Selective Orbital Imaging of Excited States with X-Ray Spectroscopy: The Example of α-MnS

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Herein we show that nonresonant inelastic x-ray scattering involving an s core level is a powerful spectroscopic method to characterize the excited states of transition metal compounds. The spherical charge distribution of the s core hole allows the orientational dependence of the intensities of the various spectral features to produce a spatial charge image of the associated multiplet states in a straightforward manner, thereby facilitating the identification of their orbital character. In addition, the s core hole does not add an extra orbital angular momentum component to the multiplet structure so that the well-established Sugano-Tanabe-Kamimura diagrams can be used for the analysis of the spectra. For α-MnS we observe the spherical charge density corresponding to its high-spin 3d⁵ (⁶A₁) ground state configuration and we were able to selectively image its excited states and identify them as ⁵T₂ (⁵T₂) and ⁵E (⁵E) with an energy splitting 10Dq of 0.78 eV.

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Transition metal (TM) compounds display a wide variety of extraordinary properties of both theoretical and technological interest. These include metal-insulator and spin-state transitions, colossal magnetoresistance, various forms of magnetism and multiferroicity, as well as superconductivity. It is generally accepted that this richness in phenomena must somehow be related to the wealth of possible electronic states created by the strong Coulomb and exchange interactions between the TM valence electrons in the d shell and the intricate interplay with the band formation in the solid [1]. Understanding how those states are formed and which ones participate in the formation of the ground state and low lying excited states is a difficult task. It is therefore highly desirable if one can at least identify the relevant local charge, spin, and orbital degrees of freedom. To this end, input from experiments is necessary. While information about the valence and magnetic states can be routinely gathered using x-ray and neutron scattering techniques, the case for the orbital state is much more delicate since spectroscopic methods have to be applied and this often requires highly complex calculations to interpret the spectral line shapes.

Recently, we have shown that nonresonant inelastic x-ray scattering (NIXS, also known as x-ray Raman scattering) involving an s core hole (s-NIXS) is an experimental method that can provide a direct image of the local d hole density in transition metal oxide single crystals [2,3]; i.e., the ground state d orbital can be determined without the need for calculations to interpret the spectral line shape. This opens up new opportunities for the investigation of the ground state, especially for those transition metal compounds that are too complex to be handled by ab initio theories. Here we will go one step further and explore the spectroscopy aspect of s-NIXS in order to study the excited states which are most often dominated by many-body atomic multiplet interactions. In particular, we aim to determine the orbital character of those states. Our idea is that the use of an s core hole should simplify the analysis of the spectra in two significant aspects. First, the presence of the s hole does not add an extra orbital angular momentum so that use can be made of

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these points, we have carried out the experiment on [sketched in Fig. 1(a)] using a Rowland geometry and P01 beam line at PETRA III (DESY). The spectrometer complete filling of the rocksalt-type antiferromagnetic insulator with far from swept from Si(311) double crystal monochromator, is continuously energy of the incident photons, monochromatized by a detector [2]. During the acquisition of the spectra, the scattering angle was set to $\theta = 155^\circ$ which yielded $|q| \approx 9.6 \, \text{Å}^{-1}$, where $q = k_{\text{fin}} - k_{\text{out}}$ is the momentum transferred. The sample was a single crystal of rocksalt-type $\alpha$-MnS grown by chemical vapor transport (see Appendix A). During the NIXS measurement the sample was kept at a temperature of 50 K in order to prevent possible radiation damage. The spectra were acquired at many $\Theta$ angles ($\Theta$ being zero when $q||[100]$) for two different orientations of the sample relative to the scattering plane, so that $q||[100], [111], \text{and } [011]$ could be reached with the first orientation [magenta plane in Fig. 1(b)] and $q||[100], [110], \text{and } [010]$ with the second orientation (dark cyan). To reach the two orientations, the crystal was rotated by inserting the sample holder (a stainless steel pin; see Fig. 8) respectively in the $0^\circ$ and $45^\circ$ slots available in the P01 cryostat. The angle between the two slots corresponds to a $45^\circ$ rotation of the crystal around its [100] axis (which remains parallel to the momentum transfer $q$ at $\Theta = 0^\circ$) and the two resulting geometries allow us to span the two planes of Fig. 1(b) by varying the angle $\Theta$ as shown Fig. 1(a).

