The multiferroic phases of Eu$_{1-x}$Y$_x$MnO$_3$

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We report on structural, magnetic, dielectric, and thermodynamic properties of Eu$_{1-x}$Y$_x$MnO$_3$ for Y doping levels 0 $\leq$ $x$ $<$ 1. This system resembles the multiferroic perovskite manganites RMnO$_3$ (with R = Gd, Dy, Tb) but without the interference of magnetic contributions of the 4f-ions. In addition, it offers the possibility to continuously tune the influence of the A-site ionic radii. For small concentrations $x \leq 0.1$ we find a canted antiferromagnetic and paraelectric groundstate. For higher concentrations $x \geq 0.3$ ferroelectric polarization coexists with the features of a long wavelength incommensurate spiral magnetic phase analogous to the observations in TbMnO$_3$. In the intermediate concentration range around $x \approx 0.2$ a multiferroic scenario is realized combining weak ferroelectricity and weak ferromagnetism, presumably due to a canted spiral magnetic structure.

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I. INTRODUCTION

In recent years multiferroics have attracted an increasing scientific and technological interest in the large community working on functional transition-metal compounds. Within this rare class of materials magnetic order coexists with long range polar order and both order-parameters are strongly coupled. Prominent examples for such multiferroics may be found among Cr-based spinels$^{22}$, the kagomé staircase compound Ni$_3$V$_2$O$_8$, rare earth manganites like hexagonal YMnO$_3$ and HoMnO$_3$, orthorhombic TbMn$_2$O$_7$, or finally perovskites like TbMnO$_3$.\footnote{In recent years multiferroics have attracted an increasing scientific and technological interest in the large community working on functional transition-metal compounds. Within this rare class of materials magnetic order coexists with long range polar order and both order-parameters are strongly coupled. Prominent examples for such multiferroics may be found among Cr-based spinels$^{22}$, the kagomé staircase compound Ni$_3$V$_2$O$_8$, rare earth manganites like hexagonal YMnO$_3$ and HoMnO$_3$, orthorhombic TbMn$_2$O$_7$, or finally perovskites like TbMnO$_3$.}$^{23}$

In this latter class of heavy rare earth compounds RMnO$_3$ (R = Gd, Tb, Dy$^{24,10}$) finite ferroelectric polarization is induced due to the partial frustration and corresponding long range modulation of the magnetic structure. The importance of the Dzyaloshinskii-Moriya interaction for the occurrence of ferroelectricity in non-collinear magnets has been pointed out recently$^{11,12,13}$.$^{24}$ Starting from the lanthanide manganite with the perovskite tolerance factor close to unity, the substitution of La at the A-sites by rare-earth elements with smaller ionic radii (from Pr to Ho) leads to a successive increase of the orthorhombic distortion, accompanied by a decrease of the Mn-O-Mn bond angles and an increase of the buckling and tilting angles of the MnO$_6$-octahedra, respectively.$^{25}$ Using high-resolution x-ray diffraction and the refinement of the oxygen positions, this angle has recently been determined for the complete series of pure rare-earth manganites.$^{26}$ Equivalent results can be obtained when continuously replacing La$^{3+}$ by smaller ions like in La$_{1-x}$Gd$_x$MnO$_3$.$^{27}$ The enhanced tilting of the MnO$_6$-octahedra leads to an increasing importance of antiferromagnetic (AFM) next-nearest neighbor interactions competing with the nearest neighbor superexchange within the ferromagnetic (FM) ab-planes of the A-type AFM structure. This weakening of the effective magnetic interaction promotes a tendency towards frustration and complex spin-states.$^{28}$ Hence, the transition temperature into the $A$-type AFM phase is not only reduced, but for the heavy rare earth compounds with smaller ionic radii an incommensurate magnetic structure is established for temperatures below $T_N \approx 50$ K. Within these incommensurate magnetic phases, magnetoelectric coupling via long-range modulation of the magnetic structure leads to the loss of inversion symmetry and the onset of ferroelectric polarization.$^{16}$ The onset of ferroelectricity is connected with the change of the magnetic structure from a sinusoidal to a helicoidal modulation.$^{16,17}$ Very recently excitations of the multiferroic state have been observed experimentally.$^{18}$ These new collective modes, which are responsible for ferroelectricity, but are of magnetic origin, have also been described theoretically.$^{19}$ The existence of a ferroelectric lattice distortion is especially remarkable due to the fact that these compounds possess a quite robust Jahn-Teller (JT) type orbital order, which sets in at temperatures well above 1000 K. From a principal point of view Jahn-Teller active orbital degrees of freedom are the "natural enemy" of off-center ferroelectric distortions.$^{20}$ Undistorted orbital electron-density distributions are point-symmetric carrying no electric dipole moment. Hence, if the lattice is able to relax into a lower symmetry via a Jahn-Teller distortion this transition is expected not to be dipolar. In this sense the ferroelectricity in the heavy rare earth manganites exists not due to, but despite the superimposed orbital order and comparing the relevant energy scales it has to be regarded as a second order effect. Therefore the ferroelectric distortion is rather weak and so far could not be proven directly using high-resolution neutron or x-ray diffraction techniques. However, the onset of ferroelectricity was documented via pyroelectric measurements and is connected to a distinct anomaly in the real part of the dielectric permittivity$^{10}$ and clear features in the anisotropic thermal expansion.$^{21}$ This underlines that the ferroelectric...
distortions are driven by frustrated magnetic interactions via local exchange-striction.

