A non-empirical calculation of 2p core-electron excitation in compounds with 3d metal transition ions by ligand-field and density functional theory (LFDFT)

Harry Ramanantoanina*^a and Claude Daul^b

^{*a*}Paul Scherrer Institute, CH-5232 Villigen, Switzerland; E-mail: harry.ra@hotmail.com ^{*b*}Department of chemistry, University of Fribourg, Chemin du musée 9, CH-1700 Fribourg, Switzerland

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Fig. S1 LFDFT results of the $3d^5$ (${}^6S_{5/2}$) $\rightarrow 2p5^3d^6$ (in green), $3d^4$ (5D_0) $\rightarrow 2p5^3d^5$ (in blue) and $3d^3$ (${}^4F_{3/2}$) $\rightarrow 2p5^3d^4$ (in red) transitions of free Mn²⁺, Mn³⁺ and Mn⁴⁺ ions: Lorentzian convolution of the oscillator strengths of the electronic transitions with a half-width of half-maximum of 0.20 eV. The calculated parameters of the ligand field Hamiltonian are listed in Table 1.



Fig. S2 LFDFT results of the $3d^5$ (${}^{6}S_{5/2}$) $\rightarrow 2p5^3d^6$ transitions of free Mn²⁺ ion obtained from DFT calculations employing the LDA (in green), GGA (in black) and Hybrid (in red) functional: Lorentzian convolution of the oscillator strengths of the electronic transitions with a half-width of half-maximum of 0.20 eV. The calculated parameters of the ligand field Hamiltonian are listed in Table 1.



Fig. S3 Radial functions of the Kohn-Sham orbitals with dominant 3*d* characters of Mn^{2+} obtained for the 3*d*⁵ (up, solid curves) and $2p^53d^6$ (down, dashed curves) electron configurations in free ion (in black) and in $(MnF_6)^{4-}$ embedded in MnF_2 (in red and blue).