Ferrielectricity in DyMn_2O_5 : A golden touchstone for multiferroicity of RMn_2O_5 family*

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The RMn_2O_5 manganite compounds represent one class of multiferroic family with magnetic origins, which has been receiving continuous attention in the past decade. So far, our understanding of the magnetic origins for ferroelectricity in RMn_2O_5 is associated with the nearly collinear antiferromagnetic structure of Mn ions, while the exchange striction induced ionic displacements are the consequence of the spin frustration competitions. While this scenario may be applied to almost all RMn_2O_5 members, its limitation is either clear: the temperature-dependent behaviors of electric polarization and its responses to external stimuli are seriously materials dependent. These inconsistencies raise substantial concern with the state-of-the-art physics of ferroelectricity in RMn_2O_5 . In this mini-review, we present our recent experimental results on the roles of the $4f$ moments from R ions which are intimately coupled with the $3d$ moments from Mn ions. DyMn_2O_5 is a golden figure for illustrating these roles. It is demonstrated that the spin structure accommodates two nearly collinear sublattices which generate respectively two ferroelectric (FE) sublattices, enabling DyMn_2O_5 an emergent ferrielectric (FIE) system rarely identified in magnetically induced FEs. The evidence is presented from several aspects, including FIE-like phenomena and magnetoelectric responses, proposed structural model, and experimental check by nonmagnetic substitutions of the $3d$ and $4f$ moments. Additional perspectives regarding possible challenges in understanding the multiferroicity of RMn_2O_5 as a generalized scenario are discussed.

Keywords: RMn_2O_5 ; multiferroic; ferrielectricity; $3d$ - $4f$ coupling; exchange striction.

1. Introduction

Multiferroic compounds of magnetically induced ferroelectricity, as promising magnetoelectric materials for immediate applications, are more or less despised currently but have been receiving continuous attention from the condensed matter physics community.^{1–4} On one hand, these compounds do enable a generation of ferroelectricity by magnetism-relevant mechanisms rather than lattice phonon-mode softening widely known in textbooks of ferroelectricity,^{5–7} since such phenomena had never been observed in realistic materials before. On the other hand, the strong coupling between electric polarization (P) and magnetization (M) plus their cross-controls via electric and magnetic stimuli routes have inspired continuous interest in the underlying mechanisms.^{8–11} It is believed that these mechanisms for ferroelectricity generation and magnetoelectric cross-controls may be useful in searching for novel multiferroics with improved performances at high temperatures (T).^{12,13}

Up to date, extensive investigations on these emergent phenomena show off two major microscopic mechanisms for ferroelectricity generation,^{8,11,14} as sketched in Figs. 1(a)

and 1(b) for a guide of eyes where a charge-ordered spin chain is chosen for illustration, although other mechanisms for individuals were proposed.^{15–17} Details for discovering these phenomena and relevant physics can be found in several recent review papers.^{1,3} Figure 1(a) shows a noncollinear spin chain where a spin-pair is bridged by a ligand ion (e.g., oxygen O) and the spins are noncollinearly ordered in counterclockwise spiral (a1) or clockwise spiral (a2) alignment.¹⁸ The relativistic correction of the spin–orbit coupling to the exchange interaction, i.e., the so-called Dzyaloshinskii–Moriya interaction (DMI), drives a small shift of the ligand ions, since the exchange interaction can be enhanced at the cost of the shift-induced lattice energy.^{8,9,14} Given the spiral spin order along the chain direction, all the ligand ions shift along the same direction, leading to a net electric polarization perpendicular to the spin chain. This is the DMI mechanism and the generated polarization $P(\Delta P) \sim e_{ij} \times (S_i \times S_j)$. The other mechanism refers to some specific collinear spin orders and one example is illustrated in Fig. 1(b) where the spin chain favors the $\uparrow\uparrow\downarrow\downarrow$ collinear order.^{11,19} The symmetric exchange striction drives the two parallel nearest spins to near

*In celebration of the eightieth birthday of Prof. Xi Yao.

Fig. 1. (Color online) Two major microscopic mechanisms for polarization generations in single phase multiferroic compounds.¹⁸ (a) The Dzyaloshinskii–Moriya interaction (DMI) mechanism associated with a noncollinear spiral spin order and the local polarization $P(\Delta P) \sim e_{ij} \times (S_i \times S_j)$ where e_{ij} is a vector connecting one neighboring spin pair S_i and S_j bridged with oxygen as a ligand. (b) The symmetric exchange striction mechanism associated with a collinear $\uparrow\uparrow\downarrow\downarrow$ (or $\leftarrow\leftarrow\rightarrow\rightarrow$) spin order and the local $P(\Delta P)$ is proportional to $S_i \cdot S_j$ where the spin pair S_i and S_j is bridged with oxygen as a ligand.

with each other and those antiparallel to apart from each other. Concomitantly, the ligand ions bridging the spin pairs will shift towards and away from the chain, respectively, leading to net polarizations $P(\Delta P) \sim (S_i \cdot S_j)$. It is called the exchange striction mechanism.

In spite of other mechanisms proposed, the above two have been well recognized for most multiferroics of noncollinear and collinear spin orders, in particular for orthorhombic manganites RMnO_3 with R being rare-earth.³ Two generic characteristics associated with the spin order induced polarization P as functions of T and magnetic field H can be highlighted. First, both the noncollinear and collinear spin orders are the compromises of multifold exchange competition which enables the spin structure highly frustrated. This leads to, in a usual way, a sequence of spin ordering starting from commensurate (C) and incommensurate (IC) antiferromagnetic (AFM) orders with noncollinear or collinear alignment becomes possible and is often identified in multiferroic oxides such as manganites, ferrites, cobaltates, vanadates, cuprates, etc.^{3,12} It certainly implies that the temperatures for these spin orderings are low, and so is the FE Curie point (T_C). Obviously, driving the transitions between these spin orders does not need much additional exchange energy on cost of lattice distortion energy for ferroelectricity, implying that the as-generated electric polarization must be small either. In consequence, the measured $P(T)$ curve would exhibit anomalies at these ordering points. Second, these spin orders are not robust against intrinsic and external stimuli due to the strong spin frustration, which can be well illustrated by the giant magnetoelectric response. Even though, the two mechanisms show distinct difference in terms of the response, and the DMI induced polarization is quite sensitive to H but the exchange striction induced one is not. Surely, details of such responses can be fascinating and materials dependent, and readers may consult recent review papers.^{1,3,4,10}

Apart from the two generic aspects, reality is that many more observed phenomena cannot be reasonably understood within the two respect frameworks. One issue to be covered in this mini-review is the very different FE behaviors in

compounds with coexisting $4f$ and $3d$ moments.^{20–23} Without losing the generality, one may take the well-known multiferroic manganite DyMnO_3 as an example. First, this material has two kinds of moments: $3d\text{-Mn}^{3+}$ and $4f\text{-Dy}^{3+}$, which unfortunately add complexity to the two mechanisms for ferroelectricity generation and are appreciated due to involvement of additional physics.^{21,22} Second, the $3d\text{-}4f$ coupling in DyMnO_3 is quite strong, which makes the Mn and Dy spin ordering sequences quite different.^{20,24} It is known that the $4f$ moments in rare-earth oxides free of $3d$ moments may not order until extremely low temperature ($T < 1.0\text{K}$).^{25,26} One assigns this ordering temperature as T_{Dy} for DyMnO_3 (also DyMn_2O_5 to be discussed here). However, this ordering in DyMnO_3 occurs at a much higher temperature $T_{\text{Dy}} \sim 10\text{K}$, which is believed to be driven by the strong Dy–Mn coupling, given that the Mn spins begin to order at $\sim 40\text{K}$ or higher.^{22,24} An immediate consequence is not only the much higher T_{Dy} , but more importantly the coherent Dy spin ordering at $T \gg T_{\text{Dy}}$, induced by the Dy–Mn coupling. For DyMnO_3 , this coherence results in the $\uparrow\uparrow\downarrow\downarrow$ Mn–Dy–Mn–Dy... spin alignment along the c -axis in the bc -plane, while the Mn spiral spin structure has its spiral wavevector along the b -axis.²² This specific Mn and Dy coherent spin structure allows the co-existence of two FE sublattices generated respectively from the DMI mechanism (P_{Mn} sublattice) and exchange striction one (P_{Dy} sublattice).^{22,27–29} Fortunately, the two components both align along the c -axis, enabling DyMnO_3 to be a system with the largest polarization $P = P_{\text{Mn}} + P_{\text{Dy}}$ ever observed in orthorhombic RMnO_3 . The relevant physics can be illustrated in Fig. 2 and details can be found in an earlier paper.²⁹

