Evidence for strong spin-lattice coupling in multiferroic RMn_2O_5 (R=Tb,Dy,Ho) via thermal expansion anomalies

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Thermal expansion measurements were done on single-crystal RMn_2O_5 (R=Tb,Dy,Ho) along the principal crystallographic axes. Distinctive anomalies were observed in the linear thermal expansivities at critical temperatures marking the onset of long-range antiferromagnetic order (T_{N1}), ferroelectricity (T_{C1}), as well as at temperatures when anomalous changes in the polarization, dielectric constant, and spin wave incommensurability have been previously reported. These observations suggest that the coupling between the magnetic orders and the dielectric properties is mediated by the lattice distortion. In particular, a possible scenario as to how ferroelectricity arises and subsequently is altered as a result of the subtle changes in the highly frustrated magnetic order, is discussed in the light of the strong spin-lattice coupling observed in these materials. Neutron diffraction measurements on $HoMn_2O_5$ show a spin reorientation at 23 K corresponding to a step-like anomaly in the dielectric constant. © *2006 American Institute of Physics*.
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Rare-earth manganites RMn_2O_5 (R=Tb,Dy,Ho) have been studied since the 1960s due to their unusual magnetic properties and complex structures. The recent resurgence of interest in these compounds is fueled by the discovery of the coexistence and mutual interference of long-range magnetic and ferroelectric orders. Further attention to these so-called multiferroics is gained due to their potential for device applications such as the magnetically recorded ferroelectric media, made possible by the controllability of the spontaneous polarization by a magnetic field or the bulk magnetization by an electric field via the magnetodielectric coupling in these materials.[1–6] The orthorhombic crystal structure (*Pbam*) of RMn_2O_5 is composed of edge-sharing $Mn^{4+}O_6$ octahedra forming ribbons along the c axis. A pair of $Mn^{3+}O_5$ pyramids, connected at a common edge of their bases, bridge the adjacent ribbons of octahedra in the a-b plane.[1] This complex structure contributes to the interplay of competing magnetic exchange interactions occurring with some degree of spin frustration. The inherent magnetic frustration in the structure has been pointed out to play a major role in the cascade of phase transitions that these manganites undergo upon temperature variation. Upon cooling, the manganese spins order in a helicoidal manner along the c axis at $T_{N1} \approx 40-43$ K. The magnetic structure is described by an incommensurate propagation vector $\mathbf{q}=(q_x,0,q_z)$, where q_x and q_z depend on the ionic size of R. This incommensurate wave vector then locks into a commensurate one $\mathbf{q}=(1/2,0,1/4)$ at $T_{C1} \approx 37-39$ K. Further cooling to $T_{C2} \approx 15-25$ K changes the commensurate wave vector back to an incommensurate one.[1,2,7] The transition at T_{C1} in RMn_2O_5 has been shown to coincide with the onset of ferroelectric order, as indicated by anomalies in the dielectric constant and by the appearance of a spontaneous polarization along the b axis.

The resulting phase diagrams of these compounds are rich indeed. However, the definite nature of the correlations among the ferroelectricity, magnetic order, and the crystal structure remains an open question. Much has been done in search for structural anomalies or a change of symmetry in these compounds in going to the ferroelectric phases. However, investigations done thus far have been only partially successful in the characterization of such anomalies.[2,8] In this work, we unambiguously show the existence of sizable lattice distortions coinciding with changes in the commensurability of the magnetic wave vector and the ferroelectric

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order implying the presence of strong spin-lattice coupling in these materials.

Single crystals of $R\mathrm{Mn_2O_5}$ (R=Ho, Dy, Tb) were grown via the high-temperature flux growth method in solution as discussed elsewhere.[3,4] Thermal expansion measurements were done using a home-made high-resolution capacitance dilatometer. The crystals were then thinned down to 0.2 mm along the b axis with gold evaporated at the surfaces to form a capacitor for the dielectric measurements. To further investigate the magnetic ordering in single-crystal $\mathrm{HoMn_2O_5}$, neutron diffraction measurements were performed using the BT9 thermal triple-axis spectrometer at the NIST Center for Neutron Research.

