Eur. Phys. J. B **52**, 361–364 (2006)
DOI: 10.1140/epjb/e2006-00318-3

THE EUROPEAN PHYSICAL JOURNAL B

Colossal magnetostriction effect in $HoMn_2O_5$

I. Radulov[1,2,a], V.I. Nizhankovskii[2], V. Lovchinov[1], D. Dimitrov[1], and A. Apostolov[3]

[1] Bulgarian Academy of Sciences, Institute of Solid State Physics, 72 "Tzarigradsko Chaussee" Blvd., 1784 Sofia, Bulgaria
[2] International Laboratory of High Magnetic Fields and Low Temperatures, 95 Gajowicka Str., 53421 Wroclaw, Poland
[3] Sofia University "St. Kl. Ohridski", Faculty of Physics, 5 "James Bourchier" Blvd., 1164 Sofia, Bulgaria

Received 26 May 2006 / Received in final form 14 July 2006
Published online 7 August 2006 –

Abstract. We have investigated the detailed field and temperature dependence of the dielectric constant, electric polarization, magnetization and magnetostriction in orthorhombic $HoMn_2O_5$ single crystals. $HoMn_2O_5$ displays incommensurate antiferromagnetic ordering below 39 K, becoming commensurate on further cooling. The commensurate-incommensurate transition takes place at low temperatures. The inherent magnetic frustration in this material is lifted by a small lattice distortion, primarily involving shifts of the Mn^{3+} cations and giving rise to a canted antiferroelectric phase. Colossal magnetostriction effect was observed and a novel phase transition diagram was build.

PACS. 75.47.Lx Manganites – 75.80.+q Magnetomechanical and magnetoelectric effects, magnetostriction

1 Introduction

The coupling between long-range magnetic and ferroelectric order has been studied since the 1960s [1,2]. Although a number of systems that are ferroelectric at high temperatures become magnetically ordered at a lower temperature [3,4], the simultaneous appearance of both kinds of order at single-phase transition is much less common. For the most part, studies of these multiferroic materials have been focused on commensurate magnets. The coexistence and mutual interference of different types of long-range order, such as ferroelectric, (anti) ferromagnetic and ferroelastic have long inspired researchers because of their fundamental interest and their significant potential applications. Recent studies of systems undergoing simultaneous ferroelectric order at a magnetic transition have identified new multiferroic compounds, including the perovskite rare earth manganites [5–7]. For example, colossal magneto dielectric effect in orthorhombic $DyMn_2O_5$ [8] was recently discovered.

Rare-earth orthorhombic manganites, with general formula $ReMn_2O_5$, are insulators. Re is situated in the holes with almost octahedron coordination with the oxygen ions. The structure consists of edge-sharing $Mn^{4+}O^6$ octahedra forming chains along the c axis crosslinked via $Mn^{3+}O^5$ pyramidal units designating the space group $D^9_{2h} - Pbam$ at room temperature (see Fig. 1).

$HoMn_2O_5$ ($Ho^{3+}Mn^{3+}Mn^{4+}O_5^{2+}$) is orthorombic with lattice parameters: $\mathbf{a} = 7.2643$ Å, $\mathbf{b} = 8.4768$ Å and $\mathbf{c} = 5.6700$ Å [9]. By X-ray diffraction we have received for our monocrystals the following values: $\mathbf{a} = 7.2563(2)$ Å, $\mathbf{b} = 8.4758(2)$ Å and $\mathbf{c} = 5.6768(1)$ Å. Therefore we have in $HoMn_2O_5$ three magnetic subsystems: Ho^{3+}, Mn^{3+} and Mn^{4+} with crystallographic position **4g**, **4h** and **4f** respectively. Magnetic interactions in the Mn subsystem are geometrically frustrated and $HoMn_2O_5$ shows complicated series of magnetic transitions involving the Mn and Ho ions on cooling below T 39 K. For the isostructural $TbMn_2O_5$ and YMn_2O_5 compounds, it was assumed that

