the ground and final state spin–orbital L–S interactions and the final state 2p core hole J–J coupling. The ab initio Hartree–Fock values of Slater integrals and spin–orbital couplings for the 3d transition metals used were tabulated values.

The calculated atomic multiplets were expressed as eigenstates appropriate for the ion in a ligand field. XMCD selection rules were imposed on the transitions to obtain the XMCD spectra. The local symmetry of the Ni and Mn sites in MgO was assumed to be Oh symmetry. In Oh symmetry, the 3d orbitals are split into t2g and eg representations with an energy difference of 10 Dq. The appropriate values for 10 Dq were optimized by comparing the calculated with the experimental spectra. The calculated spectra were convoluted with Lorentzian and Gaussian line shapes to account for the lifetime and instrumental broadening, respectively.

3. RESULTS AND DISCUSSION

A. XMCD and Multiplets. The Ni L-edge excitation spectra for Ni/MgO (I↑↑ and I↑↓) are reported in Figure 2a. The spectra are typical of previously reported high-spin (triplet state) NiII21,25,34 which can be well-described by ligand field multiplet simulations. The L3 region has a major peak near 853.4 eV, a minor peak near 855.6 eV, and some broad structure near 859−862 eV. Arroio and co-workers26,34 have shown that the latter satellite structure requires inclusion of configuration interaction with 3d4L character in the ground state in the calculations. The L2 at 869−873 eV has a partially resolved doublet structure (peaks at 870.0 and 871.6 eV). The overall feature is similar to the NiII ion inside of the magnetic materials.35,36 Although some work mentioned the possible cant spectral distortion occurs in the fluorescence detection of the f shell rare earth materials35,36. Although some work mentioned the possible distortion in 3d metals, our spectra for the dilute (0.14%) NiII ion do not show a significant distortion effect. The ratio of L3 to L2 peak heights is about 4:1, which agrees well with previous TEY results (also 4:1) on high-spin NiII compounds in the report26,27 and in our own measurements (Figure 3). The ratio of the two L3 subpeaks (slightly smaller than 4:1) also resembles the previously published or measured TEY results (4:1), suggesting no obvious fluorescence detection distortion. These data are listed in Table 1. The averages of I↑↑ and I↑↓ for NiII/MgO were also compared with the TEY measured NiII in
the ionic NiF₂ complex in the same L-edge region (Figure 3). The overall close match of the two spectra again provides credibility for fluorescence detection at low concentration, such as 0.14% Ni.

Shown in the bottom portion (dotted line) of Figure 2 is the polarization-corrected difference in fluorescence signals $\langle I^\uparrow \downarrow \rangle - \langle I^\uparrow \uparrow \rangle$, which is proportional to the X-ray magnetic circular dichroism effect (XMCD). At the $L_2$-edge peak, there is a 44% difference in polarization-corrected fluorescence intensity between the two peaks (corresponding to a 22% XMCD effect). This is not far from the previously reported 60% absorption difference for Ni$^{II}$ ions in Cs(NiCr(CN)$_6$)$_2$H$_2$O. The differences are kind of expected because (1) there was a much larger correction for the degree of circular polarization in the previous reports; (2) their averaged signal was $(L + R + z)/3$ while ours is $(L + R)/2$ instead; and (3) their sample was an unoriented powder while our sample is a (001) oriented single crystal. Nevertheless, our measurement is qualitatively consistent with theirs while also in close agreement with the ligand field calculation with $10 D_{q} = 1$ eV (Figure 2b and c). The XMCD in the $L_2$ peak is unipolar, also consistent with the Cs(NiCr(CN)$_6$)$_2$H$_2$O reports. The XMCD effect at $L_3$ is about 8%.

A bipolar XMCD signal was observed in the $L_1$ peak with an intensity ratio of 3:1, which is close to the 3.5:1 for Ni$^{II}$ in Arrio et al.’s molecular magnets. This effect is nicely reproduced in the spectral simulations of a typical Ni$^{II}$ ($^4A_2$) ground state in $D_4h$ symmetry. This can be understood qualitatively as follows. The $L$ absorption corresponds approximately to an excitation to a $2p^5 3d^9$ final state, with $J = 3/2$ or 1/2 core hole spin to further split the transition into $L_1$ and $L_2$. The signals at the $L_3$ have opposite signs because the main $L_1$ peak corresponds to excitations with the final $2p^5$ spin parallel to the $3d^9$ spin, while the shoulder is the transition with the final $2p^5$ spin antiparallel to the $3d^9$ spin. This is always the case unless there is a strong distortion (like in $D_{x2}$ or other low symmetries), which could then cancel out some of the shoulder features.

