Magnetic order in YbMnO₃ studied by Neutron Diffraction and Mössbauer Spectroscopy

X. Fabrèges¹, I. Mirebeau¹, P. Bonville², S. Petit¹, G. Lebras-Jasmin², A. Forget², G. André¹, S. Pailhès¹
¹ Laboratoire Léon Brillouin, CEA-CNRS, CE-Saclay, 91191 Gif-sur-Yvette, France and
² DSM/Service de Physique de l’Etat Condensé, CEA-CNRS, CE-Saclay, 91191 Gif-Sur-Yvette, France
(Dated: 01/04/2008)

The magnetic ordering of the hexagonal multiferroic compound YbMnO₃ has been studied between 100 K and 1.5 K by combining neutron powder diffraction, ¹⁷⁰Yb Mössbauer spectroscopy and magnetization measurements. The Yb moments of the two crystallographic sites order at two different temperatures, the 4b site together with the Mn moments (at \(T_N \approx 85\) K) and the 2a site well below (at 3.5 K). The temperature dependences of the Mn and Yb moments are explained within a molecular field model, showing that the 4b and 2a sites order via Yb-Mn and Yb-Yb interactions respectively. A simple picture taking into account the local Mn environment of the Rare earth R (4b) ion is proposed to couple R and Mn orders in hexagonal RMnO₃ manganites. The nature and symmetry of the R-Mn interactions yielding the R order are discussed.

PACS numbers: 75.25.+z,76.80.+y,75.80.+q,75.30.Kz

I. INTRODUCTION

RMnO₃ manganites, where the \(R^{3+}\) ions are either Y or a rare earth, belong to the multiferroic family, showing a coupling between magnetic and electric order parameters. This magneto-electric (M-E) coupling opens the possibility of tuning the magnetization by an electric field or vice-versa, with potential application for building new kinds of electronic devices¹-². Numerous experiments in the RMnO₃ series probe the key role of their non collinear magnetic structures, induced by frustrated magnetic interactions, in driving such M-E coupling³. The M-E coupling is also connected with a spin-lattice coupling, recently observed both in structural measurements in the triangular Mn lattice are extremely difficult to distinguish, and where the R magnetic order is intricate, owing to the presence of two different crystallographic rare earth sites⁴-⁵.

Here we present a detailed study of the magnetic order in YbMnO₃, using neutron diffraction, Mössbauer spectroscopy on the isotope ¹⁷⁰Yb and magnetization measurements. The magnetic structure of this compound has not been studied up to now, although precise predictions could be made from optical spectroscopy data⁶. By combining microscopic and macroscopic probes in a large temperature range (1.5 K<\(T<100\) K), we provide a complete determination of the magnetic structure.

The T-dependence of the Mn and Yb moments derived from our experiments can be explained quantitatively within the molecular field model. This allows us to clarify the respective roles of Mn-Mn, R-Mn and R-R interactions in this compound. Using these results, we discuss the symmetry and the possible origins of the magnetic R-Mn interactions, and we propose a simple picture, which may hold for the whole hexagonal family.

II. EXPERIMENTAL DETAILS

A polycrystalline sample of YbMnO₃ was prepared as described in Ref.¹² and characterized using X-Ray diffraction at room temperature, showing that the sample is single phased. Magnetic measurements were performed with a superconducting quantum interference device (SQUID) magnetometer between 1.5 K and 300 K.

Mössbauer spectroscopy on ¹⁷⁰Yb realises \(\gamma\)-ray resonant absorption between the ground nuclear state, with spin \(I_g=0\), and the first excited state, with spin \(I_e=2\), at an energy of 84.3 keV. We used a neutron activated Tm⁺²¹B₁₂ \(\gamma\)-ray source, mounted on a triangular velocity electromagnetic drive. ¹⁷⁰Yb Mössbauer absorption spectra were recorded in the temperature range 1.35 -
The crystal structure was determined by measuring a neutron powder diffraction (NPD) pattern at 300 K on the high resolution powder diffractometer 3T2 of the Laboratoire Léon Brillouin (LLB) at Orphée reactor, with an incident neutron wavelength $\lambda = 1.2253 \text{ Å}$. The magnetic structure was studied by collecting NPD patterns at several temperatures, between 100 K (above the magnetic transition) and 1.5 K, on the neutron diffractometer G4-1 of the LLB, with an incident neutron wavelength of $2.4226 \text{ Å}$. Both crystal and magnetic structures were refined using the FULLPROF suite.

