Modulated magnetic structure in ^{57}Fe doped orthorhombic $YbMnO_3$: A Mössbauer study

Cite as: AIP Advances 9, 035008 (2019); doi: 10.1063/1.5077005
Presented: 17 January 2019 • Submitted: 23 October 2018 •
Accepted: 3 December 2018 • Published Online: 11 March 2019

View Online Export Citation CrossMark

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Note: This paper was presented at the 2019 Joint MMM-Intermag Conference.
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ABSTRACT

In the orthorhombic manganites o-$RMnO_3$, where R is a heavy rare earth (R = Gd-Yb), the Mn^{3+} sublattice is known to undergo two magnetic transitions. The low temperature phase has an antiferromagnetic structure (collinear or elliptical), which has been well characterized by neutron diffraction in most of these compounds. The intermediate phase, occurring in a narrow temperature range (a few K), is documented for R = Gd–Ho as a collinear modulated structure, incommensurate with the lattice spacings. We report here on a ^{57}Fe Mössbauer study of 2% ^{57}Fe doped o-$YbMnO_3$, where the spin only Fe^{3+} ion plays the role of a magnetic probe. From the analysis of the shape of the magnetic hyperfine Mössbauer spectra, we show that the magnetic structure of the intermediate phase in o-$YbMnO_3$ (38.0 K < T < 41.5 K) is also modulated and incommensurate.

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I. INTRODUCTION

The physics of the orthorhombic (or perovskite) rare earth manganites o-$RMnO_3$, where R is a rare earth ion, is governed by the interplay of various interactions: the largest is the Jahn-Teller effect on the $3d^4$ Mn^{3+} ion, which can lead to orbital ordering; the interionic exchange interaction, which leads to magnetic ordering; and the magneto-electric coupling which couples ferroelectric order and magnetic order in certain given circumstances (for reviews, see Refs. 1, 2). Due to the present interest in multiferroic phenomena, *i.e.* acting on magnetic moments *via* an electric field (or vice-versa),[3] the precise determination of the lattice and magnetic properties of these interesting materials, and of their interplay, is of prime importance.

The magnetic phase diagram of the orthorhombic rare-earth manganites has been established in Ref. 4 using specific heat measurements. For the naturally occurring perovskites (R = La-Gd), the magnetic transition temperature, T_{N1}, marking the ordering of the Mn moments, decreases with the rare earth radius. In addition, for Eu and Gd, a second transition occurs at $T_{N2} > T_{N1}$. The same also happens for all of the heavier rare earth manganites for which the orthorhombic phase is only a metastable high-pressure phase. Neutron diffraction studies have shown the ground state magnetic structure of o-$RMnO_3$ to be a collinear A-type antiferromagnet (AF) for R=La-Gd,[5,6] a transverse spiral type for R = Tb and Dy[7,8] and a collinear E-type AF for R = Ho.[9] In $TbMnO_3$ and $DyMnO_3$, the spiral magnetic order is accompanied by ferroelectric order and a large magneto-electric effect.[3,5] In $HoMnO_3$, the E-type order also bears ferroelectricity.[10] The structure of the intermediate phase ($T_{N1} < T < T_{N2}$) is documented only for R = Gd–Ho, where it was shown to be incommensurate sine-wave modulated.[9] The Néel temperature

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T_{N1} therefore marks a lock-in transition below which the magnetic structure becomes commensurate.

For the last rare earths of the series, the ground magnetic structure has been determined only for R = Yb[11] (E-type AF), but the structure of the intermediate phase has not yet been elucidated. By analogy with R = Gd–Ho, it is expected to be incommensurate modulated. A Mössbauer spectroscopy study of ^{57}Fe doped o-$YbMnO_3$, with the isotopes ^{57}Fe and ^{170}Yb, was performed in Ref. 12, but could not reach a definitive conclusion about the structure of the intermediate phase.

We have performed a ^{57}Fe Mössbauer investigation of this material, doped at a 2% level with ^{57}Fe, and by analyzing the shapes of the spectra in the intermediate phase, we show they are compatible with a collinear incommensurate modulated type. Recently, we have shown the feasibility of this method by analyzing the incommensurate magnetic phases in $FeVO_4$ by Mössbauer spectroscopy[13] (see also Ref. 14).

A. Sample preparation and characterisation

The hexagonal polymorph h-$YbMn_{0.98}Fe_{0.02}O_3$ was prepared as polycrystalline powder by solid state reaction. Oxides Yb_2O_3, MnO_2 and Fe_2O_3 of at least 99.99% purity were used as precursors. The iron oxide was enriched in the ^{57}Fe isotope up to 95.5%.