Figure 1(c) displays a compilation of the NIXS spectra measured for the different sample angles. They are characterized by a broad Compton profile peaking at 350 eV, which was used to normalize the spectra and correct for the intensity variations due to self-absorption effects at different scattering geometries [2]. On top of this signal, two sharp peaks are visible, ascribable to atomiclike excitations, namely the Mn $M_{2,3}$ edge ($3p \rightarrow 3d$) at about 50 eV and, relevant to this study, the dipole-forbidden $M_1$ ($3s \rightarrow 3d$) transition at around 83 eV. Such a transition is well visible thanks to the large momentum transfer $|q|$ [5–8], which allows higher multipole excitations to gain intensity and become of use for quantitative analysis [2,3].

The Mn $M_1$ edge spectra acquired at different $\Theta$ are shown in Fig. 2(a) for the set $q||[100] \rightarrow [111] \rightarrow [011]$...
(magenta) and in Fig. 2(b) for \( q \parallel [100] \rightarrow [111] \rightarrow [011] \) (dark cyan). The Compton contribution has been subtracted from these spectra using a linear background. At first glance, there are no prominent variations in the peak intensities, but, as highlighted by the colors, the overall peak energy position varies as a function of \( \Theta \), i.e., as a function of the direction of \( q \) with respect to the crystallographic axes.

To quantitatively discuss our data, we display the integrated intensities of each Mn \( M_1 \) spectrum of Fig. 2 on a polar plot (Fig. 3, top panel). We can directly observe that there is no directional dependence; i.e., the integrated \( M_1 \) intensity is constant for all directions. As explained earlier [2], given that the core-level \( s \) orbital is spherical, the directional dependence of the integrated \( M_1 \) intensity is only determined by (and directly proportional to) the density of \( d \) holes in the direction parallel to \( q \). In other words, this directional dependence provides a direct spatial image of the local empty valence states. We thus observe from the polar plots in the top panel of Fig. 3 that the Mn \( 3d \) hole density is spherical. This is consistent with the scenario in which all five spin-up or all five spin-down \( 3d \) orbitals are unoccupied, i.e., in which the Mn\(^{2+} \) \( 3d^5 \) ion is in its Hund’s rule high-spin \( ^6A_1 \) ground state. It is important to note once again that this result does not rely on any modeling or calculations about the electronic structure of the compound, but that it is directly obtained simply by measuring the orientational dependence of the integrated intensities of the spectra.

While the integrated intensity of the spectra is constant with \( \Theta \), the energy position of the \( M_1 \) peak in Figs. 2(a) and 2(b) does vary with the direction, between 82.37 eV (blue vertical line) for the \( q \parallel [100] \) spectrum and 83.15 eV (orange vertical line) for \( q \parallel [111] \). Since no discernable dispersion can be expected for core-hole excitations, such a variation in energy indicates that the \( M_1 \) signal consists of features positioned at different energies whose relative intensities change with \( \Theta \).

We now make the ansatz that the two spectra acquired at \( q \parallel [111] \) and \( q \parallel [100] \), which show the extreme peak positions and narrowest line shapes, are the basic...
The difference between these two lines in Figs. 2(a) and 2(b). The weights (gray line).

declined by an interaction with a

The angular dependence follows the shape of the $t_2g$ and $e_g$ states with great accuracy, allowing us to directly identify the orbitals reached in each excitation. In particular, the $t_2g$ orbital shape is drawn by the angular dependence of $c_{111}(\Theta)$, the weight of the $S_{q[111]}$ component peaking at 82.37 eV. Likewise, the excitation into $e_g$ orbitals is represented by $c_{100}(\Theta)$, the weight of the $S_{q[100]}$ component peaking at 83.15 eV. The difference between these two energies is due to the $e_g - t_2g$ splitting, and it is therefore a direct measurement of the crystal field parameter $10Dq = 83.15$ eV−82.37 eV = 0.78 eV.