DyMnO_3 represents the first ever measured multiferroic compound where two FE sublattices coexist and coherently contribute to the total polarization which exhibits an unusual T -dependence, as shown in Fig. 2 (bottom).²⁹ It is usually believed that two coexisting FE sublattices most likely favor an antiparallel alignment, leading to an antiferroelectric (AFE) or ferrielectric (FIE) lattice, as often found in normal FEs.^{30,31} For a reference, a FIE lattice and its T -dependent

Fig. 2. (Color online) Well-recognized multiferric scenario for DyMnO₃ with both 4*f* Dy³⁺ spins and 4*d* Mn³⁺ spins.²⁹ (a) The spin structures on the *bc*-plane at four different *T* as indicated in (c). (b) The as-generated two FE sublattices *P*_{Mn} and *P*_{Dy} at the four *T*, respectively. The *P*_{Mn} sublattice is generated via the DMI mechanism ($P_{Mn} \sim [S_i \times S_j]_{Mn}$) and the *P*_{Dy} sublattice is generated via the exchange striction ($P_{Dy} \sim [S_{Dy} \cdot S_{Mn}]$), as respectively shown in Fig. 1. (c) The proposed *P*_{Mn}, *P*_{Dy}, and *P* = *P*_{Mn} + *P*_{Dy} as a function of *T*, respectively.

polarization are schematically shown in Fig. 3 where the two FE sublattices (blue and red) have different ordering temperatures, leading to a crossover from *P* < 0 to *P* > 0 (*P* = *P*₊ + *P*_−) upon decreasing *T*. This crossover is a prime characteristic for a FIE lattice.

An immediate motivation to this end is whether any FIE multiferric is available or not. In fact, this issue was once concerned when another class of multiferric manganites RMn₂O₅ was claimed to exhibit ferroelectricity. As early as 2004, DyMn₂O₅ was observed to exhibit a clear crossover of its *P*(*T*) behavior (*P* along the *b*-axis) and was argued to be a FIE system,³² while this phenomenon was not well characterized until recently.^{33,34} Based on the knowledge of the ferroelectricity in DyMnO₃,²⁹ one has sufficient reason to expect possible AFE or FIE behavior in DyMn₂O₅. First, DyMn₂O₅ also has 3*d* and 4*f* moments: Mn and Dy ions, and strong Dy–Mn coupling is well confirmed.^{35–40} More than this, here Mn has two valence states: Mn³⁺ and Mn⁴⁺, implying the Dy³⁺–Mn³⁺ and Dy³⁺–Mn⁴⁺ couplings in addition to the 3*d* and 4*f* exchange interactions themselves. Such multifold coupling may bring more possibilities for two

Fig. 3. (Color online) The polarization *P* in a FIE upon decreasing *T* down to the negative–positive crossover point *T*_{*P*=0}. The FIE lattice consisting of two FE sublattices *P*₊ and *P*_− at four different *T* are inserted for guide of eyes.

or more FE sublattices to develop. Second, a remarkable perturbation of polarization *P* in response to complicated magnetic ordering sequence was identified, suggesting more than one polarization component in DyMn₂O₅.^{32–34,41–43} Third, recent investigations based on extensive neutron scattering and resonant X-ray scattering data disclosed the magnetic structure and its transitions, tampering a basis to find a correlation between spin structure and FE polarization.^{35–43} Finally, some RMn₂O₅ members other than DyMn₂O₅ (R=Ga, Tb, Ho, Er, Tm, Y, Bi, etc.) have been repeatedly revealed to be multiferrics and their polarizations show unusual behaviors too,^{32,33,35,37,39,43–48} suggesting that ferrielectricity may be a common characteristic of some members of this family.

In the last several years, various attempts to figure out the microscopic origins for ferroelectricity in DyMn₂O₅ have been made^{32–34,41–43} and so far available data demonstrate the ferrielectricity in DyMn₂O₅ in a self-consistent manner. Several aspects were carefully investigated, addressing the pure, Mn-site substituted, and Dy-site substituted DyMn₂O₅.^{49,50} The major features associated with the ferrielectricity of pure DyMn₂O₅ were sorted out. Our strategy was to start from these features and propose a phenomenological framework.³⁴ The subsequent Mn-site and Dy-site substitution experiments were designed to check this framework.^{49,50} In this mini-review, we intend to present all our data on the multiferricity of DyMn₂O₅ in an integrated package, eventually revealing the FIE nature of DyMn₂O₅. The remaining part is organized as follows. In Sec. 2 are outlined the crystal structure, magnetism, dielectric and FE behaviors, and discussion on the underlying mechanisms for multiferricity in literature on RMn₂O₅ and particularly DyMn₂O₅. Our improved experiments on polarization *P* as a function of *T* and *H* and proposed FIE lattice model will be discussed in Sec. 3. Subsequently, measured data on substitution trials at the Mn site and Dy site in order to validate this

Up to date, it remains unclear whether the magnetic transitions at T_{N2} and T_{N3} are related to the Dy spin ordering or not. Most likely they are driven by the $\text{Dy}^{3+}\text{-Mn}^{4+}$ and $\text{Dy}^{3+}\text{-Mn}^{3+}$ couplings, given that the $\text{Dy}^{3+}\text{-Mn}^{4+}$ separation shorter than the $\text{Dy}^{3+}\text{-Mn}^{3+}$ distance may favor a stronger Dy–Mn coupling. The consecutive magnetic transitions can be qualitatively explained by the competing interactions. The three major Mn–Mn exchange terms are denoted

as J_3 , J_4 , and J_5 in Fig. 4(a),³⁹ while the minor Mn^{4+} – Mn^{4+} , Dy^{3+} – Mn^{4+} , and Dy^{3+} – Mn^{3+} exchanges cannot be neglected either. These exchange interactions together with the relevant frustrations and anisotropies were discussed in detail but only qualitatively.^{35–42}

Nevertheless, it is interesting to find that almost all RMn_2O_5 members with strong ferroelectricity exhibit nearly identical spin structure if the R moments are not considered.³⁹ Otherwise, the structure can be slightly different, particularly in the low- T range where the Dy spin ordering appears, as shown in Fig. 4(b) for DyMn_2O_5 .^{35–42} First, all the Mn spins have the major components lying on the ab -plane, implying that the in-plane anisotropy is dominant and the out-of-plane one is relatively weak. Second, the in-plane Mn spins are roughly collinear although the noncollinear components cannot be negligible.⁵¹ It seems that the collinear components align along the b -axis for DyMn_2O_5 but along the a -axis for other RMn_2O_5 members. The minor noncollinear alignment was claimed to be attributed to the competition between the exchanges and the DMI. Considering the DMI mechanism for ferroelectricity, this noncollinear issue was discussed but no sufficient evidence echoing the major role of the DMI has been settled down.⁵¹ Third, the Dy spins also favor the collinear alignment with the Mn spins below T_{N2} and T_{N3} , as shown in Fig. 4(b) too. The major collinear Dy spin structure developed above T_{Dy} makes the Dy spin re-ordering at T_{Dy} less essential in terms of ferroelectricity. It is thus suggested that this Dy re-ordering may even benefit to the ferroelectricity, different from the case of DyMnO_3 .

