Magnetostriction in orthorhombic manganites

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Abstract.
From the physical point of view multiferroics present an extremely interesting class of systems and problems. In the present article we report our results from magnetic properties measurements on orthorhombic ReMn$_2$O$_5$ single crystals (Re = Ho, Tb). The inherent magnetic frustration in these materials is lifted by a small lattice distortion, primarily involving shifts of the Mn$^{3+}$ cations and giving rise to a canted antiferroelectric phase. In both compounds a colossal magnetostriction effect was observed and a novel phase transition diagrams, which indicate the correlation between magnetostriction and polarization for these two compounds were build.

1. Introduction
Multiferroics are single phase compounds in which magnetism and ferroelectricity coexist. Surprisingly, orthorhombic and hexagonal manganites with general formula ReMnO$_3$ and ReMn$_2$O$_5$ (Re=rare earth) belong also to the group of multiferroics , which are currently of great interest because of the possibility to use them for the design of different kind magneto-electric devices. Among the multiferroic materials displaying the coexistence of magnetic and ferroelectric (FE) orders the rare earth manganites, ReMn$_2$O$_5$, have attracted attention because of a cascade of phase transitions originating from the wealth of fundamental physical phenomena observed in these compounds. The physical origin of this phase complexity lies in the partially competing interactions between the Mn$^{4+}$/Mn$^{3+}$ spins, the rare earth magnetic moments, and the lattice. Geometric magnetic frustration among the Mn$^{3+}$ - Mn$^{4+}$ spins leads to a ground state degeneracy of the magnetic states that can be lifted by a distortion of the lattice (magnetic Jahn-Teller effect) [1]. This is believed to be the origin of ferroelectricity in ReMn$_2$O$_5$ compounds. Strong spin-lattice coupling is needed to explain the ionic displacements in the FE state. From a fundamental point of view, however, these multiferroic manganites contain a puzzle.

2. Samples and experimental
The orthorhombic single crystals were grown by the high temperature solution growth method from pure polycrystalline ReMn$_2$O$_5$, as described elsewhere [2]. Before investigation all single crystals were characterized and oriented by using EDAX and XDR techniques. The investigated samples are of two types: cubical type with dimensions 1.2 x 1.4 x 1.5 mm$^3$ and weights 9.8 -
13.5 mg and thin rectangular specimens with typical surface area 3 - 4 mm², thickness 0.3 mm and weight 7.4 - 9.2 mg.

3. Results and discussion
At room temperature orthorhombic ReMn₂O₅ manganites have space group *Pbam*, but it is expected that in their multiferroic state the actual symmetry group is *Pb2₁m*, which allows for a macroscopic electric polarization along the *b* axis [2, 3, 4, 5, 6]. The structure consists of edge-sharing Mn⁴⁺O₆ octahedra, forming chains along the *c* axis, cross linked via Mn³⁺ pyramidal units. Recently *ab initio* calculations have shown [7], that the experimental magnetic structure of HoMn₂O₅ with *Pb2₁m* symmetry is indeed the magnetic groundstate. Mn and Re ions in ReMn₂O₅ systems form three magnetic subsystems: Re³⁺, Mn³⁺ and Mn⁴⁺ with crystallographic position 4g, 4h and 4f respectively. Magnetic interactions in the Mn subsystem are geometrically frustrated and ReMn₂O₅ shows complicated series of magnetic transitions involving the Mn and Re ions on cooling below Tₓ. The Mn³⁺ ions have a decisive importance for the ferroelectric ordering of the ReMn₂O₅ system.

**Figure 1.** Field dependencies of magnetization in HoMn₂O₅ single crystals along the three principal crystallographic directions: *a* - □ *b* - ◆ *c* - △.

**Figure 2.** Field dependencies of magnetization in TbMn₂O₅ single crystals along the three principal crystallographic directions: *a* - □ *b* - ◆ *c* - △.

Our magnetization measurements were realized by a vibrating sample magnetometer. Magnetization dependencies along the three principal crystallographic directions for HoMn₂O₅ and TbMn₂O₅ single crystals were measured in the temperature range 4.2 - 120 K and in magnetic fields up to ± 14 T. Typical field dependence curves for HoMn₂O₅ and TbMn₂O₅ are shown on Fig.1 and Fig.2 respectively. In both compounds a significant magnetic anisotropy is present. In HoMn₂O₅ monocrystal two directions of easy magnetization, along the *a* and *b* axes, were found, while for the TbMn₂O₅ monocrystal only one easy magnetization direction along the *b* axis was found. Saturation of the sample magnetization was not observed in fields up to 14 T. According to the results from our magnetostriction measurements, presented below, some peculiarities in the magnetization curves of both compounds were expected, but in fact not observed.

Aiming to eliminate any possibility for equipment fault or malfunction, a series of test magnetization and magnetostriction measurements on orthorhombic NdMnO₃ single crystal were performed. The obtained typical magnetization and magnetostriction curves are presented in Fig.3. From the presented results can be clearly seen, that in NdMnO₃ single crystal a strong
The correlation between magnetization and magnetostriction was observed, which eliminates the possibility for equipment fault or malfunction.

