Single-crystal neutron diffraction study of hexagonal YbMnO$_3$ multiferroic under magnetic field

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We report single-crystal neutron diffraction study of the magnetic structure of the multiferroic compound YbMnO$_3$, a member of the hexagonal manganite family, in zero-field and under a magnetic field applied along the c-axis. We propose a scenario for the zero-field magnetic ordering and for the field-induced magnetic reorientation of the Mn and of the two Yb on distinct crystallographic sites, compatible with the macroscopic measurements, as well as with previous powder neutron diffraction experiment and results from other techniques (optical second harmonic generation, Mössbauer spectroscopy). Our study should contribute in settling some debated issues about the magnetic properties of this material, as part of a broader investigation of the entire hexagonal RMnO$_3$ (R = Dy, Ho, Er, Tm, Yb, Lu, Y) family.

I. INTRODUCTION

The hexagonal h-RMnO$_3$ multiferroic compounds (with R = Dy, Ho, Er, Tm, Yb, Lu, Y) have produced an abundant amount of literatures since their discovery in 1963. This interest is due to their exotic static and dynamical behaviors ascribed to the combination of ferroelectricity and magnetic frustration. The latter arises from the intra-plane triangular arrangement of antiferromagnetically interacting Mn$^{3+}$ magnetic ions, weakly coupled along the c-axis, as shown in Fig. 1. Unlike multiferroics where the ferroelectricity is induced by the magnetic order, as in the orthorhombic RMnO$_3$ compounds (with larger rare-earth ions), h-RMnO$_3$ oxides become ferroelectric at much higher temperatures (around 1000 K) than their magnetic transition (Néel temperature $T_N$ below 100 K). In h-YMnO$_3$, ferroelectricity was found to be connected to the buckling of the layered MnO$_5$ polyhedra, displacements of the Y ions, and the trimerization of the Mn lattice associated to strong magnetoelastic effect. Although the exact mechanism at the origin of the ferroelectricity has been debated, it is assumed to be identical in all members of the family, which are described in the hexagonal space group $P6_3cm$ (number 185) at low temperature.

The magnetism is a complex issue in itself in this class of materials. Mn$^{3+}$ ions occupy the Wyckoff site 6c, forming triangular layers of Mn$^{3+}$ in the (a, b) planes. Between them, the R$^{3+}$ occupies two different crystallographic Wyckoff sites 4b and 2a. While decreasing the temperature, first the Mn$^{3+}$ order magnetically at $T_N$, due to superexchange antiferromagnetic interactions in a 120° magnetic structure, characterized by a $k=(0, 0, 0)$ propagation vector. Then the R$^{3+}$ (4b) are polarized in the molecular field of the Mn, while the R$^{3+}$ (2a) are believed to order at much lower temperature from their mutual interaction. Additional spin-reorientations occur at intermediate temperatures for some members of the family (e.g. Ho, Sc). Finally, metamagnetic pro-

![FIG. 1. Left panel: Perspective view of the YbMnO$_3$ crystal structure with tilted MnO$_5$ bi-pyramids and Yb atoms on the different 4b and 2a Wyckoff sites respectively (the small green spheres are the oxygens). Right panel: Two layers of Mn triangles positioned at $z = 0$ and $z = 1/2$ along the crystallographic c direction.](https://example.com/figure1.jpg)
The necessity of single-crystal neutron diffraction experiment and results coming out of D23 only are presented in the following.

II. SYNTHESIS AND EXPERIMENTAL DETAILS

The plate-like single crystals of YbMnO\textsubscript{3}, with the hexagonal c-axis perpendicular to the surface and a thickness of about 0.5 mm, were grown using flux method as described by Yen et al\textsuperscript{[20]}. The magnetization (M) measurements were performed in a commercial SQUID magnetometer and in a physical property measurement system from Quantum Design. Electric polarization (P) was measured along the crystallographic c-axis using a Keithley 6517A electrometer. Electrical contacts were attached by Ag paint on the two parallel surfaces of the c-cut sample. The measurements were performed both for zero and non-zero (±1 kV/mm) applied electric field regimes. These have not revealed a significant difference, implying the absence of ohmic currents. Note that the latter were observed in YMnO\textsubscript{3} at temperatures above 230 K and were accompanied by a negative magneto resistive effect\textsuperscript{[20]}. No preliminary poling was carried out to polarize the sample possessing a ferroelectric domain structure. Neutron diffraction measurements in zero magnetic field were performed on the CEA-CRG D15 and D23 single crystal diffractometers at the ILL (wavelength $\lambda=1.173$ and 1.27 Å respectively) in four-circle mode using a standard orange cryostat. The CEA-CRG D23 diffractometer at the ILL was also used for the measurements under magnetic field using a lifting arm detector and a vertical cryomagnet. The zero-field measurements on D15 and D23 were checked to be consistent and results coming out of D23 only are presented in the following.