2.3. Ferroelectricity and magnetoelectric responses

The ferroelectricity in RMn_2O_5 and its magnetic origin have been highly concerned since the discovery of ferroelectricity in HoMn_2O_5 , DyMn_2O_5 , and TbMn_2O_5 .^{51–64} Phenomenological theories on electric polarization has been developed, whose predictions seem to be qualitatively consistent with experimental results.^{65–67} If only the Mn^{3+} and Mn^{4+} spins are considered, the polarization is believed to be generated via the second mechanism shown in Fig. 1(b). The exchange striction effect arises from the three-spin blocks, as schematically drawn in Fig. 5 where the open dots represent the Mn^{3+} ions without exchange interactions. Despite the nearly collinear Mn spin ordering may take different configurations with two examples shown in Figs. 5(a) and 5(b), the exchange striction induced Mn^{3+} ionic displacements with respect to Mn^{4+} are majorly along the b -axis, leading to polarization P_{Mn} roughly aligned along the b -axis too. Based on this mechanism, a consensus on the ferroelectricity has been reached regarding the following several issues, while some issues remain unclear.^{51–64}

- (1) No matter magnetic or nonmagnetic R, all the multiferroic RMn_2O_5 members have their polarization along

Fig. 5. (Color online) The exchange striction induced local polarization P_{Mn} in RMn_2O_5 where the R spin if any is ignored. (a) The three ion blocks with roughly $\leftarrow\rightarrow$ ($\rightarrow\rightarrow\leftarrow$) spin chains and (b) the three ion blocks with roughly $\uparrow\uparrow$ ($\downarrow\downarrow$) spin chains. The solid (open) dots represent the ionic sites considering (ignoring) the exchange striction effect, with the Mn^{4+} ion as reference position in each block.

the b -axis without exception. A connection of this property with the spin structures allows an argument that the polarization is essentially generated by the collinear Mn moments while the noncollinear moments play only minor roles if any.

- (2) For all the cases, polarization P enters right below T_{N1} and exhibits anomalous variations at those magnetic ordering temperatures (e.g., at T_{N2} or T_{N3} for DyMn_2O_5), reflecting the intimate correlation between the spin structure and ionic displacement. This effect is particularly remarkable as R is magnetic, suggesting the substantial roles of the $4f$ electrons.
- (3) Regarding the responses of P and dielectric permeability (ϵ) to H , it has nearly no exception that remarkable $P(H)$ and $\epsilon(H)$ responses can be observed only in the low- T range, typically below ~ 20 K (below T_{N2} for DyMn_2O_5), at least for the cases under weak magnetic stimulation. Interestingly, one can find that the low- T response, if any, is strong in those members with strongly magnetic R. It implies once more the essential roles of the R moments in determining the multiferroicity of RMn_2O_5 , which is an issue less concerned so far but will be addressed in this mini-review.

Nevertheless, more than the reached consensus issues are those inconsistent and unclear issues. We highlight here several major but yet confusing points. For illustration convenience, one focuses on the $P(T)$ data, whose qualitative features are presented in Fig. 6 for a guide of eyes. It is noted that these data were measured by means of two different techniques, i.e., the Pyro method and Poling method,^{32,41} which will be discussed later. We highlight those unclear issues first.

- (1) Very different $P(T)$ dependences were identified for different RMn_2O_5 members, leaving puzzling on the complicated physics associated with ferroelectricity. These puzzles are more or less related to the techniques

Fig. 6. (Color online) Schematic traces of measured polarization $P(T)$ data along the b -axis for RMn_2O_5 : (a) $\text{R}=\text{Dy}$, Tb , and Ho ; (b) $\text{R}=\text{Dy}$; (c) $\text{R}=\text{Ho}$; (d) $\text{R}=\text{Er}$; (e) $\text{R}=\text{Gd}$; (f) $\text{R}=\text{Y}$; respectively.^{32,41,48,64} The methods (Pyro method and Poling method) for measuring the polarizations are marked aside. The magnetic field applied for the measurement in each case is labeled.

used for probing the $P(T)$ dependences. These distinct differences are shown in Fig. 6(a) for $\text{R}=\text{Ho}$, Dy , and Tb , where the three curves are taken from the data in Ref. 32 obtained using the Pyro method and those T_{N1} , T_{N2} , T_{N3} , and T_{Dy} are referred to DyMn_2O_5 . This was the first time to report the FIE-like behavior for DyMn_2O_5 , while the $P(T)$ dependences for HoMn_2O_5 and TbMn_2O_5 are unusual too.

- (2) Given the Poling method used for measurements,⁴¹ the $P(T)$ dependences of different members also show distinct differences, as shown in Figs. 6(b)–6(f). DyMn_2O_5 does show several clear anomalies at T_{N1} , T_{N2} , T_{N3} , and T_{Dy} .⁴¹ The polarization of HoMn_2O_5 becomes nearly disappeared below ~ 20 K,⁶⁸ while GdMn_2O_5 does not.⁴⁸ The most surprising is the positive-to-negative crossover of P at $T \sim 20$ K for YMn_2O_5 ,⁶⁴ noting that Y is non-magnetic.
- (3) While magnetoelectric response of RMn_2O_5 in terms of response of P to H is known to be weak, which is true in the high- T range, very remarkable responses are identified in the low- T range. A sufficiently high H can trigger off large low- T polarization for HoMn_2O_5 but suppress the low- T polarization for ErMn_2O_5 .⁶⁸

- (4) Continuous debate on the reason for nearly zero polarization in DyMn_2O_5 below T_{Dy} remains, so does it for HoMn_2O_5 below ~ 20 K.^{34,41} The “non-FE” phase below T_{Dy} for DyMn_2O_5 is called the X-phase. While Dy moment is big and believed to couple strongly with Mn moment, leading to destruction of the Mn spin exchange striction effect, no such phenomenon is observed in GdMn_2O_5 where the Gd – Mn coupling is also strong.⁴⁸

In short, a general scenario for ferroelectricity in RMn_2O_5 family seems unavailable at this stage, and a case-by-case checking on each member is needed.³⁹ In addition, the confusing issue of polarization measurement should be concerned since the two methods do prepare very different data. Finally, it should be mentioned that ferroelectricity in multiferroic oxides with strong electron correlations has both the electronic and ionic contributions.³¹ In some cases, one may be negligible with respect to the other, while the two contributions are comparable and even cancelled in other cases. The latter was predicted in HoMn_2O_5 by first principles calculations recently.⁶⁹ In the present study, this issue will not be addressed, but it can be a critical ingredient for the physics of ferroelectricity in multiferroics.

2.4. Comments on polarization measurements

As mentioned above, so far available data on polarization P as a function of T and H were measured mainly by means of two techniques. The first is the conventional pyroelectric current (Pyro) method, which has been extensively used in measuring $P(T, H)$ for multiferroics with small P (as small as $\sim 1.0 \mu\text{C}/\text{m}^2$) and low transition temperature. A schematic illustration of the Pyro method is given in Fig. 7(a). The sample covered with the top and bottom electrodes (e.g., Au) is submitted to electric poling under a field E_{pole} during the cooling run until $T = T_{\text{end}}$, and then electrically short-circuited for sufficient time at T_{end} . The T_{end} should be as low as possible and for typical case $T_{\text{end}} = 2$ K. The released current I_{pyro} from the sample under zero electric bias is probed during the subsequent warming run from T_{end} up to an assigned temperature T_0 . The $I_{\text{pyro}}(T)$ is integrated from T_0 down to T_{end} , generating polarization P as a function of T . The Pyro method is applicable only if P at T_{end} is nonzero, otherwise the electric poling down to T_{end} is almost ineffective even if P is nonzero at any T other than T_{end} .

