Analysis of the multiferroicity in the hexagonal manganite YMnO$_3$

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Abstract

We performed magnetic and ferroelectric measurements, associated with Landau theory and symmetry analysis, in order to clarify the situation of the YMnO$_3$ system, a classical example of type I multiferroics. We found that the only magnetic group compatible with all experimental data (neutron scattering, magnetization, polarization, dielectric constant, second harmonic generation) is the $P\bar{6}_3$ group. In this group a small ferromagnetic component along c is induced by the Dzyaloshinskii–Moriya interaction, and observed here in magnetization measurements. We found that the ferromagnetic and antiferromagnetic components can only be switched simultaneously, while the magnetic orders are functions of the polarization square and therefore insensitive to its sign.

Some figures may appear in colour only in the online journal.

1. Introduction

Hexagonal YMnO$_3$ presents ferroelectricity and antiferromagnetism [1, 2] and can be considered as the prototype of ‘type I’ ferroelectric antiferromagnetic materials in which the details of the magneto-electric coupling can be studied.

Despite numerous investigations since the pioneer work of Yakel et al in 1963 [1], the exact crystalline and magnetic structures are still under debate. The temperature of the ferroelectric (FE) transition is for example not completely clear. Located by some authors at 920 K [3], recent x-ray measurements proposed 1258 K [4]. These discrepancies are not fully understood and are possibly due to some changes in the oxygen deficiency when the sample is heated. Despite these discrepancies, we can try to summarize the knowledge of this ferroelectric transition as follows. (i) A transition corresponding to a unit-cell tripling and a change in space group from centrosymmetric $P6_3/mmc$ (#194) to polar $P\bar{6}_3cm$ (#185) is observed in this temperature range. In this respect YMnO$_3$ is a typical example of an improper ferroelectric [5, 6], opening the field to the new concept of hybrid improper ferroelectricity [7]. Indeed, the symmetric group $P6_3/mmc$ reduces to $P\bar{6}_3cm$ by a rotation of the MnO$_3$ polyhedra. (ii) In addition a displacement of the yttrium atoms with respect to the manganese atoms along the c axis of the structure induces a c axis polarization [8, 9]. (iii) Furthermore, a possible intermediate phase with the space group $P6_3/mcm$ can be derived from group theory [10], however it was not observed in the recent measurements [4], neither confirmed by symmetry-mode analysis [6]. The authors rather observe some evidence for an iso-symmetric phase transition at about 920 K, which involves a sharp decrease in the estimated polarization. This transition correlates with several previous
reports of anomalies in physical properties in this temperature region [11], but is not really understood.

At $T_N = 74$ K, YMnO$_3$ undergoes a paramagnetic (PM) to antiferromagnetic (AFM) transition. The magnetism arises from Mn$^{3+}$ ions, in 3d$^4$ configuration, with spins equal to 2 (high spin). Neutron diffraction measurements [12–15] showed that the structure is antiferromagnetic with moments in the ab-plane. Following Bertaut et al [16], Muñoz et al [14] proposed for the symmetry of the antiferromagnetic order the $\Gamma_1$ (totally symmetric) irreducible representation of the $P6_3/cm$ group; this order corresponds to the $V_1$ order pictured in figure 1. More recently, a spin polarized analysis showed that the group is rather $P6_3$ or $P6_3^1$ [15]. Finally, in a second harmonic optical generation work, Fröhlich et al rather concluded a very different order associated with the $P6_3/cm'$ magnetic group [17, 18]; this order corresponds to the $W_2$ order pictured in figure 1. Let us note that, while Bertaut et al and Muñoz et al performed a full symmetry analysis, checking all possible irreducible representations for the magnetic ordering, Brown and Chatterji, as well as Fiebig et al, only considered the $\Gamma_1$ representation of the tested symmetry groups. One should however remember that the magnetic order is the spin part of the system wavefunction and as such can belong to any of the irreducible representations of the magnetic symmetry group. On the other hand, the polarization behaves as the density matrix and thus can only belong to the totally symmetric $\Gamma_1$ representation in groups with only one-dimensional irreducible representations.

Associated with the AFM order, several authors reported a ferromagnetic (FM) component associated with a spin canting along the c direction. First suggested [12], and observed by Bertaut et al [16], this FM component was later observed in the isotypic compound ScMnO$_3$ by Xu et al [19] as well as Bieringer and Greedan [20]. Attributed to Mn$_3$O$_4$ impurities by Fiebig et al [18], an FM component disappearing at $T_N$ was later observed in neutron scattering by one of us [21]. The controversy about the existence of such a component is thus still open. One could argue that the weakness of the proposed canting removes most of the interest of its existence, however as we will see in the present paper the existence of an FM component has many consequences on the symmetry group of the magnetic structure as well as the interpretation of the YMnO$_3$ properties.

Let us finally quote the existence of a giant magnetoelastic coupling observed by powder neutron diffraction at the magnetic transition [22, 23]. Very large atomic displacements (up to 0.1 Å) are induced by the magnetic ordering without any identified change of the symmetry group. The influence of such displacements on the polarization or dielectric constant in the magnetic phase was however never reported on single crystal (such measurements exist in thin films) while this information is crucial for the assertion of the assumed magneto-electric coupling seen by domain imaging using second harmonic generation measurements [24].

The present paper aims at building a coherent description for the magnetic structure of the YMnO$_3$ compound, which will account for all the experimental observations and resolve their apparent contradictions.

2. Can we get some further insight from the experiments?

2.1. Experimental details

All the measurements reported in this work were performed on the same single crystal, grown a long time ago in Groningen by G Nénert, from the group of T Palstra. The sample size for dielectric measurements is $a = 1.1$ mm, $b = 1.5$ mm and $c = 0.3$ mm. Magnetic measurements were performed with a Quantum Design magnetic properties measurement system superconducting interferometer device (QD PMPS-5 SQUID) magnetometer. Dielectric and polarization measurements were respectively performed in a Quantum Design physical properties measurement system (QD PPMS-14T) with Agilent 4284A LCR meter and a Keithley 6517A. Magnetic fields above 14 T (and up to 25 T) were achieved in the LNCMI Grenoble. The experimental setup for the dielectric constant measurements was the same as in Caen, while the LNCMI setup was used for the magnetization. Antiferromagnetic neutron diffraction peaks were measured on a 4F triple axis spectrometer in Laboratoire Léon Brillouin in Saclay on the same single crystal.