However, within the scenario of partially frustrated Mn-spins the role of the magnetic A-sites is not completely clear so far. Generally, the moments of the rare-earth ions are polarized due to the coupling with the Mn subsystem resulting in a noticeable anisotropic contribution to the low-temperature magnetic and thermodynamic properties of the manganites as e.g. recently studied in detail for the systems PrMnO$_3$ and NdMnO$_3$. As analyzed for the case of TbMnO$_3$ by Quezel et al., the overall magnetic structure in the rare-earth manganites can be rather complex. They found a sine-wave ordering of the Mn$^{3+}$ moments with the ordering wave vector along the b-axis below 40 K and a short-range incommensurate ordering of the Tb$^{3+}$ moments with a different wave vector below 7 K. At the ordering temperature of the rare-earth moments significant anomalies in the dielectric constant can be found denoting the possible influence of the magnetic A-sites.

In this paper we report structural, magnetic susceptibility, magnetization, and specific heat measurements for single and poly-crystalline Eu$_{1-x}$Y$_x$MnO$_3$. Our focus is directed towards the isovalent doping of the trivalent A-site in RMnO$_3$, with R denoting elements Eu$^{3+}$ (4f$^0$) or Y$^{3+}$ ([Kr]). This allows for a systematic variation of the ionic radii and possibly of the Mn-O-Mn angle, which we relate to the development of the complex magnetic groundstates and ferroelectric phases analogous to the pure rare-earth compounds RMnO$_3$ with R = Gd, Dy, Tb. The system (Eu:Y)MnO$_3$ offers the possibility to continuously control the A-site volume of the orbitally ordered perovskite structure and thus to tune the corresponding multiferroic phases without the additional influence of a magnetic rare earth moment. A further aspect of the system Eu$_{1-x}$Y$_x$MnO$_3$ is the robustness of long-range polar order against the influence of perfectly structural A-site disorder.

II. EXPERIMENTAL DETAILS

Eu$_{1-x}$Y$_x$MnO$_3$ single crystals were grown in Ar flow by a floating-zone method with radiation heating for Y-concentrations $x = 0, 0.1, 0.2, 0.3$, and 0.5. Additional concentrations have been prepared as poly-crystals for higher concentrations up to $x = 0.95$ using conventional solid state reaction methods. Powder-diffraction experiments were performed on powder of crushed single and poly-crystals at room temperature with a STOE diffractometer utilizing Cu-K$_\alpha$ radiation with a wave length $\lambda = 0.1541$ nm. The magnetic susceptibility and the magnetization were recorded using a commercial SQUID magnetometer for temperatures $T < 400$ K and external magnetic fields up to 50 kOe. The dielectric constant has been measured employing a frequency response analyzer (NOVOCONTROL $\alpha$-ANALYZER and HP4284A) and the spontaneous electric polarization was recorded as integrated pyro-current. The specific heat was measured in a PPMS-system (QUANTUM-DESIGN).