The second is the Poling method, as drawn in Fig. 7(b). Instead of the separated poling and probing steps, here the poling and probing are carried out simultaneously. The sample under a poling field E_{pole} is gradually cooled down to T_{end} from a high T during which the total current I_{tot} across the sample is probed. This field is supposed to be small sufficiently so that the field induced leaky current I_{leaky} is much smaller than I_{pyro} over the whole T -range. A proper fitting procedure may allow an exclusion of I_{leaky} , leaving $I_{\text{pyro}}(T)$ and thus $P(T)$ to be evaluated. An immediate question is the validity of assumption $I_{\text{leaky}} \ll I_{\text{pyro}}$, which may

Fig. 7. (Color online) Schematic drawing of the (a) Pyro method and (b) Poling method for probing polarization P . In the Pyro method, the electrode-coated sample is pre-poled electrically from a sufficiently high T down to a given T_{end} at which the electric field E_{pole} is removed, followed by a sufficiently long time electric short-circuiting of the sample. Then the sample is slowly warmed up from T_{end} during which the pyroelectric current I_{pyro} released from the two electrodes is collected. In the Poling method, a low electric field E_{pole} is applied to the electrode-coated sample from a sufficiently high T , followed by a slow cooling of the sample during which the current passing across the sample is collected. Then an author-dependent procedure is taken to separate the leaky current and polarized current, so that polarization P can be obtained from the polarized current data.

not be always true for RMn_2O_5 , since a small E_{pole} implies an incomplete poling of the sample and thus the evaluated P may not be the saturated one. Furthermore, a separation of I_{pyro} from I_{tot} is anyway a matter if the dependences $I_{\text{leaky}}(T)$ and $I_{\text{pyro}}(T)$ are unknown. In fact, Higashiyama *et al.* discussed these issues in their work.⁴¹ The problem here for RMn_2O_5 is that this method may not identify correctly the FIE state.

Given the above discussion, we again come back to the Pyro method and have applied it for careful measurements of the released $I_{\text{pyro}}(T)$ data, noting that our Pyro technique is of precision as high as 0.05 pA. The details of experiments covered in this mini-review can be found in earlier literature, including samples synthesis, microstructural characterizations, and measurements on thermodynamic, magnetic, and electric properties, which will not be described here any more.

3. Results on DyMn_2O_5

Our data reported here are on well-prepared polycrystalline DyMn_2O_5 samples,³⁴ while data reported in literature on single crystals are taken for comparison. Since special emphasis will be oriented onto the Mn- and Dy-sites

substitutions, a preparation of whole set of single-crystal samples is challenging, and polycrystalline samples are much easier to access.

3.1. Magnetic and electric characterizations

The magnetic ordering sequence can be sensitively probed by specific heat data (C_p), while magnetization data are insensitive to the Mn spin ordering due to that the magnetic signals are mainly from the Dy moments much stronger than Mn moments. The T -normalized specific heat (C_p/T) and M as a function of T are plotted in Figs. 8(a) and 8(b), respectively. Earlier determined magnetic ordering points T_{N1} , T_{N2} , T_{N3} , and T_{Dy} are labeled and the assigned paraelectric (PE), ferroelectric (FE1, FE2, FE3), and X phase regions are marked too for reference, where differences of the three FE phases (FE1, FE2, FE3) remain unclear and the X phase was claimed to be non-FE.⁴¹ It is seen that the $C_p/T(T)$ curve shows clear anomalies at these points, while the $M(T)$ curve exhibits no anomaly except the broad peak at $\sim T_{Dy}$, reflecting gradual Dy spin ordering proceeding over the broad T -range in the low- T range (below T_{N2} or T_{N3}).

Fig. 8. (Color online) Measured T -normalized specific heat C_p/T (a), dc magnetization M under zero-field cooled (ZFC) and field cooling (FC) modes with measuring field of ~ 1000 Oe (b), dielectric permeability ε at 10 kHz under ac signal of 50 mV (c), and pyroelectric current I_{pyro} (d) for polycrystalline $DyMn_2O_5$, as a function of T , respectively. The measured polarizations as a function of T respectively taken from Ref. 32 using the Pyro method (e), from Ref. 41 using the P - E loop method (f), from Ref. 41 using the Poling method (g), and measured using the PUND method (h), respectively, are presented for comparison. The data in (e)–(g) were obtained for $DyMn_2O_5$ single crystal samples.

The magnetic ordering can also find sensitive response in dielectric permeability (ε), as shown in Fig. 8(c). The strongest anomaly at $\sim T_{N1}$ and broad peak at $\sim T_{N3}$ suggest the FE transitions. The transition at $\sim T_{N1}$ can be tentatively assigned as the consequence of the collinear Mn spin ordering and that at $\sim T_{N3}$ marks the induced Dy spin ordering in coherence with the Mn order. The anomalies at $\sim T_{N2}$ and $\sim T_{Dy}$ are relatively weak, indicating the minor variations of polarization P at these points. In particular, the small bump at $\sim T_{Dy}$ reflects the variation of P due to the Dy spin ordering driven by the Dy–Dy exchange interaction which is no longer negligible at low T .

The $I_{pyro}(T)$ is also sensitive to these spin orderings, and the data are plotted in Fig. 8(d). The one-to-one correspondence among the $I_{pyro}(T)$ peaks, the $\varepsilon(T)$ peaks, and the $C_p/T(T)$ anomalies is clearly identified, suggesting that the I_{pyro} signals are indeed from the variation of P on one hand and the pyroelectric current may be one of the most sensitive parameters to magnetic ordering in multiferroics on the other hand. Here, more significant are the negative peak at $\sim T_{N1}$

and the positive peaks at $\sim T_{N3}$ and T_{Dy} , immediately allowing an argument that $DyMn_2O_5$ may be a FIE rather than a FE.

In addition, the $P(T)$ data in earlier reports from various groups are reproduced for comparison purpose, as shown in Figs. 8(e)–8(h). The data in Fig. 8(e) are from Ref. 32 obtained using the Pyro method, showing the negative–positive crossover of P roughly at $\sim T_{N3}$, consistent with our results. It is noted that the assigned X phase has nonzero P , suggesting that it is FE. The $P(T)$ data in Figs. 8(f)–8(h) were obtained using the modified P - E loop method from Ref. 41, the Poling method from Ref. 41, and the so-called positive-up and negative-down (PUND) method⁶⁰ in our group on polycrystalline sample, respectively. For these cases, the measured P must be positive since the measurements were performed under an electric bias. Even though, one sees various features of these $P(T)$ curves around $\sim T_{N1}$, T_{N2} , T_{N3} , and T_{Dy} . These methods basically cannot identify the ferrielectricity if any, but the P in the low- T range is indeed small. In fact, no clear explanations for these features have been available so far. In short summary, there appears substantial difference between the results obtained using different methods, appealing for more careful handle of these issues. This is the reason for us to come back to the Pyro method which can more reliably and precisely probe the pyroelectric current without the electric bias induced leaky current and other activations.

Subsequently, the measured $I_{pyro}(T)$ data at three different warming rates (2, 4, 6 K/min) are plotted in Figs. 9(a)–9(c), given $E_{pole} = 10$ kV/cm. The three $I_{pyro}(T)$ curves almost overlap onto a master curve, demonstrating that the current is indeed from the pyroelectric effect. Furthermore, the $I_{pyro}(T)$ data given $E_{pole} = \pm 10$ kV/cm are plotted in Fig. 9(d) and a complete P reversal is demonstrated by the sign-opposite but magnitude-identical two curves, as further concurred by the as-evaluated $P(T)$ in Fig. 9(e), revealing the FIE characteristics. The negative–positive crossover occurs roughly at $T \sim T_{P=0} \sim T_{Dy}$, while this $T_{P=0}$ may vary upon the different measuring conditions. More detailed analysis on the data can be found in earlier report.³⁴

3.2. Model for ferrielectricity

Given the FIE characteristics, one is concerned with the underlying mechanism. Starting from the structural model shown in Fig. 4(b) for $DyMn_2O_5$, it is noted that the Dy spins are disordered until T_{N2} (or T_{N3}), below which the Dy spin ordering proceeds. Therefore, the spin configuration in Fig. 4(b) represents the state below T_{N2} (or T_{N3}). Without losing generality, we discuss the structural model in Fig. 4(b).