2.2. The antiferromagnetic transition

We performed neutron scattering experiments on a neutron triple axis spectrometer and checked the crystal orientation and crystalline quality. The 100 magnetic peak is associated with the antiferromagnetic order parameter. In figure 2, the temperature dependence of its amplitude is reported, showing the magnetic transition at $T_N = 74$ K. In the same figure, we report the ab component of the dielectric constant, $\varepsilon$,
which presents an anomaly at $T_N$. Let us note that the $c$ component of $\varepsilon$ does not present any anomaly at this temperature (not shown). The strong similarity, below $T_N$, between the temperature dependence of the antiferromagnetic order parameter, and the nonlinear part of $\varepsilon$, suggests that they are closely related, and thus infers the existence of a magneto-electric coupling. One should emphasize the fact that the anomaly of the dielectric constant is not a divergence as expected in the case of a linear magneto-electric coupling. This proof of a nonlinear magneto-electric coupling is of great importance as we will see in section 2.3.

2.3. The polarization and the dielectric constant

This magneto-electric coupling can also be asserted from the polarization and dielectric constant measurements in the magnetic phase.

We performed polarization measurements along the $c$-axis (the only one allowed by symmetry). A strong reduction of the polarization amplitude is observed below $T_N$ (see figure 3), i.e. $2 \mu C \cdot cm^{-2}$ at 30 K, to be compared with the $5.5 \mu C \cdot cm^{-2}$ measured at room temperature [25]. These polarization values are compatible with the estimated ones, obtained both as $\vec{P} = \sum q_i \vec{r}_i$ and from our first principle calculations. We computed the polarization using density functional theory and a Berry phases approach at the atomic structures given in [22] at 10 and 300 K. The calculations were performed with the B1PW hybrid functionals that was specifically designed for the treatment of ferroelectric oxides [26]. At 300 K we found a polarization of $5 \mu C \cdot cm^{-2}$ in full agreement with experimental values. At 10 K, the polarization is strongly reduced to $1 \mu C \cdot cm^{-2}$, to be compared with the experimental result of $2 \mu C \cdot cm^{-2}$ at 30 K.

In addition, we measured the polarization versus the magnetic field. Since this effect was expected to be very small, we used a procedure consisting of ramping the magnetic field many times from $-14$ to $+14$ T and extracting the periodic signal from the raw data. One can see on $P(H)$ taken in the magnetic phase (figure 4) an anomaly that can be associated with a meta-magnetic transition.

This anomaly can also be followed on the dielectric constant, $\varepsilon$, as a function of applied field and temperature. The meta-magnetic transition phase diagram, characteristic of an antiferromagnetic compound under magnetic field, can therefore be built (see figure 5). The search of the meta-magnetic transition is a classical method to observe the antiferromagnetism. Indeed, in the usual systems, the magnetization (or magnetic susceptibility) versus magnetic field presents an anomaly at the AFM/FM transition under applied field. In YMnO$_3$ our ability to see this transition on electric degrees of freedom (polarization and dielectric constant) clearly proves the existence of a coupling between the polarization and the magnetic order parameter, as first proposed by Huang et al [27].

2.4. The ferromagnetic component

As mentioned in section 1, one of us (Pailhès) observed, in a non-polarized neutron scattering experiment, a Bragg peak...
that was associated with a ferromagnetic component [21]. Indeed, this Bragg peak, at $\vec{q} = (2, -1, 1)$, can neither be associated with the antiferromagnetic order within the (a, b) plane, nor with the nuclear order, since the $P6_3cm$ symmetry group imposes $2l = 0$. In addition it disappears at $T_N$, as expected from a canted AFM order. One objection can however be made against this interpretation. The existence of two MnO$_3$ layers per unit cell (respectively at $z = 0$ and $z = 1/2$), forbids ruling out the possibility of an antiferromagnetic coupling between the $c$ components of the canted magnetic moments of each layer ($W_3$ versus $V_3$ order of figure 1).

We thus performed precise magnetic measurements on a SQUID magnetometer at low magnetic field, and we did observe a small FM component (see figure 6). The sample was cooled down from 100 K (still above $T_N$) to 10 K either under an applied magnetic field along the $c$ axis of the crystal (field cooled = FC) or without any field (zero field cooled = ZFC). After cooling, the magnetization was always measured ramping the temperature up under the applied field. This procedure, assuming that the applied field is too small to reverse the magnetization, clearly evidenced the existence of a ferromagnetic component along the $c$ axis (see figure 6). The applied magnetic field is 0.05 T.

Let us summarize the facts we learned from experiments.

- YMnO$_3$ exhibits a magneto-electric coupling between the AFM and the FE orders.
- This magneto-electric coupling is nonlinear. The immediate consequence of this is that the AFM order parameter cannot be in the same irreducible representation as the FE order parameter, that is the polarization. The latter being in the totally symmetric irreducible representation, $\Gamma_1$, the AFM order cannot belong to the $\Gamma_1$ irreducible representation of the magnetic group. Assuming that the magnetic order found by Bertaut [12, 16] and Muñoz [14] is correct, it means that the magnetic group is not $P6_3cm$ as assumed by these authors. See $V_1$ of figure 1 for a picture of this order.
- There is a weak FM component along the $c$ axis.
- Even if essentially quenched by the crystal field splitting of the Mn 3d orbitals, the spin–orbit coupling and thus the Dzyaloshinskii–Moriya (DM) interaction always exists provided it is symmetry allowed. This is the case with the AFM magnetic order $V_1$ found in neutron scattering, since the spin vorticity is non zero. The DM interaction should thus induce an FM component (even if small) along the $c$ direction.
- Finally the AFM and FM order parameters are not linearly coupled. Indeed, they present different behaviors around the transition (see figure 7 of [21] or figures 2 and 6 of the present paper).

According to the above analysis the $P6_3cm$ group cannot be the system magnetic group. Can we find a magnetic subgroup of the crystallographic group $P6_3cm$ compatible with all the above experimental requirements? The following symmetry group analysis tells us that only one magnetic group is compatible with (i) the $V_1$ AFM order, (ii) the fact that this order is not in the $\Gamma_1$ irreducible representation, and (iii) the existence of an FM component along the $c$ direction. This group is the $P6'_3$ magnetic group. Indeed, we
first examined the magnetic groups associated with the P63cm crystallographic group, namely:

P63cm: discarded since the AFM order V1 belongs to Γ1 and the FM component V3 is not allowed (does not belong to the same representation as V1);

P63′c′m: discarded since V1 and V3 do not belong to the same representation (FM component not allowed);

P63′cm: discarded since the FM component is not allowed; P63′cm′: discarded since the FM component is not allowed.

