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Evidence for room temperature electric polarization in RMn_2O_5 multiferroics

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It is established that the multiferroics RMn_2O_5 crystallize in the centrosymmetric $Pbam$ space group and that the magnetically induced electric polarization appearing at low temperature, is accompanied by a symmetry breaking. However, both our present X-ray study – performed on compounds with $R = \text{Pr}, \text{Nd}, \text{Gd}, \text{Tb}$ and Dy – and first principle calculations unambiguously rules out this picture. Based on structural refinements, geometry optimization and physical arguments, we demonstrate in this paper that the actual space group is likely to be Pm . This turns out to be of crucial importance for RMn_2O_5 multiferroics since Pm is not centrosymmetric. Ferroelectricity is thus already present at room temperature and its enhancement at low temperature is a spin-enhanced process. This result is also supported by direct observation of optical second harmonic generation. This fundamental result calls into question the actual theoretical approaches that describe the magneto-electric coupling in this multiferroic family.

Interests in multiferroic materials are twofold, fundamental questions that are yet to be properly addressed and potential technological applications. Both of these aspects mainly originate from one common issue, i.e. the intrinsic coupling among the different order parameters. The magnetoelectric coupling is attracting major attention not only because it opens a wide range of applications in the field of emerging spintronic materials, but also its microscopic mechanism requires exotic theories [1]. The strongest magnetoelectric effect is found in the so called magnetically induced ferroelectrics, where the electric polarization appearing at low temperature due to magnetic ordering. One of the archetypical systems is RMnO_3 (R is a the rare earth ion), for which the spin-induced ferroelectricity is theoretically ascribed to the Dzyaloshinskii-Moriya (DM) interaction (which mixes the structural and magnetic degrees of freedom [2]). This standard model describes the inversion symmetry breaking when a complex and non collinear magnetic order (cycloidal, helicoidal *etc.*) sets in. However, another family of manganites with general formula RMn_2O_5 challenges the community because in these systems the ferroelectricity is induced by a quasi-collinear magnetic order, thus ruling out the standard DM model [3]. This points to the primary importance of both magnetic and crystallographic structure determination to understand the microscopic mechanism breaking the centrosymmetry and leading to the electric polarization. It justifies the extensive studies performed on the different members of this family, especially for R from Tb to Tm [4–9]. According to the literature, all those compounds crys-

tallize in the $Pbam$ space group at room temperature and undergo a similar series of magnetic transitions at low temperature [10–12]. The electric polarization generally appears together with the incommensurate-to-commensurate magnetic-order transition (around 30K, this temperature slightly depends on the rare earth). This behaviour does not extend to lighter rare earth compositions such as PrMn_2O_5 , which has been reported to be non ferroelectric [13]. Since the space group at room temperature ($Pbam$) is centrosymmetric, no electric polarization is possible and its emergence at low temperature can only be ascribed to the quasi-collinear spin ordering. From theoretical point of view, an exchange striction mechanism is often introduced to explain the spin-induced ferroelectricity [14] : the system tends to minimize the underlying magnetic frustration by slight atomic displacements leading to the breaking of the inversion symmetry and the electric polarization.

In this letter, we report for the first time an exhaustive study of structural properties, as well as first principle geometry optimizations, of the room temperature paramagnetic phase for the RMn_2O_5 series. We rule out not only the $Pbam$ space group, but we also find that the actual space group is noncentrosymmetric. This result calls into question the origin of the magnetoelectric coupling and the spin-induced exchange striction model. More importantly, it strongly suggests a pre-existing electric polarization at room temperature.