Consulting to the exchange striction scenario shown in Fig. 5 for RMn_2O_5 with nonmagnetic R ion, one can easily propose a similar scenario for $DyMn_2O_5$, taking the Mn^{4+} ions as reference points. The spin lattice projected on the ab -plane is presented in Fig. 10(a), while the three-spin blocks to

Fig. 9. (Color online) Measured pyroelectric current $I_{\text{pyro}}(T)$ curves at warming rate of 2 K/min (a), 4 K/min (b), 6 K/min (c), respectively, using the Pyro method with $E_{\text{pole}} = 10$ kV/cm. The $I_{\text{pyro}}(T)$ curves at 2 K/min with $E_{\text{pole}} = \pm 10$ kV/cm and the corresponding polarization $P(T)$ curves are presented in (d) and (e), respectively.

be considered are plotted in Figs. 10(b) and 10(c), respectively. In spite of the non-negligible noncollinear components, the three spins in each block are roughly parallel or antiparallel along the b -axis. For the $\text{Mn}^{3+}\text{--Mn}^{4+}\text{--Mn}^{3+}$ blocks, the two Mn^{3+} ions shift upward along the b -axis with respect to the central Mn^{4+} ion due to the exchange striction, leading to a local polarization P_{MM} . Contrary to this effect, the two Dy^{3+} ions in the $\text{Dy}^{3+}\text{--Mn}^{4+}\text{--Dy}^{3+}$ blocks shift downward along the b -axis, leading to a local polarization P_{DM} . These blocks organize themselves by alternative stacking and occupy the whole ab -plane, constituting two FE sublattices P_{MM} and P_{DM} , to be discussed in detail below.

What should be reminded here is that various RMn_2O_5 members may have different spin structures. For GdMn_2O_5 and most members other than DyMn_2O_5 , the Mn spins align majorly along the a -axis instead of the b -axis.⁴⁸ However, the exchange striction model remains similar and the P_{MM} still aligns along the b -axis. In addition, for DyMn_2O_5 here, the

Fig. 10. (Color online) (a) Spin structure of DyMn_2O_5 below T_{N2} (T_{N3}) projected in the ab plane, where the solid (open) dots represent the ionic sites considering (ignoring) the exchange striction effect, with the Mn^{4+} ions as the reference positions. The four types of three-ion blocks are plotted in (b) and (c) with the exchange striction induced local electric polarizations P_{MM} and P_{DM} . The ionic sizes are shown only for guide of eyes.

P_{DM} sublattice is not generated until $T < T_{N2}$ (or T_{N3}), implying that only the P_{MM} sublattice is available above T_{N2} (or T_{N3}), which disappears at $\sim T_{N1}$.

We discuss the details of this ferroelectricity. Upon decreasing T from T_{N0} , the negative P appears at $\sim T_{N1}$ and its magnitude increases rapidly, as shown in Fig. 11, curve (a), implying that the P_{MM} sublattice aligns in opposite to the poling field (E_{pole}). The P_{DM} sublattice, opposite to the P_{MM} sublattice, enters at $T \sim T_{N2}$ (or T_{N3}) and the P_{DM} magnitude increases gradually until $\sim T_{P=0}$ below which $P_{\text{DM}} \geq |P_{\text{MM}}|$, enabling the crossover from the $P < 0$ to the $P > 0$ (Fig. 11, curve (a)).

In addition, for those RMn_2O_5 with nonmagnetic R, the magnetic ordering is far from complicated as that in DyMn_2O_5 , implying that the latter is more or less related to the Dy–Mn coupling.^{43–48} As the zero-order approximation, one may assume that the P_{MM} sublattice is irrelevant with the Dy–Mn coupling which is actually not true to some extent, and thus P_{MM} as a function of T reaches smoothly the

Fig. 11. (Color online) The proposed FIE lattice model for $DyMn_2O_5$. The measured $P(T)$ curve as well as the speculative $P_{MM}(T)$ and $P_{DM}(T)$ curves are plotted together. The proposed FIE lattice, P_{DM} sublattices and P_{MM} sublattices at $T < T_{Dy}$ and $T < T_{N1}$ are plotted in (a)–(e), respectively, only for guide of eyes.

saturated value. This $P_{MM}(T)$ dependence is shown in Fig. 11, curve (b) (dashed blue line). Consequently, the as-extracted $P_{DM}(T)$ curve is plotted in Fig. 11, curve (c). The minor features at $\sim T_{N2}$, T_{N3} , and T_{Dy} , are all due to the Dy–Mn coupling induced magnetic orderings. To this stage, the P_{MM} and P_{DM} as a function of T respectively are intentionally separated based on the several assumptions.

In correspondence to the $P_{MM}(T)$ and $P_{DM}(T)$ curves, the two FE sublattices below T_{Dy} and T_{N1} are schematically shown in Figs. 11(b), 11(c) and 11(d), 11(e), respectively, with the FIE lattice shown in Fig. 11(a). The observed $P(T)$ dependence is reasonably explained by the proposed FIE model at least qualitatively, although it may be oversimplified and many details associated with the magnetic ordering are ignored, which is questionable but the FIE scenario remains unaffected.

3.3. Magnetoelectric effect

As mentioned in Sec. 2, the $4f$ spin order in oxides is usually fragile against stimuli and the magnetic field driven re-orientation of $4f$ spins can be realized at a field far lower than ~ 1.0 T. In $DyMn_2O_5$, the Mn spin order is sufficiently high against magnetic field above ~ 10 T.^{35–42} In this case, one has reason to expect that the Dy spin order stability can be enhanced significantly by the Dy–Mn coupling, up to several Tesla. Therefore, the Dy spin re-orientation can be illustrated in Fig. 12(a), where an $H//a$ -axis drives the Dy spins along the b -axis to re-orient and thus disables the exchange

Fig. 12. (Color online) The proposed three-ion spin blocks under $H = 0$ and $H > 0$ (e.g., 10 T) are plotted in (a). The measured $P(T)$ curves under various H are presented in (b). As an example, the $P_{MM}(T)$ and $P_{DM}(T)$ curves together with the $P(T)$ curves under $H = 0$ and $H > 0$ (e.g., 10 T) are plotted in (c), where $P_{MM}(T)$ is assumed to be robust against H . The FIE lattice is given in (d), and the corresponding two sublattices under $H = 0$ and $H > 0$ are shown in (e) and (f) for illustrating the consequence of applying magnetic field.

striction induced Dy ions' shift along the b -axis, i.e., melts away the P_{DM} sublattice, resulting in significant magnetoelectric effect.

Our experiments did confirm this prediction. The sample was first electrically poled down to $T \sim 6$ K, and the poling was removed, followed by applying a given H . After the sample was sufficiently short-circuited, the pyroelectric current under the given H was collected during the warming process. The measured $P(T)$ curves under a series of H are plotted in Fig. 12(b). The magnetic field does suppress the positive P in the low T -range, leading to the negative P over the whole T -range at $H > 3.0$ T. This effect is qualitatively drawn in Fig. 12(c) where the vertical solid olive arrows indicate the H -induced suppression of P_{DM} and then P , while P_{MM} remains little suppressed. The responses of the two sublattices to H are schematically drawn in Figs. 12(d)–12(f).

3.4. Discussion

The proposed FIE model seems to reasonably explain all the observed phenomena associated with the unusual $P(T)$ and $P(H)$ dependences in DyMn_2O_5 , although those features at T_{N2} , T_{N3} , and T_{Dy} remains unclear yet. Nevertheless, additional more convincing evidence concurring with this model is required, since a connection of the polarization crossover at $T_{P=0}$ with the FIE model is far from sufficient.