III. RESULTS AND DISCUSSION

A. Structure

A typical result for the structural characterization of the samples by x-ray diffraction is shown in Fig. 1. The diffraction patterns were refined using Rietveld analysis. All samples investigated revealed the O’ orthorhombic structure (Pbnm). No impurity phases were detected above background level for Y-concentrations $x < 0.75$. For higher concentrations (as denoted in Fig. 2), small traces of the hexagonal (P63mc) phase of YMnO$_3$ show up which could be estimated to be below 2 % and will not considerably influence the regarded macroscopic properties. The lattice constants and the volume of the unit cell as derived from the profile analysis are shown in Fig. 2. In addition, the data for the system La$_{1-y}$Gd$_y$MnO$_3$, which was taken from Ref. [14], is displayed on a separate scale. Both scales, for Gd-doping y and Y-doping x are shifted to achieve an overlap of the structural data. For all concentrations we find $b > a > c/\sqrt{2}$ indicative for a static JT distortion superimposed on the high temperature O-type (i.e. not JT distorted) orthorhombic structure, which results from the buckling and tilting of the MnO$_6$ octahedra due to geometrical constraints. However, for Eu$_{1-x}$Y$_x$MnO$_3$, despite the continuous shrinking of the lattice volume $V$, the orthorhombic distortion parameterized by $\varepsilon = (b-a)/(a+b)$ tends to saturate for higher Y-concentrations. The inequality of the lattice constants a and b reflects the tilting of the octahedra around the b-axis and implies significant deviations from 180° of the Mn-O-Mn bond angle $\phi$ within the ab-
Another quantity reflecting the development of $\phi$ is the tilting distortion along $b$ of the $A$-site as obtained from the Rietveld refinement of the atomic positions. This parameter (not shown) is almost constant for the system $\mathrm{Eu}_{1-x}Y_x\mathrm{MnO}_3$ in contrast to the less distorted system $\mathrm{La}_{1-y}\mathrm{Gd}_y\mathrm{MnO}_3$. This implies, that the alteration of the spin system due to the influence of the Mn-O-Mn bond angle may not be the only valid mechanism for $\mathrm{Eu}_{1-x}Y_x\mathrm{MnO}_3$. In addition, the variation of the magnetic exchange via the reduction of the volume and the corresponding changes in the orbital overlap may also have to be considered. Also the $A$-site disorder and the corresponding variance in the $A$-site ionic radii could play an important role. The asterisks in Fig. 2 display the structural parameters of pure $\mathrm{TbMnO}_3$. The data agree with the findings for the $Y$-concentration $x \approx 0.85$. If only taking into account the averaged ionic radii, the values of the Tb-system should be located at $x \approx 0.42$. For the system $\mathrm{GdMnO}_3$, an equivalent concentration of $x \approx 0.3$ is found while the value is expected to be $x \approx 0.15$. This shows that for $\mathrm{Eu}_{1-x}Y_x\mathrm{MnO}_3$ the lattice is less contracted than it would be expected compared to the pure rare earth manganites.