III. IRREDUCIBLE REPRESENTATION ANALYSIS

Let us recall that Group theory and representation analysis\textsuperscript{[21]} reveal that the representation of the magnetic structure for Mn\textsuperscript{3+} and Yb\textsuperscript{3+}(4b) involve six possible irreducible representations (IR) denoted as $\Gamma_i$ ($i = 1, 2, ..., 6$), which are compatible with the $P6_3cm$ space group and the propagation vector $k = (0, 0, 0)$\textsuperscript{[22]}. Four of these, $\Gamma_1$ to $\Gamma_4$, are unidimensional and depicted in Fig. 2, the last two ones being two-dimensional. For the Yb\textsuperscript{3+}(2a) site, only the $\Gamma_2$, $\Gamma_3$, $\Gamma_5$, and $\Gamma_6$ irreducible representations are allowed.

Concerning the Mn\textsuperscript{3+} site, the magnetic moments are constrained in the $(a, b)$ plane for $\Gamma_1$ and $\Gamma_4$, while an out-of-plane ferromagnetic component is allowed for $\Gamma_2$, and an out-of-plane antiferromagnetic component is allowed for $\Gamma_3$. Among these configurations, those of symmetry $\Gamma_1$ and $\Gamma_3$ correspond to homometric pairs, so as $\Gamma_2$ and $\Gamma_4$. This means that these pairs are hardly distinguishable (almost identical intensities of the magnetic
FIG. 3. (a) DC magnetic susceptibility ($\chi$) along $c$-axis and in the $(a,b)$ plane. Measurements were performed in a magnetic field of 1 kOe on cooling. Inset: $\frac{d\chi_c}{dT}$ vs. $T$ to show the transition at $T_N = 80$ K. (b) $\chi(T)$ measured with a field of 100 Oe along the $c$-axis after field cooling and zero field cooling procedures, showing the low temperature anomaly associated to the Yb$^{3+}$($2a$) ordering. Magnetization ($M$) vs. applied magnetic field ($H$) for $H$ in the $(a,b)$ plane (c) and along $c$ (d). The low-field $M(H)$ curve at 2 K for $H \parallel c$ is shown in panel (e). The data are not corrected for demagnetizing field effect.

Fig. 4. Change of electric polarization ($\Delta P_c$) along the $c$-axis as a function of magnetic field ($H$) applied along the same direction (measured in an applied electric field of 1 kV/mm).

IV. RESULTS

A. Magnetization and electric polarization

Fig. 3(a) depicts the temperature ($T$) variation of the dc magnetic susceptibility $\chi$ in magnetic field of 1 kOe along the $c$ direction ($\chi_c$) and within the $(a,b)$ plane ($\chi_{ab}$), measured with a field of 100 Oe along the $c$-axis after field cooling and zero field cooling procedures, showing the low temperature anomaly associated to the Yb$^{3+}$($2a$) ordering. Magnetization ($M$) vs. applied magnetic field ($H$) for $H$ in the $(a,b)$ plane (c) and along $c$ (d). The low-field $M(H)$ curve at 2 K for $H \parallel c$ is shown in panel (e). The data are not corrected for demagnetizing field effect.