Since none of them is compatible with the experimental requirements, we looked further in their subgroups and thus abandoned the mirror planes.

The P63 group was discarded since V1 belongs to Γ1, which is incompatible with the absence of a linear magneto-electric coupling.

Finally the P63′ group is the only group compatible with all the requirements.

Let us remember that the P63′ magnetic group was strongly suggested by Brown and Chatterji [15] from the polarimetric study of neutron diffraction. In fact, they were the first to suggest that the mirror planes are incompatible with the YMnO3 magnetic group.

Let us now see whether we can account for all the experimental results in a Landau analysis. We established that the magnetic transition should be a transition between the paramagnetic (PM) phase belonging to the P63cm group, and the antiferromagnetic (AFM) phase belonging to the P63′ group. In the P63′ group the Γ4 irreducible representation, to which both the AFM (V1) and the FM (V3) order parameters belong, is three times represented, namely by the V1, V2 and V3. The Landau theory must thus involve all three magnetic order parameters in addition to the change in the ferroelectric polarization. V1 and V2 are easily represented by the toroidal (A) and divergence (B) components of the in-plane spins component, while V3 is the out-of-plane component associated with the magnetization (M). For each unit cell one can thus define

\[ \vec{A} = \frac{1}{6r} \sum_i \vec{r}_i \wedge \vec{S}_i = \frac{1}{6r} \sum_i \vec{r}_i \wedge \vec{S}_{ab,i} \]

\[ \vec{B} = \frac{1}{6r} \sum_i \vec{r}_i \cdot \vec{S}_i = \frac{1}{6r} \sum_i \vec{r}_i \cdot \vec{S}_{ab,i} \]

\[ \vec{M} = \frac{1}{2} \sum_i \vec{S}_i = \frac{1}{2} \sum_i \vec{S}_{ab,c,i} \]

where the summations over i run over the six Mn atoms of the unit cell; the \( \vec{r}_i \) refer to the in-plane components of the Mn atom position vectors (note that \( \sum r_i = 0 \) and \( \forall i \mid \vec{r}_i \mid = r \); the \( \vec{S}_i \) are the Mn atomic spins \( \vec{S}_i = \vec{S}_{ab,i} + \vec{S}_{c,i} \) where \( \vec{S}_{ab,i} \) is the in-plane component of the Mn spins and \( \vec{S}_{c,i} \) is the c axis component).

\( \vec{A} \) and \( \vec{M} \) are vectors along the c direction while \( \vec{B} \) is a scalar. Let us write \( \vec{A} = S_{ab} \cos \varphi \) and \( \vec{B} = S_{ab} \sin \varphi \) and point out that the intensity of the 001 AFM magnetic peak (figure 2) is proportional to \( S_{ab}^2 \) whatever the angle \( \varphi \). In the paramagnetic state, i.e. for \( T > T_N \), \( S_{ab} = 0 \), but the polarization \( P \) is not zero. This is one of the important issues of this compound. \( P \) is not a driving order parameter for the magnetic transition; however, since its value presents a singularity at \( T_N \), it is a secondary order parameter. Its contribution should thus be taken into account in the Landau free energy and can only contain even powers of \( P \), as imposed by the higher temperature paraelectric to ferroelectric transition. The free energy can thus be expressed up to the power 4 of the order parameters.

For the free energy change in the FE energy

\[
F = \alpha_2(T - T_N)(A^2 + B^2) + \alpha_4(A^2 + B^2)^2
\]

the FE coupling

\[
The FM energy

\[
F = -\beta_2(P^2 - P_0^2)^2 + \beta_4(P^1 - P_0^1)^2 + \gamma_2M^2 + \gamma_4M^4
\]

Finally the \( S_{ab} \) and \( P \) expressions are

\[
F = M\left[2\gamma + 4\gamma_4M^2 + 2\alpha_2S_{ab}^2 + 2\alpha_4S_{ab}^4 + 2\alpha_6S_{ab}^6\right]
\]

where \( \alpha_2, \alpha_4, \beta_2, \beta_4, \gamma_2, \gamma_4, \alpha_6, \beta_4, \) are the temperature independent Landau expansion coefficients. If one notes \( t = T_N - T \), and \( \delta P = P - P_0 \) the gradient of the free energy writes as

\[
\frac{\partial F}{\partial S_{ab}} = S_{ab} \left[-2\alpha_2P + 4\alpha_4S_{ab}^2 + 2\alpha_6S_{ab}^4 + 2\alpha_2P_0^2 + 2\alpha_6S_{ab}^4\right]
\]

\[
\frac{\partial F}{\partial \delta P} = \left[-2\beta_2 + 4\beta_4P_0^2 + 2\beta_6\delta P\right]
\]

\[
\frac{\partial F}{\partial \delta M} = M\left[2\gamma + 4\gamma_4M^2 + 2\alpha_2S_{ab}^2 + 2\alpha_4S_{ab}^4 + 2\alpha_6S_{ab}^6\right]
\]

From the experimental results we know that \( M \ll S_{ab} \) and \( \delta P \). We thus expect that if \( S_{ab} \propto t^0, \delta P \propto t^0 \) and \( M \propto t^0 \), we will have in the vicinity of the transition \( \eta > \mu \) and \( \eta > 2\nu \). In an order by order expansion of the free energy gradient as a function of one, we can thus suppose either that \( \eta > \nu + 1 \) (\( M \ll S_{ab} \)) or that \( \eta \sim \nu + 1 \) (\( M \sim S_{ab} \)). It is easy to show that the first hypothesis leads to a contradiction. Let us thus assume that \( M \sim S_{ab} \). One gets at the zeroth order in \( t \)

\[
\frac{\partial F}{\partial \delta P} = P_0 \left[-2\beta_2 + 4\beta_4P_0^2\right] = 0 \Rightarrow P_0^2 = \frac{\beta_2}{2\beta_4}
\]

and at the following order

\[
\frac{\partial F}{\partial S_{ab}} = S_{ab} \left[-2\alpha_2P + 4\alpha_4S_{ab}^2 + 2\alpha_6S_{ab}^4 + 2\alpha_2P_0^2 + 2\alpha_6S_{ab}^4\right] = 0
\]

\[
\frac{\partial F}{\partial \delta P} = 8\beta_4P_0^2\delta P + 2\alpha_2P_0^2\delta P = 0
\]

\[
\left\{ S_{ab}^2 = \frac{\alpha_2P_0^2}{2\alpha_4P_2^2}, \delta P = \frac{\alpha_2P_0^2}{4\alpha_4P_2^2}\right\}
\]
\[ \frac{\partial F}{\partial \varphi} : 2z_{\text{c}} P_0 S_{ab} M \sin \varphi P = 0 \iff \sin \varphi = 0 \]
\[ \frac{\partial F}{\partial M} : 2\gamma_2 M + 2z_{\text{c}} P_0 S_{ab} \cos \varphi P = 0 \]
\[ \iff M = \frac{\alpha_2^2 \beta_2^2 c_{\text{c}}^4 P_0^2}{2\gamma_2 (2\alpha_4 \beta_2 - c_{\text{c}}^4 P_0^2)^{3/2}} \cos \varphi t^{3/2}. \]