A proper interpretation of the spectra must include the effects of Coulomb and exchange interactions between the electrons within the $d$ shell, meaning that we need to put our results in a many-body framework which takes into account both the full atomic multiplet theory and the local effect of the lattice. In particular, starting from the $(3s^2)3d^6$ configuration for the ground state of the Mn ion in $\alpha$-MnS, the $s$-NIXS process leads to a $3s^13d^6$ final state. Since the $s$ core hole does not add an extra orbital angular momentum component, the multiplet structure of the final state will be closely related to the one of the $3d^6$ configuration.

Therefore, one could make use of the well-established Sugano-Tanabe-Kamimura diagrams [4] for a quantitative analysis of $s$-NIXS spectra, after taking into account for some modifications due to the presence of the extra $3s$ spin. We exemplify this in Figs. 5(a) and 5(b), where we reproduce the total energy diagrams for a Mn ion in $3d^6$ and $3d^13d^6$ configuration calculated with the QUANTY code [9]. The corresponding Slater integrals $F_{3d^6}^2$ and $F_{3d^13d^6}^4$ for the $3s^13d^6$ configuration have been obtained using the code by Cowan [10] and reduced to 80% of their Hartree-Fock value to account for configuration interaction effects not included in the calculation [11,12]. A simplified version of these diagrams, containing only a selection of the multiplets to improve readability, is displayed in Fig. 9 and can be found together with a brief explanation in Appendix B.

To ease the comparison between the diagrams of the two configurations, the lowest energy state is not fixed at 0 eV for every $10Dq$. Instead, the lowest state of the $3d^6$ configuration is put to zero only for $10Dq = 0$ eV, and serves as reference energy. In this way, the multiplets are split by the action of $10Dq$, but the average energy of the diagram is kept constant.

The energy levels are labeled for zero crystal field ($10Dq = 0$ eV, spherical symmetry) with the $(2S_{j}+1)L_d$ term symbols, where $S_d$ and $L_d$ represent the quantum numbers of the $3d$ shell and the orbital quantum numbers $L_d$ are indicated with the usual letter notation ($S$, $P$, $D$, $F$, $G$, etc.). The subscript in parentheses indicates the degeneracy of each term symbol, also including the degeneracy given by the $3s$ hole. In total, the $3d^6$ configuration has $(^6D_{6}) = 210$ states, while $3s^13d^6$ has $2 \times (^6D_{6}) = 420$ states, due to the extra multiplicity of the $3s^1$ spin. The colors group the states in the diagrams of Figs. 5 and 9 according to their $3d$ spin multiplicity $(2S_{j}+1)$: singlets are purple, triplets green, and quintets orange.

Starting from the singlets, it is straightforward to notice that the energy scheme within the set of singlets, as well as the dependence of each state on $10Dq$, is essentially the same between the two configurations $3d^6$ and $3s^13d^6$. This agrees with the fact that singlet states cannot be modified by an interaction with a $3s$ spin, given by $\langle S_j \cdot S_s \rangle$, which is zero for $S_d = 0$. The minor changes between the two groups ($\lesssim 10\%$ of the energy splittings) is due to the different values of the Slater integrals $F_{3d^6}^2$ and $F_{3s^13d^6}^4$ between the two configurations.

The sets of triplets (green lines) and quintets (orange lines) of the $3s^13d^6$ configuration in Figs. 5 and 9, instead, are further divided in two subgroups depending on the relative alignment of $S_j$ and $S_s$. The states having the two spins parallel are represented with thick lines, while the thin dashed lines represent the states with opposite $S_j$ and $S_s$. These subgroups are each a replica of the corresponding $3d^6$ triplet or quintet set, rigidly shifted in energy due to the spin interaction.
To understand and predict these energy shifts due to the Coulomb interaction between the $d$ electrons and the electron of the open $3s$ shell, one can relate the Coulomb operator to the spin operators of the $d$ shell and $s$ shell. We have

$$H_{\text{Coulomb}}^{3s-3d} = -\frac{2}{5} \hat{S}_d \cdot \hat{S}_s G_{3s-3d}^2 + n_d \left( F_{3s-3d}^0 - \frac{1}{10} G_{3s-3d}^2 \right).$$