The field dependence of the magnetization for various temperatures are shown in Fig. 3(c) and Fig. 3(d) for a field applied perpendicular and parallel to the $c$-axis respectively, and is again consistent with previous reports\cite{10,13,14,19,23}. No anomaly, nor hysteretic behavior, are measured for the magnetic field applied in the $(a,b)$ plane. This is at variance with the behavior observed for the other orientation of the field where two step-like features are visible in the magnetization curve at low temperature. The low field magnetization step is observed only for temperatures below about 5 K. As seen on the 2 K curve (Fig. 3(e)), the magnetization reaches $\sim$0.4 $\mu_B$/f.u. almost instantly after increasing the magnetic field (as soon as the applied field reaches $H_{c1} \sim 300$ Oe, which means that the internal field is even smaller). The magnetization step value as well as the magnetization hysteresis seen on Fig. 3(e) point to ferrimagnetic alignment between Yb$^{3+}$($4b$) and Yb$^{3+}$($2a$) moments. The second step like anomaly appears near $H_{c2} = 30$ kOe.

Bragg reflections) by neutron diffraction when the Mn$^{3+}$ coordinate $x_{Mn}$ is close to 1/3. For the two-dimensional representations $\Gamma_5$ and $\Gamma_6$, the Fourier components of the magnetic moments are written as a linear combination of 6 basis functions. The corresponding magnetic structures are reported in ref. 22. For $\Gamma_5$, there are four magnetic modes with the magnetic moments in the $(a,b)$ plane, displaying either a ferromagnetic or a 120° arrangement. The coupling is ferromagnetic between the planes. The two other modes are discarded since they concern non equal moments along the $c$-axis. Similar solutions are found for $\Gamma_6$ but with an antiferromagnetic coupling of the in-plane magnetic structures along the $c$-axis. Concerning the Yb$^{3+}$ $4b$ and $2a$ sites, the one dimensional IR correspond to magnetic moments along the $c$-axis. Importantly, only $\Gamma_2$ configuration allows a ferromagnetic component along the $c$-axis for the three sites (cf. Fig. 2).
for the 2 K curve. At this field, a jump of magnetization takes place and it increases with about 1.2 $\mu_B$/f.u. above its low field step value of $\sim$0.4 $\mu_B$/f.u. and becomes closer to the (a, b) plane magnetization. This step-like feature actually reveals a field induced spin reorientation that has been addressed through our neutron diffraction measurements presented below. It smears out with increasing temperature along with the shift of $H_{c2}$ towards higher field.

The field dependence of the electric polarization change $\Delta P_c(H)$ along the c-axis is presented in Fig. 3 for several temperatures. The magnetic field was applied along the same direction. A sharp jump of the polarization is observed at $\sim$30 kOe at the lowest temperatures. It is clearly correlated to the field-induced magnetic phase transition since its threshold field coincides with the second step-like anomaly in the magnetization curves at $H_{c2}$. The polarization anomaly smears out with increasing temperature. Its field-dependence changes character between $T_c \sim$ 4 K and 6 K revealing a broad maximum in $\Delta P_c(H)$ at higher temperatures. These modifications are probably associated to a change in the nature of the field-induced transition above and below the Yb$^{3+}$($2a$) ordering at $T_c$.

### TABLE I. Results of the refinement of the single crystal neutron diffraction Bragg peak intensities recorded above (100 K) and below (30 K, 13 K, and 2 K) the transition temperature ($T_N = 80$ K) under zero magnetic field condition. $R_F$, $R_{FP}$, and $R_{FPw}$ are the agreement factors of the fits. $M$ is the magnetic moment, and $x_{Mn}$ is the x coordinate of the Mn$^{3+}$.

| $T$ (K) | $x_{Mn}$ | $R_F$ | $R_{FP}$ | $R_{FPw}$ |
|---------|----------|-------|----------|-----------|
| 100     | 0.3345(20) | 4.7% | 5.5% | 6.3% |
| 30      | 0.3343(14) | 3.8% | 5.3% | 6.0% |
| 13      | 0.3350(15) | 3.9% | 5.3% | 6.4% |
| 2       | 0.3349(15) | 3.5% | 4.9% | 5.5% |

FIG. 5. Neutron counts at the peak maximum versus temperature for three types of Bragg reflections. They are site-specific for the magnetic arrangements corresponding to $\Gamma_2$ and $\Gamma_4$: (a-b) (1, 0, 3) and (1, 0, 1) contributed solely by ordered Mn$^{3+}$ (c-d) (1, 0, 2) and (-2, -1, 0) contributed by all Mn$^{3+}$, Yb$^{3+}$($4b$) and Yb$^{3+}$($2a$), and (e) (-1, 0, 0) contributed solely by Yb$^{3+}$($4b$) and Yb$^{3+}$($2a$). Note that $\Gamma_4$ configuration is not allowed by symmetry for the Yb$^{3+}$($2a$) magnetic order.