We thus retrieve the \( V_1 \) order for the AFM spin arrangement \((\sin \varphi = 0)\), the decrease in the polarization amplitude under the Néel transition \((\delta P < 0)\), the fact that the FM order parameter is much weaker than both the AFM one and the change in the polarization \((v = 1/2, \mu = 1, \eta = 3/2)\), and finally the fact the FM and AFM order parameters are not linearly related at \( T_N \). The polarization and the square of the AFM order parameter are predicted to vary linearly in \( t \) at the magnetic transition, as a classical second order phase transition. In fact, as it is for most magnetic phase transitions, higher order terms in the free energy make the temperature dependence over a large scale of temperature different from the mean field prediction. Here for example, the best fit for \( S_{ab}^2 \) is a power law in \( t^{1/3} \) (not shown in figure 2).

Coming back to the anomaly of the dielectric constant at \( T_N \) and using the second derivative of \( F \) with respect to \( P \), one gets in the first order in \( t \)
\[ \frac{1}{\kappa_e} = \frac{\partial^2 F}{\partial P^2} = 4\beta_2 - 6c_{\text{c}}^4 S^2 + 2c_{\text{c}} S^2 = 4(\beta_2 - c_{\text{c}}^4 S^2) \]
\[ \text{and} \quad \varepsilon = 1 + \chi_e = 1 + \frac{4\beta_2}{4\beta_2^2} = 1 + \frac{c_{\text{c}}^4 S^2}{4\beta_2}. \]

Comparing the above expression with the experimental data of figure 2, the Landau analysis correctly predicts the critical shape of \( \varepsilon \) versus the AFM order parameter \( S_{ab}^2 \).

As a first conclusion one can state that the above Landau analysis seems in perfect agreement with all the experimental data. The most important consequence of it is that one cannot switch the direction of any of the magnetic orders—clockwise versus counter clockwise rotation of the antiferromagnetic order (sign of \( A \)) or direction of the magnetization (sign of \( M \)—by switching \( P \). Indeed, one has \( P = P_0 \left( 1 - \frac{c_{\text{c}}^4 S_{ab}^2}{4\beta_2} \right) \), and \( M = -\frac{\alpha_2^2 \beta_2^2}{2\alpha_4 \beta_2} P_0 \delta P \), thus a change in the sign of \( P \) will leave the sign of both \( A \) and \( M \) unchanged. In contrast, \( A \) and \( M \) are switched simultaneously.

4. Are there other options?

If one supposes that the weak FM component is artefactual, then there are three different groups compatible with the \( V_1 \) AFM order and the absence of a linear magneto-electric coupling, these are: \( P6\text{f}c'm', P6\text{c}4cm' \) and \( P6\text{mc}4cm' \). In such a case however it is difficult to explain why the \( \vec{D}_{ij} \cdot (\vec{S}_i \wedge \vec{S}_j) \) Dzyaloshinskii–Moriya interaction does not yield an FM component along the \( c \) direction. Giving up the FM component thus means giving up the \( V_1 \) ordering for the AFM order.

Is there another AFM order compatible with the neutron scattering experiments? Following Bertaut [28] and Muñoz [14], there is indeed another AFM order possibly compatible with the neutron diffraction data, though with a significantly worse agreement factor than \( V_1 \) (\( R_{\text{MAG}} \) = 10.8% instead of 7.6% [14]). This order is pictured as \( W_2 \) in figure 1. It is compatible with a nonlinear magneto-electric coupling in the \( P6\text{f}cm, P6\text{f}c'm, P6\text{mc}4cm' \) and \( P6\text{mc} \) magnetic groups. In the \( P6\text{f}cm, P6\text{f}c'm, P6\text{mc}4cm' \) it is associated in its irreducible representation with the \( W_3 \) order, while in the \( P6\text{mc} \) magnetic groups both the \( W_1 \) and \( W_3 \) orders belong to the representation of \( W_2 \). At this point let us note that the \( W_3 \) AFM order is compatible with the \((2, -1, 1) \) peak observed by Paillhès et al [21] in neutron scattering.

4.1. What Landau’s theory tells us

In the \( P6\text{f}cm, P6\text{f}c'm, P6\text{mc}4cm' \) groups the Landau analysis yields
\[ F = \alpha_2 (T - T_N) B^2 + \alpha_4 B^4 + \gamma_2 M^2 + \gamma_4 M^4 \]
\[ - \beta_2 (P_0^2 - P^2) + \beta_4 (P_0^4 - P^4) + c_4 B^2 M^2 \]
\[ + c_4 B^2 (P_0^2 - P^2) + d_4 M^2 (P_0^2 - P^2) + e_4 B^2 M^2 \]
\[ \text{where} \quad B' \quad \text{and} \quad M' \quad \text{are the order parameters respectively associated with} \quad W_2 \quad \text{and} \quad W_3. \]
\[ B' = \frac{1}{6\beta} \sum_i (-1)^i \vec{r}_i \cdot \vec{S}_i = \frac{1}{6\beta} \sum_i (-1)^i \vec{r}_i \cdot \vec{S}_{e,i} \]
\[ M' = \frac{1}{\beta} \sum_i (-1)^i \vec{S}_i = \frac{1}{\beta} \sum_i (-1)^i \vec{S}_{e,i} \]
\[ \frac{\partial F}{\partial S_{ab}} = S_{ab} \left[ \frac{\alpha_2 t + 4\alpha_4 S_{ab}^4 + 2c_4 \delta P (2P_0 + \delta P)}{2\alpha_4 \beta_2} \right] = 0 \]
\[ \frac{\partial F}{\partial \delta P} = (P_0 + \delta P) \left[ \frac{-2\beta_2 + 4\beta_4 (P_0^2 + 2P_0\delta P + \delta P^2)}{2c_4 S_{ab}^2 + 4d_4 M^2} \right] = 0 \]
\[ \frac{\partial F}{\partial M'} = M' \left[ \frac{2\gamma_2 + 4\gamma_4 M^2 + 2d_4 \delta P (2P_0 + \delta P)}{4\gamma_4 M^2 + 2d_4 \delta P (2P_0 + \delta P)} \right] = 0. \]