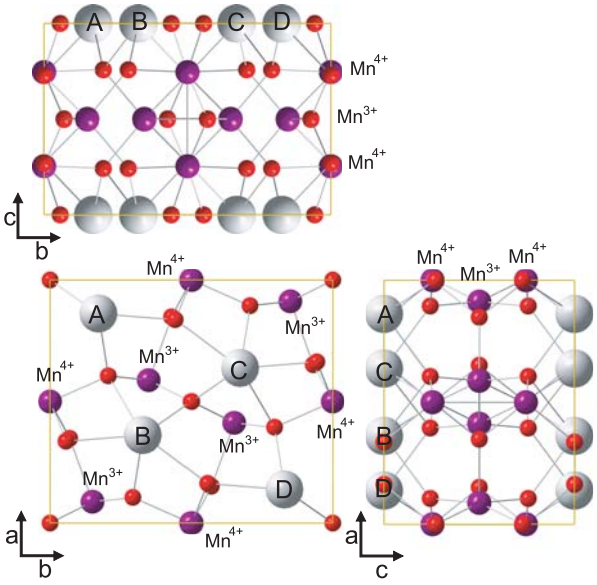

Fig. 1. Structure of $HoMn_2O_5$.

[a] e-mail: radulov@issp.bas.bg

the ferroelectric (FE) state exhibits canted antiferroelectric displacements of the Mn^{3+} ions. These displacements are expected to lift the magnetic degeneracy by lowering the crystal symmetry to *Pb21m*, thus stabilizing the FE state via the magnetic Jahn-Teller effect. However, the actual structure of the FE state is as yet unknown.

2 Samples and experiment

Herein we report a significant magnetostriction effect observed in $HoMn_2O_5$ single crystals. Pure polycrystalline $HoMn_2O_5$ was synthesized by a solid state reaction of Ho_2O_3 and MnO_2, and further annealed for 24 h at 1150 °C in oxygen atmosphere. The single crystals were grown by the high temperature solution growth method using $PbF_2/PbO/B_2O_3$ flux. The flux was mixed with $HoMn_2O_5$ powder and annealed in platinum crucible at 1280 °C for 24 h in oxygen and then slowly cooled down to 950 °C at a rate of 0.5 °C/h. All single crystals were orientated at first by X-ray diffraction. The magnetization was measured by Foner-type magnetometer at frequency of 3.6 Hz on a cubical sample $1.15 \times 1.40 \times 1.50$ mm^3 and weight 9.8 mg. For our dielectric constant measurements we have used thin rectangular specimens of single domain crystals with typical area of 3–4 mm^2, thickness of 0.3 mm and weight of 7.4 mg. The dielectric constant was measured with a high precision capacitance bridge AH 2550 A in fields 0–14 T and temperatures 4.2–300 K. To probe the ferroelectric order, we have measured both the sample polarization at fixed H and fixed T using a Keithly 617 electrometer. The magnetostriction (MS) data were obtained by use of high precision capacitance dilatometer at different temperatures below 100 K in fields up to ±14 T. The unexpected large values of linear magnetostriction led to the destruction of many of our samples.

3 Result and discussion

The magnetization data have been obtained as function of the temperature in the range 4.2–120 K and as function of the magnetic field in the range 0–14 T. Saturation of the sample magnetization in fields up to 14 T was not observed. The magnetization of $HoMn_2O_5$ at 4.2 K and at 3 T along the three principal crystallographic directions are shown in Figures 2a and 2b respectively. A significant magnetic anisotropy is observed. Our results for magnetization in the **a** direction differ from the results other authors [7,8], but are in a good agreement with our results from dielectric constant measurements discussed below. We suppose that the small differences in the magnetization values in both **a** and **b** directions are probably due to the symmetry reduction that is expected to appear at low temperatures. This effect can be proved by crystallographic measurements at low temperatures which are planned. According to this we can speak about a plane of easy magnetization **ab**, and an axis of hard magnetization, that is perpendicular to it, which is not common a case