#### B. Single-crystal neutron diffraction

1. **In zero magnetic field**

About 700 Bragg reflections were recorded at 100 K, 30 K, 13 K, and 2 K (the magnetic Bragg peaks associated to the $k=(0, 0, 0)$ propagation vector rise on top of the nuclear ones). All the refinements were performed using the FullProf Suite software package and we used the formalism of Becker-Coppens to refine the anisotropic extinction. The refined atomic positions of the 100 K data (above $T_N$) were found very similar to the ones reported from X-ray diffraction at room temperature. In particular, the z coordinate of Mn$^{3+}$ is almost 0 and thus kept to zero for the lower temperature refinements. The x coordinate of the Mn$^{3+}$($x_{Mn}$) is also very close to 1/3 (see Table I) but it was allowed to vary in the
lower temperature refinements as its variation is believed to be intricately linked to the selection of the magnetic order.\textsuperscript{91}

To get a deeper insight on the contribution of the different sublattices to the magnetic order in zero field, we chose to study the thermal evolution of some characteristic site-specific reflections (see Fig. \textsuperscript{7}). We followed the (1,0,1) and (1,0,3) reflections, which are forbidden in the \textit{P6}_3\textit{cm} space group. As can be seen, they start to become non-zero only below \(T_N\) reflecting their magnetic character and have a temperature dependence compatible with that of a magnetic order parameter. Under \(\Gamma_2\) and \(\Gamma_4\) symmetry, those two reflections are entirely dependent on the ordering of Mn\(^{3+}\) magnetic moments. Therefore, the rise of these reflections below \(T_N\) is consistent with the coincidence of the Néel temperature with the magnetic ordering of the Mn\(^{3+}\) in one of these two IR. In contrary, the \((-1,0,0)\) reflection shown in Fig. \textsuperscript{5c} only depends, for its magnetic component, on the Yb\(^{3+}\) magnetic moments for \(\Gamma_2\) (2a and 4b sites) and \(\Gamma_4\) (only 4b site). The intensity of this reflection increases very slowly when decreasing the temperature down to \(\sim 20 - 30\) K, below which, it shows a sharp increment. Such a behavior is consistent with the magnetic ordering of the Yb\(^{3+}\) in the Mn\(^{3+}\) molecular field.\textsuperscript{13} Note that, as the transition at \(T_N\) is second order, the two Mn\(^{3+}\) and Yb\(^{3+}\) (4b) sublattices must order with the same IR (\(\Gamma_2\) or \(\Gamma_4\)) since they are coupled. No anomaly can be seen in \((-1,0,0)\) at \(T_c\). Two other characteristic reflections viz. \((1,0,2)\) and \((-2,-1,0)\) combine the features of the previous two kinds of reflections, thus involving magnetic contributions from both Mn\(^{3+}\) and Yb\(^{3+}\).

We checked the information deduced from the temperature dependence of selected reflections through the refinement of all the Bragg reflections below \(T_N\). To obtain the best refinements, all the possible one-dimensional IR as predicted for Mn\(^{3+}\) and Yb\(^{3+}\) were tested. In addition to the magnitude of the magnetic moments, the \(x\) coordinate of the Mn\(^{3+}\) ions were also refined. At 30 and 13 K, the best refinements with similar agreement factors were obtained for the representations \(\Gamma_4\) or \(\Gamma_2\) for Mn\(^{3+}\)/Yb\(^{3+}\) (homometric Mn\(^{3+}\) IR), with an enhancement of the Yb\(^{3+}\) (4b) moment from 30 to 13 K and no magnetic moment on the Yb\(^{3+}\) (2a) sites. However, in the \(\Gamma_2\) magnetic configuration, the Yb\(^{3+}\) (4b) are ferromagnetically coupled. From the neutron refinement, they should give rise to a ferromagnetic contribution amounting to \(\sim 0.7\) \(\mu_B\) at 30 K and \(\sim 0.9\) \(\mu_B\) at 13 K, which is not observed in the magnetization measurements. A small bifurcation of the field-cooled and zero-field-cooled susceptibilities has been reported\textsuperscript{13} below \(T_N\) but it cannot be accounted by such a large magnetization and is rather due to field-polarized defective magnetic moments for instance in the domain walls.\textsuperscript{19} Our finding thus points out to the \(\Gamma_4\) magnetic configuration for Mn\(^{3+}\) and Yb\(^{3+}\) (4b) (see Figs. \textsuperscript{6} and \textsuperscript{7}), which is consistent with previous powder neutron diffraction\textsuperscript{13} and SHG results.\textsuperscript{13} The good quality of the fits obtained using \(\Gamma_4/\Gamma_2\) configurations allowed us to limit our analysis to solutions corresponding to one-dimensional IR over the more complex two-dimensional ones.

