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Resonant x-ray scattering at the forbidden reflections in Mn^{3+} perovskites REMnO_3 (RE:La and Tb).

M. C. Sánchez¹, G. Subías¹, V. Cuartero¹, J. García¹, J. Blasco¹, J. Herrero-Martin², K. Hatada³, Hayakawa K³, S. Di Matteo⁴ and C. R. Natoli^{1,3}

¹Instituto de Ciencia de Materiales de Aragón, Departamento de Física de la Materia Condensada, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain.

²European Synchrotron Radiation Facility, Grenoble Cedex 38042, France.

³Laboratori Nazionali di Frascati INFN, C.P. 13, I-00044 Frascati Roma, Italy

⁴Univ Rennes 1, Inst Phys Rennes, UMR UR1 CNRS 6251, F-35042 Rennes, France

Abstract. We here report a combined experimental and theoretical resonant x-ray scattering study in two isomorphous compounds, LaMnO_3 and TbMnO_3 . The two samples show an orthorhombic $Pbnm$ structure with four Mn^{3+} atoms at equivalent positions. The Mn sites have a local inversion symmetry and they are surrounded by nearly tetragonal-distorted oxygen octahedron. The tetragonal distortion is larger in TbMnO_3 than in LaMnO_3 . Resonances were measured at the Mn K-edge of the $(h,0,0)$, $(0,k,0)$ and $(0,0,l)$ ($h,k,l=3,5$) reflections. All the reflections show a resonance only in the $\sigma\text{-}\pi'$ polarization channel. The observed resonant intensities exhibit a $\sin^2\phi$ dependence on the azimuth angle ϕ . The $(h,0,0)$ and $(0,k,0)$ reflections have identical energy dependence but markedly different than the $(0,0,l)$ reflections. Differences in the energy line shape and width of these resonant reflections between La and Tb samples are explained in terms of the different tetragonal distortion and the different ionic radius of the rare-earth. The origin of the two types of reflections (related to two different non-zero non-diagonal elements of the scattering tensor) is explained within the multiple scattering theory considering long-range order of structural distortions in a cluster up to 63 atoms without invoking any d-orbital order.

1. Introduction.

Rare-earth manganese oxides show exciting phenomena that arise from competing interactions. LaMnO_3 is the parent compound to a series of materials featuring colossal magnetoresistance and shows a d -orbital order (OO) ground state, giving rise to layered antiferromagnetic ordering [1]. This compound adopts an orthorhombic $Pbnm$ structure. The Mn atoms occupy the $4b$ (point symmetry $\bar{1}$, i.e. a local inversion symmetry) sites and the MnO_6 octahedra are tetragonal-type short and two long Mn-O distances) distorted due to the Jahn-Teller effect of the Mn^{3+} , suggesting an orbital e_g electronic ordering. The most significant effect by decreasing the rare-earth ionic radius is the increase of both, the orthorhombic distortion and the tetragonal distortion of the MnO_6 octahedron. The enhancement of these distortions in TbMnO_3 leads to an incommensurate spin ordering which gives rise to a ferroelectric ordering [2].

Resonant x-ray scattering (RXS) probes the local electronic levels coherently throughout the whole crystal. The observation of resonance in the scattered intensity of the (3,0,0) forbidden reflection at Mn *K* edge in LaMnO₃ was initially interpreted as a direct probe of the OO[3]. However, the original idea that OO could be directly probed by this technique turned out to be incorrect. Detailed numerical calculations[4,5] have shown that the observed splitting of Mn 4*p* levels was by far due to the structural distortion and just a negligible contribution come from OO.

