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Magnetocaloric effect in orthorhombic manganese compounds

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Two type monocrystals of $TbMn_2O_5$ and $HoMn_2O_5$ manganites were investigated from 4.2 to 180 K. The crystals have orthorhombic structure and display antiferromagnetic transition in the investigated interval. Curie-Weiss law calculations show different type ordering along the crystallographic directions. Magnetocaloric effect computations carried out with the help of $\mathbf{c_p}$ investigations display three times higher values of the adiabatic temperature change for the $TbMn_2O_5$ compound. This result is attributed to the features of the rare-earth elements which present the same behaviour in pure mode at higher temperatures.

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1. Introduction

Modern society relies on readily available refrigeration. Magnetic refrigeration, based on the magnetocaloric effect (MCE), has latterly received increased attention as an alternative to the well-established compression-evaporation cycle for room-temperature applications. The great scale of advantages described by [1, 2, 3] etc. which this novel refrigeration method affords is the reason for the rising interest. Research investigations after the first Conference on the magnetic refrigeration at room temperatures (2005) held by Prof. Egolf in Montreux, Swiss [4] were split into two ways: creating and study of appropriate compounds with Giant MCE and developing of systems for practical applications. Thorough understanding of the magnetocaloric properties of the magnetic refrigerant materials are an important issue in magnetic refrigerant technology. Main attention in this direction was paid recently to produce magnetic refrigerants (MR) with large magnetocaloric effect. Further efforts to find out a close connection between structures, electronic and magnetic properties of potential MR are substantial for understanding of the physical processes. Cooperative interactions of this type are reflected integrally by the MCE. The latter is related to the magnetic properties of the material through the thermodynamic Maxwell relation

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B . \quad (1)$$

For magnetization measurements made at discrete temperature intervals, ΔS_m can be calculated by means

$$\Delta S_m(T,B) = \sum_i \frac{M_{i+1}(T_{i+1},B) - M_i(T_i,B)}{T_{i+1} - T_i} \Delta B, \quad (2)$$

where $M_{i+1}(T_{i+1}, B)$ and $M_i(T_i, B)$ represent the values of the magnetization in a magnetic field B at the respective temperatures. Usually this relation is used in calculation of the magnetic entropy. On other hand, the magnetic entropy change can be obtained more directly from the calorimetric measurements of the field dependence of the heat capacity:

$$\Delta S_m(T,B) = \int_0^T \frac{C(T,B) - C(T,0)}{T} dT \quad (3)$$

where C(T,B) and C(T,0) are the values of the heat capacity measured in field B and in zero field, respectively. This expression defines the MCE as a bulk feature of the unit cell. Its application leads to assignation of the adiabatic temperature change ΔT_{ad} which is more correct reflection of the MCE than the magnetic entropy change.

$$\Delta T_{ad}(T,B) = -\int_0^B \frac{T}{C(T,B)} \left(\frac{\partial M}{\partial T}\right)_B dB . \quad (4)$$

Therefore, we should concentrate on finding a material with low value of the heat capacity and with large change in magnetization at corresponding temperature.

Nevertheless, having in mind that large amount of the investigated compounds possesses large anisotropy; it is interesting to compare the results for the magnetic entropy along different directions when investigated materials are single crystals. Crystal structure also is of high importance for the transport, magnetic and thermodynamic properties of MR, as it was mentioned earlier [5, 6, 7]. Investigations of this type can be implemented on new class materials – so called multiferroics which are very appropriate because of the large number of cascade magnetic transitions which they exhibit. In our case we have chosen $HoMn_2O_5$ and

$TbMn_2O_5$ as comparable in their atomic radii and compounds with orthorhombic structure which are missing in the almost thorough review on the manganite materials by [3].

2. Samples and experimental conditions

Single crystals of $HoMn_2O_5$ and $TbMn_2O_5$ were grown as described elsewhere [8]. The samples were characterized and oriented by X-rays diffraction. The magnetization measurements were realized whit Foner-type magnetometer on a frequency 3.6 Hz. The investigated samples are of two types: cubical type with typical dimensions 1.2 × 1.4 × 1.5 mm^3 and weights 9.8 - 13.5 mg used, and thin rectangular specimens of single domain crystals with typical area 3 - 4 mm^2, thickness 0.3 mm and weight 7.4 - 9.2 mg. At room temperature $REMn_2O_5$ single crystals have space group P*bam*. The structure consists of edge-sharing $Mn^{4+}O_6$ octahedra, forming chains along the c axis, cross linked via $Mn^{3+}O_5$ pyramidal units. Fig. 1 shows the crystal structure of the compounds obtained by the X-ray diffraction analyses.

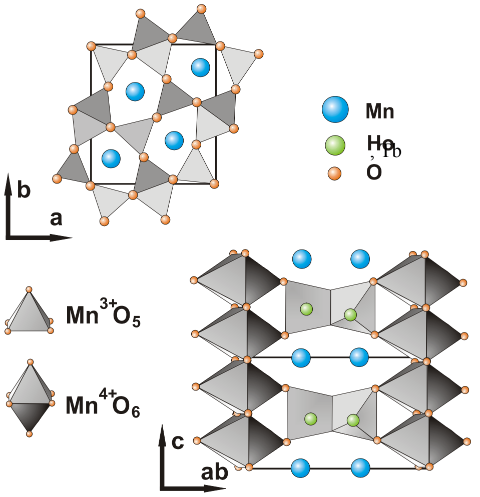

Fig. 1. Structure of $ReMn_2O_5$,Re is Ho or Tb.