B. Magnetism

Fig. 2 shows the magnetic DC susceptibilities $\chi = M/H$ for concentrations $x \leq 0.5$. At elevated temperatures all susceptibilities follow a Curie-Weiss (CW) law as revealed by the inverse representation in the lower frame of Fig. 2. The corresponding effective paramagnetic moments $p_{\text{eff}}$ are plotted in the lower inset of Fig. 2. $p_{\text{eff}}$ is decreasing due to the decreasing rare-earth contribution. $\mathrm{Y}^{3+}$ is nonmagnetic and for $\mathrm{Eu}^{3+}$ the $4f^n$-configuration leads to $J = 0$. However, for Eu low-lying multiplets give rise to a Van-Vleck type of contribution, which in this temperature regime is nearly Curie-like and thus enhances the effective paramagnetic moment. For a more detailed analysis the paramagnetic high temperature behavior was fitted by a sum of the contribution of $\mathrm{Eu}^{3+} (\propto (1 - x))$ and the CW type contribution of $\mathrm{Mn}^{3+}$. For the Eu-contribution we used the well known free ion susceptibility of $\mathrm{Eu}^{3+}$ determined by its excited multiplets with $E_1 \approx 500$ K and $E_2 \approx 3E_1$ for $J = 1$ and $J = 2$ respectively. At high temperatures it is linear in $1/T$ while at low $T$ it is determined by a temperature...
AFM structure remains incommensurate or locks in at a commensurate wave vector. It should be noted that at least for the composition $x = 0.5$ additional small anomalies can be found at the FE transitions at 24 K and 18 K, indicative for a partial rearrangement of the magnetic structure.

Fig. 4 shows the magnetization $M(H)$ for Eu$_{0.8}$Y$_{0.2}$MnO$_3$ in magnetic fields up to 5 T as measured after zero-field cooling. At $T = 34$ K (upper frame of Fig. 4) an apparently paramagnetic magnetization behavior is detected. As can be deduced from the specific heat data (presented below) the magnetic state of the sample at this temperature is in fact the IC phase. At 25 K the CAFM state can be induced by the magnetic field as reflected by the twofold hysteresis loop with the typical signature of a smeared out metamagnetic phase transition at $H \approx 30$ kOe. On further decreasing temperature this metamagnetic transition becomes fully irreversible and the two loops are merged into one as it is characteristic for a weak ferromagnet. After the initial increase of the field the CAFM state persists and only the ferromagnetic component is switched at a sharply defined coercive field, which increases up to $H_c \approx 40$ kOe for the lowest temperatures. At 2 K (lower frame of Fig. 4) even an intermediate state with a smaller ferromagnetic component is stabilized after the initial increase of the magnetic field leading to an asymmetric shape of the hysteresis loop.

C. Dielectric properties

Fig. 5 displays the real part of the dielectric constant as measured in the radio-frequency range for various concentrations of Eu$_{1-x}$Y$_x$MnO$_3$. All $\varepsilon'(T)$ curves show a steplike increase with increasing temperature along the $c$-direction. Its point of inflection is located around 50 K but as shown exemplarily for the concentration $x = 0.5$ (lower right frame of Fig. 5) its position is strongly frequency dependent. Similar phenomena have already been found e.g. for TbMnO$_3$ and have been ascribed to the relaxation of localized polarons. In the following we will concentrate on the anomalies below 45 K. For pure EuMnO$_3$ only a tiny kink can be found near $T \approx 43$ K. This coincides with the onset of weak ferromagnetism in the CAFM phase as revealed from the magnetic susceptibility measurements. For $x = 0.2$ a similar anomaly at $T_{CAFM} \approx 22$ K can be observed, which can hardly be recognized, but a much more prominent peak occurs at 30 K. For $x = 0.3$ this anomaly is located at 26 K and for $x = 0.5$ it forms a double-peak structure at roughly 23 K and 19 K. A similar double structured peak can also be detected along the $a$-direction, however with shifted
weight from higher to the lower temperature peak. These anomalies in $\varepsilon'(T)$ coincide with the onset of ferroelectricity as will be described later. For the concentrations $x = 0.2$, 0.3, and 0.5 the electric polarization $P(T)$ is shown in Fig. 4. As revealed by the uppermost frame of Fig. 4 obviously the double structure in $\varepsilon'(T)$ for Eu$_{0.5}$Y$_{0.5}$MnO$_3$ (lower right frame of Fig. 4) corresponds to the partial spontaneous reorientation of $P$ from the $c$- to the $a$-direction. This is in accord with recent results obtained for $x \approx 0.4$ by Kuwahara and coworkers. Such a spontaneous reorientation of the electric polarization is not reported for the pure systems RMnO$_3$. For the compositions Eu$_{1-x}$Y$_x$MnO$_3$ with $x = 0.3$ and 0.2 no temperature dependent reorientation of the polarization could be observed as it is shown in the lower frames of Fig. 4. It is remarkable that despite the magnetoelectric origin of the FE order no clear anomaly in $P(T)$ can be observed for $x = 0.2$ around 23 K where a spontaneous FM component sets in. However, as can be seen from Fig. 4 the values for the spontaneous magnetization stay below $0.2 \mu_B$ per Mn$^{3+}$ ion. This is only 1/20th of the maximal ordered moment of $4 \mu_B$. Thus the effective FM moment can be explained by a canting of the presumably spiral magnetic structure of less than $3^\circ$, which represents an only small modification of the magnetic structure.