Single crystals of a fraction of mm^3 for different members of the RMn_2O_5 series ($R = \text{Pr}, \text{Nd}, \text{Gd}, \text{Tb}$ and Dy) were selected. These samples were synthesized either by

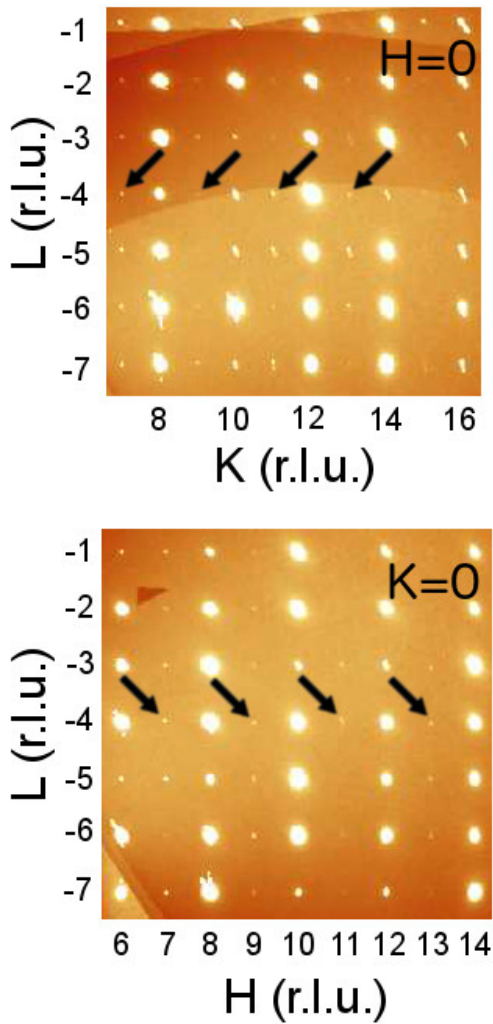


FIGURE 1: (Color online) Reconstructions of the lattice node planes (0,K,L) (top) and (H,0,L) (bottom) of DyMn_2O_5 , taking into account absorption correction.

flux method (small R size) or electrolysis (large R size). Details of the synthesis procedure are given in references [15, 16]. We performed X-ray diffraction measurements with four-circle diffractometers, either at the SOLEIL synchrotron CRISTAL beamline (for R = Tb, Gd, and Dy) or using the $\text{MoK}\alpha$ radiation from laboratory sources (for R = Pr and Nd). The measurements were performed at room temperature for all compounds, and at 100 K for TbMn_2O_5 .

In the $Pbam$ space group, H0L and 0KL Bragg reflections are forbidden whenever H and K are odd. These forbidden reflections were however systematically observed for every measured compounds. Figure 1 displays reciprocal lattice reconstructions of the 0KL and H0L planes for DyMn_2O_5 , in which the presence of the forbidden reflections is the most prominent. Before going any further, we checked for the possibilities of different exper-

imental artefacts which could have been at the origins of these additional intensities. Neither a wavelength harmonic contamination ($\lambda/2$) nor the twinning of the crystal could explain the presence of such forbidden reflections. The possibility of multiple scattering effect was also ruled out using an azimuthal scan (rotation of 10° with a step of 2° around the (007) reciprocal wave vector) since the intensity of the Bragg reflection was found to be nearly constant within the whole azimuthal range. The observed forbidden reflections thus cannot be associated with an experimental artefact, and since they are observed in the different members of the family, we can conclude that this superstructure is an intrinsic structural property of the RMn_2O_5 compounds at 300 K. It is important to notice that the presence of forbidden reflections was also observed in previous work, but without any reliable explanation of their origin [17]. We underline that all measured reflections present the experimental resolution while no diffuse scattering has been observed. This demonstrates the high quality of our crystals without significant disorder, or other defects such as nano-twinning. Despite their systematic observation, the intensity of the superstructure peaks is 0.2 to 1.5% stronger in the middle angle range than in the small angle region. This behavior can neither be related to thermal factor effects, nor to an order-disorder transition, but rather suggests a displacive origin. In such a case, the intensity of the forbidden reflections is expected to be proportional to the square of the atomic displacements from the mean $Pbam$ space group positions. The average intensity of the forbidden reflections yields the order of magnitude of the atomic displacements to be about 0.05 \AA . These displacements are larger than the ones generally observed for structural transitions like the Peierls transitions in the blue bronze [18] or in the TTF-TCNQ [19]. Table I shows the intensity ratios of the forbidden reflections compared to the allowed Bragg reflections for various compounds. It is noteworthy that this ratio does not seem to depend on the nature and on the size of the rare earth R atoms. Indeed, for the Nd, Gd, and Tb based compositions, the ratio is of the same order of magnitude. However, for Dy, it is 5 times greater than for the other members of the series. On the other hand, the mean intensity increase of the forbidden reflections destabilizes the ferroelectricity : the low temperature electric polarization is weaker in compounds where the ratio is stronger.