We have examined the evolution of the resonant intensity at the (odd,0,0), (0,odd,0) and (0,0,odd) forbidden reflections around the Mn *K* edge for rare-earth perovskites REMnO₃ (RE=La and Tb), which present the GdFeO₃-type distortion, as a function of the ionic radius of RE. We show that the RXS signal at the (0,0,odd) reflections shows a different energy dependence than the (Odd,0,0) and (0,odd,0) ones for both La and Tb samples. The analysis of the energy, azimuth, and polarization dependences of the RXS signals was performed by calculating the components of the anomalous atomic scattering factor tensor. The scattered intensity at the (0,0,odd) and the (0dd,0,0) [or (0,odd,0)] reflections depends on different off-diagonal terms of the scattering tensor. Long-range ordered distortions of just a MnO₆ cluster qualitatively describe the RXS signals. A bigger cluster must be considered to explain quantitatively the RXS reflections. In addition, we have found differences in the energy line shape of these resonant reflections between La and Tb samples, which can be related to the different tetragonal distortion induced by the different ionic radius of the rare-earth. We also show that the principal axis of the electric quadrupole tensor in the excited states, when no local symmetry axis are present, depends on the photon energy.

2. Experimental section.

Single crystals of LaMnO₃ and TbMnO₃ were grown at our own laboratory ICMA, using a halogen lamp floating zone furnace[6]. The crystals were characterized by means of x-ray powder diffraction and ac magnetic susceptibility. The lattice parameters at 300 K were $a=5.531$ Å, $b=5.740$ Å, $c=7.688$ Å for LaMnO₃ and $a=5.316$ Å, $b=5.831$ Å, $c=7.375$ Å for TbMnO₃. Two crystals were cut and polished to either (100)/(010) or (001) flat surfaces. We note that (100) and (010) domains occur at the same surface in LaMnO₃ because of twinning, but an untwinned crystal was obtained for TbMnO₃. However, (*h*,0,0) and (0,*k*,0) reflections also occurs at different angles in LaMnO₃.

RXS experiments were performed at the beamline ID20 of ESRF (Grenoble, France). The σ -polarized incident beam was monochromatized by a double crystal Si(111). Single crystals were mounted inside a closed-cycle helium refrigerator, allowing us to measure the temperature dependence of the studied reflections from 10 K up to 300 K, with the vector normal to the surface lying in the scattering plane. Azimuth scans were measured by rotating the sample around the scattering vector **Q**. A Cu (220) crystal analyser has been used to analyze the polarization of the scattered beam, i.e., perpendicular (σ) or parallel (π) to the scattering plane. We have also measured the polarized absorption spectra along the three crystallographic axis of the untwinned TbMnO₃ sample.

3. Results and discussion.

Figures 1 shows the energy dependence of the forbidden reflections (0,*k*,0), and (0,0,*l*) and the unpolarized (LaMnO₃) and polarized (TbMnO₃) absorption spectra. A strong enhancement of the scattered intensity in all reflections has been observed only at energies close to the Mn *K* absorption edge. No intensity was observed for the σ - σ' polarization channel. The (*h*,0,0) and (0,*k*,0) reflections have identical energy dependence. On the other hand, the resonance observed at the (0,0,*l*) reflections is different, either for LaMnO₃ or TbMnO₃ samples, indicating their different origin. Moreover, the energy line shape of the RXS spectra of the two samples are different as expected for their rare-earth atom. The most striking difference is the largest width of the RXS signals in TbMnO₃. The resonant intensity of all reflections exhibits characteristic $\sin^2 \phi$ dependence, ϕ being the azimuth angle (not reported here).

The anomalous atomic scattering tensor for a Mn atom in the crystallographic frame has in general six components different from zero (three diagonal and three off-diagonal). In the *Pbnm*

setting, there are four Mn^{3+} atoms at equivalent positions: $\text{Mn1}=(0,0,0)$, $\text{Mn2}=(1/2,1/2,0)$, $\text{Mn3}=(0,0,1/2)$, and $\text{Mn4}=(1/2,1/2,1/2)$.