The magnetoelectric effect reported above suggests an alternative strategy. While the suppression of the collinear Dy spin order contributing to the P_{DM} can be realized by applying a magnetic field, it would be done too by nonmagnetic substitution of Dy, which can definitely inactivate the exchange striction in the $\text{Dy}(\text{R})^{3+}\text{--Mn}^{4+}\text{--Dy}(\text{R})^{3+}$ blocks and thus remove gradually the P_{DM} sublattice with increasing substitution level. Stimulated by this approach, one can consider a nonmagnetic substitution of Mn^{3+} too, which can surely remove gradually the P_{MM} sublattice. Given a proper

design of the substitution experiments, one may reach a status in which one sublattice is gradually removed while the other remains less affected so that an FIE–FE transition is expected at certain substitution level. In addition, for the latter case, a critical issue is that the Mn-site substitution has to exclude the replacement of Mn^{4+} ions since the two sublattices would be removed simultaneously of the Mn^{4+} site is occupied with nonmagnetic ion.

The above discussion can be highlighted in Fig. 13, where the double-line arrows denote the P_{MM} and P_{DM} , respectively and their coarseness scales the magnitude. The exchange striction modes for P_{MM} and P_{DM} in DyMn_2O_5 are shown in Fig. 13(a), while the consequences of nonmagnetic substitutions at Mn^{4+} -site, Mn^{3+} -site, and Dy^{3+} -site, respectively, are shown in Figs. 13(c)–13(e). The substitution at either Mn^{3+} site or Dy^{3+} site is clearly illustrated. For comparison, the consequence of imposing a magnetic field is re-given in Fig. 13(b). A realization of these roadmaps relies on several pre-requisites, while a reliable check of the FIE model will be questioned otherwise. First, the substitution should distort the lattice as weakly as possible so that the exchange interactions remain less perturbed. Second, the valence state should be maintained to avoid any charge doping. Third, the correct site occupation is critical since DyMn_2O_5 is an occupation-ordered compound.

Fig. 13. (Color online) The proposed substitution strategy for DyMn_2O_5 , as illustrated by the three-ion spin blocks. The solid (open) dots represent the ionic sites considering (ignoring) the exchange striction effect, with the Mn^{4+} ions as the reference positions. The spin structures in these blocks for (a) $x = 0$ and $H = 0$, (b) $x = 0$ and $H > 0$ (e.g., 5–10 T), (c) Al substitution of Mn^{4+} and $H = 0$, (d) Al substitution of Mn^{3+} and $H = 0$, and (e) Y substitution of Dy^{3+} and $H = 0$, are schematically drawn, respectively. The blue $\downarrow$ and red $\uparrow$ arrows denote the P_{MM} and P_{DM} for these cases, with the coarseness representing the Magnitudes.

4. The Al Substitution of Mn: Proof Test I

4.1. Structural distortion, chemical valence states, and magnetism

As the one side of the evidence coin for the FIE model, the Mn^{3+} -site substitution by Al^{3+} is considered.⁴⁹ It is noted that Al^{3+} is only slightly smaller than $\text{Mn}^{3+}/\text{Mn}^{4+}$ and the electronegativity values of Mn and Al are similar too. While details of the polycrystalline $\text{DyMn}_{2-x}\text{Al}_x\text{O}_5$ sintering were described previously, we present in Fig. 14(a) the room temperature $\theta - 2\theta$ X-ray diffraction patterns for a series of samples. All the reflections can be indexed by the standard database of DyMn_2O_5 , and peak shifting towards the high-angle side is observed as seen in the insert of Fig. 14(b). Substitution up to $x \sim 0.20$ does not change the lattice symmetry and induce any minor impurity phase. As an example, the Rietveld refining of the data for sample $x \sim 0.04$ is as shown in Fig. 14(b), with the refining reliability as high as $R_{\text{wp}} \sim 4.48\%$.

The evaluated lattice unit volume V as a function of x plotted in Fig. 14(c) shows a linearly decreasing dependence consistent with the Vegard's law, implying the favored substitution of Mn^{3+} ions by Al^{3+} ions. Additional careful checking of the valence states of Mn using the XPS determination upon the substitution is performed, revealing no trace of intensity from Mn^{5+} or Mn^{2+} within the apparatus resolution. Since the binding energies for the $\text{Mn}^{3+}2p_{1/2}/\text{Mn}^{4+}2p_{1/2}$ and $\text{Mn}^{3+}2p_{3/2}/\text{Mn}^{4+}2p_{3/2}$ are close

Fig. 14. (Color online) The consequences of Al substitution of Mn: (a) measured XRD θ - 2θ spectra for a series of $\text{DyMn}_{2-x}\text{Al}_x/2\text{O}_5$ samples; (b) the Rietveld refined data for $x=0.04$ and the insert shows the local reflections of three samples $x=0.00, 0.10$, and 0.16 ; (c) the fitted unit volume V as a function of x with uncertainties; (d) measured XPS spectrum for sample $x=0.0$ as an example, where the Mn^{3+} and Mn^{4+} core energy levels are labeled and the measured peaks are decomposed as the superimposition of the contributions from the Mn^{3+} and Mn^{4+} excitations, respectively; (e) the local peaks around 642 eV corresponding to the Mn ($2p_{3/2}$) core level. The peak shifting toward the high energy with increasing x is shown, indicating the increasing $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio; (f) measured M for samples $x=0.00, 0.04, 0.08$, and 0.20 , as a function of T , respectively.

to each other, a highly reliable fitting of the XPS peaks associated with Mn is required. Figure 14(d) shows this fitting for sample $x=0.0$, and the $\text{Mn}^{3+}/\text{Mn}^{4+} \sim 1.0$ is suggested by comparing the shadow area below peaks $\text{Mn}^{3+}2p_{1/3}$ and $\text{Mn}^{3+}2p_{3/2}$ with that below peaks $\text{Mn}^{4+}2p_{1/3}$ and $\text{Mn}^{4+}2p_{3/2}$. The same fitting procedure is applied to other samples and the fitted $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratios are consistent with the nominal ones with an uncertainty of $\sim 10\%$, suggesting that the Al^{3+} ions do occupy the Mn^{3+} sites rather than the Mn^{4+} ones. The amplified Mn $2p_{3/2}$ peaks for several samples are summarized in Fig. 14(e). The gradual peak shifting towards the high-energy side with increasing x is concededly identified, indicating more Mn^{4+} ions than Mn^{3+} ions in samples with higher x and confirming again that the Al^{3+} ions substitute the Mn^{3+} ions rather than Mn^{4+} ions.⁴⁹

Although the possibility for minor occupation of the Mn^{4+} sites by Al^{3+} for higher x cases cannot be excluded, the Al^{3+} -occupation of Mn^{3+} is dominant. By the way, the magnetization response to the substitution can be used to measure the impact on the Dy–Dy exchange interaction, as shown in Fig. 4(f) for several samples. The T_{Dy} is remarkably suppressed with increasing x down to ~ 2 K at $x=0.20$.