One can thus unambiguously assert that the actual space group cannot be $Pbam$. Among the orthorhombic space groups, only 3 are compatible with all the experimentally observed reflections, namely $Pmmm$, $P2mm$ and $P222$. However none of them are consistent with the mean $Pbam$ structure. We therefore considered lower symmetry space groups. However we are unable to detect a symmetry deviation from the orthorhombic cell parameters, the cell angles remaining 90° within a 0.1° accuracy. In the monoclinic setting, only 3 candidates are fully

TABLE I: Critical temperature (T_{FE}), maximum electric polarization of various RMn_2O_5 compounds [20–22], and ratio between the mean integrated intensity of the forbidden reflections (I_S) and the mean integrated intensity of the allowed Bragg reflections (I_{Bragg}).

Sample	T_{FE} (K)	$\frac{I_S}{I_{\text{Bragg}}}$ (%)	Polarization ($\mu\text{C}\cdot\text{m}^{-2}$)
PrMn_2O_5	–	0.58	0
NdMn_2O_5	25	0.27	3.5
GdMn_2O_5	33	0.20	3600
TbMn_2O_5	38	0.36	450
DyMn_2O_5	39	1.40	200

compatible with the observed Bragg reflections : $P2/m$, $P2$ and Pm (unique c axis). Lattice angles of 90° is unusual when considering monoclinic space groups. Nevertheless, a careful analysis of the reciprocal space reconstructions revealed minute deviation from 90° . Indeed, large segments instead of points are visible when the reciprocal space is projected along the a axis. This indicates that the γ angle is not exactly 90° but distributed around 90° , supporting the hypothesis of a monoclinic space group.

Among the 3 possible monoclinic space groups a distinction has to be made between $P2/m$ on one hand and $P2$ and Pm on another hand. Indeed the former one is centrosymmetric while the latter are not. This question of centrosymmetry is the central issue regarding the ferroelectric properties of these materials, as glimpsed in the introduction.

Slight departure from the Friedel law should be observed thanks to the anomalous components of the atomic form factors, $f'(E)$ and $f''(E)$, for noncentrosymmetric groups. [23]. Because of the strong absorption of RMn_2O_5 at the Mn K-edge and rare earth L-edge (both around 6 keV), anomalous scattering measurements at these edges is difficult. Therefore, we performed anomalous X-ray measurements on the DyMn_2O_5 and TbMn_2O_5 compounds just above the K edge energy of the rare earth atom (respectively 53794 ± 35 eV and 52007 ± 35 eV). These compounds were chosen for their prominent forbidden reflections (see Table I). For both compounds, the differences between the intensities of the measured Friedel pairs were calculated. For the Dy compound, we observed that 1% of the 7000 measured Friedel pairs present a significant discrepancy above the 3 sigmas level. The average difference for these pairs was estimated to be 1%, with a maximum of 2% for the (2,0,0). Several reasons can explain this weak difference. i) In the absence of any external electric field, there exist twinned domains that may compensate the expected anomalous signal [23]. ii) When the resonant atom stays close to a centrosymmetric position, the corresponding $f''(E)$ terms nearly compensate one another, weakening the intensity difference between the Friedel pair. Nevertheless, this non

negligible deviation of the Friedel law has to be taken into account and is in favor of a noncentrosymmetric structure.

TABLE II: Atomic positions of DyMn_2O_5 at 300 K in the Pm space group ($R=1.95\%$, $wR=3.21\%$, $N=28763$, $2\theta_{\text{min}}=1.47^\circ$, $2\theta_{\text{max}}=41.44^\circ$). The lattice parameters are $a=7.2931$ Å $b=8.5025$ Å and $c=5.6743$ Å $\gamma=90^\circ$.