Stoichiometric quantities of the starting materials were thoroughly mixed and ground together, then pressed into pellets and heated up to 950°C, in air, for 12h. After an intermediate grinding, the mixture was pressed again into pellets and further heated at 1100°C for 48h in air, which completed the synthesis. According to powder x-ray diffraction the h-$YbMnO_3$ sample was single phase, with a=b=6.068(1) Å and c=11.364(1) Å.

The orthorhombic phase of $YbMnO_3$ was prepared by heating the hexagonal phase h-$YbMnO_3$ under high pressure. The powder was packed into a platinum capsule surrounded by pyrophillite (a good pressure transmitter and thermal insulator) and heated at 1100° (ramp rate 40°/min) during 40 min under an applied pressure of 5 GPa. The XRD pattern was entirely compatible with the orthorhombic Pnma space group with lattice parameters (with the Pnma setting): a = 5.7988(1) Å, b = 7.3094(1) Å and c = 5.2197(1) Å, in good agreement with published values.[11,12] The Bragg peaks are narrow, showing negligible nonstoichiometry.

B. Magnetic susceptibility

The polycrystal magnetic susceptibility was measured with a field of 20 G in the temperature range 5 – 70 K. It shows a monotonic decrease as temperature rises, with a small feature around 40 K (see Fig. 1).

The structure of the feature is clearer in the derivative $d\chi/dT$ shown in the inset of Fig. 1. On cooling, one observes a jump at 41.5 K, which is identified as T_{N2}, the transition to the intermediate phase, and a maximum at 38 K, which is identified as T_{N1}, the transition to the collinear E-type AF phase. Thus, in our o-$YbMnO_3$ sample, the intermediate magnetic phase occurs in the range 38.0 K < T < 41.5 K. These boundaries match the T_N of 43 K reported in Ref. 11 and the two values T_{N1} ≃36 K and T_{N2} ≃ 40 K inferred from Ref. 4, showing that the intermediate phase transition temperatures may vary slightly from sample to sample.

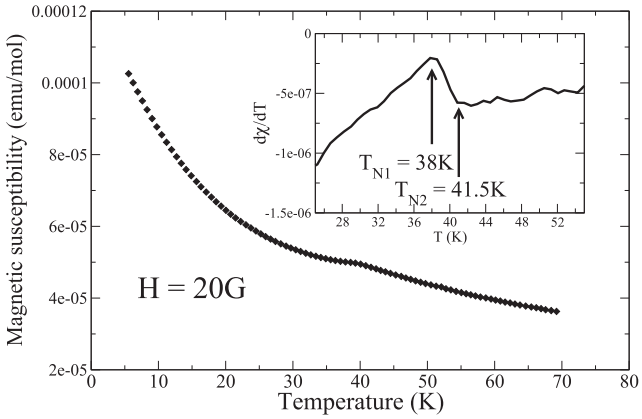

FIG. 1. Thermal variation of the magnetic susceptibility $\chi(T)$ in o-$YbMnO_3$ doped with 2% ^{57}Fe, in a field of 20 G. The inset shows the derivative of $\chi(T)$.

II. MÖSSBAUER MEASUREMENTS

The Mössbauer spectra were recorded with a linear velocity electromagnetic drive using a commercial ^{57}Co*:Rh γ-ray source. A standard liquid He cryostat with temperature regulation was used.

A. The electric field gradient tensor

o-$YbMnO_3$ crystallizes into the orthorhombic space group Pnma, where the Mn 4b-site has triclinic C_i point symmetry. Fe substitutes for Mn in the doped material, and since Fe^{3+} and Mn^{3+} have approximately the same radius (0.645 Å), one can reasonably assume that the Fe site is not appreciably distorted with respect to the Mn site. On this basis, the authors of Ref. 12 performed a Point Charge Model (PCM) calculation using the o-$YbMnO_3$ crystal parameters to obtain the Electric Field Gradient (EFG) tensor V_{ij} (principal axes and diagonal values) at the Fe/Mn site. This tensor is needed in order to evaluate the quadrupole hyperfine interaction which characterizes the Mössbauer spectrum in the paramagnetic phase. It has zero trace and it is usually determined by two quantities: V_{ZZ}, where OZ is the principal axis and $\eta = |\frac{V_{YY}-V_{XX}}{V_{ZZ}}|$.