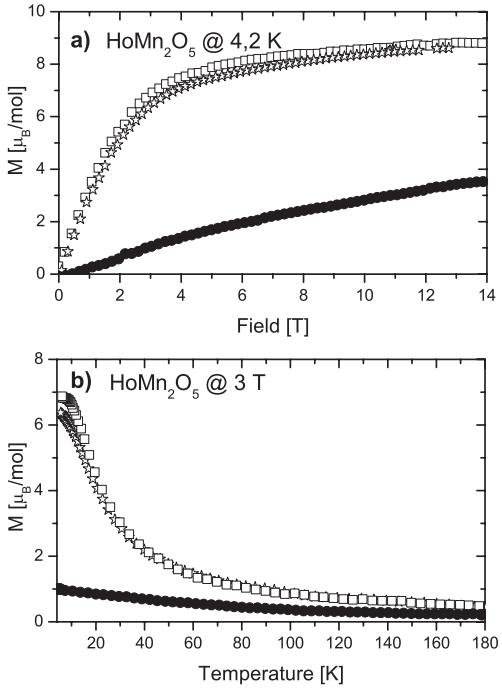

Fig. 2. Magnetization vs. magnetic field (2a) and temperature (2b) along the three principal crystallographic directions as following along axis **a** — open star, **b** — open square, **c** — filed circle.

for orthorhombic crystals. The value of the total magnetic moment of the compound, derived from our measurements is 17.4 μ_B, which is in a good agreement with the expected one: $M_{Ho^{3+}} = 10.6\ \mu_B$ and $\sqrt{M^2_{Mn^{3+}} + M^2_{Mn^{4+}}} = 6.24\ \mu_B$. The asymptotic temperature is $P = -190$ K, which implies predominant negative exchange interaction.

The typical curve of the dielectric constant is shown in Figure 3a. As mentioned before, the values of the dielectric constant measured in both magnetic easy directions **a** and **b** do not vary considerably. They exhibit a number of successive phase transitions in $HoMn_2O_5$. By arrows we have indicated in Figure 3a the phase transitions, observed also by our measurements of magnetization, polarization and dielectric properties, as well as in previously published results [10,11]. Long-range antiferromagnetic (AFM) of the Mn^{3+}/Mn^{4+} spins occur at $T_N = 43$ K, and subsequently the FE transition takes place at $T_C = 39$ K slightly below T_N. The pure ferroelectric transition, observed at 39 K, is not influenced by magnetic fields. 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 [10]. $HoMn_2O_5$ is characterized by the existence of another magnetic transition at $T'_N = 22.5$ K, at which commensurate AFM (c AFM) ordering becomes "incommensurate" (ic AFM) [10]. Below 19 K a phase transition to canted AFM (CAFM I) take places. It was found from our measurements that second CAFM-type ordering (CAFM II) of the Ho ions occurs at T_N(Ho) below 12 K. Measurements at low magnetic fields show peculiarities at

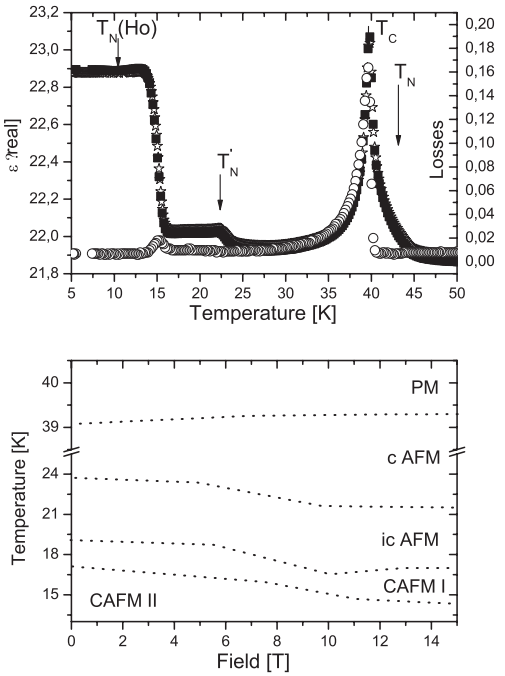

Fig. 3. (a) T dependence of dielectric constant at 1 kHz along **a** (open star) and **b** (filled square) axis and losses (open circle), measured by cooling the sample in presence of 7 T field–field cooling (FC). (b) Phase diagram based on the dielectric constant measurements (from data obtained by sample heating).