III. CRYSTAL STRUCTURE

The refined NPD pattern at 300 K is shown in Fig. 1. All Bragg reflexions of the pattern can be indexed within the hexagonal space group $P6_3cm$. The lattice constants at 300 K are $a = 6.0629(1) \text{ Å}$ and $c = 11.3529(1) \text{ Å}$.

The refined atomic positions are reported in Table I. They are in good agreement with previous determinations from X-ray diffraction. As already stated in Ref. 16, the lattice unit cell consists of 6 formula units. Each Mn atom is surrounded by oxygen ions forming a MnO$_5$ bipyramidal structure, with 3 O (2 O$_4$ and one O$_3$) ions close to the Mn plane, and two O (O$_1$ and O$_2$) ions at the apexes. Corner sharing MnO$_5$ bipyramids form layers separated along the c-axis by Yb layers. In the space group $P6_3cm$, Yb occupies the two crystallographically inequivalent sites 2a and 4b, with trigonal local symmetry around the hexagonal c-axis. The Yb(4b) site consists of 4 equivalent atomic positions inside the hexagonal unit cell, and the Yb(2a) site, of two equivalent atomic positions along the c-axis-edges of the cell.

| Atoms   | x    | y    | z    |
|---------|------|------|------|
| Yb(2a)  | 0    | 0    | 0.274(2) |
| Yb(4b)  | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.232(2) |
| Mn(6c)  | 0.345(4) | 0    | 0    |
| O$_1$(6c) | 0.307(2) | 0    | 0.165(3) |
| O$_2$(6c) | 0.640(1) | 0    | 0.336(3) |
| O$_3$(4b) | 0    | 0    | 0.475(2) |
| O$_4$(2a) | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.020(2) |

Discrepancy Bragg R-factor 4.32%
Factors RF-factor 3.21%

TABLE I: Atom positions and discrepancy factors at room temperature

FIG. 1: (Color online) Observed and Fullprof calculated NPD pattern at room temperature. The Bragg reflections (tics), and the difference between the observed and calculated patterns are plotted at the bottom.

IV. MAGNETIC SUSCEPTIBILITY AND $^{170}$YB MÖSSBAUER DATA

The thermal variation of the magnetic susceptibility $\chi(T)$, measured in a field of 20 G, is shown in Fig. 2. The inverse susceptibility follows a Curie-Weiss law in the temperature range 200-300 K, with an effective moment $\mu_{eff} = 6.1(1) \mu_B$ and $\theta_p = -220(5)$ K (antiferromagnetic). As will be shown in section V, the Neél temperature in YbMnO$_3$ is $T_N \simeq 85$ K. The large negative $\theta_p$ value, such that $|\theta_p|/T_N \simeq 2.5$, could be linked with the frustration of the Mn moments on their triangular lattice. Assuming for Yb$^{3+}$ the free ion value $\mu_{eff} = 4.54 \mu_B$, we obtain an effective moment of 4.1(1) $\mu_B$ for the Mn$^{3+}$ ion ($S=2$), which is lower than the value 4.9 $\mu_B$ expected for $g=2$. This deviation could be due to our limited experimental temperature range where the Curie-Weiss law holds; indeed, susceptibility measurements performed in a single crystal up to 350 K obtain the correct effective moment with the free ion values for both ions. No anomaly
in $\chi(T)$ is found at the magnetic transition, in contrast with magnetic measurements in single crystals\textsuperscript{17,18}, where $\chi_c(T)$ exhibits a small peak at $T_N$. At low temperature, a ferromagnetic like increase of $\chi(T)$ occurs at 3.5 K (inset of Fig. 2), signalling the onset of magnetic ordering among the Yb(2a) ions, as confirmed by the Mössbauer data to be described next.