Atom	Site	x	y	z
Dy1 ₁	1a	0.138964(10)	0.171696(7)	1
Dy1 ₂	1a	-0.138953(10)	-0.171402(7)	-1
Dy1 ₃	1a	0.638754(10)	0.328455(7)	-1
Dy1 ₄	1a	-0.638650(10)	-0.328396(7)	1
Mn1 ₁	2c	0.00027(4)	0.49993(3)	1.25550(3)
Mn1 ₂	2c	0.50034(4)	0.00017(3)	-1.25549(3)
Mn2 ₁	1b	0.41162(4)	0.35041(3)	0.5
Mn2 ₂	1b	-0.41197(4)	-0.35002(3)	-0.5
Mn2 ₃	1b	0.91181(4)	0.14942(3)	-0.5
Mn2 ₄	1b	-0.91191(4)	-0.15032(3)	0.5
O1 ₁	2c	0.0003(2)	-0.00065(15)	0.27409(18)
O1 ₂	2c	0.5002(2)	0.50265(14)	-0.27048(16)
O2 ₁	1a	0.16290(15)	0.44480(12)	0
O2 ₂	1a	-0.1674(2)	-0.44552(17)	0
O2 ₃	1a	0.66178(19)	0.05594(13)	0
O2 ₄	1a	-0.6592(2)	-0.05567(18)	0
O3 ₁	1b	0.14701(16)	0.41971(14)	0.5
O3 ₂	1b	-0.1514(2)	-0.43336(14)	-0.5
O3 ₃	1b	0.65281(16)	0.06249(13)	-0.5
O3 ₄	1b	-0.6548(2)	-0.0612(2)	0.5
O4 ₁	2c	0.39543(17)	0.20296(11)	0.25333(19)
O4 ₂	2c	-0.40123(12)	-0.20960(9)	-0.23719(15)
O4 ₃	2c	0.89595(17)	0.29307(11)	-0.2425(2)
O4 ₄	2c	-0.89174(13)	-0.29566(10)	0.24629(14)

Full data collection on DyMn_2O_5 was performed at 28 KeV, for structural determination (and at 21.4 KeV for TbMn_2O_5 and GdMn_2O_5 compounds). Structure refinements were performed with the Jana software reference [24], considering the contributions of the different twins likely present in the samples (the introduction of twins only weakly improved the refinement and did nearly not modified the atomic positions). The anomalous scattering factors were taken from the Sasaki tables [25]. In the following, we will focus on the DyMn_2O_5 data which were of the highest quality. Our refinements were not able to distinguish among the different possible monoclinic structures. A joint refinement, using the data collected at 28 keV and at 53.8 KeV, however shows slightly better R factors for Pm and $P2$ than for $P2/m$ and $Pbam$ ($R=3.32\%$, 3.41% and 3.94% and 4.82% respectively).

Simultaneously to these X-ray measurements we performed density functional calculations in order to theoretically confirm the symmetry breaking. We optimized the DyMn_2O_5 geometry in different subgroups of $Pbam$, using the CRYSTAL code [26, 27]. We performed spin-polarized calculations using both ferromagnetic (FM) and antiferromagnetic (AFM) orders compatible with the $Pbam$ space group. Let us note that since our calculation do not include spin orbit coupling all magnetisation

axis are equivalent and there is an AFM order similar to the one of ref. 11 compatible with $Pbam$. In order not to be biased by the magnetic ordering (the high temperature phase is paramagnetic) we searched along line between the FM and AFM optimum geometries, the structure associated with the lowest average energy : $[E(FM) + E(AFM)]/2$. In all cases deviations from orthorhombic parameters remain very small ($< 0.01^\circ$ [27]). Our calculations easily ruled out the $Pbam$ and $P2/m$ space groups. Indeed, the optimized Pm and $P2$ structures are about 500 meV per unit cell lower in energy than the $Pbam$ one and 28 meV lower than the $P2/m$. The $P2$ optimized geometry is only 5 meV higher in energy than the Pm one. This energy difference is too small to be truly significant within a DFT scheme. Among the 3 possible monoclinic space groups, first principle calculations thus rule out the centrosymmetric group ($P2/m$). One can notice that the remaining Pm and $P2$ candidates are both polar groups (Pm with a polarisation in the (\mathbf{a}, \mathbf{b}) plane and $P2$ in along the \mathbf{c} axis).