**Figure 3.** Field dependencies of magnetization (solid line) and magnetostriction (dashed line) in NdMnO$_3$ single crystals along the $b$-axis.

It is characteristic for all ReMn$_2$O$_5$ compounds that the various magnetic phase changes are reflected in sharp and distinct anomalies of the dielectric constant, as shown for HoMn$_2$O$_5$ and TbMn$_2$O$_5$ in Fig. 4, which exhibit distinct anomalies at all magnetic transitions temperatures, with the strongest peaks observed at the FE transitions. Our data provide striking evidence for the existence of extraordinarily large spin-lattice interactions in ReMn$_2$O$_5$.

**Figure 4.** Temperature dependency of dielectric constant for TbMn$_2$O$_5$ - □ and HoMn$_2$O$_5$ - ○ single crystals at 1 kHz along the $b$ axis measured by sample cooling in the presence of 1 T magnetic field.

This is a clear indication of strong magneto-electric coupling due to large spin-lattice interactions. Long-range antiferromagnetic (AFM) ordering of the Mn$^{3+}$/Mn$^{4+}$ spins occur at $T_N = 43$ K. This transition into a high Néel temperature phase is a common features for all ReMn$_2$O$_5$. Subsequently the FE transition takes place at $T_C$ slightly below $T_N$. The pure ferroelectric lock-in transition is not influenced by magnetic fields. With further temperature decreasing, another magnetic transition takes place at $T'_N$ (22.4 K for HoMn$_2$O$_5$ and 24 K for TbMn$_2$O$_5$), where commensurate AFM ordering becomes low temperature incommensurate. This transition is accompanied by a significant decrease of the FE polarization and is often referred to a second FE phase transition. $T'_N$ turns out to be associated with a commensurate-incommensurate transition. This is very surprising in that the typical incommensurate-commensurate transition results in the commensurate state being the low-T ground state. This is a consequence of the "locking in" of magnetic and lattice modulations that is energetically favored at low T. Under $T'_N$ the spin wave vector remains unchanged and the transition involves an increase in the ordered moments of the Mn$^{4+}$/Mn$^{3+}$ sublattice. It has been assumed that the long-range magnetic ordering of Mn$^{3+}$/Mn$^{4+}$ induces the FE transition via an additional Jahn-Teller distortion of Mn$^{3+}$ ions [8]. The FE state exhibits canted antiferromagnetic displacements...
of the Mn$^{3+}$ ions. These displacements lift the magnetic degeneracy by lowering the crystal symmetry to $Pb\bar{2}1m$, thus stabilizing the FE state via the magnetic Jahn-Teller effect.

The spontaneous polarization along the $b$ axes appears by cooling the sample below $T_N$, where a long-range anti-ferromagnetic (AFM) ordering of the Mn$^{3+}$/Mn$^{4+}$ spins occurs. As shown in Fig.5 the spins of two Mn$^{3+}$ per unit cell are each frustrated with two neighboring Mn$^{4+}$ with the same spin direction. Reducing this frustration by moving the Mn$^{3+}$ away from the Mn$^{4+}$ generates a dipolar moment $P$ between the Mn$^{3+}$ and the surrounding oxygen ions. The $P_a$ components of this dipolar moments cancel out while the $P_b$-components add up to the macroscopic polarization and ferroelectricity along the $b$ axis. The proposed displacement lowers the symmetry to the space group $Pb\bar{2}1m$. The AFM modulation along the $a$ axis with $q_x=0.5$ leads to the frustration and displacement of both Mn$^{3+}$ and the net polarization along the $b$ axis. In the temperature range $4.2 - 43$ K a number of magneto-elasto-electric phase transitions was observed. It was pointed out that all the ferroelectric phases are strongly tied to the antiferromagnetic Mn$^{3+}$/Mn$^{4+}$ spin structure, with the latter being dominated by the f-d exchange interaction [9]. It is important to emphasize that the described above mechanism leads to the appearance of a spontaneous polarization in both investigated compounds HoMn$_2$O$_5$ and TbMn$_2$O$_5$.

In general the values of the macroscopic polarization $P$, for nonmagnetic ferroelectrics, computed by $ab$ initio band-structure methods [7] are in good agreement with the experimentally observed ones [10]. According to the big difference between this both values, the class of multiferroic manganites can be considered as an exception to this rule. They are two possible explanations for this large discrepancy: On the one hand, it can be due to experimental artifacts, for instance the formation of ferroelectric domains, but on the other hand it can be due to an incompleteness in our understanding of the physical properties of these magnetic ferroelectric materials.