The results of the dilatometric measurements are summarized in Fig. 1. These data show clear evidence of sizable lattice distortions with the onset and changes in the ferroelectric order as shown by the correspondence of the thermal expansion with the dielectric anomalies. The main phase transitions common to the three compounds as seen in Fig. 1 are the onset of long-range magnetic order at T_{N1}, the onset of ferroelectricity at T_{C1}, and another phase transition at T_{C2} associated with a sharp change in the ferroelectric polarization.[5,6] Additional anomalous lattice strain coincident with subtle changes in the magnetic structure were also observed at T_{N2} and T_{C3} and will be discussed later. The data clearly show that the largest lattice distortions occur at the ferroelectric transitions. This is expected because it is the ionic displacements that give rise to the ferroelectricity. Since the role of these structural anomalies is one of the main issues involved in understanding these multiferroics, much work has been done to resolve such anomalies. From both the dielectric and thermal expansion measurements, these anomalies associated with distinct changes in the dielectric constant and ferroelectric polarization (T_{C1}, T_{C2}, and T_{C3}), exhibit hysteretic behaviors (not shown in Fig. 1) coupled with sharp peak-like changes in the thermal expansion coefficient in all three axes, indicative of a change in the unit cell volume. Only heating data were shown for clarity. In contrast, the thermal expansivity at T_{N1} and T_{N2} exhibit a qualitatively different anomaly. At T_{N1}, α_b is unaffected while α_a and α_c show a step-like increase. At T_{N2}, the main anomaly is along the c axis, which is a smooth step-like change.

In addition, Fig. 1 also shows that the thermal expansion anomalies are anisotropic. At T_{C1}, the anomaly in α_c is opposite in sign to that in α_a and α_b for all three compounds. Therefore, a strong uniaxial pressure effect is expected and it could be used to selectively tune the ferroelectric transitions in the compounds. There are differences between the three compounds (e.g., the c axis contracts for R=Ho, Dy but it expands for R=Tb at T_{C1}) which indicate the important role of the rare earth ion that seems to largely influence the magnetic modulation along the c axis.[2,10] In addition, the critical temperatures determined from the said measurements were confirmed through specific-heat measurements, in perfect agreement with previous polarization, specific-heat, and neutron diffraction data.[1–3,5–9]

Although the most distinct anomalies are associated with the ferroelectric transitions, there are substantial lattice distortions at T_{N1} as well. These anomalies imply the existence of strong spin-lattice correlations in the material. Strong magnetic correlations as well as long-range order are known to be a common origin of lattice strain when the magnetic