The noncentrosymmetry was finally confirmed by the presence of optical second harmonic generation (see Supporting Information). Together with the first principle calculations and the anomalous X-ray measurements; these results definitely rule out the centrosymmetric nature of the $R\text{Mn}_2\text{O}_5$ systems at room temperature.

Unfortunately, neither our refinements nor our calculations can distinguish Pm from $P2$ with enough confidence, even if in both cases the Pm group is favored. The structure of DyMn_2O_5 for the Pm space group obtained from the 28 KeV high resolution data set is presented in Table II ($P2$ experimental structure as well as Pm and $P2$ theoretical ones can be found in the supplementary information). The atomic deviations from the $Pbam$ structure of ref. [28] is analyzed in the following. As expected a small deviation of the rare earth from its centrosymmetric position is observed (0.1 ± 0.02 pm). In fact, for both structures, the main atomic displacement concerns the oxygens labeled O3 and to a less extent the oxygens O4, respectively located at the 4h and 8i Wyckoff positions in the $Pbam$ space group. Their displacements ($\sim 7 \pm 1$ pm for O3 and $\sim 5 \pm 1$ pm for O4) are one or two orders of magnitude larger than the rare earth one. The Mn^{4+} ions are also slightly displaced (0.5 ± 0.05 pm). Naturally, the direction of the atomic displacements totally differs in the $P2$ and the Pm space groups. The same kind of displacements have been observed for TbMn_2O_5 and to a lesser extent (because of poorer quality data) for GdMn_2O_5 . The role of the oxygen atoms in the deviation from the mean $Pbam$ structure explains the lack of accuracy and statistics using X-ray scattering, as well as the difficulty to discriminate between the Pm and $P2$ space groups. The prominent role of the O3 (O4) oxygens in the deviation from the $Pbam$ structure may have a strong impact in the multiferroic properties. Indeed, these oxygens are located between the Mn^{3+} and Mn^{4+} magnetic sites.

Thus, they actively participate in the superexchange interactions J_4 (O3) and J_3 (O4) [10]. Consequently, any change in the oxygens positions largely influences the values of J_4 and J_3 . As the superstructure magnitude is nearly 4 times stronger in DyMn_2O_5 than in TbMn_2O_5 , J_4 and J_3 should significantly differ between these two compounds. Due to the presence of magnetic frustration, the magnetic order at low temperature is expected to be particularly sensitive to any variation of the J_i couplings. In light of these considerations, it appears natural that DyMn_2O_5 and TbMn_2O_5 exhibit completely different magnetic orders [11].

Despite the lack of experimental and theoretical accuracy to discern $P2$ from Pm , we can present other physical arguments in favour of the Pm symmetry. When a polarisation is observed [20–22] it systematically points along the \mathbf{b} axis (compatible with the Pm group, but not with the $P2$ one). It is likely that the high temperature symmetry is compatible with the symmetry of the low temperature polarization. There is however a subtlety in TmMn_2O_5 as it presents a polarization flip from the \mathbf{b} to the \mathbf{a} direction at low temperature [29]. Nevertheless this flip is still compatible with Pm , but not with $P2$ (where \vec{P} is along the \mathbf{c} axis). These considerations therefore definitely preclude the $P2$ space group.

In conclusion, our study reveals that the universal space group of the $R\text{Mn}_2\text{O}_5$ series at ambient temperature is not the expected $Pbam$, but the noncentrosymmetric Pm space group. The direct consequence of the noncentrosymmetric symmetry is the presence of electric polarization above the Néel temperature and even at room temperature. This fundamental result calls into question all theoretical approaches that deal with the origin of the magneto-electric coupling in this multiferroic family. In addition, it gives a comprehensive understanding of the difference of magnetic orders among different members of the $R\text{Mn}_2\text{O}_5$ series. Finally, since the inversion symmetry is already broken at room temperature, it is obvious that the magneto-electric coupling in the $R\text{Mn}_2\text{O}_5$ originates from a spin-enhanced process rather than from the spin-induced effect.

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