The last term in the equation is constant for all multiplets within a $3s^1 3d^{p2}$ configuration and as such does not lead to a splitting between the different states. The eigenvalues of $\hat{S}_d \cdot \hat{S}_s$ can be obtained simply by inverting the formula \cite{13} $(\hat{S}_{\text{tot}})^2 = (\hat{S}_d)^2 + (\hat{S}_s)^2 + 2\hat{S}_d \cdot \hat{S}_s$, where $\hat{S}_{\text{tot}}$ can be $S_d + S_s = S_d + \frac{1}{2}$ or $|S_d - S_s| = |S_d - \frac{1}{2}|$, and remembering that the eigenvalue of $(\hat{S})^2$ is $S(S + 1)$. By applying these formulas, one obtains the eigenvalues listed in Table I for each possible value of $S_d$.

Typical values of $G_{3s-3d}^2$ for the $3d$ series, after a reduction to 80% of their Hartree-Fock values, range from 8.5 to 10.2 eV. In general, $\Delta E$ is larger for larger spin multiplicities. With these ingredients, one can easily build the Sugano-Tanabe-Kamimura diagrams of the NIXS final configuration from the ones without the $3s$ core hole, listed, for example, in Figs. 5.1–5.7 of the famous book of Sugano, Tanabe, and Kamimura \cite{4}. This allows the diagram of the possible $s$-NIXS final states to be reproduced without the need for performing new calculations and, by comparing the diagrams to the spectra, quantitatively determine the value $10Dg$.

The next step toward a complete understanding of the $s$-NIXS spectra is to realize that not all states depicted in Fig. 5(b) can be reached starting from the ground state of Mn 3d$^6$ (in absence of the core 3s hole) and of (b) Mn 3s$^1$3d$^6$ (the $s$-NIXS final state). The 0 eV energy reference is the same for both panels, and it is fixed to the lowest state of Mn 3d$^6$ at 10Dg = 0 eV. Each multiplet is labeled with the corresponding term symbol at 10Dg = 0 eV and in parentheses is indicated its degeneracy. The colors indicate each state’s spin multiplicity: purple for singlets, green for triplets, and orange for quintets. In panel (b), the thick full lines represent the states having parallel $\hat{S}_d$ and $\hat{S}_s$, the thin dashed lines the states with $\hat{S}_d$ antiparallel to $\hat{S}_s$, and the thin full lines the states not affected by $\hat{S}_s$. The stars indicate, for several 10Dg, the possible final states of the s-NIXS process, and the vertical gray line at 10Dg = 2.7 eV is the transition between the high- and low-spin configurations of the 3d$^5$ ground state. The Slater parameters used for Mn 3d$^6$, after reduction to 80% of their atomic value, are $F_{2p-3d}^0 = 7.258$ eV and $F_{3d-3d}^1 = 4.472$ eV. The reduced Slater parameters for Mn 3s$^1$3d$^6$ are $F_{3d-3d}^1 = 8.426$ eV, $F_{3d-3d}^1 = 5.244$ eV, and $G_{3s-3d}^2 = 8.856$ eV.
Table I. Eigenvalues of $\hat{S}_d \cdot \hat{S}_s$, related to the energy splitting due to the Coulomb interaction of pure spin multiplets (i.e., neglecting spin-orbit interaction) in the $d$ shell with the open 3$s^1$ core shell for states with the $d$ spin either parallel ($S_{\text{tot}} = S_d + S_s$) or antiparallel ($S_{\text{tot}} = S_d - S_s$) to the core $s$ spin.