Ferroelectricity (FE) does not occur for concentrations below $x < 0.2$. Nevertheless, it is remarkable that a canted, i.e. weakly ferromagnetic state and FE are not mutually exclusive. For $x = 0.2$ the system first becomes ferroelectric at $T_{FE} \approx 30$ K and then the ferromagnetism evolves roughly 8 K below. In a strict sense, this is the only multiferroic system among the rare earth perovskite manganites where the ground state seems to combine the properties of ferromagnetism and ferroelectricity. The most prominent examples like TbMnO$_3$ never show a finite spontaneous FM and FE order-parameter at the same time.

### D. Specific heat

Fig. 6 presents the results of heat-capacity measurements in Eu$_{1-x}$Y$_x$MnO$_3$ as function of temperature. The heat capacity, plotted as $C/T$, is shown for temperatures $T < 65$ K and concentrations $0 \leq x \leq 0.5$. A well defined lambda-like anomaly shows up between 45 K and 50 K for all concentrations under investigation. In agreement with magnetization data and deduced from observations in other rare-earth manganites this anomaly has to be interpreted as onset of the IC spin structure, which gives no macroscopic FM moment. The transition temperature is slightly decreasing with increasing Y-concentration. Below 45 K for each concentration a further anomaly appears at lower temperatures which for pure EuMnO$_3$ is characterized by a sharp peak in $C/T$ at 44 K corresponding to the transition into the A-type AFM-phase (see

![FIG. 6: (Color online) Electric polarization as measured on heating after cooling down in a poling field of about 100 V/mm for the Y-concentrations $x = 0.2$, 0.3, and 0.5.](image)
Fig. [3]. For the Y doped samples this feature gets considerably smeared out presumably due to the influence of disorder. Again the corresponding transition temperature as denoted by the onset of the broad shoulder-like contribution is monotonously decreasing with increasing \( x \) down to about 20 K for \( x = 0.5 \). However, even though the shape of this anomaly in \( C/T \) is not altered qualitatively, the corresponding transition refers to different ground states for different compositions. As it was already revealed in Figs. 4 and 5 the onset of spontaneous magnetization corresponds to the transition into a new magnetic ground state with FM and FE components for concentrations \( x \approx 0.2 \). For higher concentrations the spiral IC structure persists down to lowest temperatures in analogy to the pure rare earth compounds, but the onset of a FE polarization corresponds to a change from a sinusoidal to a helicoidal magnetic structure. The absence of any qualitative differences in the curvature of \( C/T \) for the different compositions reflects that the corresponding ground states together with their partially frustrated spin structures are nearly degenerate.