The splitting ΔE_Q of the doublet observed in the paramagnetic phase, due to the electric quadrupolar hyperfine interaction is given by:

$$\Delta E_Q = \frac{eQV_{ZZ}}{2}\sqrt{1+\frac{\eta^2}{3}}. \quad (1)$$

The experimental value ΔE_Q ≃1.54 mm/s, obtained above 43 K in Ref. 12 as well as in the present work (not shown), is in rather good agreement (ΔE_Q ≃1.59 mm/s) with the PCM calculation,[12] which also yields η=0.175. Furthermore, the ordered Mn^{3+} magnetic moment lies along the orthorhombic **a** axis in the low temperature E-type collinear AF phase.[11] The impurity Fe moment and the hyperfine field (B_{hf}), proportional to the moment for Fe^{3+}, are expected to lie along **a** as well. Stewart *et al*[12] also determined the values of the polar and azimuthal angles of B_{hf} (the **a** axis) in the EFG frame: θ ≃37.8° and φ ≃270°.

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B. Mössbauer spectra in the magnetic phases

Selected spectra are represented in Fig. 2, in the ground collinear E-type AF phase at 4.2 K, and for three temperatures inside the intermediate phase: 38.1, 39.1 and 40.3 K. They are in good agreement with those in Ref. 12.

The spectra show no significant variation in the E-type phase, between 4.2 K and 36 K, showing only a single B_{hf}, as expected for the collinear E-type magnetic structure,[11] with moments directed along the **a** axis. A good fit is obtained using the quadrupolar parameters and the polar and azimuthal angles of B_{hf} determined in Ref. 12. B_{hf} at 4.2 K is 44.3 T, a value lying at the lower end of the typical range for Fe^{3+} in insulators (50 ± 5 T).

Above 38 K, in the intermediate phase, the spectra show a drastic change: the lines broaden and the resonant absorption strongly increases in the center of the spectrum, *i.e.* near zero velocity. At 40.3 K, the spectrum is an almost featureless asymmetric doublet. These characteristics point to the presence of a distribution of B_{hf} with a rather strong weight near zero and low values. Generally speaking, in a magnetically ordered phase, this very specific feature is generated in a Mössbauer spectrum solely by an incommensurate collinear magnetic structure, like that observed in $FeVO_4$ in the intermediate magnetic phase, for 15.7 K < T < 23 K.[13] Other types of incommensurate orderings (for instance elliptical) do not yield an enhanced weight near zero B_{hf}.

The distribution corresponding to a collinear incommensurate sine-wave modulation of B_{hf} is shown in Fig. 3a, for a maximum B_{hf} of 38 T, and the associated simulated spectrum, with the same quadrupolar parameters and orientation of B_{hf} as determined for o-$YbMnO_3$:Fe, in Fig. 3b. Comparison of the simulated spectrum in Fig. 3b and of the experimental spectra in the intermediate phase of o-$YbMnO_3$:Fe at 38.1 K and 39.1 K shows a clear similarity: not only, as mentioned above, the presence of a large spectral weight at the center of the spectrum, but also the left-hand central line being broader than the right-hand one. There is however an important difference: the outer and intermediate lines in the simulation of Fig. 3b have an asymmetric shape, whereas those in the spectra are rather symmetrically broadened. Such a broadening could be caused by fluctuations in B_{hf}, but the two other spectral features mentioned above clearly cannot, thus excluding relaxation effects as a cause for the observed peculiar spectral shapes.

The simulated spectrum in Fig. 3b actually corresponds to the case of a modulated magnetic structure in a pure material, where