| $S_d$  | $2S_d + 1$ | $S_{\text{tot}} = S_d + S_s$ | $S_{\text{tot}} = S_d - S_s$ |
|--------|-----------|-------------------------------|-------------------------------|
| 0      | 1         | 0                             | 0                             |
| $\frac{1}{2}$ | 2         | $\frac{3}{2}$ $- \frac{1}{2}$ | $\frac{3}{2}$ $- \frac{1}{2}$ |
| 1      | 3         | $\frac{5}{2}$ $- \frac{3}{2}$ | $\frac{5}{2}$ $- \frac{3}{2}$ |
| $\frac{3}{2}$ | 4         | $\frac{7}{2}$ $- \frac{5}{2}$ | $\frac{7}{2}$ $- \frac{5}{2}$ |
| 2      | 5         | $\frac{9}{2}$ $- \frac{7}{2}$ | $\frac{9}{2}$ $- \frac{7}{2}$ |
| $\frac{5}{2}$ | 6         | $\frac{11}{2}$ $- \frac{9}{2}$ | $\frac{11}{2}$ $- \frac{9}{2}$ |

Mn$^{2+}$ in $\alpha$-MnS. In our case, the addition of one extra 3$d$ electron ($s = 1/2$) to the high-spin $^6A_1$ ($S_d = 5/2$) ground state can only lead to quintet final states ($S_d = 2$), with the $3s^1$ spin parallel to the majority spin of the 3$d$. Figure 10 in Appendix C describes this excitation process in more detail. Therefore, $-\frac{3}{5} G^2_{3s-3d}(\hat{S}_d \cdot \hat{S}_s) < 0$, and the low energy replica of the quintet set is reached. The possible $s$-NIXS final states for different values of $10Dq$ are indicated with stars in Fig. 5(b), where the values of $10Dq$ corresponding to the initial $3d^5$ high-spin configuration $^6A_1$ are to the left of the gray vertical line, and low-spin on the right. The size of each star is proportional to the intensity of the excitation, averaged over all directions. There are only two states in the diagrams that can be reached with a $s$-NIXS excitation, namely the $5T_2$ (the extra 3$d$ electron occupying $t_{2g}$ orbitals) and $5E$ (the extra electron in the $e_g$). From the shape of the final state orbitals as imaged in Fig. 3 (bottom panels), we can immediately that the lower energy peak belongs to the $^5T_2$ state and the higher to the $^5E$. It is then straightforward to understand, as predicted above, that in our case the experimental peak energy separation of 0.78 eV corresponds one to one to the $10Dq$ value.

It is worth looking into Fig. 5(b) in more detail. For $10Dq$ values on the right-hand side of the gray vertical line, the ground state will no longer be the high-spin but the low-spin $3d^4$. The consequence for the $s$-NIXS spectrum is dramatic. It switches from a two-peak structure (two stars) into a five-peak feature (five stars); Fig. 10 in Appendix C explains the occurrence of these peaks. This demonstrates that the line shape of the $s$-NIXS spectrum is an extremely sensitive indicator of the ground state symmetry. The value of $10Dq$ can be determined directly from the spread of the five peaks. Consequently, the ground state hole density will also change in going from high to low spin, i.e., from spherical ($l^2_e g^2_e$-like) to highly nonspherical ($l^2_g$-like), which can be revealed directly by the image obtained from the directional dependence of the integrated $s$-NIXS intensity.

![Graphical representation of the integrated intensity of the Mn $M_1$ spectra](image)

**FIG. 6.** Mn $M_1$ simulations using a Mn$_6$ cluster calculated for various degrees of covalency. Left: Polar plot of the integrated intensity of the Mn $M_1$ in the [100] $\rightarrow$ [110] $\rightarrow$ [010] plane: from ionic (most outer circle) to strongly covalent (most inner distorted circle, $\Delta = 1$ eV) case. Middle: Mn $M_1$ spectra along the $q \parallel [100]$ (orange) and $q \parallel [111]$ (blue) directions: from ionic (bottom curves) to strongly covalent (top curve, $\Delta = 1$ eV). The $\Delta$ and corresponding ionic $10Dq$ values are indicated, together with the resulting $e_g$ and $t_{2g}$ occupation numbers. The energy splitting between the $q \parallel [100]$ (orange) and $q \parallel [111]$ (blue) peaks is fixed at 0.78 eV. Right: The directional dependence of the high (orange) and low energy peak (blue) of Mn $M_1$ spectra, for the ionic (bottom) and strongly covalent (top, $\Delta = 1$ eV) cases.
We now investigate the influence of covalency on the s-NIXS image of the local d hole density and the spectra. To this end, we have carried out configuration interaction calculations [9,11,12,14] using an octahedral MnS₆ cluster which includes explicitly the hybridization between the Mn 3d and the S 3p orbitals. We have set the hopping integrals for the e₉ orbital at 1.92 eV and for the t₂g at 1.15 eV [9] and varied the energy difference between the d⁹ and d⁶L configurations (charge transfer energy Δ). Here L denotes the S 3p ligand hole states. The results are shown in Fig. 6.

