Magnetic and electronic orderings in orthorhombic $\text{R MnO}_3$ ($R = \text{Tm, Lu}$) studied by resonant soft x-ray powder diffraction

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(Received 7 May 2012; revised manuscript received 26 June 2012; published 17 August 2012)

Resonant soft x-ray powder diffraction experiments on orthorhombic $\text{TmMnO}_3$ and $\text{LuMnO}_3$ are presented. Experiments were performed in the vicinity of the $\text{Tm} M_2$ and the $\text{Mn} L_{2,3}$ edges to study the $\text{Tm}$ and $\text{Mn}$ magnetic moments, respectively. These experiments show that for the heavy rare-earth perovskite with an E-type ordered ground state, the $\text{Tm}$ magnetic moments order already in the nonferroelectric incommensurate magnetic phase. Additionally, deviations from the collinear E-type $\text{Mn}$ magnetic structure at low temperatures are found for both compounds. These experiments show the power of resonant soft x-ray diffraction, extended to polycrystalline 4$f$ materials.

DOI: 10.1103/PhysRevB.86.054425

PACS number(s): 75.25.–j, 75.85.+t

I. INTRODUCTION

Multiferroic materials have attracted a great deal of scientific interest due to the presence of more than one intrinsic order parameter, e.g., the magnetic and electric dipole moment. These can be divided into two main groups. In the first group, the coupling of magnetism and ferroelectricity is rather weak, hence the onset of ferroelectricity is unrelated to the magnetic order. In the second group, ferroelectricity is induced by magnetic order, which corresponds to a gigantic coupling order. The latter group is the most challenging with regard to a basic understanding. It includes materials in which ferroelectricity is found to be caused by particular types of magnetic order. Prototype examples of such multiferroics are the orthorhombic o-$\text{R MnO}_3$ perovskites, with $R$ denoting a rare-earth ion. They exhibit versatile multiferroic phases driven by different interactions, such as exchange striction and Dzyaloshinski-Moriya interactions. In these systems, generic transitions of the ground state with respect to the size of the ionic radius of the $R$ ions are demonstrated. They range from an $ab$, $bc$ cycloidal to the E-type antiferromagnetic (AFM) phase where larger electric polarization (P) appears.

In this work, the individual magnetic and orbital order of $\text{Mn}$ and $R$ sublattices is investigated in polycrystalline o-$\text{TmMnO}_3$ and o-$\text{LuMnO}_3$ by resonant soft x-ray powder diffraction (RSXPD). Resonant x-ray diffraction has turned out to be a powerful technique to study magnetic, orbital, and charge order phenomena of numerous compounds. RSXPD has been successfully applied to multiferroic manganite materials and even enabled the study of in situ interaction of electric fields with magnetism. By selecting particular energies of the x-ray beam, it is possible to probe directly either the 3$d$ $\text{Mn}$ or the 4$f$ $R$ states at the $\text{Mn} L_{2,3}$ or $\text{Mn} M_{4,5}$ edge resonances, respectively. Resonant diffraction has so far not been applied to these two compounds due to the lack of single crystals that are of a sufficient size and quality. The crystal structure of o-$\text{TmMnO}_3$ and o-$\text{LuMnO}_3$ has the space group $\text{Pnma}$ at room temperature. For o-$\text{TmMnO}_3$, neutron diffraction found an AFM incommensurate (ICM) phase with an ordering wave vector of $(h \, 0 \, 0)$ that sets in at the Néel temperature ($T_N^{\text{Mn}} = 40$ K), whereas below $T_C = 32$ K a further transition locks the system into a commensurate (CM) E-type AFM structure with collinear $\text{Mn}$ magnetic moments. Additionally, $\text{Tm}^{3+}$ magnetic moments were found to order along the $c$ axis at 2 K. Regarding o-$\text{LuMnO}_3$, it is AFM below $T_N \approx 40$ K, and below $T_C = 35$ K it possesses an E-type AFM order with the $\text{Mn}$ moments antiferromagnetically aligned along the $a$ and $b$ axes, as has been shown by neutron scattering experiments. Furthermore, in the same study, no satellite peaks were found at 8 K, indicating a single-phase magnetic E-type structure at low temperatures.

Finally, both materials were found to exhibit quite high values of electric polarization, which can be attributed to the E-type phase, making these materials interesting for further studies.

