Table I. Slater integrals obtained from DFT and spin–orbit coupling constants in the Hartree-Fock approximation for the Mn^{2+} ion (in units of eV).

ion	state	configuration	$F_{dd}^{(2)}$	$F_{dd}^{(4)}$	ζ_{3d}	$F_{pd}^{(2)}$	$G_{pd}^{(1)}$	$G_{pd}^{(3)}$	ζ_{2p}
Mn^{2+}	initial	$2p^6 3d^5$	9.4323	5.8132	0.040				
	final	$2p^5 3d^6$	10.1963	6.2899	0.053	5.3354	3.8379	2.1773	6.846

Mn d and ligand p orbitals. The resulting $3d$ electron filling is $n_d = 5.31$, corresponding to an effective 1.69+ valence. We obtain $m_{\text{eff}}^{\text{spin}} = \sqrt{\langle \mathbf{m}^2 \rangle} = 5.67\mu_{\text{B}}$ for the local effective moment, as well as $m^{\text{spin}} = g_s \langle S_z \rangle = 4.68\mu_{\text{B}}$ and $m^{\text{orb}} = g_l \langle L_z \rangle = 0.008\mu_{\text{B}}$ for the maximal z-projections of the spin and orbital moments, respectively.

Finally, we observe that the electron filling and the magnetic moments resulting from our MLFT analysis are in excellent agreement with those calculated based on the DFT-GGA+U calculations in sec. II C: We obtain $n_d = 5.3$ and $m^{\text{spin}} = 4.7\mu_{\text{B}}$ using the same interaction parameters as in MLFT. These results are also in good agreement with the bulk magnetometry data (see sec. II B and Fig. 2), as well as with published neutron diffraction data [34, 48].

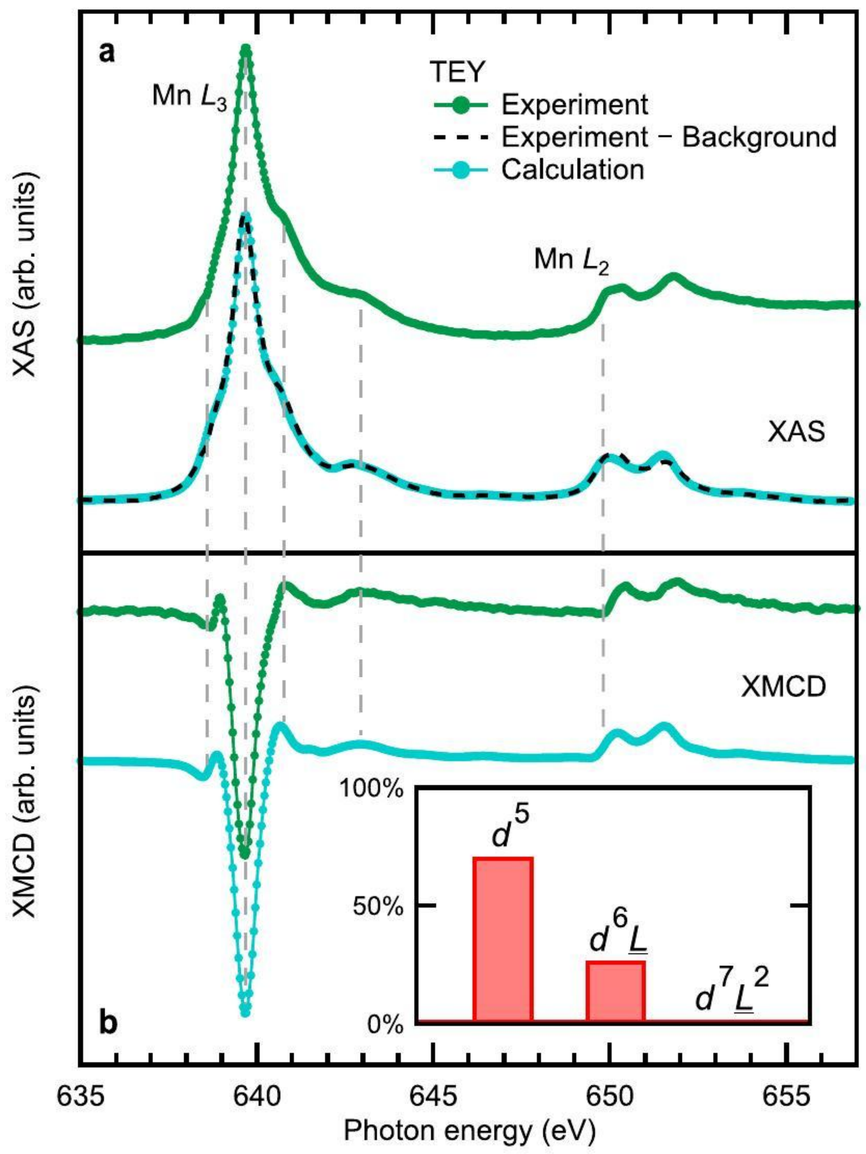

FIG. 5. MLFT analysis. (a) Background-corrected polarization-averaged experimental XAS spectrum (dashed line) together with a calculated MLFT spectrum (blue). The original, uncorrected data is shown above (green line). (b) Corresponding experimental and calculated XMCD spectra. The inset shows the contributions of different electronic configurations to the ground state. The vertical dashed lines highlight the positions of particular features of the spectra.