Starting with the ionic calculation, we have for the ground state an electron occupation of 3.000 for the t₂g orbital and 2.000 for the e₉ (values listed in the central panel of Fig. 6). The corresponding ground state hole density is spherical (left-hand panel, red line), and the directional dependence of the low and high energy peaks in the calculated s-NIXS spectra follow the t₂g (blue) and e₉ (orange) orbital shapes, respectively, as we have seen already in Fig. 2. Switching on the hybridization between the d⁹ and d⁶L configurations, we can see that the electron occupation in the ground state increases with lowering the Δ values. It increases faster for the e₉ than for the t₂g (values listed in the central panel), consistent with the fact that the hopping integral with the ligand is larger for the e₉ than for the t₂g. In the strongly covalent case of Δ = 1 eV we have 3.136 in the t₂g and 2.287 for the e₉. Accordingly, the ground state hole density, proportional to the NIXS signal, decreases for lower Δ values and becomes strongly nonspherical (left-hand panel). This also means that the amount of hybridization can be extracted from the precise shape of the hole density as measured by s-NIXS.

Perhaps a surprising result is that the presence of hybridization does not have much influence on the s-NIXS spectrum, even for the hybridization does not have much influence on the configurations (charge transfer energy Δ). Here L denotes the S 3p ligand hole states. The results are shown in Fig. 6. The middle and right-hand panels of Fig. 6 show that the intensity of the high energy peak (e₉, orange) becomes smaller relative to that of the low energy peak (t₂g, blue) with decreasing Δ values. The s-NIXS spectrum can therefore be used to help determine quantitatively the parameter values describing the hybridization process.

In the ionic calculations, we have used a 10Dq value of 0.78 eV in order to get a separation of 0.78 eV between the two peaks in the Mn M₄ NIXS spectrum. We will name this the ionic-10Dq parameter. Upon switching on the hybridization, we must decrease the value of the ionic-10Dq parameter to simulate the spectrum. The reduction of the Slater integral was optimized in order to best reproduce the experimental spectrum was obtained for 10Dq = +0.64 eV. The 10Dq values that we have obtained from the s-NIXS and L₂,₃ XAS measurements are quite close, lending confidence to the validity of our analysis. Yet, it is also worth noting that there is a difference in the values of the two experiments. We would like to infer that this has a physical origin, namely that the influence of the 2p core hole on the 3d electrons differs from that of the 3s core hole. An indication that this might indeed be the case comes from the observation that the Hartree-Fock value for the
Slater integral for the $2p^5 3d^6$ configuration is different from that of the $3s^1 3d^6$, namely (before reduction) 11.15 versus 10.53 eV, signaling that the radial extent of the $3d$ electrons is smaller in the presence of a deep $2p$ core hole than with a more shallow $3s$. This in turn then explains why the crystal field felt by the $3d$ electrons is smaller if measured in the presence of the $2p$ core hole instead of the $3s$. Similar remarks can be made when comparing crystal field values extracted from spectroscopies with or without a core hole in the final state\(^{[9,17,19–23]}\).

In conclusion, we have shown that s-NIXS has the unique ability to directly provide a spatial image of also the local excited states of transition metal ions, thereby simplifying the identification of the multiplet character of those states. We also have shown that the well-established Sugano-Tanabe-Kamimura diagrams can be used for the analysis of the spectra since the $s$ core hole does not add an extra orbital angular momentum. The present study thus demonstrates that one can extract from the analysis of s-NIXS spectra (1) the character of the excited states, (2) the relevant energy parameters, and (3) the character of the ground state. In addition, the integrated s-NIXS also gives (4) direct information about the character of the ground state. Information (4) can then be used to check the information obtained from (3). Alternatively, in case the spectra are extremely complex, information (4) can be used as a constraint for the analysis of the spectra so that (1) and (2) can be extracted more reliably. Therefore s-NIXS opens up new opportunities to determine the local electronic structure in a wide range of transition metal compounds.