The $^{170}$Yb Mössbauer spectra at selected temperatures are shown in Fig. 3. Between 1.35 K and 25 K, they show two subspectra with relative weights close to the ratio 1:2, that we attribute respectively to Yb(2a) and Yb(4b) sites. Above 25 K, the spectra no longer resolved and consist of a single line. In Fig. 3, the Yb(2a) subspectrum corresponds to the red line, the Yb(4b) to the blue line. At 1.35 K, both subspectra are five-line magnetic hyperfine patterns, with a small quadrupolar hyperfine interaction. The weakness of the latter precludes any reliable information about the orientation of the hyperfine field with respect to the c-axis to be obtained. The hyperfine fields are respectively 117(3) T and 180(3) T for site Yb(2a) and Yb(4b). Using the proportionality constant $C=102 T/\mu_B$ linking the hyperfine field and the Yb$^{3+}$ magnetic moment\textsuperscript{19}, the saturated moment is 1.15(3) $\mu_B$ for Yb(2a) and 1.76(3) $\mu_B$ for Yb(4b).

As temperature increases, the Yb(2a) hyperfine field, and thus the moment, slowly decreases down to 3 K, reaching 1.00(3) $\mu_B$ at 3 K. A spectral change occurs between 3 and 3.5 K on the Yb(2a) subspectrum: the hyperfine field pattern transforms into a single unresolved broad line at 3.5 K (see the red subspectrum at 4.2 K in Fig. 3). Therefore, the hyperfine field vanishes on this site above 3.5 K, and the Yb(2a) ion becomes paramagnetic. The Mössbauer lineshape then reflects the ionic fluctuations within the ground Kramers doublet, and its interpretation is postponed until the end of this section.

The ordering of the Yb(2a) moments below 3.5 K is also observed on the magnetic susceptibility, which shows a large ferromagnetic-like anomaly at the transition (see insert of Fig. 2). The Yb(4b) subspectrum shows no qualitative change from 1.35 K to 25 K: the hyperfine field decreases, reaching 59(5) T (i.e. a moment of 0.58(5) $\mu_B$) at 25 K. At higher temperature, it is not possible to distinguish the Yb(2a) and Yb(4b) sub-spectra. The thermal variation of the Yb(4b) moment is presented in section VI in comparison with the moment values derived from neutron diffraction. Our 4.2 K spectrum is in agreement with that of a recent $^{57}$Fe and $^{170}$Yb Mössbauer study\textsuperscript{22}.

The behaviours of the Yb ions at the two sites are thus rather different: above 3.5 K, there is a vanishing molecular field at the 2a site, which means that the exchange field from the Mn ions is zero. This is not the case for the Yb ions at the 4a sites, which are polarized by Mn exchange up to at least 20 K. The neutron study described below shows that this exchange field is present up to 40 K, and probably up to $T_N$. This behaviour is similar to that in HoMnO$_3$.

The paramagnetic relaxation of the Yb(2a) ion can be interpreted using the Mössbauer relaxational lineshape developed in Ref\textsuperscript{20}. Since the Yb(2a) subspectrum consists of a single line, the “extreme narrowing” regime
holds for the fluctuation rate $\frac{1}{2\pi\tau}$, i.e. $h/\tau \gg A$, where $A$ is the hyperfine constant associated with the Yb$^{3+}$ ground Kramers doublet and the excited nuclear state of the $^{170}$Yb isotope. It is related to the above mentioned proportionality constant $C$ by $A = C g\mu_B g_n\mu_n$, where $g$ and $g_n$ are respectively the electronic and nuclear gyromagnetic ratios (or g-factors), and $\mu_n$ the nuclear Bohr magneton. Using the Yb(2a) saturated moment value $1.15 \mu_B$, yielding $g=2.3$, one gets $A = 580$ MHz. Since the width of the Yb(2a) line narrows as temperature increases, the spin relaxation rate increases, according to the expression for the dynamical broadening $\Delta \Gamma_R = 3A^2\tau$. The fitted values of the relaxation rate $\frac{1}{2\pi\tau}$ are represented in Fig. 4. It slows down abruptly when approaching the transition near 3.5 K from above (“critical slowing down”); the $T=0$ “extrapolated” value of $\approx 6$ GHz is due to exchange-driven spin-spin relaxation and the increase above 10 K can be caused by phonon driven relaxation.

V. MAGNETIC STRUCTURE

The thermal evolution of the NPD patterns is shown in Fig. 5. The temperature dependences of the integrated intensities of typical Bragg peaks (100), (101) and (102) are shown in Fig. 6. Strong changes occur around $T_N = 86$ K, which corresponds to the magnetic transition. Below this temperature, an intensity of magnetic origin grows at the (100) and (101) Bragg positions, where the nuclear reflections are forbidden by the $P\bar{6}_3cm$ symmetry, and the intensity of the (102) peak strongly increases due to an additional magnetic contribution. All peaks can be indexed within the hexagonal space group $P\bar{6}_3cm$ and a propagation vector $\vec{k} = \vec{0}$; this points to an AF structure having the same unit cell as the chemical one, since a ferromagnetic ordering can be excluded from the absence of anomaly in the susceptibility at the transition.