II. EXPERIMENTAL DETAILS

Polycrystalline o-$\text{TmMnO}_3$ and o-$\text{LuMnO}_3$ samples have been prepared under high pressure as described in Ref. 9. RSXPD at low temperatures is performed at the RESOX end station at the SIM beamline of the Swiss Light Source at Paul Scherrer Institut in Switzerland. For the experiment, a polycrystalline pellet of 10 mm diameter was first pressed and then glued on a copper sample holder, which was then mounted on a cold finger of a He flow cryostat. To investigate the magnetic and orbital order, the incident light polarization was chosen to be horizontal ($\pi$) or vertical ($\sigma$) with respect to the horizontal scattering plane. A commercial Roper Scientific in vacuum water-cooled CCD camera was used to collect sections of the Debye-Scherrer powder diffraction rings and then integrated perpendicular to the ring to obtain reflection intensities.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray absorption spectra of $\text{TmMnO}_3$ taken in the fluorescence mode as well as the photon energy dependence of the magnetic ($\frac{1}{2} \, 1 \, 0$) reflection in the vicinity of the $\text{Tm} M_5$ edge. Three main features appear in the x-ray absorption data at the exact energies where there are local minima in the energy dependence of the ($\frac{1}{2} \, 1 \, 0$) reflection.
FIG. 1. (Color online) Top: x-ray absorption collected in fluorescence yield. Bottom: energy dependence of (1/2 1 0) reflection taken at the Tm $M_5$ edge at 9 K, in $\sigma$ and $\pi$ incident polarization. Both: The lines are guides to the eyes. Inset: intensity of a cut through the Debye-Scherrer diffraction ring of the magnetic (1/2 1 0) reflection in TmMnO$_3$ at 9 K. The scan was performed in the vicinity of the Tm $M_5$ edge at 1464.25 eV. The line corresponds to a fit with a Lorentzian function.

These features correspond to multiplet transitions from the 3$d_{5/2}$ core to 4$f$ valence states at the Tm $M_5$ edge. An integrated section of the Debye-Scherrer ring of the magnetic (1/2 1 0) reflection taken in the E-type AFM phase at 9 K of TmMnO$_3$ is illustrated in the inset to Fig. 1. This represents a magnetic reflection and has contributions solely from the Tm$^{3+}$ magnetic moments, as the measurement was performed with incident $\pi$ light polarization. The shape of the reflection is well described by a Lorentzian function (solid line). The diffraction measurements were performed both with $\pi$ and $\sigma$ incident light polarization. The diffracted signal measured with $\pi$ incident light polarization is larger than the one with $\sigma$. The large difference of the scattered intensity in those two incident light polarizations in all the spectral features confirms the pure magnetic origin of the signal, a result attributed to the zero magnetic intensity in the $\sigma$-$\sigma'$ channel. These data show nicely that resonant magnetic powder diffraction can be successfully performed at the $M$ edges of 4$f$ systems, even for rather weak induced magnetic ordered moments.

To further verify the magnetic origin of the features present in the spectra (Fig. 1), the temperature dependence of the reflection at two different energies is collected as shown in Fig. 2. The drop in intensity for increasing temperatures is direct and reliable evidence of the magnetic origin of the spectral features. A concave increase in the scattered intensity below 32 K implies an induced magnetic order character of Tm$^{3+}$ moments, possibly correlated with the onset of ferroelectricity at the corresponding temperature. Similar induced 4$f$ moments have already been demonstrated in TbMnO$_3$, DyMnO$_3$, or other 3$d$-4$f$ systems such as NdNiO$_3$. A clear nonzero intensity is observed above $T_C$ in the ICM phase. This result is not expected, since above $T_C$ no magnetic order of Tm$^{3+}$ ions occurs. This is caused by very weak ordered Tm moments, which have not been observed with neutrons. Note that contrary to neutron scattering, RSXPD is element-selective. To verify that the observed nonzero intensity in the ICM phase originates from the Tm$^{3+}$ magnetic order, the temperature dependence of the Miller index, $h$, of the magnetic (h 1 0) reflection is illustrated in Fig. 2 (bottom). A shift of the (h 1 0) reflection is observed from $h = 0.5$ to 0.46 when the structure enters into the ICM phase at $T \approx 32$ K, verifying that the diffracted intensity departs indeed from the E-type magnetic order also for the Tm$^{3+}$ ions above $T_C$. This is consistent with the proposed phase diagram, even when above $T \approx 37$ K no reliable x-ray diffracted intensity is observable.
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In addition to the magnetic $(\frac{1}{2}, 1, 0)$ reflection, the structural forbidden $(1, 0, 0)$ reflection is also observed. Figure 3(a) shows the energy dependence of $(1, 0, 0)$ reflection in the vicinity of the Tm $M_5$ edge. The intensity reflects scattering caused by the anisotropic tensor of susceptibility (ATS) or Templeton and Templeton scattering. It has already been shown that the resonant diffraction intensity can be related to the octahedra tilt in Pr$_{1-x}$Ca$_x$MnO$_3$ and LaMnO$_3$ when the x-ray energy is tuned to the $L$ absorption edge of the $R$ (Pr, La) ion. In that case, the resonant intensity arises from splitting of the unoccupied $5d$ states of Pr and La, induced by the crystal field related to the octahedra rotation. In our case here, the resonant diffraction intensity of the $(1, 0, 0)$ reflection is attributed directly to the orbital order of Tm $4f$ states. This order, caused by the crystal field splitting, is also induced by the octahedra tilts, but it concerns the crystal field splitting in the open valence shell. An almost constant temperature dependence of the orbital reflection occurs through the magnetic phase transitions, implying that there is no significant depopulation of the $4f$ ground states in this temperature region. This indicates that there is likely a gap in the $4f$ excitation spectra larger than 10 meV.