3. Results and discussion

Magnetization data for $HoMn_2O_5$ and $TbMn_2O_5$ single crystals have been obtained as temperature dependence in range 4.2 - 120 K and as magnetic field dependence in range 0 - 14 T. Saturation of the sample magnetization in fields up to 14 T was not observed. Typical temperature dependence curves for $HoMn_2O_5$ and $TbMn_2O_5$ along the three principal crystallographic directions are shown respectively in Fig. 2 left block and Fig. 1 right block.

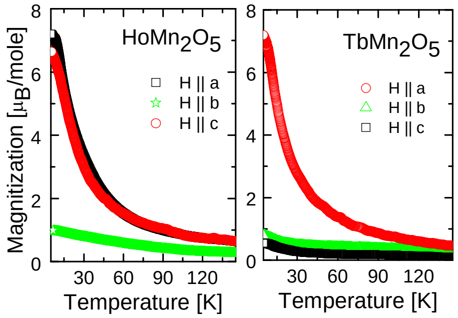

Fig. 2. Magnetization of $ReMn_2O_5$ (Re=Ho,Tb).

In both compounds a significant magnetic anisotropy is demonstrated. Main difference between the presented results is that for the $HoMn_2O_5$ monocrystal two directions of easy magnetization were found along the a and b axes while for the $TbMn_2O_5$ monocrystal there exists only one easy magnetization direction – along the b axis. Next Fig. 3 presents the development of the magnetisation derivatives versus temperature at 4 T magnetic field for $TbMn_2O_5$ compound. It is consequent that the contribution of the derivative along the **a** axis which is the direction of easy magnetization (EMD) is determinative. The other two directions **b** and **c** of the hard magnetization (HMD) are much lower and give lower contribution to the magnetocaloric effect. Propagation of the maximum of the EMD derivative with the external magnetic field follows logarithmic law as shown on Fig. 4. The derivative values for the $HoMn_2O_5$ sample are situated higher than those for $TbMn_2O_5$. This result can be ascribed to the influence of the rare-earth material in the investigated system. The difference in the same derivatives for the pure Ho and Tb at temperatures much closer to the room temperature is even higher. The peaks for each point of the curves given in (dM/dT)=f(T) coordinates at constant magnetic field become widen with the propagation of the field. At very low temperatures (around 5 K) the HMDs show a slight peak at low fields (2 ÷ 6 T) followed by further lowering of the $\partial M/\partial T$ values. The ratio of the easy and hard magnetization $\partial M/\partial T$ values is about 10% at B = 2 ÷ 4 T. Thus, the contribution of the EMD to the magnetic behaviour of the monocrystal is much higher than HMD values.

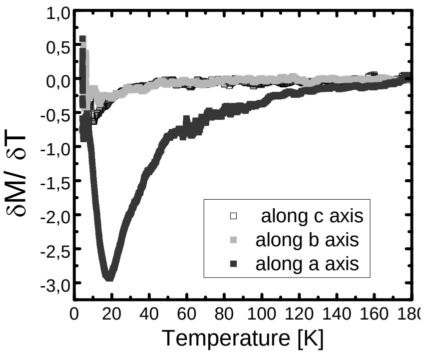

Fig. 3. Temperature dependencies of the magnetization derivative for $TbMn_2O_5$ monocrystal at 4T.

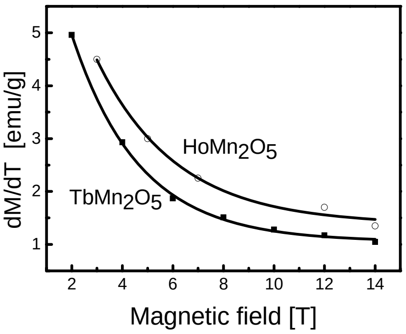

Fig. 4. Displacement of the derivatives (dM/dT)=f(T) maxima for the both compounds.

Fig. 5 presents ∂M/∂T values for the $HoMn_2O_5$ monocrystal at 3 T magnetic field. The EMDs in this case are **a** and **b** axes, i.e. easy magnetization plane - **ab** while **c** is the HMD. The values are higher than those obtained for the $TbMn_2O_5$ monocrystal. The differences are illustrated by the respective curve in Fig. 4.

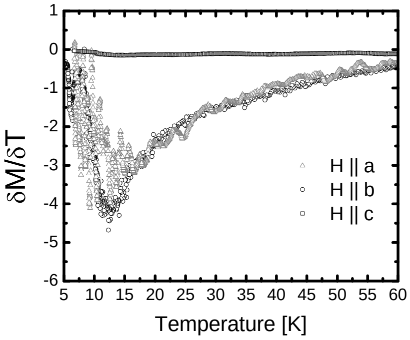

Fig. 5. Temperature dependencies of the magnetization derivative for $HoMn_2O_5$ - at 3T.