4.2. Suppression of P_{MM} sublattice and polarization reversal

The measured $I_{\text{pyro}}(T)$ and $P(T)$ curves for a series of samples are presented in Figs. 15(a)–15(g), with the $I_{\text{pyro}}(T)$ curve for $x=0.0$ in each plot for comparison. The Al-substitution leads to several interesting features. First, the negative I_{pyro} peak right below T_{N1} is suppressed and downshifted with increasing x , indicating the suppression of P_{MM} , suggesting the damage of the exchange striction of the $\text{Mn}^{3+}\text{--Mn}^{4+}\text{--Mn}^{3+}$ blocks. Second, the positive I_{pyro} peak around T_{Dy} at $x=0.0$ indicated by the arrow in Fig. 15(a) becomes weak at $x=0.02$ and disappears at $x=0.04$ and higher. Third, the broad current bump around T_{N3} at $x=0.0$ is evolved into a sharp peak locating in-between T_{N2} and T_{N3} for low x ($x < 0.08$), increasing in height and shifting rightward, in contrast to the variations of the negative peak right below $\sim T_{N1}$. Eventually, the two peaks meet and annihilate with each other. The last ‘moment’ of the two peak

Fig. 15. (Color online) Measured pyroelectric current $I_{\text{pyro}}(T)$ and evaluated polarization $P(T)$ for a series of samples in (a)–(g), where the $I_{\text{pyro}}(T)$ data for sample $x=0.0$ are inserted for reference. The P data at several T as a function of x are plotted in (h).

annihilation is at $x \sim 0.08$. The two peaks correspond respectively to the polarization generation at the higher- T side and disappearance at the lower- T side, and their simultaneous evolutions illustrates how P_{MM} is suppressed upon the substitution.

The Al-substitution certainly damages the P_{DM} too because the spin structure is gradually diluted. The measured P ($=|P_{DM}| - |P_{MM}|$) in the low- T range does not show substantial increase with the gradual suppression of P_{MM} , implying the deterioration of P_{DM} with increasing x . Nevertheless, P_{DM} is more robust than P_{MM} against the substitution, suggesting that the Al-substitution does not change much the Dy³⁺–Mn⁴⁺ coupling. Furthermore, the Al-substitution induced suppression of P_{MM} certainly leads to a negative–positive crossover of P , illustrated by the $P(x)$ curves in Fig. 15(h). Reasonably, the $P(x)$ at $T \sim 2$ K is always positive due to $|P_{DM}| > |P_{MM}|$ but the $P(x)$ curves at both $T \sim 15$ K and $\sim T_{N3}$ change their signs at certain x ($x \sim 0.04$ and 0.065).

5. The Y Substitution of Dy: Proof Test II

As the other side of the evidence coin for the FIE model, the Y³⁺-substitution of Dy³⁺ is a proper approach.⁵⁰ The Y³⁺ ionic radius (~ 0.090 nm) is slightly smaller than Dy³⁺ (~ 0.091 nm), and the Y substitution allows the induced lattice distortion as small as possible. Nevertheless, the Dy–Mn coupling and Dy–Dy interactions can be substantially manipulated by the substitution, and the direct consequence is gradual suppression of the P_{DM} sublattice but the P_{MM} sublattice remains less perturbed.

5.1. Structural, specific heat, and magnetization

The crystallinity and lattice distortion for several samples were checked by the XRD θ - 2θ spectra in Fig. 16(a). The substitution up to $x \sim 0.20$ does not change the lattice symmetry and all the reflections can be indexed. The gradual peak shifting with increasing x is shown in the inset of Fig. 16(c), with the data refinement for sample $x = 0.10$ shown in Fig. 16(b). The evaluated unit lattice volume V as a function of x is presented in Fig. 16(c), following the Vegard's law, suggesting the Y substitution of Dy rather than Mn.

The specific heat $C_P(T)$ and magnetization $M(T)$ data are presented in Fig. 16(d). For $x = 0$, the $C_P(T)$ data feature the spin orderings at T_{N1} , T_{N2} , T_{N3} , and T_{Dy} , respectively. The positions of T_{N1} and T_{N2} do not depend on x , but the transition at T_{N3} becomes vague and the T_{Dy} is down-shifted remarkably, suggesting the instability of the Dy spin order and the weakened Dy–Mn coupling, obviously due to the Dy network dilution by the substitution. The $M(T)$ curves for these samples are plotted in Fig. 16(e), and again no identifiable spin ordering features can be observed except the shifting of the broad peak at T_{Dy} associated with the Dy spin ordering. A substitution up to $x = 0.20$ does not yet collapse

Fig. 16. (Color online) The consequences of Al substitution of Mn: (a) measured XRD θ - 2θ spectra for a series of samples; (b) the Rietveld refined data for sample $x = 0.10$; (c) the fitted unit volume V as a function of x , and the insert shows the local reflections around $2\theta \sim 29^\circ$ for samples $x = 0, 0.10$, and 0.20 ; (d) measured specific heat C_P/T and (e) measured M for several samples, as a function of T , respectively.

the Dy spin ordering, implying that the Dy–Mn coupling in DyMn_2O_5 is strong enough. However, the P_{DM} sublattice will most likely be destabilized in prior to the disordering of the Dy spins, since the ferroelectricity is anyhow a second-order effect with respect to the spin order and the inter-dipole interactions must be much weaker than the exchange interactions.

5.2. Modulation of electric polarization

The measured $P(T)$ (blue curves) and $I_{\text{pyro}}(T)$ (red curves) for several samples are plotted in Figs. 17(a) to 17(f), respectively,⁵⁰ with several clear features in terms of ferroelectricity. First, the sharp I_{pyro} peaks at $\sim T_{Dy}$ and $\sim T_{N1}$ for $x = 0$ become gradually suppressed as $x > 0.05$ until $x = x_c \sim 0.13$ where the peak reversal occurs, signing the polarization reversal. Second, the magnitude of P over the whole T -range decays gradually until $x = x_c \sim 0.13$, and then increases gradually. At $x \sim 0.15$ and ~ 0.20 , the $P(T)$ data no longer exhibit the FIE-like behavior but more FE-like, regardless the anomalous features around T_{N3} . The substitution induced P reversal can be more clearly identified by plotting the $P(x)$ data at several T , as shown in Fig. 17(g). The reversal at $T \sim 15$ K and T_{N3} occurs round $x_c \sim 0.13$, while the $P(x)$ at $T \sim 2$ K, which is always positive, exhibits a valley around $x_c \sim 0.13$ too.

Fig. 17. (Color online) Measured pyroelectric current $I_{\text{pyro}}(T)$ and evaluated polarization $P(T)$ for a series of samples (a)–(f), where the $I_{\text{pyro}}(T)$ data for sample $x = 0$ are inserted for reference. The P data at several T as a function of x are plotted in (g).

5.3. Domain model for polarization modulation

The $P(T, x)$ data presented above do show substantial variations upon the Y substitution, including the polarization reversal around x_c . However, a connection between the observed behaviors and the proposed FIE model is not straightforward, appealing for a bridge of the polarization reversal with the sublattice instability. It is noted that all the samples were electrically pre-poled down to $T_{\text{end}} \sim 2 \text{ K}$ in prior to the pyroelectric current collection. This implies that the P_{DM} sublattice aligns along E_{pole} (upward), opposite to the P_{MM} sublattice. Nevertheless, the two sublattices each consist of mesoscopic domains, i.e., the P_{DM} -domains and P_{MM} -domains. The whole FIE lattice contains overlapped P_{DM} -domains and P_{MM} -domains which are inter-coupled and antiparallel. The random Y-substitution allows those P_{DM} -domains with higher Y concentration to be unstable and replaced by PE phase, while the P_{MM} -domains remain less perturbed. Here two specific temperatures are chosen for illustrating the domain evolutions associated with the polarization modulation.

First, at a low- T ($\sim T_{Dy}$) where $P = P_{DM} + P_{MM} > 0$ (Fig. 18).⁵⁰ Each domain is denoted by one square dot, and the aligned squares constitute the P_{DM} sublattice (top row) and P_{MM} sublattice (bottom row). The Y substitution damages some P_{DM} domains so that the local $P_{DM} = 0$ (white squares) while the P_{MM} -domains may be reversed by E_{pole} , as labeled by the orange squares, and thus the local $P_{MM} > 0$. The averaged P_{DM} and P_{MM} over the whole lattice decrease slightly with increasing x . At $x \sim x_c$, all the P_{MM} -domains with $P_{MM} < 0$ are reversed by E_{pole} and those P_{DM} -domains will be reversed too to follow the antiparallel alignment with the corresponding P_{MM} -domains, due to the ferroelectricity nature. In consequence, the $P(x)$ remains positive but a minimal will appear at $\sim x_c$. The whole sequence is schematically drawn in Figs. 18(a)–18(e), consistent with the measured $P(x)$ data at $T \sim 2 \text{ K}$ in Fig. 18(g).