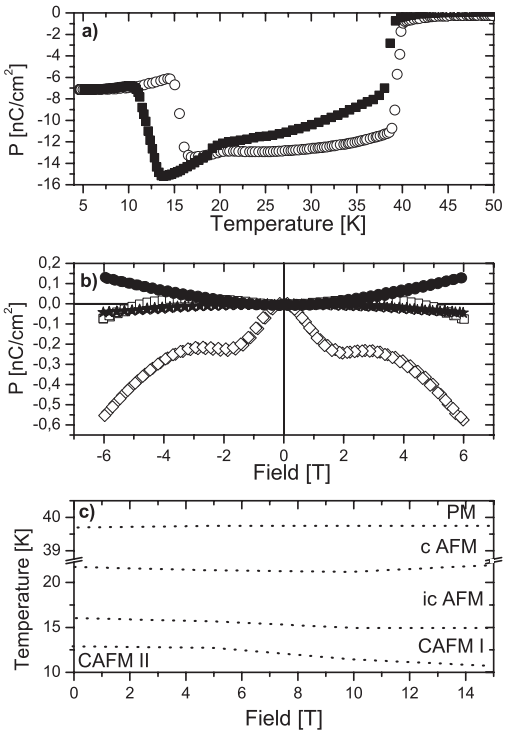

Fig. 4. (a) Temperature dependence of polarization along **b** axis (5 T magnetic field is applied parallel to the **b** axes) by sample cooling/heating (filed square/open star). (b) Field dependence of polarization along **b** axis by 4.2 K (diamond), 18 K (square), 28 K (circle) and 45 K (star) The magnetic field is applied parallel to the **b** axes. (c) Phase diagram based on the polarization measurements (from data obtained by sample heating).

11.3 K. In zero fields, the dielectric permittivity has hysteresis in the range 4.2–20 K, which becomes broader in higher fields, up to 12 T, where it disappears. The last two transitions, at T_N(Ho) and T'_N, change significantly their shape and place depending on the intensity of the applied magnetic field which means that they have magnetic origin. The phase diagram build from data received by dielectric constant measurements of $HoMn_2O_5$ is shown in Figure 3b.

The temperature and field dependencies of $HoMn_2O_5$ polarization are shown in Figures 4a and 4b respectively. The heating (cooling) of samples by polarization measurements was made with constant velocity of 1 K/min. The spontaneous polarization along the **b** axes appears by cooling the sample below $T_N = 43$ K. The spontaneous polarization remains negative for all fields in the range 4.2–50 K. $HoMn_2O_5$ undergoes a transition to a ferroelectric phase at $T_C \approx 39$ K, where the absolute value of the spontaneous polarization increases vastly. Further it changes slightly to temperatures about 20 K, where a new sharp change takes place. This change can be explained with the spontaneous reorientation of the magnetic lattice at T'_N (commensurate/incommensurate AFM ordering, accompanied by changes in the dielectric properties). The maximum value of polarization –16 nC/cm^2 is reached at temperature of about 13 K, where a phase transition to CAFM (CAFM I) ordering take place. By further cooling the polarization of the sample increases fastly to –8 nC/cm^2, and after a small change in the region of 10 K, which can be explained by T_N(Ho) (CAFM II), remains near by constant down to 4.2 K. Also here a hysteresis in the range 4.2–20 K and fields up to 12 T was observed, which disappears in higher fields. The phase diagram built from $HoMn_2O_5$ polarization measurements is shown in Figure 4c.

Data from magnetostriction measurements are presented in Figure 5. At 4.2 K the magnetostriction (MS) along the **b** axes (magnetic field is applied parallel to **b**) has a phase transition in the filed of 1.5 T and then increases rapidly reaching a value of $\lambda = 1.8 \times 10^{-3}$ at 2 T. We note that at 4.2 K λ for pure holmium single crystal reaches the value of 1.8×10^{-3} in magnetic fields about 6 T [12]. The MS along the **b** axis in magnetic fields applied perpendicularly to **b** was in the limits of 10^{-6} for magnetic fields up to 14 T and temperatures between 4.2 K and 100 K. The temperature increase shifts the phase transition point to higher fields, decreasing the slope and widening the hysteresis curve. Above 85 K colossal magnetostriction (CMS) effect was not observed.