As it is well known, the total polarization $P$ for a given material is the sum of the ionic and electronic polarization which originates from the lattice displacements and the valence electrons respectively. The ionic contribution $P_i$ to the total polarization is easily obtained by summing the product of the ionic displacements from the centrosymmetric to the ferroelectric structure with the nominal charge of the ions rigid core. The calculation of the electronic contribution $P_e$, which is is induced by the magnetic superstructure is more complicated. The electronic polarization $P_e$ arises from a reorganization of valence charges caused by both ferroelectric lattice distortions and magnetic ordering. Both these cause changes in covalency, which in turn cause a flow of valence electron charge across the material. Therefore the effective charge that is displaced by a distortion can be much larger than just the bare ionic value. In the magnetically ordered high symmetry phase the ionic contribution is $P_i=0$, but the electronic part is not required to vanish. In fact, the material is bound to have a magnetically induced ferroelectric polarization as it is a dislocated spin density wave system in which the center of symmetry of the magnetic and lattice structure does not coincide, providing a basic mechanism for multiferroicity [11, 12]. An equivalent point of view is that in this oxide symmetry allows for a purely electronic part to the magnetostriction [13, 14]. As a consequence the spin ordering...
induces a redistribution of charge on crystallographically inequivalent manganese sites.

Recent calculations have shown \cite{7} that the Hubbard U causes a near cancellation of the electronic and ionic contributions to the polarization and effectively reduces the polarization in the multiferroic manganites by over an order of magnitude. Therefore we can conclude that the electron-electron interactions decimate the polarization in the multiferroic RE\text{Mn}_2\text{O}_5 manganites. Electronic correlation effects are thus of prime importance and quantitatively dominate the physical properties of these multiferroic transition metal compounds.

As recently reported \cite{2} a colossal magnetostriction effect in HoMn$_2$O$_5$ single crystals was observed. According to our assumption about the existing correlation between polarization and magnetostriction, we carried out a number of experiments on HoMn$_2$O$_5$ and TbMn$_2$O$_5$ single crystals in the temperature range 4.2 - 10 K. In Fig.6 and Fig.7 typical polarization and magnetostriction dependence curves from our measurements on HoMn$_2$O$_5$ and TbMn$_2$O$_5$ single crystals are shown. As clearly can be seen in Fig.6, for HoMn$_2$O$_5$ the place of the peculiarities in polarization field dependencies and the magnetostriction phase transition at 4.2 K is nearly the same. For TbMn$_2$O$_5$ (Fig.7) where the peculiarities in polarization are not so clear indicated, the exact transition fields can be determinate by dielectric constant derivative. More detailed measurements corroborated our assumption for possible correlation between the peculiarities in polarization and the magnetostriction phase transition. In our opinion, the observation of polarization peculiarities below 10 K only is a direct consequence of the RE (Ho,Tb) spin reorientation.

As discussed in \cite{2} the reason for observing such a colossal magnetostriction effect is the total effect of the exchange magnetostriction of the manganese ions and the holmium single ion magnetostriction. Holmium and Terbium in metal state showed gigantic single-ion magnetostriction, which is due to both the strong spin-orbit coupling between orbital magnetic moment $M_L$ and the non-spherical charge cloud of 4f - electron shell (which is highly anisotropic), and strong spin-lattice interactions. When a Ho ion is placed in the crystal lattice the anisotropy of the 4f -electron shell remains practically unchanged. In an external magnetic field the spin moment MS changes its orientation and this leads to reorientation of $M_L$. This causes a strong perturbative effect on the crystal field (the spin - lattice interactions in the HoMn$_2$O$_5$ and TbMn$_2$O$_5$ compound are strong) and a colossal magnetostriction effect appears.

The phase diagram build from magnetostriction (line) and polarization (circle) measurements on HoMn$_2$O$_5$ and TbMn$_2$O$_5$ single crystals is shown in Fig.8.
4. Conclusions
In the present article the temperature dependencies of the magnetization and the dielectric constant, as well the field dependencies of the polarization and magnetostriction for two series of HoMn$_2$O$_5$ and TbMn$_2$O$_5$ monocrystals are discussed. As is evident, by temperature lowering these orthorhombic manganites undergo cascade phase transitions, whose complexity originates from in the partially competing interactions between Mn$^{3+}$/Mn$^{4+}$ spins, rare earth magnetic moments and the lattice [1]. We also observed a colossal magnetostriction effect in both HoMn$_2$O$_5$ and TbMn$_2$O$_5$ monocrystals. This effect results from the reorientation of the spin moments in an external magnetic field and its strong perturbative effect on the crystal field. Compared to HoMn$_2$O$_5$ monocrystals the observed in TbMn$_2$O$_5$ monocrystals magnetostriction effect appears at lower magnetic fields (as shown in Fig. 6 and fig. 7). The same magnetostrictive behavior was observed in pure Ho/Tb monocrystals in metal state [15]. The more detailed measurements of magnetization, polarization and magnetostriction of HoMn$_2$O$_5$ and TbMn$_2$O$_5$ monocrystals in the temperature range 4.2 - 10 K gave us the possibility to build the phase diagrams for both monocrystals. These diagrams clearly demonstrate the correlation between the peculiarities in polarization and the magnetostriction phase transition. In our opinion, the field couples to the magnetic order resulting in field-induced spin reorientations and magnetic phase transitions, which in turn should affect the lattice via the spin-lattice interaction. In this way they realize the correlation observed between the polarization and magnetostriction. Knowing the signature and the nature of the magnetoelastic effect we acquit essential information about the intrinsic magnetoelastic and magnetoelectric interactions. To elucidate the role of the rare earth ions in this processes further investigations are necessary.

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