In previous studies on Fe$_5$Gd$_3$O$_{12}$ garnets, the presence of peaks with an opposite sign of the XMCD effect was interpreted as arising from the antiferromagnetic coupling between the tetrahedral and octahedral Fe sites. There is no reason to question that interpretation. However, the Ni results show that there is no simple correspondence between the sign of a peak and the presence of a component in the sample with a particular magnetic coupling. For interpretation of the XMCD of Ni complexes, simulations becomes essential to distinguish between detailed small effects and possible artifacts.

The fluorescence-detected XMCD spectrum for Mn/MgO was recorded as in Figure 4. At the $L_1$-edge maximum, there is a 50% difference in polarization-corrected intensities, corresponding to a 25% XMCD effect. There is also very rich multiplet structure that is only partially resolved at the beamline resolution. As with Ni/MgO at $L_3$, the secondary peak has an XMCD of opposite sign to the main peak. However, the spectra are too complex for a simple interpretation because of the $d^5$ configuration of Mn$^{II}$. Unfortunately the strong Mg second-
order K-edge absorption (1303 → 651.5 eV) overlaps with the L_{2,3}-edge of Mn II (650 eV); therefore, no spectrum has been obtained in the Mn L_{2,3} region for Mn^{II}/MgO. The simulations again reproduce both the sign and amplitude of the XMCD "magnetic dipole term" (octahedral) Ni^{II} ions as well.26,27 Omitting the last term can again reproduce both the sign and amplitude of the XMCD

The corresponding integrals are illustrated in Figure 5. With these integrals the integral range. The following integrals are defined

\begin{align}
A &= \int_{L_2} (I^{11} - I^{11}) \, d\omega \\
B &= \int_{L_2} (I^{11} - I^{11}) \, d\omega \\
C &= \int_{L_2} [(I^{11} + I^{11})/2] \, d\omega
\end{align}

where \(\omega\) is the incident photon energy and \(L_i (i = 2, 3)\) denotes the integral range. The corresponding integrals are illustrated in Figure 5. With these integrals

\begin{align}
\langle L_x \rangle &= -n_h(A + B) / 2C \\
\langle S_x \rangle &= -(3/2)n_h[(A - 2B) / 2C](1 + \langle T_z \rangle / \langle S_z \rangle)^{-1}
\end{align}

where \(n_h\) represents the number of 3d vacancies in the metal ion. As these doped samples are oriented, the last term containing \(\langle T_z \rangle\) in general, cannot be averaged to zero as for the "powder" samples. However, Arroio and co-workers pointed out that this term is often very small for the highly symmetric (octahedral) Ni^{II} ions as well.26,27 Omitting the last term and using the common symbols in the XMCD literature (\(A, B, C\)) the XMCD sum rules can be re-expressed in the following manner, in units of \(\hbar\) per atom

\begin{align}
\langle L_x \rangle &= -n_h(A + B) / 2C \\
\langle S_x \rangle &= -(3/2)n_h[(A - 2B) / 2C](1 + \langle T_z \rangle / \langle S_z \rangle)^{-1}
\end{align}

As illustrated in Figure 5, \(A = 4.5 \pm 0.3, B = -3.0 \pm 0.2,\) and \(C = 20.8 \pm 0.6.\) Using a value of 1.8 for \(n_h\) (assuming 90% covalency) in the calculations, we found \(\langle L_x \rangle\) and \(\langle S_x \rangle\) to be 0.06 ± 0.02 and 0.68 ± 0.06, respectively. The number for the \(\langle L_x \rangle\) and \(\langle S_x \rangle\) per \(n_h\) were also derived as 0.03 ± 0.01 and 0.38 ± 0.03. The error analysis is based on the statistical error plus 10% instrumental error. The ratio of \(\langle L_x \rangle / \langle S_x \rangle\) is ~0.08, regardless of the number of holes \(n_h.\) These sum rule analyzed values are summarized in Table 1, along with reported results for a TEY measured Ni^{II} ion. Besides the many other similarities in between the L-edge absorption/XMCD spectra for Ni^{II}/MgO and for the Ni^{II} ions inside of Cs(NiCr-(CN)_{6})2H_{2}O,26,27 the above calculated spin angular momenta for these two Ni^{II} ions have comparable values (0.38\(\hbar\) versus 0.40\(\hbar\)). However, more difference exists for the orbital angular momenta between them (0.03\(\hbar\) versus 0.10\(\hbar\)).