These equations give
\[ P_0^2 = \frac{\beta_2}{2\beta_4} \]
\[ S_{ab}^2 = \frac{\alpha_2 \beta_2}{2\alpha_4 \beta_2 - c_4^2 P_0^2} \]
\[ \delta P = -\frac{\alpha_2 c_4 P_0}{4\alpha_4 \beta_2 - 2c_4^2 P_0^2} \]
and finally \( M' = 0 \).

One sees that these results are equivalent to the previous derivation as far as \( S_{ab} \) and \( P \) are concerned. However, if \( M' = 0 \) is coherent with the neutron scattering results of [14], it is not compatible with the existence of the \((2, -1, 1) \) peak observed by Paillhès et al [21]. Indeed, in this representation the \((2, -1, 1) \) peak measures the intensity of the order parameter \( M' \).
The detailed calculations can be found in the appendix.

The second harmonic spectra are due to d–d electronic transitions within the Mn$^{3+}$ ions (see figure 7). The nonlinear susceptibility is dominated by the term starting from the atomic ground state ($S = 2$) and can be written as

$$\chi_0 = \sum_{m, \ell} \frac{\langle 0 | \hat{P}_\ell | m \rangle \langle m | \hat{P}_\ell | k \rangle \langle k | \hat{P}_\ell | 0 \rangle}{(\hbar \omega_i - \hbar \omega)(\hbar \omega_j - \hbar \omega)}$$

where $|0\rangle$ is the Mn$^{3+}$ atomic ground state; $|k\rangle$ and $|m\rangle$ span the d–d Mn$^{3+}$ excited states, $\hbar \omega_i$ and $\hbar \omega_j$ being their excitation energies; $\hat{P}_\ell$ are the dipolar moment operators along the $\alpha$ direction.

We thus evaluated both the in-plane, $\chi_{xxx}$ and $\chi_{xxy}$, and the out-of-plane components, $\chi_{zxx}$, $\chi_{zyy}$, for the different magnetic groups and orders discussed in this paper. The detailed calculations can be found in the appendix.

For the magnetic groups associated with the P6$_3$cm space group we found

$$\chi_{xxx}(z = 0) = \chi_{xxy}(z = 0) = \chi_{zxx}(z = 0),$$

$$\chi_{zyy}(z = 0) = \chi_{zxy}(z = 0) = 0.$$

The following form for the $\chi$ components (only the contributions associated with the $V_1$ and $V_3$ magnetic orders compatible with the P6$_3$cm magnetic group are retained)

$$\chi_{xxx}(z = 0) = \chi_{xxy}(z = 0) = \chi_{zxx}(z = 0),$$

$$\chi_{zyy}(z = 0) = 0.$$

and similarly for the $z = 1/2$ layer (Mn$_1$ being replaced by Mn$_4$). $\chi_{xxx}(z = 0)$ is the spin independent (FE) tensor, $\varepsilon_i$ the energy of the iron orbital $\varepsilon_i \approx 3d_i$ and $(\varepsilon'_m)_{Mn_4}$, the $\alpha$ component of the spin of the Mn$_4$ atom. $x, y, z$ are orthogonal axes, $x$ being along the crystallographic $a$ direction and $k$ along the crystallographic $c$ direction.

From these results one can derive the following conclusions.

- Within the symmetry rules associated with a P6$_3$cm crystal group the second harmonic signal can only be sensitive to magnetic orders in which $(S_z)_{Mn_1} \neq 0$ and/or $(S_z)_{Mn_4} \neq 0$.
- The experimental data [17] that see a magnetic contribution to the in-plane component of $\chi$ are thus incompatible with the $V_1$ magnetic order as previously shown by Iizuka-Sakano [29] and coherently with our previous analysis.
- We showed that the only possible magnetic order compatible with a P6$_3$cm crystal group is $W_2$ in which $(S_z)_{Mn_1} = (S_z)_{Mn_4} \neq 0$. According to equation (1) this order predicts a magnetic contribution to the in-plane component of $\chi$, but also to the out-of-plane one $\chi_{zxy} = \chi_{xyy}$. While the first one is in agreement with the experimental findings, no magnetic signal was found in the out-of-plane SHG signal.
- The P6$_3$cm crystal group and associated magnetic groups are thus not only incompatible with the existence of an FM order predicts a magnetic contribution to the in-plane

Let us thus go back to the P6$_3$ magnetic group and remember that, up to now, this group was found compatible with all experimental facts. The calculation yields the following form for the $\chi$ components (only the contributions associated with the $V_1$ and $V_3$ magnetic orders compatible with the P6$_3$ magnetic group are retained)

$$\chi_{xxx}(z = 0) = \chi_{xxy}(z = 0) = \chi_{zxx}(z = 0),$$

$$\chi_{zyy}(z = 0) = 0.$$

and similarly for the $z = 1/2$ layer (Mn$_1$ being replaced by Mn$_4$). $\chi_{xxx}(z = 0)$ is the spin independent (FE) tensor, $\varepsilon_i$ the energy of the iron orbital $\varepsilon_i \approx 3d_i$ and $(\varepsilon'_m)_{Mn_4}$, the $\alpha$ component of the spin of the Mn$_4$ atom. $x, y, z$ are orthogonal axes, $x$ being along the crystallographic $a$ direction and $k$ along the crystallographic $c$ direction.