The temperature dependence of the (100) and (101) Bragg peaks strongly differ from each other. The (100) peak remains rather weak down to about 20 K, then suddenly increases below. In contrast, the (101) peak increases abruptly below 86 K. These variations suggest that the (100) and (101) peak intensities are controlled by Yb and Mn ordering, respectively, the (102) Bragg peak involving contributions of both orderings. Moreover, one observes a strong (101) peak in YbMnO$_3$, with thermal evolution akin to that of the (100) peak in YMnO$_3$. Recalling that in YMnO$_3$, the Mn order does not induce a strong (101) magnetic peak, it means that Mn order is affected by Y/Yb substitution. Finally, the temperature dependence of all magnetic peaks is monotonic, in contrast with HoMnO$_3$ where Mn magnetic moments reorient at low temperature.

A. Mn order

To analyze the magnetic structure we searched for all irreducible representations (IR) compatible with the crystal symmetry using the theory of group representation analysis and the program Basireps. Description of this analysis for hexagonal RMnO$_3$ compounds was already given in Ref. [16]. The atomic positions in the unit cell were kept fixed and equal to those determined above. In the space groupe $P\bar{6}_3cm$ with $\vec{k} = \vec{0}$ propaga-

![NPD patterns between 1.5 K and 100 K. The Bragg reflections (tics), and the difference between the observed and calculated patterns are plotted at the bottom.](https://example.com/fig5)
tion vector, one finds 6 irreducible representations (IR), corresponding to the 6 possible configurations of the Mn moments reported in Fig. 7. In these configurations, the Mn moments lie in the (a,b) plane and their vectorial sum is zero. This results from the frustration of the Mn moments in their triangular lattice.

It is important to notice that the $\Gamma_2$ and the $\Gamma_4$ configurations are homometric (namely cannot be distinguished by NPD) as well as $\Gamma_1$ and $\Gamma_3$. The best fit of the data was obtained assuming Mn ordering which corresponds to the irreducible representation $\Gamma_2$ or $\Gamma_4$, in contrast with YMnO$_3$ where it corresponds to a $\Gamma_1$ or $\Gamma_3$ IR. The saturated Mn moment value is $3.25 \mu_B$, lower than the value $4 \mu_B$ expected for $g=2$ and $S=2$.

**B. Yb order**

The magnetic order of Yb moments is more intricate and difficult to determine unambiguously using neutron diffraction only, since the two crystallographic 2$a$ and 4$b$ sites order independently. Space group symmetry allows two types of magnetic orders: along the c-axis or in the (a,b) plane, and the coupling between the Yb ions can be antiferromagnetic or ferromagnetic (F), leading to six possibilities. The Mössbauer spectroscopy data show that the low temperature Yb magnetic moments are small: 1.76 $\mu_B$ for Yb(4$b$) and 1.15 $\mu_B$ for Yb(2$a$), as compared to the saturated Mn moment value of $3.25 \mu_B$. Then the magnetic ordering of the Yb sublattices only gives incremental contributions to the NPD spectra, and their magnetic structure was solved with the help of Mössbauer spectroscopy.

In the temperature range $3.5 \text{ K} < T < 86 \text{ K}$, we considered contributions only from ordered magnetic moments on the Yb(4$b$) sites. For $T < 3.5 \text{ K}$, we considered also ordered moments on the Yb(2$a$) sites. As to the 4$b$ sites, the best agreement with the NPD patterns is obtained for Yb moments oriented along the c-axis. We find that the Yb moments of the 4$b$ sites are antiferromagnetically coupled within a given layer, and that the z and z+$\frac{1}{2}$ layers are ferromagnetically coupled. At $T = 3.7 \text{ K}$, this refinement yields a discrepancy factor $R_{Mag}$ of about 3.1 $\%$, much better than the values around 20 $\%$ given by alternative solutions. As shown in Fig. 8 the moment values on the Yb(4$b$) sites deduced from NPD patterns are in excellent agreement with those obtained from the Mössbauer spectra.