C. Magnetization Curves. The samples’ magnetization was also investigated by analyzing the field-dependent XMCD effects, as shown in Figure 6. As expected, the spin S/2 Mn^{II} ion shows a much steeper magnetization curve (magnetization versus B/T) than the spin 1 Ni^{II}, which is then steeper than the spin 1/2 Cu^{II} (from a previous experiment17). For more quantitative understanding, we fit these magnetization data to a Brillouin function as below.40

\begin{align}
R &= \frac{X M C D}{X M C D_{max}} \\
&= (2J + 1)/(2J) + \text{coth}[(2J + 1)/2] - 1/(2J) \\
&\times \text{coth}(a/2) \\
\text{in which } x &= x = (\mu_B B/kT), a = g \chi, \text{coth}(a) = (e^x + e^{-x})/(e^x - e^{-x}) \\
g &= 1 + [J(J + 1) + S(S + 1) - L(L + 1)]/2J(J + 1), \text{which}
\end{align}
is called the Landé factor. In the formula, \( \mu_B \) is the Bohr magnetron, \( k \) the Boltzmann constant, \( B \) the magnetic field, and \( T \) the sample’s temperature. As the orbital angular momentum for a ligand chemical complex should be close to zero in comparison with its spin contribution, for the first-order approximation, we omit \( L \) and let \( J = S \) and \( g = 2 \) approximately. Under this special circumstance \( (L = 0, g = 2) \), we obtain

\[
R = \frac{(2S + 1)}{(2S)} \coth\left([2S + 1]x\right) - 1/(2J) \coth(x) \tag{8}\]

A least-squares fit of our measured XMCD data (using the temperature from the reading, 0.5 K) to eq 8 yields estimated spin values of 0.4\( \hbar \), 0.9\( \hbar \), and 2.0\( \hbar \) per metal ion. Although the spin values are not equal to the nominal values, their ratio 0\( \leq 0.9:2.0 \) is very close to the nominal values 0.5:1.0:2.5 (\( \leq 0.4:0.8:2.0 \)). The error may come from the estimation of the ground state, the estimation for the magnetic saturation is directly proportional to the temperature \( (0.5 \text{ K}) \) to eq 8 yields estimated temperature reading as well as the slightly different temperatures for different samples. The errors could also be due to the XMCD measurement/analysis error and/or an oversimplified model for \( L \) and \( g \) values. Nevertheless, the magnetization curves may be a very useful tool to distinguish different spin species under the same experimental conditions. By using the nominal spin values, the temperature for this study is estimated to be 0.45 K. This assumes that other second-rank tensor zero field splitting(s) do not dominate the ground-state spin Hamiltonian. Although the temperature estimation depends on the spin value as well as the zero field splitting(s) in the ground state, the estimation for the magnetic saturation is directly from the observed magnetization curve and is not affected by these factors. In our XMCD measurement, a 99% magnetic saturation is achieved for the Ni\(^{II}\) doped MgO crystal.

**D. Helicity Curves.** Under conditions of constant sample temperature (0.5 K) and constant magnetic field (2 T), the magnitude of the XMCD effect is directly proportional to the helicity of the incoming X-ray photons. The XMCD of Ni\(^{II}\) was measured at different first mirror positions (in the beamline) to examine the degree of beam polarization at different “out-of-plane” observation angles (\( \psi \) or \( \gamma \psi \)). The measured XMCD effect for Ni\(^{II}\) is shown as in Figure 7b (solid symbols), and the corresponding beam intensities (measured with a gold grid) are also shown in Figure 7a. These data constitute the basis for estimating the degree of polarization at a given mirror position.

**Figure 6.** Experimental magnetization curve measured with the XMCD effect (solid symbols) as a function of the ratio of the magnetic field over the temperature \( (B/T) \), along with a Brillouin function fit (solid line).