Let us remember that the $V_1$ and $V_3$ orders cannot be reversed independently $(S_z)_{Mn} (S_z)_{Mn_4} > 0$ whatever the magnetic domain), and that $(S_y)_{Mn_1} = -(S_y)_{Mn_4}, (S_z)_{Mn_1} = (S_z)_{Mn_4}$. One thus sees immediately that $\chi_{zxy}$ and $\chi_{xyy}$ depend only on $(S_z)_{Mn_1}$ and should thus be insensitive to the magnetic domains. In contrast, $\chi_{zxy}$ depends on $(S_z)_{Mn_4}$ and should thus exhibit a sensitivity to the magnetic domains at two different frequencies; namely $2\hbar \omega = \varepsilon_{z2} - \varepsilon_{xy}$ and $2\hbar \omega = \varepsilon_{z2} - \varepsilon_{z2-y2}$.
differing by $\Delta E'$. Those results are in full agreement with the experimental data reported in [17].

5. Conclusion

In this paper we show from joint experimental evidence and theoretical analysis that the AFM transition in YMnO$_3$ is associated with three order parameters, namely the AFM one (primary order parameter), the extra-component of the polarization along $c$ and the ferromagnetic component along the $c$ axis induced by the Dzyaloshinskii–Moriya interaction (secondary order parameters). Moreover the analysis of the magnetic transition shows the absence of linear coupling between them and thus a hierarchy. Taking into account the different experimental observations (magnetic and transport macroscopic measurements, neutron scattering data, optical second harmonic responses), as well as the presence of the DM coupling, it appears that the $P6_3$ magnetic group is the only possible one. In the past, many publications tried to address this question with different conclusions, but all of them presented unsolved questions or problems which we have tried to address in the present work. For example, the importance of a ferromagnetic component was underlined by Bertaut, but corresponds in his samples to a parasitic phase; importance of a ferromagnetic component was underlined by them presented unsolved questions or problems which we address this question with different conclusions, but all of

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Appendix

A.1. General considerations

In the following appendix the SHG equations are expressed in terms of an orthogonal $x, y, z$ set of axes. The $x$ axis is along

the $a$ direction, that is associated with one of the O–Mn bonds in the $z = 0$ layer (O is the (0, 0, z = 0) in-plane oxygen), the $y$ axis is in-plane orthogonal and the $z$ axis is along the $c$ direction.

The three-fold rotation axis is present in any of the groups proposed in this paper. We can thus use it in order to express the $\chi_{\alpha\beta\gamma}$ tensor for the $z = 0$ layers as a function of its value for the Mn$_1$ ion (see figure 1 for the ion labeling), and for the $z = 1/2$ layer as a function of its value for the Mn$_4$ ion. One gets easily

$$
\chi_{xxz}(z = 0) = \frac{3}{4} \left( \chi_{xxz}(\text{Mn}_1) - \sum \chi_{xyy}(\text{Mn}_1) \right)
$$

$$
\chi_{zzz}(z = 0) = \frac{3}{4} \left( \chi_{xxz}(\text{Mn}_1) + \chi_{yyz}(\text{Mn}_1) \right)
$$

$$
\chi_{zzz}(z = 0) = 0
$$

and similarly for $z = 1/2$ with Mn$_4$ or for $\chi_{xyy}, \chi_{yyz}, \chi_{xxz}$. The summation $\sum \chi_{xyy}$ must be intended as a sum over all similar terms, that is $\sum \chi_{xyy} = \chi_{yyz} + \chi_{zyy} + \chi_{xyz}$.

Starting from the high temperature phase, we will proceed in perturbation (up to the first order in the wavefunctions, second order in energy) to include the different symmetry breaking at the FE and AFM transitions, as well as the spin–orbit interaction. In the $P6_3/mmc$ high temperature group, the Mn ions are located on sites of $D_{3h}$ symmetry and one gets the following 3d zeroth order orbitals (associated with a nil nonlinear susceptibility tensor)

$$
\varphi_x^z = d_{z^2}^z
$$

$$
\varphi_{xz} = d_{xz}
$$

$$
\varphi_{yz} = d_{yz}
$$

$$
\varphi_{x^2} = c d_{x^2} + c' p_x
$$

$$
\varphi_{xy} = c d_{xy} + c' p_y.
$$

At this point let us notice that the $d_{x^2} + c'$ and $p_x$ (as well as the $d_{xy}$ and $p_y$) Mn orbitals belong to the same irreducible representation and are thus hybridized through the metal–ligand interactions.

A.2. The magnetic groups with the $P6_3cm$ crystal group

Going through the FE transition toward the $P6_3cm$ group, the Mn ion goes from a $D_{3h}$ site to a $C_s$ symmetry site, thus the degeneracies between $\varphi_{xz}/\varphi_{yz}$ and the $\varphi_{x^2}/\varphi_{xy}$ orbitals are lifted by respectively $\delta E$ and $\delta E'$. At the first order of perturbation in this symmetry breaking and in the spin–orbit coupling, one gets the following orbitals:

$$
\varphi_x^z = d_{z^2} + s_0 t_x + \mu_{d_{z^2}} + \nu(c d_{x^2} + c' p_x)
$$

$$
+ \frac{\sqrt{3}N}{\Delta E_2} \left[ (S_z) d_{z^2} + (S_y) d_{y^2} \right]
$$

$$
\varphi_{xz} = d_{xz} + \lambda(c d_{x^2} + c' p_x) - \mu_{d_{z^2}} + c' p_x
$$

$$
- \frac{\sqrt{3}N}{\Delta E_2} \left[ (S_z) d_{z^2} + (S_y) d_{y^2} \right]
$$

$$
+ \frac{cN}{\Delta E_1} \left[ (S_z)(c d_{x^2} + c' p_x) + (S_y)(c d_{y^2} + c' p_y) \right]$$
\[ \varphi_{\chi z} = d_{\chi z} + \lambda (\text{cd}_{\chi y} + c' p_{\chi y}) \]
\[ - \frac{\sqrt{3} N}{\Delta E_2} \langle S_y \rangle d_{\chi z} + \frac{N}{\delta E} \langle S_y \rangle d_{\chi z} \]
\[ + \frac{N}{\Delta E_1} \left[ \langle S_y \rangle (\text{cd}_{\chi y} + c' p_{\chi y}) + \langle S_x \rangle (\text{cd}_{\chi y} + c' p_{\chi y}) \right] \]
\[ \varphi_{\chi z - \chi y} = c d_{\chi y} + c' p_{\chi y} - \lambda d_{\chi y} - v d_{\chi y} + \zeta'' p_{\chi y} \]
\[ - \frac{c N}{\Delta E_1} \left[ \langle S_y \rangle d_{\chi y} - \langle S_z \rangle d_{\chi y} \right] + \frac{c^2 N}{\delta E} \langle S_y \rangle (\text{cd}_{\chi y} + c' p_{\chi y}) \]
\[ \varphi_{\chi y} = c d_{\chi y} + c' p_{\chi y} - \lambda d_{\chi y} - \frac{c N}{\delta E} \langle S_y \rangle d_{\chi y} + \frac{c^2 N}{\delta E} \langle S_y \rangle (\text{cd}_{\chi y} + c' p_{\chi y}) \]
\[ \times \left[ \langle S_y \rangle d_{\chi y} + \langle S_z \rangle d_{\chi y} \right] + c^2 N \langle S_y \rangle (\text{cd}_{\chi y} + c' p_{\chi y}) \]
\]
\[ (2) \]