As to the 2$a$ sites, which order below 3.5 K with much smaller moments, we fixed the moments to the values deduced from the Mössbauer spectra. The orientation of the moments was refined using our NPD data. There are two possibilities for the Yb(2$a$) to orient : along the c-axis or in the (a,b) plane. Taking into account the ferromagnetic-like increase of the susceptibility at 3.5 K, we assume a F coupling between two adjacent Yb(2$a$) layers. We obtain a discrepancy factor of $R=3.05 \%$ for the 2$a$ moments in the (a,b) plane, slightly better than for the moments along the c-axis ($R=3.44 \%$). It suggests that the Yb(2$a$) moments are perpendicular to the c-axis.

Finally, the moment values at 1.5 K are $m_{Mn}=3.23(5) \mu_B$, $m_{Yb(4b)}=1.77(5) \mu_B$ and $m_{Yb(2a)}=1.13(5) \mu_B$. The evolution of the moments versus temperature is plotted in Fig. 8.
VI. DISCUSSION

The thermal variations of the Mn and Yb magnetic moments derived from both neutron and Mössbauer data are shown in Fig. 8. The Yb(4b) moment values derived from both techniques are in remarkable agreement, and their thermal variation has an unusual shape, with upwards curvature in a large temperature range. We applied the molecular field model in order to calculate these thermal variations. We first obtained the T dependence of the Mn moment by a self consistent mean field calculation using the Brillouin function $B_{2}(x)$ for $S=2$ and a molecular field constant $\lambda_{0}$ representing Mn-Mn exchange. The standard formula has to be slightly modified because the saturated Mn moment of $m_{sat}=3.23(5) \mu_{B}$ is lower than $g\mu_{B}=4 \mu_{B}$. So we used the following expression:

$$m_{Mn}(T) = m_{sat} B_{2}\left[\frac{g\mu_{B} S \lambda_{0} m_{Mn}(T)}{k_{B}T}\right]$$

which ensures that saturation occurs at $m_{sat}=3.3 \mu_{B}$.

We obtain a good fit of the experimental data (blue line in Fig. 8) with $\lambda_{0}=19 T/\mu_{B}$. Then we fitted the $T$ dependence of the Yb(4b) moment assuming that the ground crystal field doublet alone is populated, i.e. describing the Yb ion by an effective spin $S=1/2$, with a g-factor $g_{Yb}$ in the direction of the net exchange field from the Mn ions. Since the saturated Yb(4b) moment is $m_{0}=\frac{1}{2}g_{Yb}\mu_{B}=1.75 \mu_{B}$, then: $g_{Yb}=3.5$. The Yb(4b) ion is submitted to a molecular field $\lambda_{1} m_{Mn}$ from Yb-Mn exchange, since we neglect Yb-Yb exchange. Its moment is then calculated using the expression:

$$m_{Yb}(T) = \frac{1}{2}g_{Yb}\mu_{B} \tanh\left[\frac{g_{Yb}\mu_{B} \lambda_{1} m_{Mn}(T)}{2k_{B}T}\right]$$

where $m_{Mn}(T)$ is obtained from expression (1). We obtain a good fit to the data (magenta line in Fig. 8) with $\lambda_{1}=2.1 T/\mu_{B}$. The unusual upwards curvature comes from the tanh function with a small argument, the constant $\lambda_{1}$ being much smaller than $\lambda_{0}$. With this model, a small ordered Yb moment should persist up to $T_{N}=86 K$, with a value below 0.3 $\mu_{B}$, beyond the accuracy of neutron and Mössbauer probes. We conclude that the Yb ions on the 4b sites orient in a non-vanishing net molecular field through Yb-Mn exchange. As to the Yb moment on the 2a sites, their much lower ordering temperature (3.5 K) strongly suggests that they orient in their own molecular field, through Yb-Yb interactions. From this analysis follows the hierarchy of exchange interactions in

A. Molecular field analysis

In YbMnO$_{3}$, the Mn magnetic order with $\Gamma_{2}$ or $\Gamma_{4}$ symmetry agrees with expectations from optical measurements. Such a type of order is also expected from the general tendency observed in hexagonal RMnO$_{3}$ compounds versus the rare earth ionic radius. Magnetic orders seem to be stabilized for low ionic radius (Er, Y, Yb, Lu), and $\Gamma_{1-3}$ for higher ionic radius (Ho, Y, Yb, Er). This could be related to the amplitude of the distortion of the Mn lattice with respect to triangular symmetry.