Mössbauer and far-infrared spectroscopies have proven the ordering of the Yb\(^{3+}\) (2a) below \(\sim 5\) K.\textsuperscript{14,15,13} Moreover, the onset of a ferromagnetic component along the \(c\) axis is associated to this ordering, which suggests that the Yb\(^{3+}\) (2a) moments order in the \(\Gamma_4\) IR. The last uncertainty concerns the ordering of the Mn\(^{3+}\) and Yb\(^{3+}\) (4b) below \(T_c\). Do they remain in the \(\Gamma_4\) IR or do they reorient due to a coupling with the Yb\(^{3+}\) (2a) in the \(\Gamma_2\) IR? We checked both possibilities: Although the agreement factor is only slightly better for the \(\Gamma_2\) solution for all sites versus the solution with \(\Gamma_4\) for Mn\(^{3+}\) and Yb\(^{3+}\) (4b) and \(\Gamma_2\) for Yb\(^{3+}\) (2a), the former is more consistent with the magnetization data yielding an almost 0.5 \(\mu_B\) per

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**FIG. 6.** Observed versus calculated intensity (square of the structure factor) of the magnetic Bragg reflections in arbitrary units. Top panel: Data recorded in zero field at \(T = 30\) K (red diamond) and 2 K (back circle) using the 4-circles mode. Bottom panel: Data recorded at \(T = 2\) K with \(H = 20\) kOe (black circle) and 60 kOe (red diamond) in the cryomagnet using the lifting-arm detector. The agreement factors and magnetic configurations for the three sites are indicated.
formula unit as shown in Fig. 3(d). Indeed, the total ferromagnetic component deduced from the neutron refinement for the $\Gamma_2$ solution is found equal to $0.68(8) \mu_B$ per formula unit, instead of $0.06(3) \mu_B$ obtained for the $\Gamma_4/\Gamma_2$ solution. We have also tested the possibility of an in-plane configuration of Yb$^{3+}(2a)$ magnetization that had been suggested, but found a worse agreement with our data. The results of the fits are shown in Fig. 6 with the associated magnetic configuration in Fig. 7 and the details of the important refined parameters are given in Table I.

2. Under magnetic field

Fig. 8 depicts the magnetic field dependence of characteristic reflections measured at 1.5 K and 4.5 K, i.e. below and close to the transition $T_c$, with a field applied along the c-axis. The results are identical: The $(1,0,-1)$ reflection, which depends solely on Mn$^{3+}$, remains practically insensitive to the field sweep. On the other hand, the $(1,0,0)$ reflection, which is associated with Yb$^{3+}(4b)$ and Yb$^{3+}(2a)$ magnetic moments in the $\Gamma_2$ IR, strongly decreases at 30 kOe and almost vanishes above this field. This field corresponds to $H_{c2}$ marking the high field step-like anomaly observed in the macroscopic measurements for a field applied along the c-axis. The last reflection $(2,1,0)$ combines the two contributions from the Mn$^{3+}$ and from the Yb$^{3+}$. It is therefore evident that only the Yb$^{3+}$ moments are affected by the application of an external magnetic field.