APPENDIX A: SAMPLE PREPARATION

Single crystals of $\alpha$-MnS were grown via chemical transport reaction using iodine as transport agent. The starting material was synthesized by direct reaction of the elements manganese (powder 99.8% Alfa Aesar) and sulfur (pieces 99.99% Alfa Aesar) at 975 °C in evacuated fused silica tubes with an inset of glassy carbon for 7 days. The obtained microcrystalline powder was recrystallized via chemical transport reaction in a temperature gradient from 1000 °C (source) to 800 °C (sink). The transport agent iodine (Alfa Aesar 99,998%) was introduced at a concentration of $8.5 \text{ mg/cm}^3$ of the fused silica ampoule. After 14 days, the experiment was stopped by quenching the ampoule in cold water. The obtained crystals showed a well-defined truncated octahedral shape depending on the growth location inside the ampoule. The largest crystals have edges of approximately 1 mm length. A photograph of the sample measured is displayed in Fig. 8. Few selected small crystallites were ground and the obtained x-ray powder pattern clearly confirmed the rocksalt-type crystal structure of $\alpha$-MnS with a lattice parameter of 5.224 Å.

FIG. 7. Mn $L_{2,3}$ x-ray absorption spectrum of $\alpha$-MnS (black line) and simulations for different values of $10Dq$. The best fit is obtained for $10Dq = 0.64$ eV (turquoise line).

FIG. 8. Top view of the $\alpha$-MnS sample (black) glued onto a stainless steel pin. The size of the mesh in the background is $1 \times 1$ mm.
APPENDIX B: SUBSECTION OF THE SUGANO-TANABE-KAMIMURA DIAGRAM

For more clarity on the relation between the Sugano-Tanabe-Kamimura diagrams in the absence and in the presence of the 3s core hole, the diagrams of Fig. 5 are reproduced in Fig. 9 only for the multiplets relevant for the analysis of the NIXS spectra. Figure 9(a) shows the evolution with $10Dq$ of a singlet (purple lines), triplet (green lines), and quintet (orange lines) of the Mn $3d^6$ configuration. Figure 9(b) shows the corresponding states of the Mn $3s^13d^6$ configuration (i.e., the states characterized by the same $L_d$ and $S_d$). The triplets and quintets are split into two replicas, one with parallel $S_d$ and $S_s$ (thick full lines) and the other with $S_d$ antiparallel to $S_s$ (dashed lines). The arrows indicate the shift in energy of the replicas. The singlets (purple thin lines) are not affected by the presence of the 3s hole. The minor energy shift between the energy of the singlet states in the two panels is due to the different calculated values of the $F_{3d-3d}^2$ and $F_{3d-3d}^1$ Slater integrals for the two configurations. This is also the cause for the small difference between the energy of the triplet state at $10Dq = 0$ eV in Fig. 9(a) and the reference energy for the splitting of the corresponding replicas (starting point of the vertical green arrows) in Fig. 9(b). Since the Slater integrals always have to be finely tuned to fit the experimental data, these minor effects do not affect the analysis of NIXS spectra and are shown here only for the sake of completeness.

APPENDIX C: s-NIXS EXCITATION PROCESS

Figure 10 shows a schematic diagram of the s-NIXS excitation process for a $3d^5$ system. The left-hand panel displays the system in the high-spin state, and the
right-hand panel in the low-spin state. From the high-spin ground state, it is only possible to excite a $3s$ electron with the spin opposite to that of the half filled $3d$ shell. This leads to final states with $S_d = 2$ (quintet in the $3d$ shell) and $\langle \hat{S}_d \cdot \hat{S}_s \rangle > 0$ (parallel $3s$ and $3d$ spins), corresponding to the solid orange lines in Figs. 5(b) and 9(b). There are two possibilities to do this, namely to excite the electron into a $t_{2g}$ (arrow 1 in Fig. 10) or into an $e_g$ (arrow 2 in Fig. 10) orbital, giving rise to two peaks in the spectrum, as indicated by the two stars in Figs. 5(b) and 9(b).