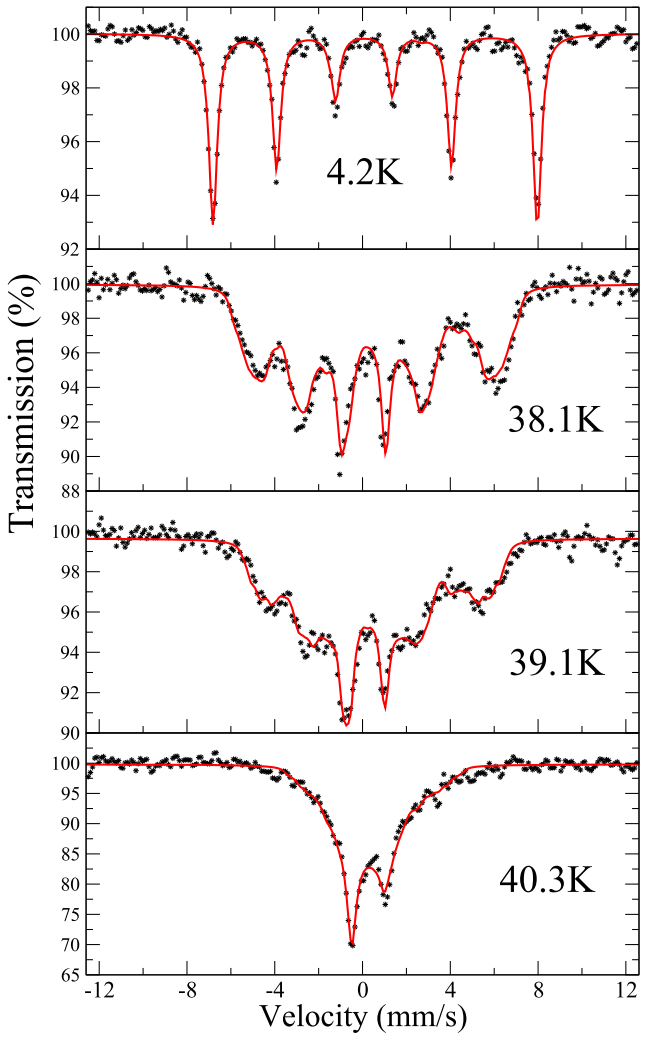

FIG. 2. ^{57}Fe Mössbauer spectra in o-$YbMnO_3$:Fe at selected temperatures. The fits, shown by a solid red line, are as explained in the text.

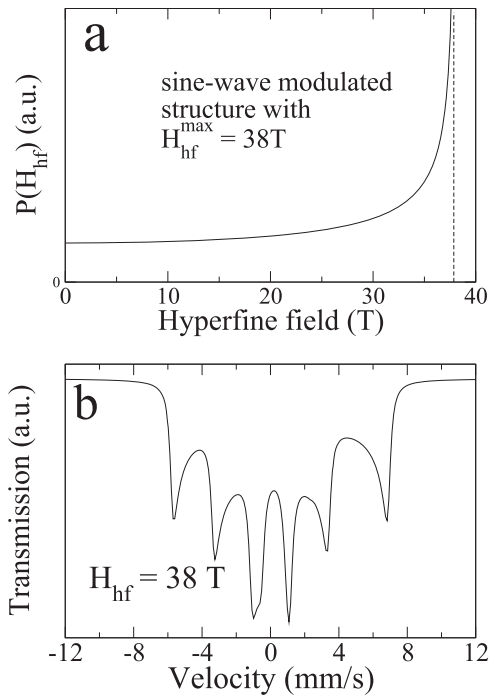

FIG. 3. In the presence of a sine-wave modulated collinear magnetic structure: a Distribution of B_{hf} at the Fe site, with a maximum value of 38 T; b Simulated ^{57}Fe Mössbauer spectrum in the presence of this distribution.

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there is only one sort of magnetic ion, as in $FeVO_4$. In o-$YbMnO_3$:Fe, we observe the spectrum of Fe *dopants* which might perturb the magnetic structure of the matrix Mn ions. Furthermore, we assume that the Mn magnetic structure is locally reflected in the magnitude of B_{hf} at the Fe site. This assumption means that while the dilute Fe doping does not perturb the superexchange interaction, it could blur the modulation of the Fe moments all over the sample.

For these reasons, we have fitted the spectra in the intermediate phase using the four following assumptions:

i) the quadrupole interaction tensor is fixed to its value at 4.2 K.
ii) the magnetic structure is collinear incommensurate with the moments, and hence B_{hf}, along the **a** axis, *i.e.* the same as in the collinear E-type ground structure.
iii) the modulation is described by a Fourier expansion up to the 3 first (odd) harmonics, as a function of the abscissa x along the propagation vector **k**:

$$B_{hf}\ (kx) = \sum_{p=0}^{2} b_{2p+1}\ \sin[(2p+1)kx], \qquad (2)$$

in order to account for possible deviations from a pure sine-wave.
iv) a small random deviation of the form: $\delta B_{\rm hf} = x\,\Delta B_{\rm hf}$, where x is chosen at random in the interval [0;1] accounts for impurity-induced defects. $\Delta B_{\rm hf}$ is a fitted parameter. The mean value of the deviation is therefore $\sigma = \frac{1}{2}\,\Delta B_{\rm hf}$.