It is worth mentioning that the low temperature specific heat in this system differs essentially from that of GdMnO\(_3\) or TbMnO\(_3\) due to the missing contribution of the magnetic rare earths. Neither a Schottky-type contribution as found due to the rare earth spins, which are polarized in the effective exchange field from the CAFM Mn-sublattice, nor an anomaly due to the subsequent ordering of the magnetic rare earth sublattice in the temperature range below 10 K can be detected for Eu\(_{1-x}\)Y\(_x\)MnO\(_3\). For comparison the inset of Fig. 4 shows data for pure GdMnO\(_3\) and EuMnO\(_3\). Besides the mentioned differences at low temperatures for EuMnO\(_3\) an additional contribution at higher temperatures is observed. This contribution can not be explained by the slight differences of the phonon spectrum because Gd and Eu have very similar masses. \( \Delta C(t) \) shows a broad peak at around 120 K and can be explained by the relatively small splitting of the Eu-multiplet, which also gives rise to the Van-Vleck contribution to the magnetic susceptibility, discussed above.

**IV. PHASE DIAGRAM**

Based on the results shown above, from the magnetic and dielectric measurements as well as from the heat capacity, a detailed \( (x,T) \)-phase diagram can be constructed and is shown in Fig. 8. The paramagnetic regime above \( T_N \approx 45 \) – 50 K, is followed by the sinusoidal IC structure of the manganese moments, an interpretation guided by results for TbMnO\(_3\) and o-TbMnO\(_3\). For small Y-concentrations, \( x \leq 0.2 \), this incommensurate spin-structure locks into the weakly ferromagnetic A-type CAFM phase. For higher concentrations, \( x \geq 0.3 \), the ground state is ferroelectric but no ferromagnetic component can be found. Obviously, the spin-structure does not lock into the CAFM anymore. However, like in TbMnO\(_3\) it remains unclear so far, if the magnetic structure still is incommensurate or if a commensurate long wavelength magnetic vector is established. In a small regime around \( x \approx 0.2 \) weak ferromagnetism (CAFM) and weak ferroelectricity coexist in contrast to the pure multiferroic rare earth manganites. Regarding the volume of the unit cell, the series Eu\(_{1-x}\)Y\(_x\)MnO\(_3\) covers the values of GdMnO\(_3\) and TbMnO\(_3\). Pure EuMnO\(_3\) is not ferroelectric. GdMnO\(_3\) is ferroelectric along \( a \) in a weak external magnetic field along \( b \), which destroys the A-type AFM structure. For Eu\(_{1-x}\)Y\(_x\)MnO\(_3\) a concentration slightly
lower than \( x = 0.2 \) probably will reproduce this property of GdMnO\(_3\). However, according to Fig. 2 the Eu-Y-system corresponding to GdMnO\(_3\) should have \( x \approx 0.2 \). This composition is already ferroelectric without magnetic field even though a canted AFM structure persists. Pure TbMnO\(_3\) is ferroelectric along \( c \). However, concerning the volume of the unit cell it could not be reproduced by pure single crystalline Eu\(_{1-x}\)Y\(_x\)MnO\(_3\) close to \( x \approx 0.85 \) as shown in Fig. 2. In TbMnO\(_3\) there is an additional anisotropy due to Tb-ions and Tb-Mn exchange which could lead to the observed electric polarization along the \( c \)-axis. This should be taken into account for the comparison between TbMnO\(_3\) and Eu\(_{1-x}\)Y\(_x\)MnO\(_3\) systems. However, the tendency towards a spontaneous ferroelectric component along \( c \) is already indicated also for Eu\(_{1-x}\)Y\(_x\)MnO\(_3\) at lower Y-concentrations like \( x = 0.5 \) (Fig. 6).