**Figure 7.** (a) X-ray beam intensity at different out-of-plane observation angles (\( \gamma \psi \)) (green square symbols) measured with a gold grid at bent magnet SSRL BL8.2, along with a simple Gaussian fit (dotted—dashed green line) and the theoretical prediction (solid green line); (b) the degree of polarization at different \( \gamma \psi \) measured with fluorescence detection on Ni\(^{II}\)/MgO XMCD (red round solid symbols), along with the theoretical prediction of the degree of polarization (solid red line).

To better understand the observations, the degree of polarization for radiation from a bend magnet was calculated theoretically by solving modified Bessel functions.\(^{33}\) The horizontal (\( E_x \)) and vertical (\( E_y \)) components of the electric fields were followed by calculation of circular polarization \( P = 2r/(1 + r^2) \), where \( r = E_x/E_y \) and the photon flux \( F \propto E_x^2 + E_y^2 \). The angular distribution of the final formula is obtained as follows:

\[
P = \frac{(2\chi^2)/\left(1 + \chi^2\right)K_{1/3}(\xi)/K_{2/3}(\xi)}{[1 + \chi^2/(1 + \chi^2)K_{1/3}(\xi)/K_{2/3}(\xi)]^{-1}} \tag{9}\]

\[
F = \text{const} \left[1 + \chi^2 K^2_{2/3}(\xi)K_{2/3}(\xi) + \chi^2/(1 + \chi^2)K^2_{1/3}(\xi)\right] \tag{10}\]

In the formulas, \( K_n(x) \) is the \( n \)-th order Bessel function, \( \psi \) is the observation angle in the vertical plane, \( \varepsilon \) is photon energy (854 eV for \( L_2\text{-Ni}^{III}\)), \( \varepsilon_C \) is the critical energy (SSRL = 4.72 KeV), \( \gamma = \varepsilon/\varepsilon_C = 0.1809 \), \( \gamma \) is the ratio of electron energy/rest energy (SSRL = 5870.84), \( \chi = \gamma \psi \), and \( \xi = \gamma (1 + \chi^2)^{2/3} \). As it is a standard calculation, we omit further details.\(^{33}\) The calculated polarization (solid red line) and intensity (solid green line) are also shown in Figure 7. Our polarization and intensity curves are in close agreement with the previous TEY measurement for this beamline on ferromagnetic samples.\(^{39}\) The least-squares fit of the measured XMCD data to calculated polarization with two adjustable parameters, the XMCD scaling factor and mirror position offset, gives an almost-perfect agreement in the aspect of the polarization. The discrepancy in the intensity curve is...
understandable because once the mirror is moved out of its optimal position, the beam may encounter more intensity cutoff by slits than theoretically predicted.

4. CONCLUSIONS

XMCD spectra have been recorded for the well-defined Ni\textsuperscript{II} and Mn\textsuperscript{II} doped into a single crystal MgO under a sub-Kelvin temperature (0.5 K) using a very high magnetic field (B = 2 T) and with X-ray fluorescence measurements. The fluorescence-detected L-edge absorption spectrum of Ni\textsuperscript{II} in MgO has been comparable with the TEY measurements of Ni\textsuperscript{II} L-edge absorption spectra in similar systems (with a similar octahedral crystal field).\textsuperscript{17,26,27} The fluorescence-detected XMCD also shows little difference between the two cases (Table 1), at least qualitatively validating the use of this sensitive technique for the study of a dilute later 3d transition-metal matrix, such as the various biological samples.

Large XMCD effects have been observed for both Ni\textsuperscript{II} and Mn\textsuperscript{II}, and the multiplet simulations have reproduced the observed XMCD with multiplet simulations. Meanwhile, XMCD sum rule analyses have also yielded comparable results, showing that X-ray fluorescence-detected XMCD is similar to the total electron yield detected XMCD on similar Ni\textsuperscript{II} site. XMCD measurements have also been utilized to obtain and understand the sample’s magnetization curve (as a function of the B/T) and the beamline’s helicity curve (as a function of the X-ray takeoff angle). These measurements are also very comparable with theoretical calculations and with the reported TEY measurements.

Although, nowadays, use of an elliptically polarized undulator beamline for XMCD experiments is a trend, this work has illustrated well that a bent magnet beamline is still useful and practical for performing XMCD measurements even for dilute samples.

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Notes
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