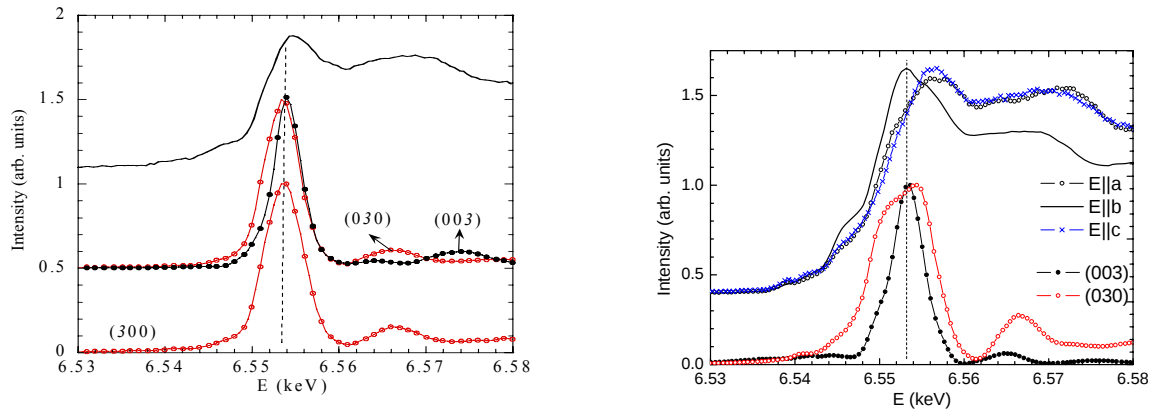


Figure 1. (a) Energy dependence of the forbidden (3,0,0), (0,3,0), and (0,0,3) reflections in the σ - π channel at the Mn K edge of LaMnO_3 for $\phi=0^\circ$, together with the average fluorescence spectrum (upper curve). (b) Energy dependence of the forbidden (3,0,0), and (0,0,3) reflections in the σ - π channel at the Mn K edge of TbMnO_3 for $\phi=0^\circ$, together with the polarized fluorescence spectra (upper curves).

The structure factor at both (odd,0,0) and (0,odd,0) reflections is $F(\text{odd},0,0)=F(0,\text{odd},0)=f_{\text{Mn1}}+f_{\text{Mn3}}-f_{\text{Mn2}}-f_{\text{Mn4}}$, while the structure factor at (0,0,odd) is $F(0,0,\text{odd})=f_{\text{Mn1}}+f_{\text{Mn2}}-f_{\text{Mn3}}-f_{\text{Mn4}}$. Since the four sites are related by mirror planes orthogonal to a, b and c axes, the structure factor tensor for the two reflections contain only one element different from zero: $f_{xy} \neq 0$ for $F(\text{odd},0,0)=F(0,\text{odd},0)$ and $f_{yz} \neq 0$ for $F(0,0,\text{odd})$. The intensities in the σ - σ polarization channel are equal to zero, while in the σ - π polarization channel, they are given by $I(\text{odd},0,0) = I(0,\text{odd},0) = 16|f_{xy}|^2 \cos^2 \theta \sin^2 \phi$ and $I(0,0,\text{odd}) = 16|f_{yz}|^2 \cos^2 \theta \sin^2 \phi$. Here, θ and ϕ are the Bragg and azimuth angles, respectively. For the two types of reflections, only the σ - π polarization channel is active and the azimuth dependence is of a $\sin^2 \phi$ type, as it was experimentally measured. The azimuth and polarization dependences are only determined by the crystallography.