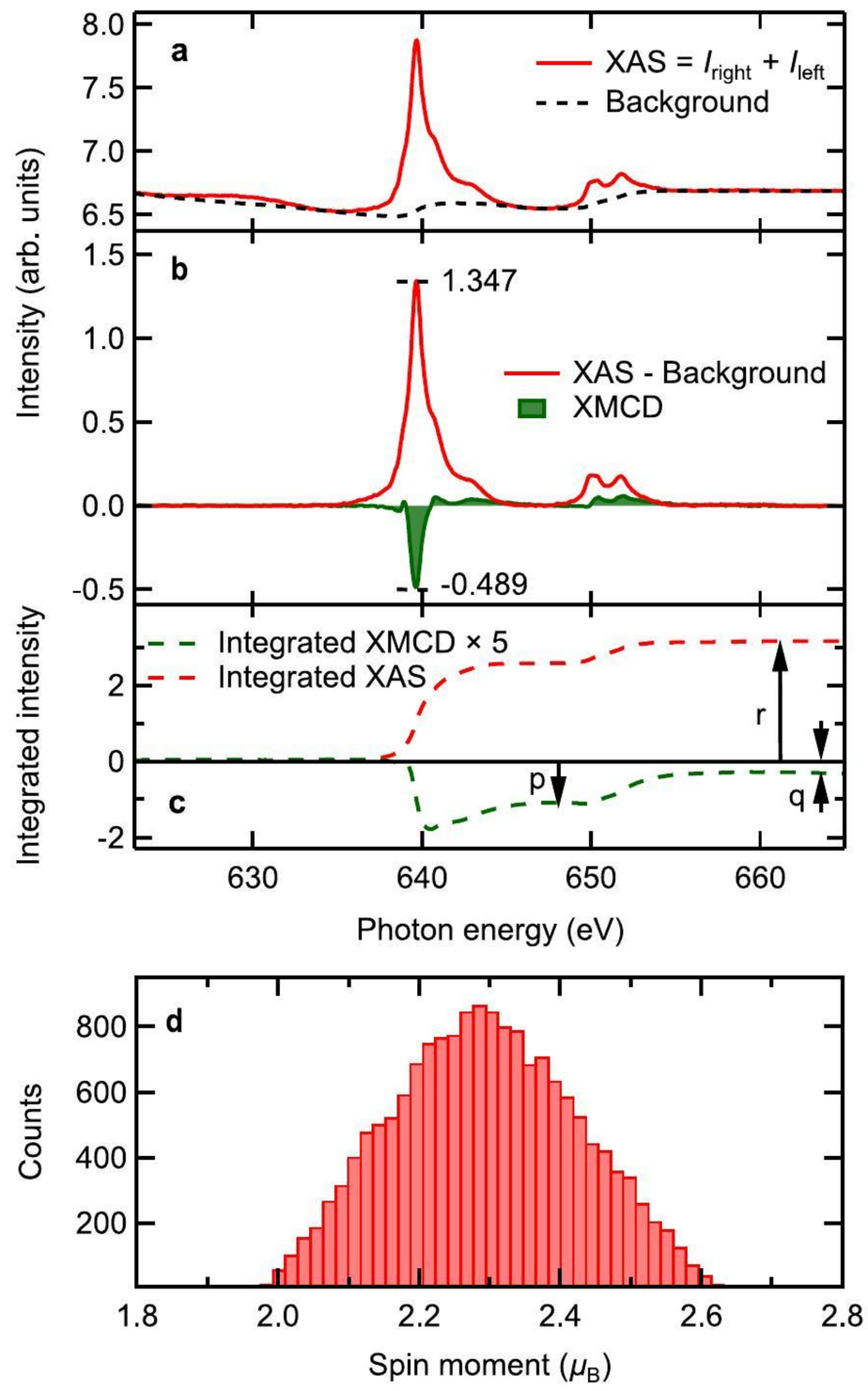

FIG. 6. Sum rule and peak asymmetry analysis of data measured on sample #4 at $T \approx 3.5\,\text{K}$ and $\mu_0 H = 0.15\,\text{T}$. (a) Polarization-averaged XAS intensity I (red line) together with the background (dashed line). (b) XAS spectrum after background correction, together with the XMCD signal I_{XMCD} (filled green curve). The peak intensities necessary for the asymmetry analysis are marked. (c) Integrated intensities of the XAS and the XMCD (multiplied by 5) spectra. The integrals p, q and r necessary for the sum rules are indicated with arrows. (d) Distribution of $m_{\text{XM}}^{\text{spin}}$ obtained by randomly varying the sum rule parameters within reasonable error margins, but not considering the uncertainty in the background choice (sec. II F and sec. S.V).