where \( N \) is the spin–orbit coupling constant, and \( \langle S \rangle \) the average values of the spin operators associated with ground state spin order. \( \Delta E_1 \) is the excitation energy from the degenerated \( \varphi_{\chi y} \) or \( \varphi_{\chi y} \) orbitals toward the \( \varphi_{\chi y + \chi y} \) one, \( \Delta E_2 \) is the excitation energy from the degenerated \( \varphi_{\chi y - \chi y} \), \( \varphi_{\chi y} \) orbitals toward the \( \varphi_{\chi y} \) or \( \varphi_{\chi y} \) ones. \( \lambda, \mu, \nu, \zeta, \zeta', \zeta'' \) are the first order mixing coefficients associated with the \( P6_3/mmc \rightarrow P6_3cm \) symmetry breaking.

For any of the magnetic groups associated with the \( P6_3cm \) spatial group, the nonlinear susceptibility tensor will involve the following transitions (authorized light polarization is shown on top of the arrows while the orbital irreps are given in parentheses)

\[
\begin{align*}
&\varphi_{\chi y}(A) \xrightarrow{\lambda} \varphi_{\chi z}(A) \quad \varphi_{\chi y}(A) \xrightarrow{\lambda} \varphi_{\chi z - \chi y}(A) \\
&\varphi_{\chi y}(A') \xrightarrow{\lambda} \varphi_{\chi z - \chi y}(A') \quad \varphi_{\chi y}(A') \xrightarrow{\lambda} \varphi_{\chi z + \chi y}(A')
\end{align*}
\]

Using the above diagram and the orbitals given in equation (2) one can show that

\[ \epsilon_0 \chi_{zzzz}(z = 0) = \epsilon_0 \chi^0_{zzzz}(z = 0) \]
\[ + \frac{\epsilon^2}{2} \frac{A}{\epsilon^2 - \epsilon_2} + \frac{A'}{\epsilon^2 - \epsilon_2 - 2 \hbar \omega} \langle S_z \rangle_{\text{Mn}_1} \]
\[ + \frac{\epsilon^2}{2} \frac{B}{\epsilon^2 - \epsilon_2} + \frac{B'}{\epsilon^2 - \epsilon_2 - 2 \hbar \omega} \langle S_z \rangle_{\text{Mn}_1}^2 \]
\[ \epsilon_0 \chi_{yyyy}(z = 0) = 0 \]
\[ \epsilon_0 \chi_{zxx}(z = 0) = \epsilon_0 \chi^0_{zxx}(z = 0) \]
\[ + \frac{\epsilon^2}{2} \frac{C}{\epsilon^2 - \epsilon_2} + \frac{C'}{\epsilon^2 - \epsilon_2 - 2 \hbar \omega} \langle S_z \rangle_{\text{Mn}_1} \]
\[ + \frac{\epsilon^2}{2} \frac{D}{\epsilon^2 - \epsilon_2} + \frac{D'}{\epsilon^2 - \epsilon_2 - 2 \hbar \omega} \langle S_z \rangle_{\text{Mn}_1}^2 \]
\[ \epsilon_0 \chi_{yxy}(z = 0) \]
\[ + \frac{\epsilon^2}{2} \frac{E}{\epsilon^2 - \epsilon_2} + \frac{E'}{\epsilon^2 - \epsilon_2 - 2 \hbar \omega} \langle S_z \rangle_{\text{Mn}_1}^3 \]

and similarly for the \( z = 1/2 \) layer. \( \chi^0_{zzzz}(z = 0) \) is the spin independent (FE) tensor and \( \epsilon_i \) the energy of the orbital \( \varphi_i \).

For the \( W_2 \) magnetic order one has \( \langle S_z \rangle_{\text{Mn}_1} = \langle S_z \rangle_{\text{Mn}_4} \) thus if \( \epsilon_0 \chi^0_{zzzz} \) and \( \chi_{zzzz} \) include all the magnetic domain independent terms

\[ \epsilon_0 \chi_{zzzz} = \epsilon_0 \chi^0_{zzzz} \]
\[ + 2 \left[ \frac{A}{\epsilon^2 - \epsilon_2 - 2 \hbar \omega} + \frac{A'}{\epsilon^2 - \epsilon_2 - 2 \hbar \omega} + \frac{B}{\epsilon^2 - \epsilon_2} + \frac{B'}{\epsilon^2 - \epsilon_2 - 2 \hbar \omega} \right] \langle S_z \rangle_{\text{Mn}_1} \]
\[ \epsilon_0 \chi_{yyyy} = 2 \left[ \frac{C}{\epsilon^2 - \epsilon_2 - 2 \hbar \omega} \langle S_z \rangle_{\text{Mn}_1} \right] \]
\[ + 2 \left[ \frac{D}{\epsilon^2 - \epsilon_2} + \frac{D'}{\epsilon^2 - \epsilon_2 - 2 \hbar \omega} \right] \langle S_z \rangle_{\text{Mn}_1}^2 \]

It results that in this scheme both the in-plane and out-of-plane signal should be sensitive to the magnetic domains.

In contrast, the \( V_1 \) magnetic order should not display any SHG signal since \( \langle S_z \rangle_{\text{Mn}_1} = \langle S_z \rangle_{\text{Mn}_4} = 0 \).