As concerns the rare earth moments, we found that the 4b and 2a sites order independently. This is also the case in HoMnO$_{3}$, where ordered Ho moments on 4b sites are observed below 35-40 K, whereas Ho 2a sites remain paramagnetic down to 5 K. In HoMnO$_{3}$, a change of the Mn structure (from $\Gamma_{2-4}$ above 38 K to $\Gamma_{1-3}$ below) occurs together with the rare earth ordering. This is not the case for YbMnO$_{3}$, possibly due to the lower value of the Yb moment.

In spite of a very large amount of experimental and theoretical work, the nature of the interactions which control the magnetic structure in RMnO$_{3}$ compounds is still unclear. To shed some light on this point, we first compare the measured temperature dependence of Mn and Yb moments with calculations from a molecular field model. Then we briefly discuss the symmetry of interactions necessary to explain the observed magnetic orders. Finally we propose possible origins for the magnetic interactions in RMnO$_{3}$, compatible with both experiment and calculations.

![Diagram showing symmetry allowed Mn spin orders in hexagonal RMnO$_{3}$](image)

**FIG. 7:** (Color online) Symmetry allowed Mn spin orders in hexagonal RMnO$_{3}$. In YbMnO$_{3}$, $\Gamma_{2}$ or $\Gamma_{4}$ IR yield the best fit to experiment.
in environments with identical (resp. opposite) A-pairs align parallel (resp. antiparallel) along c, one can predict the R magnetic order on a 4b site for a given Mn order. This is reported in Table II. This description provides a simple way to distinguish two homometric configurations, knowing the order on the 4b sites. Experimentally, the intraplane Yb(4b) coupling is AF while the interplane coupling is F. Therefore, the Mn order must be of $\Gamma_4$ type and $\Gamma_2$ can be discarded. This description also agrees with recent experiments\cite{29,30} in HoMnO$_3$ and can be easily extended to the rest of the RMnO$_3$ family.

C. Origin of the molecular field

The exchange energy between a Yb ion and its Mn first neighbors is classically written as a sum over Mn sites $\sum_{\text{Mn}} J \mathbf{S}_{\text{Mn}} \cdot \mathbf{S}_{\text{Yb}}$, where $J$ is the isotropic first neighbor exchange interaction. Each Yb atom (either on a 2a or 4b site) is at the top of a pyramid with an equilateral triangular basis of Mn ions. Therefore, the exchange field induced at either Yb site cancels by symmetry for any of the $\Gamma_{1-4}$ representations of the Mn magnetic order. Moreover, the classical exchange term cannot explain the perpendicular orientations of the R and Mn moments.

Experimentally, the exchange field is effectively zero at the Yb(2a) site (above 3.5 K), but it is not at the Yb(4b) site. So, in order to explain the R(4b) magnetic order, we have to introduce an interaction which is not isotropic, i.e. which depends on $\mathbf{r}_{ij}$, the radius vector linking a R(4b) to a Mn ion. This is the only way to obtain an out of plane effective field.

In the following we consider two interactions fulfilling this condition: the magnetic dipolar interaction and the Dzyaloshinskii-Moriya (DM) coupling between R(4b) and Mn spins. The magnetic dipolar interaction is defined as:

$$ \mathcal{H}_{\text{dip}} = -\sum_{i,j} \mathbf{\sigma}_i \cdot \mathbf{B}_{ij}, $$

where $\mathbf{B}_{ij}$ is the dipolar field induced by Mn moment $j$ at R(4b) site $i$, and $\mathbf{\sigma}_i$ the spin of the R(4b) ion at site $i$.

The Dzyaloshinskii-Moriya (DM) interaction between
the Yb(4b) and the Mn moments is written as
\[
\mathcal{H}_{DM} = \sum_{i,j} \vec{D}_{ij}.(\vec{\sigma}_i \times \vec{S}_j). \tag{5}
\]

According to the crystal symmetry and the rules defined by Moriya, \(\vec{D}_{ij}\) is perpendicular to the mirror plane including both R and Mn sites, i.e. to the c-axis, and defined as \(\vec{D}_{ij} = \eta \vec{c} \times \vec{r}_{ij}\), where \(\eta\) is a spin-orbit coupling constant.