From the low-spin ground state, the excitation of the $3s$ electron to the $3d$ shell leads to $S_d = 1$ and $\langle \hat{S}_d \cdot \hat{S}_s \rangle < 0$ final states (triplet in the $3d$ shell), dashed green lines in Figs. 5(b) and 9(b), or $S_d = 1$ final states (singlet in the $3d$ shell), purple lines in Figs. 5(b) and 9(b). In terms of orbital degrees of freedom, an excitation into a $t_{2g}$ orbital is only possible (arrow 3 in Fig. 10) for the $3s$ electron having the spin opposite to the $3d$ shell, producing the low-spin $3s^33d^1(t_{2g})^6$ configuration. This excitation is marked by the star lying on the purple line with the steepest downward slope in Figs. 5(b) and 9(b).

An excitation into an $e_g$ orbital will produce a $3s^33d(e_g)^1(t_{2g})^5$ state, which can be a spin singlet or triplet as far as the intra $3d$ shell configuration is concerned. This gives rise to two peaks. These two peaks will have an intensity ratio of 1:3 reflecting the degeneracies of the spin singlet versus triplet states. This can be understood in more detail as follows. An excitation of the $3s$ electron with the spin parallel to that of the $3d$ shell (arrow 4 in Fig. 10) reaches a state with more up spins than down spins in the $3d$ shell; i.e., this is a spin triplet state. On the other hand, an excitation of the $3s$ electron with the spin opposite to that of the $3d$ shell (arrow 5 in Fig. 10) results in a state with equal amounts of up and down spins. This state belongs half to the spin singlet state and half to the triplet. The excitation into an $e_g$ orbital thus yields $\frac{1}{2} : \frac{3}{2}$ or 1:3 intensity ratio for the spin singlet versus triplet states. Next we need to consider the orbital aspect of the Coulomb interactions. In this case, the Coulomb attraction between the $e_g$ electron and the $t_{2g}$ hole (in the otherwise full $t_{2g}$ subshell) depends on their relative orientations (the $x^2-y^2$ electron and $xy$ hole versus $3z^2-r^2$ electron and $xy$ hole). This orbital degree of freedom will then split each of those spin singlet and triplet states further into two. So the excitation to an $e_g$ orbital results in two small stars on the purple lines (spin singlet in the $3d$ shell) and two large stars on the dashed green lines (spin triplet in the $3d$ shell) as indicated in Figs. 5(b) and 9(b).

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The Slater integrals for the simulations have been calculated using a Hartree-Fock code \cite{10} and reduced to take into account configuration interaction effect not included in the calculation. The parameters $F_{3d-3d}^{2}$ and $F_{3d-3d}^{4}$ describing the ground state $3d^{5}$ configuration have been reduced down to 80% of their atomic value, while for the $2p^{5}3d^{6}$ final state configuration the $F_{3d-3d}^{2}$ and $F_{3d-3d}^{4}$ integrals have been reduced to 71%, $G_{2p-3d}^{1}$ and $G_{2p-3d}^{3}$ to 75%, and $F_{2p-3d}^{2}$ kept unchanged. The corresponding values are $F_{3d-3d}^{2}(3d^{5}) = 8.252$ eV, $F_{3d-3d}^{4}(3d^{5}) = 5.1304$ eV, $F_{3d-3d}(2p^{5}3d^{6}) = 7.920$ eV, $F_{3d-3d}(2p^{5}3d^{6}) = 4.929$ eV, $F_{2p-3d}(2p^{5}3d^{6}) = 6.320$ eV, $G_{2p-3d}(2p^{5}3d^{6}) = 3.452$ eV, and $G_{2p-3d}(2p^{5}3d^{6}) = 1.962$ eV. The intrinsic Lorentzian (full width at half maximum) linewidth varies from 0.25 to 1.3 eV for the $L_{3}$ edge and from 0.6 to 1.1 eV for the $L_{2}$ edge.

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