**The \( P6_3 \) magnetic group**

Let us now look at the \( P6_3 \) magnetic group. The associated crystal group is \( P6_3 \) in which the Mn ions are on a \( P_1 \) symmetry site. In this group the Fe 3d orbitals can be expressed as

\[ \varphi_{\chi y} = d_{\chi y} + \zeta p_{\chi y} + \mu d_{\chi y} + v (\text{cd}_{\chi y} + c' p_{\chi y}) \]
\[ + \mu' d_{\chi y} + v' (\text{cd}_{\chi y} + c' p_{\chi y}) + \frac{\sqrt{3} N}{\Delta E_2} \left[ \langle S_y \rangle d_{\chi y} + \langle S_y \rangle d_{\chi y} \right] \]
\[ \varphi_{\chi z - \chi y} = d_{\chi y} + \lambda (\text{cd}_{\chi y} + c' p_{\chi y}) - \mu d_{\chi y} + \zeta'' p_{\chi y} \]
\[ - \tau d_{\chi y} + v (\text{cd}_{\chi y} + c' p_{\chi y}) + \frac{\sqrt{3} N}{\Delta E_2} \langle S_y \rangle d_{\chi y} + \frac{N}{\delta E} \langle S_y \rangle d_{\chi y} \]
\[ \varphi_{\chi z} = d_{\chi y} + \lambda (\text{cd}_{\chi y} + c' p_{\chi y}) - \mu d_{\chi y} + \zeta'' p_{\chi y} \]
\[ - \mu' d_{\chi y} + \zeta'' p_{\chi y} - \tau d_{\chi y} + v (\text{cd}_{\chi y} + c' p_{\chi y}) \]
\[ - \frac{\sqrt{3} N}{\Delta E_2} \langle S_y \rangle d_{\chi y} + \frac{N}{\delta E} \langle S_y \rangle d_{\chi y} \]
\[ \varphi_{\chi z - \chi y} = [\text{cd}_{\chi y} + c' p_{\chi y}] - \lambda d_{\chi y} - \nu d_{\chi y} + \zeta'' p_{\chi y} \]
\[ - \nu' d_{\chi y} + \tau' (\text{cd}_{\chi y} + c' p_{\chi y}) \]
\[ - \frac{\sqrt{3} N}{\Delta E_2} \langle S_y \rangle d_{\chi y} + \frac{N}{\delta E} \langle S_y \rangle d_{\chi y} \]
\[ \varphi_{\chi y} = [\text{cd}_{\chi y} + c' p_{\chi y}] - \lambda d_{\chi y} - \nu d_{\chi y} + \zeta'' p_{\chi y} \]
\[ - \nu' d_{\chi y} + \tau' (\text{cd}_{\chi y} + c' p_{\chi y}) \]
\[ - \frac{\sqrt{3} N}{\Delta E_2} \langle S_y \rangle d_{\chi y} + \frac{N}{\delta E} \langle S_y \rangle d_{\chi y} \]

where \( \mu', \nu', \tau', \nu, \zeta', \zeta'', \zeta''' \) are the first order perturbation coefficients associated with the \( P6_3/mmc \rightarrow P6_3cm \) symmetry breaking. The nonlinear susceptibility tensor will thus involve
the following transitions:

\[
\begin{align*}
\varphi_{x\zeta} & \xrightarrow{z,\zeta} \varphi_{z\zeta} \\
\varphi_{x\zeta} & \xrightarrow{y,\zeta} \varphi_{y\zeta}
\end{align*}
\]

As it is expected that the \(P6_3cm \rightarrow P6_3\) point symmetry breaking is very weak (not observed in x-ray diffraction up to now), in the calculation of the second harmonic susceptibility tensor we will thus neglect the terms in \(\mu', \nu', \tau', \nu, \nu', \xi'', \nu''\). Using the above diagram and the orbitals given in equation (3) one can show that the SHG tensor has the following form (only the contributions associated with the \(V_1\) and \(V_3\) magnetic orders compatible with the \(P6_3\) magnetic group are retained)

\[
\begin{align*}
\epsilon_0 \chi_{xxx}(z = 0) + \epsilon_0 \chi_{xyy}(z = 0) + \epsilon_0 \chi_{yyy}(z = 0) = & \\
+ & \left[ A \left( \frac{\epsilon_z - \epsilon_{x^2-y^2}}{2 \hbar \omega} + \frac{\epsilon_z - \epsilon_{xy}}{2 \hbar \omega} \right) + C' \left( \frac{\epsilon_z - \epsilon_{x^2-y^2}}{2 \hbar \omega} + \frac{\epsilon_z - \epsilon_{xy}}{2 \hbar \omega} \right) \right] (S_y)_{Mn_1}^2 \\
+ & \left[ D \left( \frac{\epsilon_z - \epsilon_{x^2-y^2}}{2 \hbar \omega} + \frac{\epsilon_z - \epsilon_{xy}}{2 \hbar \omega} \right) + D' \left( \frac{\epsilon_z - \epsilon_{x^2-y^2}}{2 \hbar \omega} + \frac{\epsilon_z - \epsilon_{xy}}{2 \hbar \omega} \right) \right] (S_y)_{Mn_1}^2 \\
+ & \left( \frac{E}{\epsilon_z - \epsilon_{x^2-y^2}} + \frac{E'}{\epsilon_z - \epsilon_{xy}} \right) (S_z)_{Mn_1}^2
\end{align*}
\]

\[
\begin{align*}
\epsilon_0 \chi_{xyy}(z = 0) = & \\
+ & \left[ A' \left( \frac{\epsilon_z - \epsilon_{x^2-y^2}}{2 \hbar \omega} + \frac{\epsilon_z - \epsilon_{xy}}{2 \hbar \omega} \right) \right] (S_x)_{Mn_1}^2
\end{align*}
\]

Using \((S_y)_{Mn_1} > 0\) whatever the magnetic domain, \((S_y)_{Mn_1} = -(S_z)_{Mn_1}\) and \((S_z)_{Mn_1} = (S_x)_{Mn_1}\), one gets

\[
\begin{align*}
\epsilon_0 \chi_{xxx} = & \epsilon_0 \chi_{xyy} \\
\epsilon_0 \chi_{yyy} = & \epsilon_0 \chi_{yyy} \\
+ & 2i \left[ \frac{D(S_y)_{Mn_1}^2 + E}{\epsilon_z - \epsilon_{x^2-y^2}} + \frac{D'(S_y)_{Mn_1}^2 + E'}{\epsilon_z - \epsilon_{xy}} \right] (S_z)_{Mn_1}^2
\end{align*}
\]

\[
\begin{align*}
\epsilon_0 \chi_{xyy} = & \epsilon_0 \chi_{xyy} = \epsilon_0 \chi_{xyy}.
\end{align*}
\]

One sees immediately that \(\chi_{xxx}\) and \(\chi_{xyy}\) should be insensitive to the magnetic order, while \(\chi_{yyy}\) should exhibit a sensitivity to the magnetic domains at different frequencies.

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