Similar analysis can be applied to the cases at higher T where P is negative. At this temperature, sample $x = 0$ offers $|P_{DM}| \ll |P_{MM}|$ although $|P_{DM}| > |P_{MM}|$ at low T . The $P_{DM}(T)$ will decay more rapidly than the $P_{MM}(T)$ and eventually becomes disappeared respectively at $\sim T_{N3}$ and $\sim T_{N1}$. Since

Fig. 18. (Color online) Schematic drawing of domain structure evolution of the P_{DM} sublattice (top row) with the P_{DM} -domains (square dots) and P_{MM} sublattice (bottom row) with the P_{MM} -domains (square dots) in the FIE domain structure for a series of samples from $x = 0.00$ to $x \sim 0.20$, at low T ($\sim T_{Dy}$). The solid and dashed arrows aside each sublattice represent the polarizations P_{DM} and P_{MM} of the two sublattices under electric field $E = 0$ and $E > 0$, respectively. The proposed P_{DM} and P_{MM} , and the measured P , as a function of x , are plotted in (f) for the guide of eyes.

the samples were pre-poled down to the lowest T (~ 2 K), the P_{DM} -domains (red squares) still align along E_{pole} at $x = 0$. In this case, the evolution of the domain structure with x is similar to the low- T cases described above, but the $P(x)$ curve reverses its sign at $\sim x_c$. This explains reasonably the observed crossover of the $P(T)$ curves at $T \sim 15$ K and $\sim T_{N3}$, as shown in Fig. 17(g).

6. Conclusion and Perspectives

6.1. Conclusion

Motivated by the introduction in Sec. 1, possible ferrielectricity in DyMn_2O_5 has been thoroughly discussed in Sec. 2 and then demonstrated by a series of experiments in the framework of the FIE lattice consisting of two FE sublattices in Secs. 3–5, respectively. To the end stage of this mini-review, we can reach the following points of conclusion.^{34,49,50}

- (1) The clear sign-reversal of polarization as a function of T has been confirmed by highly reliable pyroelectric current data probed using the Pyro method. Along this line, an FIE behavior of DyMn_2O_5 has been identified.
- (2) Based on available data on the lattice and spin structures of DyMn_2O_5 , an FIE model has been proposed, which consists of two antiparallel FE sublattices. One sublattice is composed of ordered local P_{MM} generated from the $\text{Mn}^{3+}\text{--Mn}^{4+}\text{--Mn}^{3+}$ blocks with the major $\uparrow\uparrow\downarrow$ spin components along the b -axis or a -axis, and the other is occupied with ordered local P_{DM} generated from the $\text{Dy}^{3+}\text{--Mn}^{4+}\text{--Dy}^{3+}$ blocks with the major $\uparrow\uparrow\downarrow$ spin components along the b -axis or a -axis. Both sublattices are generated via the exchange striction mechanism and their total polarizations are aligned along the b -axis.
- (3) The FIE lattice model has been confirmed by the nonmagnetic substitution of Mn^{3+} by Al^{3+} , which suppresses gradually the P_{MM} sublattice and thus drives the polarization reversal at certain substitution level.
- (4) The nonmagnetic Y^{3+} substitution of Dy^{3+} has been performed also to check the FIE lattice model, which dilutes gradually the P_{DM} sublattice. This dilution also enables the reversal of the P_{MM} domains and thus a polarization reversal at certain substitution level has been revealed too.

The conclusion is ended with the two FE phase diagrams on the (x, T) plane for the Mn^{3+} -site substitution and Dy^{3+} -site substitution, as shown in Figs. 19(a) and 19(b), respectively. One can see that the phase plane for both cases can be divided into four regions: the PE region and regions I, II, and III. The major characters in terms of polarizations P_{MM} , P_{DM} , and $P = P_{MM} + P_{DM}$, are clearly marked in these regions, not needing any additional description. One may address that such a polarization reversal in multiferroics with magnetically induced ferroelectricity has rarely been observed so far and

Fig. 19. (Color online) Evaluated ferroelectric phase diagrams on the (x, T) plane for the Al-substitution of Mn (a) and Y substitution of Dy (b). The whole phase plane are divided into four regions for each case, and the properties of the two sublattices P_{DM} and P_{MM} are labeled, while the polarization reversals are indicated by the solid double head arrows.

this is the first experimental evidence for the polarization reversal by chemical substitution.

6.2. Perspectives

The complexity of multiferroic physics in DyMn_2O_5 , which accommodates both $4f$ spins and $3d$ spins, has been demonstrated in this work in addition to earlier reports.^{35–42} We present a simple framework for this physics in terms of ferrielectricity, which allows opportunities for any potential manipulations of FE polarization in RMn_2O_5 . Nevertheless, at least several major issues remain not yet well touched so far and some of them closely related to the present work can be outlined:

- (1) The contribution of the noncollinear components of Mn and Dy spins, if any, is entirely out of consideration in the present model. This contribution remains to be a debated issue for long time.
- (2) The spin structure variations and magnetic transitions around T_{N2} , T_{N3} , and T_{Dy} are not well understood and in fact entirely ignored in the FIE lattice model here. All of our discussions start from the lattice and spin structures shown in Figs. 4 and 10, but these structures may not be applicable above T_{N2} (T_{N3}). Uncertainties in terms of the

spin structure and microscopic mechanism for ferroelectricity cannot be excluded.

- (3) The role of the Dy–Dy ($4f$ – $4f$) interaction has not yet been clearly identified in the present work, which may be non-negligible with respect to the Dy–Mn and Mn–Mn interactions. Usually, independent Dy spin ordering due to the Dy–Dy interaction is possible in spite of appearance at extremely low T . This effect is not considered in the present work.

Even though, it should be mentioned that the proposed ferrielectric model and the simple substitution strategy in this work enable our understanding of the physics of multiferroicity in a quite simplified framework. This framework seems to grasp the core of the physics. Its significance may be embarrassed from several aspects highlighted below:

- (1) The RMn_2O_5 members with $\text{R}=\text{Gd}$, Tb , Ho , and Er , have similar spin structure as DyMn_2O_5 . The present model would be of generality to some extent and can be used to explain most of the multiferroic behaviors observed in these materials.
- (2) Some additional ingredients of physics should be taken into account. First, the R ionic size variation is critical for the lattice distortion and thus the delicate balance of the multifold interactions. Second, the $4f$ – $3d$ coupling between R and Mn ions is different for different members. The Gd – Mn , Dy – Mn , and Ho – Mn couplings are strong while the Tb – Mn and Er – Mn couplings are relatively weak. For the latter cases, the polarization arisen from the R – Mn coupling may be small and thus the underlying physics becomes different.
- (3) Possible application of ferrielectricity can be recognized. Usually, ferrielectricity represents a property much less favorable than ferroelectricity for practical applications. Nevertheless, the present work suggests that a proper chemical substitution may make a ferrielectricity–ferroelectricity transition possible. In other words, by a critical substitution, the FE states as low-energy excitations of the FIE ground states may be reached, triggering possible multi-state memories applications. A similar example in BaFe_2Se_3 was recently reported,⁷⁰ where two FIE states and two slightly metastable FE states can be easily inter-switched.

Finally but not the least, one is reminded of a recent work on ferroelectricity in RMn_2O_5 , which claims the room temperature ferroelectricity associated with the lattice symmetry breaking.⁷¹ The magnetically induced polarization below T_{N1} does add a component to the existing polarization. This issue, critical if true, deserves for critical checking.

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