Although nearly 140 reflections were recorded at 2 K for $H = 0.25$ kOe ($H < H_{c2}$), and 60 kOe ($H > H_{c2}$), the small coverage of the reciprocal space due to the limited aperture of the cryomagnet did not allow us to perform a reliable refinement of the data. Instead, we tested the most reasonable assumption agreeing with the magnetization data: a reorientation of the Yb$^{3+}(2a)$ magnetic moments above $H_{c2}$ in a way that they become parallel to the Yb$^{3+}(4b)$ ones while keeping the Mn$^{3+}$ magnetic moments unaltered in the $(a, b)$ plane. This reorientation would lead, keeping the Yb$^{3+}(4b)$ and Yb$^{3+}(2a)$ magnetic moments to their absolute values refined in zero field, to a total magnetization per f.u. equal to 1.65 $\mu_B$ in agreement with the magnetization data of Fig. 3. As starting point for the analysis of the data under field, we tested the magnetic configuration found previously in zero-field using the 4-circles mode. This configuration yields comparable agreement factors using the data recorded with the cryomagnet and lifting-arm detector in zero field and under a magnetic field of 20 kOe ($R_F/R_{F2}/R_{Fw} = 13.7/15.4/18.7\%$ and $13.6/14.5/24.3\%$ respectively). At 60 kOe, i.e. above $H_{c2}$, the same configuration does not hold good any longer as evidenced by worse agreement factors ($R_F/R_{F2}/R_{Fw} = 24.2/17.9/43.8\%$). Those improve significantly ($R_F/R_{F2}/R_{Fw} = 12.7/11.8/25\%$) by reversing the Yb$^{3+}(2a)$ magnetic moments and making them parallel to the Yb$^{3+}(4b)$ ones (see bottom panel of Fig. 6), hence validating the model. It is to be noted that the strong decrease of the $(1,0,0)$ Bragg reflection above $H_{c2}$, as depicted in Fig. 5, is obtained within this model (where all the Yb$^{3+}$ magnetic moments are aligned along the field) due to the destructive interference between the two Yb$^{3+}$ sublattices.

At 10 K ($T_c < T < T_N$) the same set of reflections was recorded at field values of 4 T and 8 T, i.e. below and above the critical field corresponding to $H_{c2}$ for this temperature (see Fig. 3(c)). Again, a full refinement is impossible but the data unambiguously show that the Yb$^{3+}(4b)$ and Yb$^{3+}(2a)$ moments order in the $\Gamma_2$ IR and are aligned parallel to each other and to the field for both values of the field. It is impossible to determine whether the Mn$^{3+}$ magnetic moments are in $\Gamma_2$ or $\Gamma_4$. At 8 T, the data are compatible with the same configuration than the one inferred from that data at 2 K and 6 T which...
corresponds to the full polarization of the two Yb\(^{3+}\) sites. Note that the low field phase with both Yb\(^{3+}\) moments antiparallel to each other seems not to exist at 10 K.

C. Summary and discussion

In summary, we have achieved a good description of the magnetic properties of the h-YbMnO\(_3\) compound through our single-crystal neutron diffraction study. We have found that the Mn\(^{3+}\) magnetic moments order below \(T_N = 80\) K, polarizing the Yb\(^{3+}\)(4\(b\)) moments whose ordered component strongly increases below 20-30 K. Both Mn\(^{3+}\) and Yb\(^{3+}\)(4\(b\)) moments are described with respect to \(\Gamma_4\) in this temperature region. Below 5 K, the Yb\(^{3+}\)(2\(a\)) moments order in \(\Gamma_2\) dragging the Mn\(^{3+}\) and Yb\(^{3+}\)(4\(b\)) into a new kind of magnetic configuration also corresponding to \(\Gamma_2\). It consists of a ferromagnetic ar-

gangement of the Yb\(^{3+}\)(2\(a\)) and Yb\(^{3+}\)(4\(b\)) moments along \(c\) in a way that the Yb\(^{3+}\)(2\(a\)) and Yb\(^{3+}\)(4\(b\)) magnetic sublattices are antiparallel to each other. There happens also to be an important spin-reorientation of the in-plane Mn\(^{3+}\) moments by 90°, as well as an additional change of its interlayer coupling from AFM to FM. Under a magnetic field applied along the \(c\)-axis, our magnetization and neutron diffraction data are compatible with a spin-flip of the Yb\(^{3+}\)(2\(a\)) moments that become aligned with the field and with the Yb\(^{3+}\)(4\(b\)) magnetic moments. This correlates well with the observed step-like change in the electric polarization accompanying the field-induced magnetic transition. These polarization changes could originate from small alterations in the atomic/electronic positions due to spin-lattice coupling together with a change in Yb-Mn and Yb-Yb magnetic interactions.