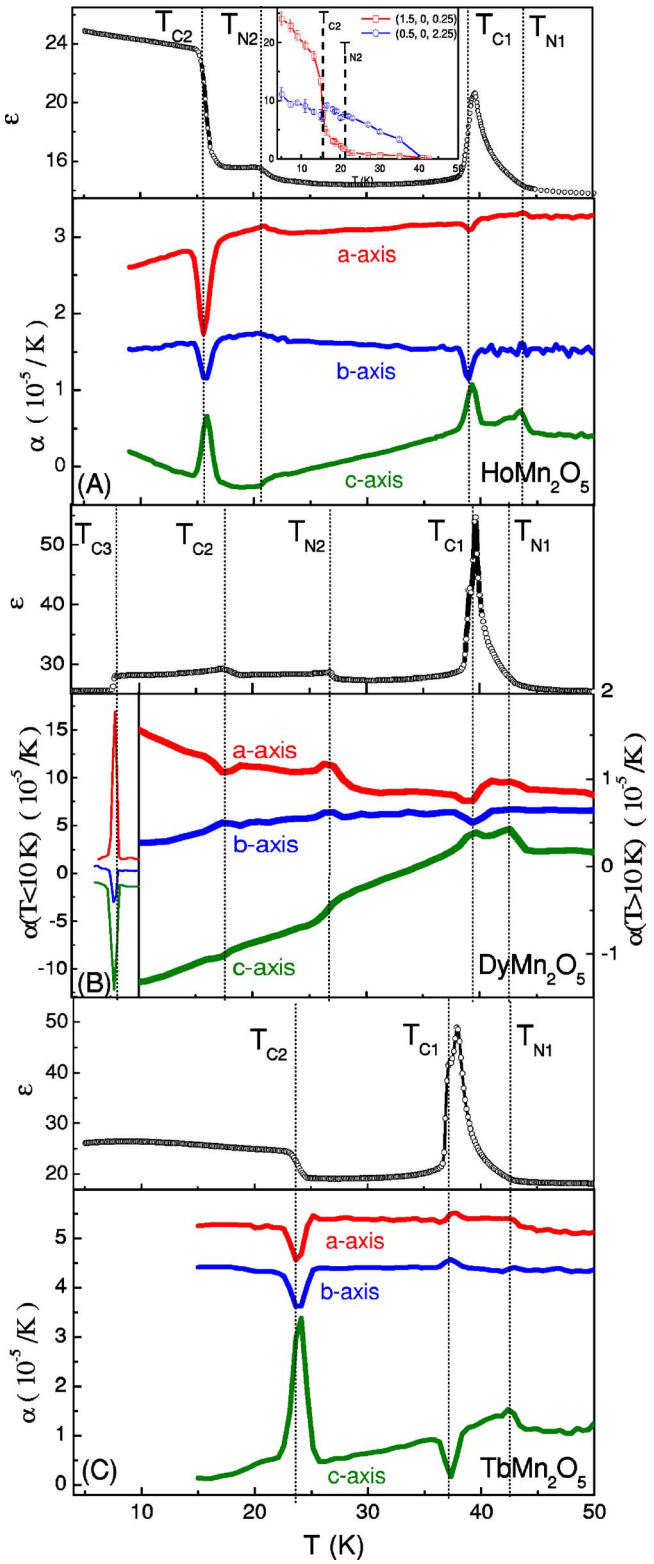

FIG. 1. (Color online) Anomalies in the thermal expansion and dielectric constant for $R\mathrm{Mn_2O_5}$ (A) R=Ho, (B) R=Dy, and (C) R=Tb. a and b axis data are offset for clarity. Inset shows the anomalies in the integrated intensity of the magnetic scattering peaks at 16 and 23 K interpreted as spin reorientations of the Mn^{3+} spins. Data shown are collected upon heating.

energy of the system of interacting moments is lowered by a change in interatomic distances. The observed striction of the *c* axis and *a* axis common to all three compounds, is consistent with the proposed magnetic structure in the incommensurate phase below T_{N1}, described by $\mathbf{q}=(0.5+\gamma,0,0.25+\delta)$. The onset of this antiferromagnetic order along the *a* and *c* axes results to the sudden increase in α_a and α_c. On the other hand, the absence of a detectable anomaly along the *b* axis can be explained by the absence of magnetic modulation along this axis. In addition to the onset of magnetic order at T_{N1}, there are other anomalies in Fig. 1, associated with subtle changes in the magnetic structure and/or polarization. There are two additional anomalies for $DyMn_2O_5$, the correlations of which with current neutron diffraction data ascribe them to spin reorientations.[7] In particular, a sharp change in the ferroelectric polarization is seen at T_{C3}[5,6] which coincides with the strongest anomalies of the thermal expansivity. For $HoMn_2O_5$, there is an additional expansion anomaly at $T_{N2}=23$ K corresponding to a small step in the dielectric constant. This was investigated through elastic neutron diffraction measurements on the single-crystal $HoMn_2O_5$. The inset to Fig. 1(a) shows the integrated intensity for two magnetic peaks that are approximately orthogonal. The data show sharp changes of the intensities at T_{C2} that is of the opposite sign for each magnetic peak with similar changes at T_{N2} with a smaller magnitude. This implies a spin reorientation at these temperatures. The data obtained at higher temperatures were consistent with those previously reported.[8]

Recent work on these manganites was focused on understanding how the ferroelectricity relates to the magnetic order. It has been suggested, via symmetry arguments, that the ferroelectricity arises from the off-center displacement of the Mn^{3+} that results to a net polarization in the Mn-O sublattices. The two ferroelectric anomalies at T_{C1} and T_{C2}, have been interpreted as that resulting from the polarization arising from two Mn sublattices.[3,5,6] Following the proposed magnetic structure,[8] an illustration of which is shown in Fig. 2, we conclude that the ferroelectricity arises mainly due to the displacement of the two frustrated Mn^{3+} ions, in such a way as to relieve the frustration between the Mn^{3+} spins and the two Mn^{4+} spins of the same sign (the exchange interactions between these spins shown are all antiferromagnetic in the *a*-*b* plane) resulting to canted polarizations (wide arrows in Fig. 2) at each of the two $Mn^{3+}O_5$ bipyramids, which lead to a net polarization along the *b* axis.[3,5,6]

In summary, the thermal expansion measurements done on RMn_2O_5 (R=Ho,Dy,Tb) show strong anomalies corresponding to the onset and changes in the ferroelectric order as well as subtle changes in magnetic structure. Specific differences between the lattice strains observed in the three compounds, due to the different ionic size needs further understanding. A closer look at the differences in the exchange interactions leading to the particular temperature-dependent magnetic structures needs to be done.

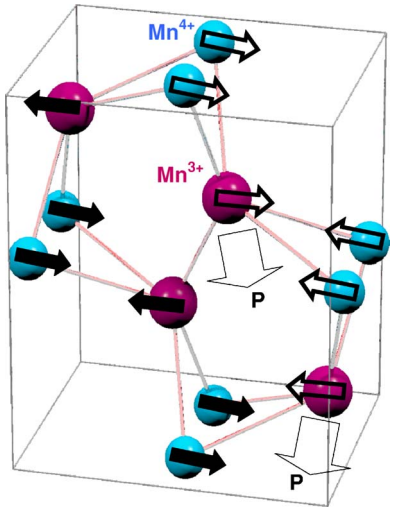

FIG. 2. (Color online) Network of Mn^{3+}-Mn^{4+} (Mn^{4+} are smaller in size). Horizontal arrows denote the Mn spins. Two sets of spins (unfilled arrows) are magnetically frustrated. The wide arrows show the proposed displacement of frustrated Mn^{3+}, resulting in a net polarization along the *b* axis.

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