Although the dipolar and DM interactions are intrinsically different, they may be expressed in similar ways in terms of the A factors:
\[
\mathcal{H}_{dip} = \sum_i \sigma_i (A_i \sigma^u \downarrow + A_i \sigma^u \uparrow) \tag{6}
\]
\[
\mathcal{H}_{DM} = \eta \sum_i \sigma_i (A_i^{up} + A_i^{down}) \tag{7}
\]

Minimizing the energy for these interactions should therefore lead to the same configurations as found in section B. To confirm this, we have rewritten both interactions in terms of a matrix \(J_{ij}^{\sigma}\) such that \(\mathcal{H} = \sum_{i,j} \sigma_i J_{ij} \sigma_j\), where \(J_{ij}^{\sigma}\) is expressed as:
\[
J_{ij}^{\sigma} = \begin{pmatrix}
0 & D_{ij}^x & -D_{ij}^y \\
-D_{ij}^x & 0 & D_{ij}^z \\
D_{ij}^y & -D_{ij}^z & 0
\end{pmatrix}
\]
\[
J_{ij}^{\sigma_{up}} = \begin{pmatrix}
r_{ij}^{x} & r_{ij}^{y} & -r_{ij}^{z} \\
r_{ij}^{x} & r_{ij}^{y} & -r_{ij}^{z} \\
r_{ij}^{x} & r_{ij}^{y} & -r_{ij}^{z}
\end{pmatrix}
\]
\[
J_{ij}^{\sigma_{down}} = \frac{1}{r_{ij}^{3}}.
\]

It is worth noting that the above matrixes both have non-diagonal terms, which depend on the R-Mn pair considered. This is a necessary condition to ensure a non-zero interaction between Mn moments in (a,b) planes and R(4b) moments along the c-axis.

We determined the stable Yb(4b) configuration for each IR of the Mn order. We find that both dipolar and DM interactions give the same result, in agreement with our analysis of the magnetic environment made above (see Table I). Namely they stabilize the \(\Gamma_4\) configuration of the Mn moments for the Yb(4b) order determined experimentally.

The analysis described here provides the conditions required for the magnetic interactions to yield the R and Mn magnetic orders observed experimentally. To go further, a quantitative calculation of the energy should be made. Our estimations made for the dipolar interaction show that it is too weak by one order of magnitude to fully account for the molecular field constant \(\lambda_{\text{Mn}^2-\text{Yb}}(=\lambda_1) = 2.1 T\mu\) found in section A, Fig. 8. As for the DM interaction, an estimation would require an evaluation of the relevant spin-orbit coupling constant.

We hope that this analysis will stimulate further theoretical work on the R-Mn interactions at the origin of the molecular field. This will allow one to understand the microscopic origin of the rare earth magnetic order in the hexagonal RMnO\(_3\) family.

VII. CONCLUSION

We have studied the magnetic order in YbMnO\(_3\) and found a consistent description by combining Mössbauer and neutrons probes. The temperature dependences of the Yb and Mn magnetic moments are well fitted in a molecular field approach, showing that Yb(4b) moments order due to the Mn molecular field, whereas the Yb(2a) moments order at much lower temperature through Yb-Yb interactions.

We could determine the Mn magnetic structure and distinguish between two homometric configurations by considerations about the magnetic environment of each R(4b) sites. In YbMnO\(_3\), we found a \(\Gamma_4\) configuration for Mn moments associated with F stacking of AF Yb(4b) layers. This approach can be extended to the whole hexagonal RMnO\(_3\) family. We propose possible mechanisms for the R-Mn interactions to be studied by further theories.

Aknowledgements : We thank D. Colson for the sample preparation, F. Porcher and F. Bourée for the measurement on 3T2.