The \(H - T\) phase diagram described above is consistent with the SHG results and very similar to the one reported for the h-ErMnO\(_3\) compound\(^{34}\). It has been rationalized phenomenologically through the Landau theory of phase transition\(^{35}\). An important microscopic parameter seems to be the Mn-rare earth coupling. In the present study, it is evidenced through the polarization of the Yb\(^{3+}\)(4\(b\)) moments by the Mn\(^{3+}\) ones and through the reorientation of the Mn\(^{3+}\) moments triggered by the Yb\(^{3+}\)(2\(a\)) magnetic ordering. This coupling has also signatures in the dynamical properties of YbMnO\(_3\)\(^{33,35,37}\), whereas it confers its electroactivity to a magnon in ErMnO\(_3\)\(^{38}\). A puzzling issue remains in the mutual orthogonal orientation of the Mn\(^{3+}\) and Yb\(^{3+}\) magnetic moments which excludes a coupling mechanism by isotropic exchange interactions and calls for more subtle mechanisms. The deviation of the \(x_{Mn}\) coordinate from \(1/3\) has also been proposed as an important parameter in the selection of the Mn\(^{3+}\) magnetic configuration, either by triggering the sign of the inter-layer Mn\(^{3+}\) magnetic effective interaction\(^{31}\), or by determining the orientation of the Mn\(^{3+}\) within the \((a, b)\) plane through spin-lattice coupling\(^{39}\). In our study, this parameter does not seem to vary significantly with the temperature, impeding a definite conclusion on this issue.