4 Conclusions

A novel phase diagram has been established in orthorombical $HoMn_2O_5$ by our magnetostriction measurements.

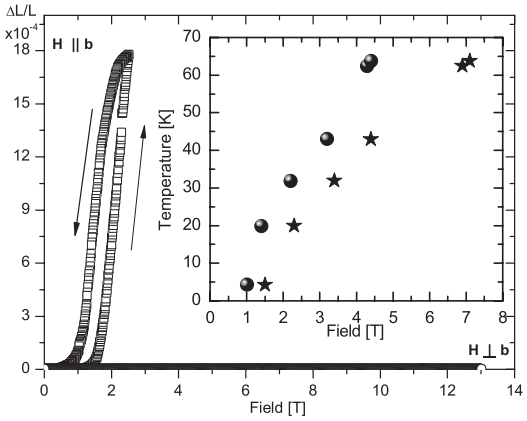

Fig. 5. Magnetostriction of $HoMn_2O_5$ at 4.2 in fields applied parallel (open square) and perpendicular (open circle) to the **b** axis. Inset show the phase diagram built from data received by magnetostriction measurements. Stars/circles means points obtained by field increasing/decreasing respectively.

Our results unambiguously show that the magnetoactive ions in the compound at the **b** axis direction are "unstable", but they are practically "static" along the **c** axis. We assume that the reason of observing such an CMS effect is the total effect of the exchange MS of the manganese ions and the holmium single-ion MS. Holmium in metal state shows gigantic single-ion MS [12], which is due to both, the strong spin-orbit coupling between orbital magnetic moment M_L and 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 external magnetic field the spin moment M_S 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 $HoMn_2O_5$ compound are strong [13]) and a CMS appears. A characteristic feature of holmium in paramagnetic state is that it preserves its large magnetostriction at room temperatures (at 300 K $\lambda = 0.17 \times 10^{-3}$). The colossal value of the $HoMn_2O_5$ magnetostriction mostly due to the holmium ions shows that the rare earth metal role should not be neglected as a strong structure determines, despite its untidy status at temperatures between 12 K and 45 K. The magnetostriction of $HoMn_2O_5$ at 4.2 K changes rapidly at 1.5 T. Comparing the polarizations and magnetostriction results obtained by us at 4.2 K, we have observed a small peculiarity in the magnetic polarization at 1.5 T. This can be an indication for a possible correlation between the field-induced polarization and magnetostriction. To confirm this correlation we plan more detailed measurements in this temperature region.

The authors are very grateful for sample preparation by M. Gospodinov and crystallographic investigations by A. Damm and M. Daszkiewicz. The work of I. Radulov is supported by NATO EAP.RIG.981824.

References

1. R.R. Briss, *Symmetry and Magnetism* (North-Holland, Amsterdam, 1966), 2nd edn.
2. H. Schmid, Ferroelectrics **162**, 317 (1994)
3. G.A. Smolenskii, I.E. Chupis, Sov. Phys. Usp. **25**, 475 (1982)
4. T. Lottermoser et al., Nature **430**, 541 (2004)
5. M. Fiebig, J. Phys. D, Appl. Phys. **38**, R123 (2005)
6. T. Goto et al., Phys. Rev. Lett. **92**, 257201 (2004)
7. N. Hur et al., Nature **429**, 392 (2004)
8. D. Higashiyama et al., Phys. Rev. B **70**, 174405 (2004)
9. J.A. Alonso et al., J. Phys.: Condensed Matter **9**, 8515 (1997)
10. E.I. Golovenchits et al., Sov. Phys. Solid State **34**, 56 (1992)
11. I. Kagomiya et al., J. Phys. Soc. Jpn **70**, Suppl. A, 145 (2001)
12. S.A. Nikitin, JETF, **43**, 31 (1962) (in Russian)
13. De la Cruse et al., Phys. Rev. B **73**, 100406 (2006)