To gain more insight into the magnetic structure of the Mn ions for both o-TmMnO$_3$ and o-LuMnO$_3$, we also collected data of the magnetic $(\frac{1}{2}, 0, 0)$ reflection in the vicinity of the Mn $L_{2,3}$ edges. For both materials, the temperature dependence of the magnetic $(\frac{1}{2}, 0, 0)$ reflection is shown in Fig. 4. Note that the onset of magnetic order for both materials is at $T_N = 40$ K. For o-TmMnO$_3$ the intensity increases sharply below 32 K, in agreement with neutron scattering, whereas for o-LuMnO$_3$ the sharp increase in intensity starts at 35 K. This result is consistent with magnetoelectric measurements, which showed a slightly higher transition temperature compared to Tm. It might arise from the different ionic radius of the $R$ ion, and correspondingly it could be due to different octahedra tilts and Jahn-Teller distortions.

For the resonant magnetic scattering, electric dipole transitions (E1) dominate and the magnetic scattering amplitude can be written as:

$$ F \propto -i(\epsilon' \times \epsilon) \cdot F_m, $$

where $\epsilon'$ and $\epsilon$ are unit vectors of the incident and scattered polarization, respectively.

Calculations of the magnetic structure factor $F_m$ provide quantitative information about the measured intensity, with

$$ F_m = \sum_j m_j e^{i\mathbf{r}_j \cdot \mathbf{q}}, $$

where $m_j$ is a tensor representing the magnetic moment at site $j$ at the position $\mathbf{r}_j$ and having $\mathbf{q}$ as a wave vector.

FIG. 3. (a) Energy dependence and (b) temperature dependence of the structural forbidden $(1, 0, 0)$ reflection with $\sigma$ light polarization in the vicinity of the Tm $M_5$ edge. The lines are guides to the eyes.

FIG. 4. (Color online) Temperature dependence of the magnetic $(\frac{1}{2}, 0, 0)$ reflection in TmMnO$_3$ and LuMnO$_3$ taken at the Mn $L_3$ edge at 643.25 eV. The lines are guides to the eyes. Inset: the canted E-type antiferromagnetic structure of TmMnO$_3$ below $T_C$. The spin canting is toward the long $b$ axis.
The photon energy dependence of the magnetic ($\frac{1}{2} 0 0$) reflection of LuMnO$_3$ is collected in $\pi$ and $\sigma$, incident light polarizations at 9 K. Having a single moment component along the $b$ axis results in a calculated powder average of $I_\pi/I_\sigma = 0.277$, which is consistent with the observed ratio (Fig. 5). The difference of the diffracted intensity in $\pi$ and $\sigma$ polarization implies that the magnetic scattering indeed originates from moment components along the $b$ axis. It would be interesting to use ab initio methods to investigate if and how this spin canting influences the exchange striction that produces the enhanced polarization in E-type magnetic structures. Moreover, the energy dependence of the ($\frac{1}{2} 0 0$) reflection of LuMnO$_3$ around the Mn $L_{2,3}$ edges in Fig. 5 is very similar compared to other RMnO$_3$ compounds, such as TbMnO$_3$. This shows that additional Fourier components of magnetic moments do not strongly affect the energy dependence of the magnetic reflection, as in the case of TbMnO$_3$.

IV. CONCLUSION

Resonant soft x-ray powder diffraction experiments have been used to study the electronic and magnetic ground state of o-TmMnO$_3$ and o-LuMnO$_3$. The data of the ($h 1 0$) reflection taken at the Tm $M_5$ edge show that the Tm magnetic moments already order in the incommensurate magnetic phase, with a clear induced characteristic in the temperature dependence below $T_C$. The observation of the (1 0 0) reflection at the same resonance is directly related to the orbital order of the Tm 4$f$ electrons, caused by the tilts of the oxygen octahedra. The observed ($\frac{1}{2} 0 0$) magnetic reflection at the Mn $L_3$ edge indicates that the magnetic structure is not purely collinear E-type, but there is an additional spin canting along the $b$ axis in the ferroelectric phase. This canting is significantly larger for the o-LuMnO$_3$ with nonmagnetic Lu compared to the o-TmMnO$_3$. These experiments demonstrate that resonant soft x-ray powder diffraction can be used to study electronic and magnetic ordering phenomena also in 4$f$ polycrystalline materials, which is important as there is a lack of single crystals of the orthorhombic heavy rare-earth perovskite manganites.

ACKNOWLEDGMENTS

We have benefited from the experimental support of the X11MA beamline staff. We acknowledge fruitful discussions with M. Kenzelmann and V. Pomyakushin. The financial support of the Swiss National Science Foundation and its NCCR MaNEP is gratefully acknowledged.


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