---

1. M. Fiebig, J. Phys. D : Appl. Phys., 38, R123-R152 (2005)
2. S.W. Cheong, M. Mostovoy, Nature, 6, 13-20 (2007)
3. J. Park, J.G. Park, Gun Sang Jeon, Han-Yong Choi, Changhee Lee, W. Jo, R. Bewley, K. A. McEwen, T. G. Perring, Phys. Rev. B, 68, 104426 (2003)
4. S. Lee, A. Firogov, M. Kang, K.H. Jang, M. Yonemura, T. Kamiyama, S.-W. Cheong, F. Gozzo, N. Shin, H. Kimura, Y. Noda, J.G. Park, Nature, 451, 06507 (2008)
5. A. Pimenov, T. Rudolf, F. Mayr, A. Loidl, A. A. Mukhin, A. M. Balbashov, Phys. Rev. B, 74, 100403(R) (2006)
6. H. Katsura, A. V. Balatsky, N. Nagaosa, Phys. Rev. Lett., 98, 027203 (2007)
7. S. Petit, F. Moussa, M. Hennion, S. Paillés, L. Pinsard-Gaudart, A. Ivanov, Phys. Rev. Lett., 99, 266604 (2007)
8. T. Kimura, G. Lawes, T. Goto, Y. Tokura, A. P. Ramirez, Phys. Rev. B, 71, 224425 (2005)
9. Z. J. Huang, Y. Cao, Y. Y. Sun, Y. Y. Xue, C. W. Chu, Phys. Rev. B, 56, 2623 (1997)
10. E. F. Bertaut, Physics Letters, 5, 27-29 (1963)
11. M. Fiebig, D. Frohlich, K. Kohn, S. Leute, T. Lottermoser, V. V. Pavlov, R. V. Pisarev, Phys. Rev. Lett., 84, 5620 (2000)
12. J. A. Alonso, M.J. Martinez-Lope, M.T. Casais, M.T. Fernandez-Diaz, Inorg. Chemistry, 39, 917-923 (2000)
13. J. Rodriguez-Carvajal, Physica B, 192, 55-69 (1993)
14. M. Isobe, Kimizu, M. Nakamura, T. Mohri, Acta Cryst. Sect. C, 47, 423-424 (1991)
15. B. B. Van Aken, A. Meetsma, T. T. M. Palstra, Acta
Cryst. Sect. E, 57, i87-i89 (2001).

16 A. Munoz, J. A. Alonso, J. Martinez-Lope, T. Casais, J. L. Martinez, M. T. Fernandez-Diaz, Phys. Rev. B, 62, 9498 (2000)

17 J. Fontcuberta, M. Gospodinov, V. Skumryev, J. App. Phys., 103, 07B722 (2008)

18 T. Katsufuji, S. Mori, M. Masaki, Y. Moritomo, N. Yamamoto, H. Takagi, Phys. Rev. B, 64, 104419 (2001)

19 P. Bonville, P. Imbert, G. Jéhanno, F. Gonzalez-Jimenez, F. Hartmann-Boutron, Phys. Rev. B, 30, 3672 (1984).

20 F. Gonzalez-Jimenez, P. Imbert, F. Hartmann-Boutron, Phys. Rev. B 9, 95 (1974).

21 A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions (Clarendon, Oxford, 1969)

22 H. A. Salama, G. A. Stewart, D. H. Ryan, M. Elouneg-Jamroz, A. V. J. Edge, J. Phys. : Condens. Matter, 20, 255213 (2008)

23 E. F. Bertaut, C. R. Hebd. Séances Acad. Sci., 252, 76 (1961); J. Phys. Radium, 22, 321 (1961).

24 J. Rodriguez-Carvajal, http://www.ill.eu/sites/fullprof/php/programsfa7c.

25 E. F. Bertaut, edited by G.T. Rado and H. Shul (Academic, New York), Vol. 3, Chap. 4, p. 149. (1963)

26 D. P. Kozlenko, S. E. Kichanov, S. Lee, J. G. Park, B. N. Savenko, J. Phys. : Condens. Matter, 19, 156228 (2007)

27 M. Fiebig, C. Degenhardt, R. V. Pisarev, Phys. Rev. Lett., 88, 027203 (2001)

28 O. P. Vajk, M. Kenzelmann, J.W. Lynn, S.B. Kim, S.-W. Cheong, Phys. Rev. Lett., 94, 087601 (2005)

29 A. Munoz, J.A. Alonso, M.J. Martinez-Lope, M.T. Casais, J.L. Martinez, M.T. Fernandez-Diaz, Chem. Matters, 13, 1497-1505 (2001)

30 P.J. Brown, T. Chatterji, J. Phys. : Condens. Matter, 18, 10085-10096 (2006)

31 S. Nandi, A. Kreyssig, L. Tan, J.W. Kim, J.Q. Yan, J.C. Lang, D. Haskel, R. J. McQueeney, A. I. Goldman, Phys. Rev. Lett., 100, 217201 (2008)

32 T. Moriya, Phys. Rev., 120, 91 (1960)