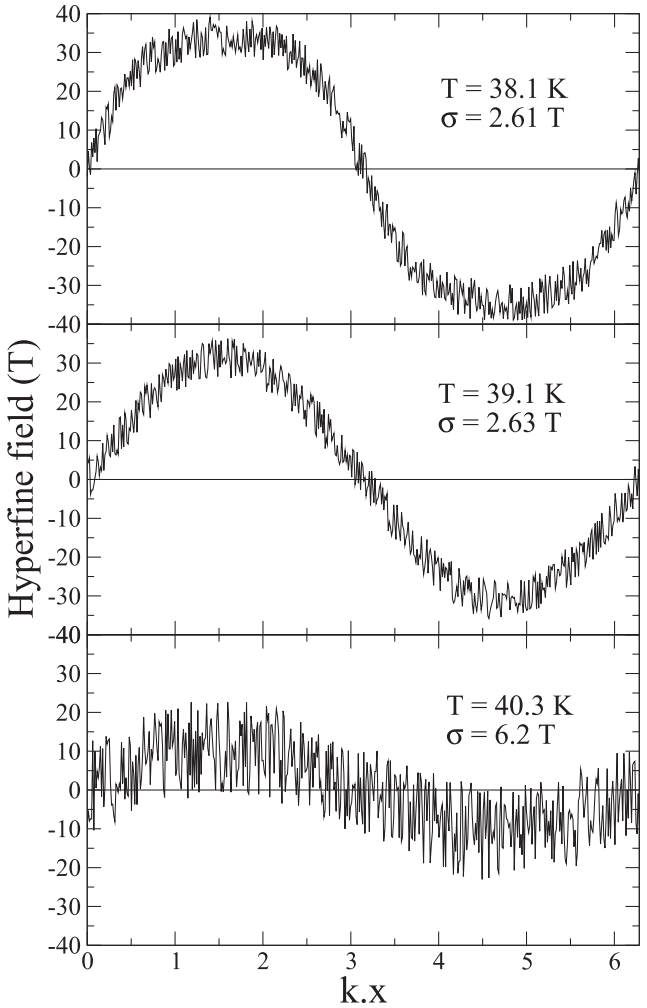

FIG. 4. Fitted hyperfine field (or moment) modulations in the intermediate phase of o-$YbMnO_3$:Fe at 38.1 K, 39.1 K and 40.3 K showing the random deviations from the nominal modulation with their mean value σ.

The spectra in the intermediate phase were successfully fitted, as shown by the solid red lines in Fig. 2. The corresponding B_{hf} (or moment) modulations are shown in Fig. 4. At 38.1 K, just above T_{N1} = 38.0 K, the modulation is somewhat squared, (as the commensurate E-type AF ground state starts to break down) and 3 harmonics are needed to reproduce the spectral shape: b_1 = 38.0 T, b_3 = 4.32 T and b_5 = 0.80 T. At 39.1 K, in the middle of the intermediate phase, the modulation is close to pure sine wave with b_1= 31.2 T. In both cases the mean deviation σ was ≃6% of B_{hf}^{max}. By 40.3 K, just below T_{N2} = 41.5 K, the first harmonic has decreased to ≃11 T and the mean value of the deviation is rather large: $\sigma \simeq 6.2$ T, so that the magnetic hyperfine structure has almost disappeared, leaving an asymmetric doublet with a broad base.

III. CONCLUSION

Using ^{57}Fe Mössbauer spectroscopy, we have shown that the lineshapes in the intermediate magnetic phase (38.0 K < T < 41.5 K) of orthorhombic $YbMnO_3$ (doped with 2% ^{57}Fe) are compatible with a collinear incommensurate magnetic structure. The Fe hyperfine field, and hence the Mn spontaneous moment, has the same direction as in the ground E-type AF phase, *i.e.* the crystal **a** axis. The modulation is mainly sine-wave, but we could detect some "squaring" just above the lock-in transition. Since this type of magnetic structure has been found for the intermediate phase in orthorhombic $RMnO_3$ with R = Gd–Ho,[5–9] we think our Mössbauer spectra demonstrate its presence in orthorhombic $YbMnO_3$. However the wave vector of this modulation can only be determined using neutron diffraction.

ACKNOWLEDGMENTS

We thank the "Service Synthèses Hautes Pressions" of the ICMCB (Bordeaux, France) for the preparation of the orthorhombic $YbMnO_3$ sample.

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