It is interesting that only the weak FE component along \( a \) coexists with spontaneous weak ferromagnetism, namely within the concentration range around \( x \approx 0.2 \), while for higher concentrations, where at least an intermediate FE component along \( c \) is detected, no weak ferromagnetism shows up. According to the symmetry properties of the magnetoelectric coupling for the rare earth manganites, the ferroelectric polarization vector is orthogonal to both, the vector of the magnetic spiral and the magnetic modulation vector, which points along the \( b \) axis. For TbMnO\(_3\) and analog for the higher Y-concentrations of Eu\(_{1-x}\)Y\(_x\)MnO\(_3\) the ferroelectric component points along the \( c \)-direction, which is compatible with a spiral vector along \( a \) (i.e. the spins rotating in the \( bc \)-plane). For GdMnO\(_3\) (in small magnetic fields along \( c \)) and similarly for the concentrations around \( x \approx 0.2 \) of Eu\(_{1-x}\)Y\(_x\)MnO\(_3\), the ferroelectric component points along the \( a \)-direction. This would be compatible with a spiral vector along \( c \) (i.e. the spins rotating in the \( ab \)-plane). The homogeneous canting of this helicoidal spin structure out of the \( ab \)-plane could then generate the observed ferromagnetic moment along \( c \).

V. CONCLUSION

In summary, we have characterized poly- and single-crystalline samples of the system Eu\(_{1-x}\)Y\(_x\)MnO\(_3\) by means of structural, magnetic, thermodynamic, and dielectric measurements. In comparison with recently published results for the pure rare earth systems we constructed a \((T, x)\)-phase diagram for compositions \( x \leq 0.5 \). The ground state Eu\(_{1-x}\)Y\(_x\)MnO\(_3\) changes from a canted A-type AFM without long range polar order for concentrations \( x < 0.15 \) towards a presumably incommensurate spiral magnetic structure coexisting with a ferroelectric component for \( x \geq 0.3 \). For these higher Y-concentrations the orientation of the ferroelectric component changes spontaneously from the \( c \)-axis at higher temperatures towards the \( a \)-axis for low temperatures. The regime with \( P \parallel c \) increases with increasing Y-concentration. In this sense Eu\(_{1-x}\)Y\(_x\)MnO\(_3\) resembles the development of the ferroelectric orientation with decreasing ionic \( A \)-site radius as in the system Tb\(_{1-x}\)Gd\(_x\)MnO\(_3\). Hence, all essential magnetoelectric properties existing in the pure rare earth compounds GdMnO\(_3\) and TbMnO\(_3\) are reproduced. The influence of the magnetic rare earth seems to be restricted to the distortion of the magnetic structure connected with the magnetic \( A \)-site ordering at low temperatures. The modulation of the magnetic structure related to the onset of ferroelectricity is realized due to the Mn sublattice only. However, the contraction of the lattice with increasing \( x \) in Eu\(_{1-x}\)Y\(_x\)MnO\(_3\) is less effective than estimated from the average ionic \( A \)-site radii in comparison to the pure rare earth compounds, which points towards the importance of disorder effects. The latter may also influence the properties in the concentration range around \( x \approx 0.2 \) where a finite spontaneous magnetic moment and ferroelectricity coexist. The details of the underlying magnetic structure are not yet verified but it is plausible to expect a spontaneously canted spiral. Such a FM and FE ground state has not been found in the pure rare earth compounds so far and deserves further study.