For the both directions of easy magnetization results show lowering of the ∂M/∂T maximum value with rising B and widening of the peak. Simultaneously, the maximum is shifted with the field increase from 12 K for 2 T to 40 K at 14 T. This is an interesting feature which can be useful in some cases of the practice.

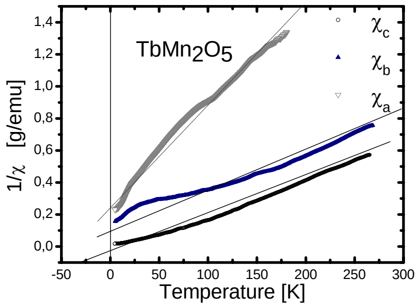

Fig. 6. Curie Weiss law calculations for $TbMn_2O_5$ monocrystal.

The observed differences are in consequence of the anisotropy of the monocrystals and can be further illustrated by the Curie-Weiss law. Figs. 6 and 7 show the Curie-Weiss law for $TbMn_2O_5$ and for $HoMn_2O_5$ compounds obtained along the three crystallographic directions. Results for the EMD on Fig. 6 for the first type monocrystal determine antiferromagnetic ordering in this direction with much higher value of the Curie constant than at the other two directions.

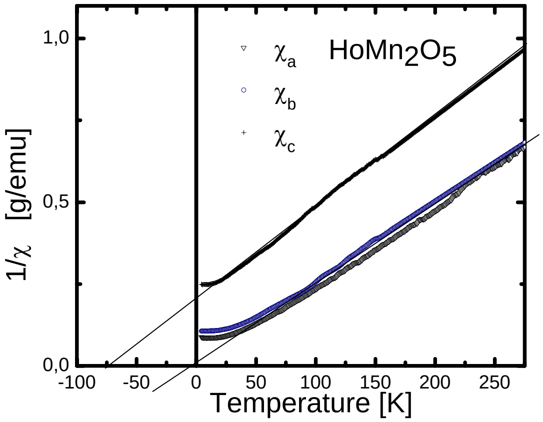

Fig. 7. Curie Weiss law calculations for $HoMn_2O_5$ monocrystal.

The $HoMn_2O_5$ compound shows different behaviour – two EMDs order ferromagnetically and the HMD orders antiferromagnetically. These features reflect in the total magnetic behaviour of the investigated samples. The values of the total magnetic moment of the compounds, derived from our measurements, are 17.4 μ_B and 14.6 μ_B for $HoMn_2O_5$ and $TbMn_2O_5$ respectively, which is in a good agreement with the expected one.

To compare the magnetocaloric response for the investigated materials we have used the specific heat data for them presented by Hur et al. [9]. Calculations have been conducted following equation (4). Magnetization derivative data were taken from our experiments. Obtained results for the adiabatic temperature change are presented at Fig. 8. They show that the maximum of ΔT_{ad} for the $HoMn_2O_5$ monocrystal is 2 times higher than that for the $TbMn_2O_5$ one. This result recur the thermal behaviour of Tb and Ho at high temperatures. It is represented by the $\Delta T_{ad}(T)$ curves for the Ho and Tb binary systems with nickel at room temperatures [10]. The polarization measurements on the same samples give the same ratio of the values between the Tb and Ho based compounds [11]. All this, probably, reflects the influence of the different rare-earth materials.

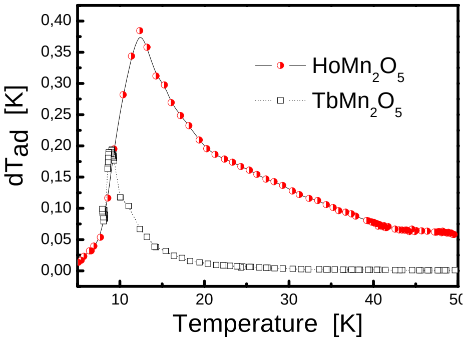

Fig. 8. Adiabatic temperature change for $HoMn_2O_5$ and $TbMn_2O_5$ monocrystals.

Obviously, the EMD plane existent in the holmium sample contributes much considerably in its magnetic behaviour but is not enough to overcome the lower $\mathbf{c_p}$ values and to give rise of ΔT_{ad}. Consequently, the monocrystal has to be orientated before its magnetocaloric usage and it should work under external magnetic field of different order applied along the different axes.

4 Conclusions

We have investigated the magnetocaloric features of rhombohedral rare-earth monocrystal manganites because of their interesting physical properties. Naturally, in monocrystal form these features are manifested in the clearest way on one side, and it seems that just the monocrystal materials can prove to be extremely of benefit for practical usage based on the magnetocaloric effect. These monocrystals can prove more useful for the practice especially because of the well defined physical properties.

Concerning our samples we regard them as a model of fundamental importance because of their low Neel temperatures. Thus, they elucidate the existence of two easy directions of magnetization for the $TbMn_2O_5$ samples and one – for the $HoMn_2O_5$ samples which probably results in their magnetocaloric properties, despite that they are of one and the same crystal structure.

Acknowledgements

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