We have calculated the energy dependence of the RXS spectra for the two samples and the polarized absorption spectra for TbMnO_3 in the multiple scattering approach. Both, FDMNES[7] and CONTINUUM [8] codes were used to calculate the different terms of the scattering tensor for a cluster radius of 5.75 Å, i.e., 63 atoms. The two codes gave equivalent results. We report here the analysis for TbMnO_3 since that regarding to LaMnO_3 was been already published [9]. Figure 3 shows the comparison between the experimental data of forbidden (0,3,0) and (0,0,3) reflections and the calculated f_{xy}^2 and f_{yz}^2 terms, respectively, obtained from the CONTINUUM program. Figure 4 compares the experimental and calculated polarized spectra (imaginary part of the diagonal terms). There is a quite good agreement either for the absorption or for the RXS spectra. Using a MnO_6 cluster, the agreement is only qualitative and no differentiation between the (0,odd,0) and (0,0,odd) reflection is obtained. Further distant neighbours (up to about 6 Å) are necessary to reproduce the experiments.

In order to determine the axis of the electric quadrupole moment of the Mn excited states, we have diagonalized the symmetric scattering tensor, which provides us the main directions of the quadrupole moment. We obtained that the principal axes of the ellipsoid representing the quadrupole show different directions at different photon energies. This clearly demonstrates that such a RXS measurement is not directly related to the ground-state average of the electric quadrupole, which, of course, has a unique direction of the principal axes. Indeed, due to the large energy spread of the

continuum intermediate excited states observed in RXS, the anisotropy will depend on the photon energy.

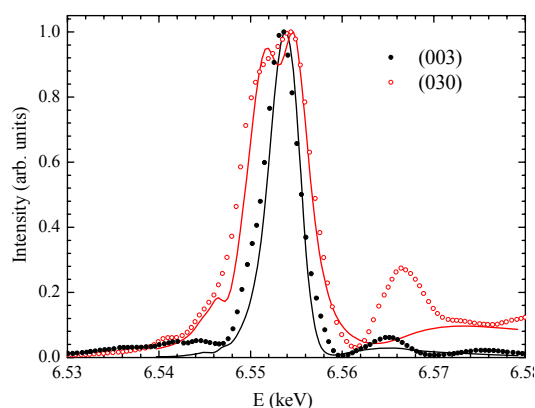


Figure 3. Experimental and calculated (solid lines) energy dependence RXS spectra of the (003) and (030) forbidden reflections of TbMnO_3 .

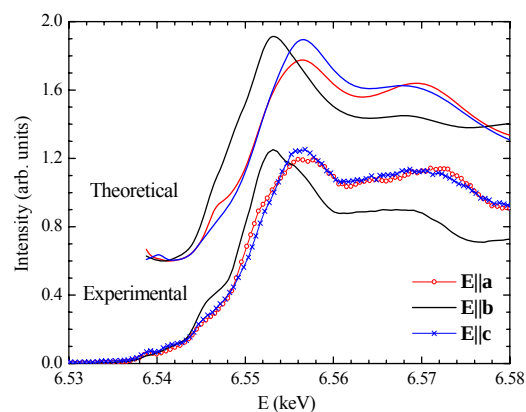


Figure 4. Comparison between the experimental and polarized XANES spectra of TbMnO_3 .

4. Conclusions.

Three conclusions can be derived from the present study: i) The RXS signal is mainly a consequence of the short and intermediate range distortions around the resonant atom. The anisotropy energy shift in the p density of states determined by the underlying OO through the Coulomb $3d-4p$ repulsion is found to be negligible when compared to the structural distortion. ii) The observation of two independent forbidden reflections implies two different nonzero off-diagonal elements in the rank-2 tensor, which are needed to completely describe the RXS signal. iii) The principal axes of the anisotropic tensor for scattering atoms with no point-symmetry elements, as occurs in LaMnO_3 , and TbMnO_3 , are not constant with the photon energy. From the general point of view, this means that it is not possible to determine the direction of the principal axes for the ground-state electric quadrupole from a K -edge RXS measurement and that only indirect information can be inferred.

In conclusion, all measured resonant forbidden reflections at the Mn K edge in REMnO_3 ($\text{RE}=\text{La}$ and Tb) can be explained within the multiple-scattering theory in terms of long-range order of structural distortions around Mn atoms without invoking any kind of d -OO.

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