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1 M. Fiebig, J. Phys. D: Appl. Phys. 38, R123 (2005).
2 J. Hemberger, P. Lunkenheimer, R. Fichtl, H.-A. Krug von Nidda, V. Tsurkan, and A. Loidl, Nature 434, 364 (2005).
3 P. Lunkenheimer, R. Fichtl, J. Hemberger, V. Tsurkan, and A. Loidl, Phys. Rev. B 72, 060103(R) (2005).
4 G. Lawes, A. B. Harris, T. Kimura, N. Rogado, R. J. Cava, A. Aharony, O. Entin-Wohlman, T. Yildirim, M. Kenzelmann, C. Broholm, et al., Phys. Rev. Lett. 95, 087205 (2005).
5 T. Lottermoser, T. Lonkai, U. Amann, D. Hohlwein, J. Ihringer, and M. Fiebig, Nature 430, 514 (2004).
6 M. Fiebig, T. Lottermoser, D. Frohlich, A. V. Guitsev, and R. V. Pisarev, Nature 419, 818 (2002).
7 N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S. W. Cheong, Nature 429, 392 (2004).
8 T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature 426, 55 (2003).
9 T. Goto, T. Kimura, G. Lawes, A. P. Ramirez, and Y. Tokura, Phys. Rev. Lett. 92, 257201 (2004).
10 T. Kimura, G. Lawes, T. Goto, Y. Tokura, and A. P. Ramirez, Phys. Rev. B 71, 224425 (2005).
11 I. A. Sergienko and E. Dagotto (cond-mat/0508075).
12 H. Katsura, N. Nagaosa, and A. V. Balatsky, Phys. Rev. Lett. 95, 057205 (2005).
13 C. Ederer and N. A. Spaldin (cond-mat/0602400).
14 J. Hemberger, S. Lobina, H.-A. Krug von Nidda, N. Tristan, V. Y. Ivanov, A. A. Mukhin, A. M. Balbashov, and A. Loidl, Phys. Rev. B 70, 024444 (2004).
15 T. Kimura, S. Ishihara, H. Shintani, T. Arima, K. T. Takahashi, K. Ishizaka, and Y. Tokura, Phys. Rev. B 68, 060403(R) (2003).
16 M. Mostovoy, Phys. Rev. Lett. 96, 067601 (2006).
17 M. Kenzelmann, A. B. Harris, S. Jonas, C. Broholm, J. Schefer, S. B. Kim, C. L. Zhang, S. W. Cheong, O. P. Vajk, and J. W. Lynn, Phys. Rev. Lett. 95, 087206 (2005).
18 A. Pimenov, A. A. Mukhin, V. Y. Ivanov, V. D. Travkin, A. M. Balbashov, and A. Loidl, Nature Physics 2, 97 (2006).
19 H. Katsura, A. V. Balatsky, and N. Nagaosa (cond-mat/0602547).
20 N. A. Hill and A. Filippetti, J. Magn. Magn. Mater. 242, 976 (1998).
21 J. Baier, D. Meier, K. Berggold, J. Hemberger, A. Balbashov, J. A. Mydosh, and T. Lorenz, Phys. Rev. B 73, 100402(R) (2006).
22 J. Hemberger, A. Krimmel, T. Kurz, H.-A. Krug von Nidda, V. Y. Ivanov, A. A. Mukhin, A. M. Balbashov, and A. Loidl, Phys. Rev. B 66, 094410 (2002).
23 S. Quezel, F. Tcheou, J. Rossat-Mignod, G. Quezel, and E. Roudaut, Physica B 86-88, 916 (1977).
24 V. Y. Ivanov, A. A. Mukhin, V. D. Travkin, A. S. Prokhorov, A. M. Kadomtseva, Y. F. Popov, G. P. Vorobiev, K. I. Kamilov, and A. M. Balbashov, Phys. Status Solidi B 243, 107 (2006).
25 K. Noda, M. Akaki, T. Kikuchi, D. Akahoshi, and H. Kuwahara (cond-mat/0512139).
26 K. Taylor and M. Darby, Physics of Rare Earth Solids (Chapman and Hall Ltd., London, 1972).
27 A. Herpin, Theorie de magnetism (Presses Universitaires de France, Paris, 1968).
28 I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. Lett. 76, 4825 (1996).
29 V. Skumryev, F. Ott, J. M. D. Coey, A. Anane, J.-P. Renaud, L. Pinsard-Gaudart, and A. Revcolevschi, Eur. Phys. J. B 11, 401 (1999).
30 T. Arima, T. Goto, Y. Yamasaki, S. Miyasaka, K. Ishii, M. Tsubota, T. Inami, Y. Murakami, and Y. Tokura, Phys. Rev. B 72, 100102(R) (2005).
31 H. W. Brinks, J. Rodriguez-Carvajal, H. Fjellvag, A. Kjekshus, and B. C. Hauback, Phys. Rev. B 63, 094411 (2001).
32 T. Goto, Y. Yamasaki, H. Watanabe, T. Kimura, and Y. Tokura, Phys. Rev. B 72, 220405(R) (2005).