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FIG. 8. Neutron counts at the peak maximum versus magnetic field at 1.5 K (left) and 4.5 K (right) for different types of Bragg reflections that are site-specific in the 2\(^{\text{nd}}\) and 4\(^{\text{th}}\) IRs for their magnetic contribution.
1. F. Bertaut, F. Forat, and P. Fang, C. R. Acad. Sci. 256, 1958 (1963).
2. B. B. van Aken, T. T. M. Palstra, A. Filippetti, and N. A. Spaldin, Nat. Mat. 3, 187 (2004).
3. C. J. Fennie, and K. M. Rabe, Phys. Rev. B 72, 100103 (2005).
4. S. Lee, A. Pirogov, M. Kang, K.-H. Jang, M. Yonemura, T. Kamiyama, S.-W. Cheong, F. Gozzo, N. Shin, H. Kimura, Y. Noda, and J.-G. Park, Nature 451, 305 (2008).
5. M. Lilienblum, T. Lottermoser, S. Manz, S. Selbach, A. Cano, and M. Fiebig, Nat. Phys. 11, 1070 (2015).
6. H. Sim, J. Oh, J. Jeong, M. Duc Le, and J.-G. Park, Acta Cryst. B Struct. Sci. Cryst. Eng. Mater. 72, 3 (2016).
7. D. Bansal, J. L. Niedziela, R. Sinclair, V.O. Garlea, D. L. Abernathy, S. Chi, Y. Ren, H. Zhou, and O. Delaire, Nat. Commun. 9, 15 (2018).
8. H. Sim, J. Jeong, H. Kim, S.-W. Cheong, and J.-G. Park, J. Phys.: Condens. Matter 30, 105601 (2018).
9. S. H. Skjærvø, Q. N. Meier, M. Feygenson, N. A. Spaldin, S. J. L. Billinge, E. S. Bozin, and S. M. Selbach, arXiv:1707.09649v2 (2018).
10. H. Sugie, N. Iwata, and K. Kohn, J. Phys. Soc. Japan 71, 1558 (2002).
11. N. Hur, I. K. Jeong, M. F. Hundley, S. B. Kim, and S. W. Cheong, Phys. Rev. B 79, 134120 (2009).
12. P. J. Brown, and T. Chatterjy, J. Phys.: Condens. Matter 18, 10085 (2006).
13. J. Fontcuberta, M. Gospodinov, and V. Skumryev, J. App. Phys. 103, 07B722 (2008).
14. X. Fabrèges, I. Mirebeau, P. Bonville, S. Petit, G. Lebrasa-Jasmin, A. Forget, G. André, and S. Pailhès, Phys. Rev. B 78, 214422 (2008).
15. M. Fiebig, D. Fröhlich, K. Khon, St. Leute, Th. Lottermoser, V. V. Pavlov, and R. V. Pisarev, Phys. Rev. Lett. 84, 5620 (2000).
16. M. Fiebig, Th. Lottermoser, and R. V. Pisarev, J. App. Phys. 93, 8194 (2003).
17. U. Adem, M. Mostovoy, N. Bellido, A. A. Nugroho, C. Simon, and T. T. M. Palstra, J. Phys.: Condens. Matter 21, 496002 (2009).
18. G. Qiang, Y. Fang, X. Lu, S. Cao, and J. Zhang, App. Phys. Lett. 108, 022906 (2016).
19. F. Yen, C. R. de la Cruz, B. Lorenz, E. Galstyan, Y. Y. Sun, M. M. Gospodinov, and C. W. Chu, J. Mater. Res. 22, 2163 (2007).
20. Z. J. Huang, Y. Cao, Y. Y. Sun, Y. Y. Xue, and C. W. Chu, Phys. Rev. B 56, 2623 (1997).
21. E. F. Bertaut, Acta Crystallogr. Sect. A 24, 217 (1968).
22. A. Muñoz, J. A. Alonso, M. J. Martínez-Lope, M. T. Casáis, J. L. Martínez, and M. T. Fernández-Díaz, Phys. Rev. B 62, 9498 (2000).
23. V. Skumryev, M. D. Kuz’min, M. Gospodinov, and J. Fontcuberta, Phys. Rev. B 79, 212414 (2009).
24. N. Abramov, V. Chichkov, S. E. Loftand, and Y. M. Mukovskii, J. Appl. Phys. 109, 07D912 (2011).
25. A. Midya, S. N. Das, P. Mandal, S. Pandya, and V. Ganesan, Phys. Rev. B 84, 235127 (2011).
26. B. Lorenz, ISRN Condensed Matter Physics 2013, Article ID 497073 (2013).
27. J. Rodríguez-Carvajal, Phys. B (Amsterdam) 192, 55 (1993).
28. P. J. Becker and P. Coppens, Acta Crystallogr., Sect. A 30, 129 (1974).
29. M. Isose, N. Kimizuka, M. Nakamura, and T. Mohri, Acta Cryst. C47, 423 (1991).
30. B. B. van Aken, A. Meestam, and T. T. M. Palstra, Acta Cryst. sect. E 57, 164 (2001).
31. X. Fabrèges, S. Petit, I. Mirebeau, S. Pailhès, L. Pinsard, A. Forget, M. T. Fernandez-Diaz, and F. Porcher, Phys. Rev. Lett. 103, 067204 (2009).
32. H. A. Salama, C. J. Voyer, D. H. Ryan, and G. A. Stewart, J. App. Phys. 105, 07E110 (2009).
33. E. C. Standard, T. Stanislavchuk, and A. A. Sirenko, Phys. Rev. B 85, 144422 (2012).
34. D. Meier, H. Ryll, B. Klemke, J.-U. Hoffmann, R. Ramesh, and F. Fiebig, Phys. Rev. B 86, 184415 (2012).
35. I. Munawar, and S. H. Curnoe, J. Phys.: Condens. Matter 18, 9575 (2006).
36. M. Diviš, J. Hölsä, M. Lastusaari, A. P. Litvinchuk, and V. Nekvasil, J. Alloys Compounds 451, 662 (2008).
37. J. Liu, C. Toulouse, P. Rovillain, M. Cazayous, Y. Gallais, M.-A. Measson, N. Lee, S. W. Cheong, and A. Sacuto, Phys. Rev. B 86, 184410 (2012).
38. L. Chaix, S. deBrion, S. Petit, R. Ballou, L.-P. Regnault, J. Ollivier, J.-B. Brubach, P. Roy, J. Debray, P. Lejay, A. Cano, E. Ressouche, and V. Simonet, Phys. Rev. Lett. 112, 137201 (2014).
39. I. V. Solovyev, M. V. Valentynuk, and V. V. Mazurenko, Phys. Rev. B 86, 054407 (2012).
