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Magnetic and transport properties of $HoMnO_3$ monocrystals

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This paper presents results from measurements of the magnetization, specific heat and dielectric constant, and their temperature and magnetic field dependence, for $HoMnO_3$ single crystals. The results are discussed in the framework of existing data on magnetic symmetries and the interactions between the Mn-spins, the rare earth moments, and the lattice. From the resulting data, the magnetic phase diagram of $HoMnO_3$ was built.

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1. Introduction

The simultaneous mutual existence of ferro-electric and magnetic ordering in hexagonal rare earth manganites caused an increased interest in these compounds. As a result of the mutual coupling and interference between magnetism and ferroelectricity, a strong magnetoelectric (ME) effect appears [1]. Most simply, the ME-effect could be represented by the opportunity to control the electric properties by the magnetic field [2] or to control the magnetic properties of the compound by the electric field [3]. There are two the major structural peculiarities of the hexagonal rare earth manganites of the type $ReMnO_3$ (Re = rare earth), which contribute to the presence of multiferroicity. The first is ferroelectric ordering at high temperatures, when the ions are shifted from their equilibrium positions and the inverse symmetry of the lattice is damaged. The second is the presence of geometric frustration due to the antiferromagnetic ordering in Mn spins in the planar triangle lattice at temperatures of 70-130 K [4].

In the present study, an attempt is made to illustrate the effect of these structural peculiarities on the magnetization, specific heat and dielectric permittivity of $HoMnO_3$ single crystal samples. Using the experimental results, the magnetic phase diagram of this system was built.

2. Samples and experimental

The magnetic measurements were performed in temperature range 1.5 K to 300 K, and magnetic fields up to 9 T, using single crystal samples of $HoMnO_3$ with typical dimensions 2.5 x 2 x 0.2 mm^3 and weight ≈ 8-10 mg. Sample preparation and its characterization is described in [5]. For magnetic measurements, a vibration magnetometer was used. The specific heat was measured by a PPMS Quantum Design and the dielectric permittivity by a novel system described elsewhere [6] using a capacity bridge AH2500A from Andeen-Hagerling.

3. Results and discussion

In Fig. 1, the adjusted Curie – Weiss plot of the reverse magnetizations $1/\chi$ for the temperature interval 1.5 – 300 K are presented, being measured with magnetic fields applied parallel and perpendicular to the hexagonal plane (where χ is the magnetic susceptibility of the sample). The intercept of the Curie-Weiss straight lines with the axis determines the value of the Curie paramagnetic temperature for a magnetic field perpendicular to the hexagonal plane θ = -117.4 K, being a direct consequence of the antiferromagnetic (AFM) orientation of the spins along the **c**-axis. The value of θ is significantly higher than that for polycrystalline samples [7] but comparable to results for single crystal samples [8, 9].

A possible reason for the difference observed for θ is the random orientation of the different domains in the polycrystalline samples. If we assume that the magnetization along each axis of the sample has an equal contribution to the total magnetization, as in the present case, $\chi \| c$ and $\chi \| a$ participate in ratios of 2/3:1/3 and it is possible to recalculate the average magnetization of the sample. The dependence is shown in Fig. 1.

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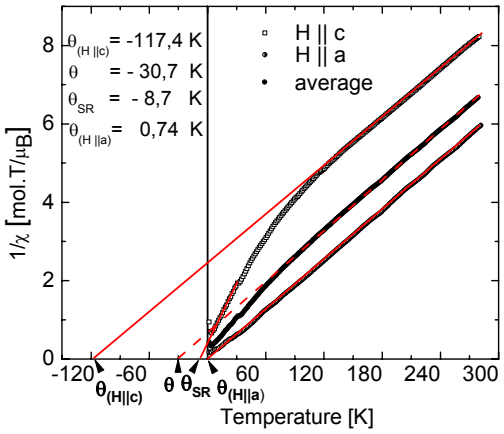

Fig.1. Curie-Weiss plot of the $HoMnO_3$ single crystal sample. The graphically determined Curie paramagnetic temperatures are also shown.

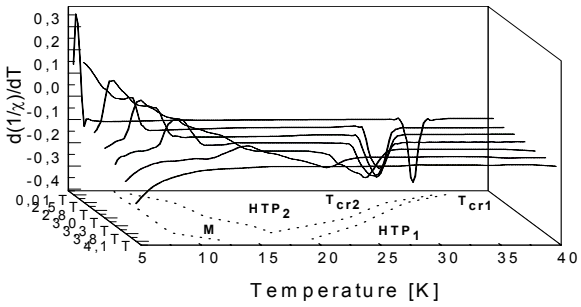

Fig.2. Temperature dependences of the magnetization derivative in a $HoMnO_3$ sample for different values of the external magnetic field perpendicular to t he hexagonal plane.

It is obvious from the results obtained that a strong magnetic anisotropy is present single in the hexagonal plane the magnetization reaches twice as high values compared to those along the **c**-axis (8 и 4 μ_B/mol at T = 5 K and H = 8 T, respectively). The value of the experimentally found effective magnetic moment is μ_{eff} = 11.5μ_B, which corresponds very well to the theoretically determined one μ_{eff} = 11.7 μ_B and the values cited in [8].

For a better illustration of the magnetization peculiarities, the results for the hexagonal $HoMnO_3$ samples are presented in d(1/χ)/dT = f(T, H) coordinates in Fig. 2.

As can be seen, in the interval from 300 K to the temperature of the spin re-orientation T_{SR} = 32.8 K, no peculiarity in the behavior of the magnetization, both parallel and perpendicular to the hexagonal plane field, is observed. The magnetization within the whole interval is inversely proportional to the temperature. At a temperature T_N = 76 K, where the ordering of the moments of Mn^{3+} ions takes place, no changes are observed, which confirms the results by other authors [7, 8, 10]. At temperatures lower than T_N, the sample magnetization is dominated by the paramagnetic contribution of the magnetic moments of Ho^{3+} ions.

At a temperature of T_{SR} = 32.8 K, the magnetization measured perpendicular to the hexagonal plane field indicates a slight but distinct decrease, followed by a monotonic increase.

Since, at temperatures lower than T_N, the spins of all Mn^{3+} ions are oriented, the paramagnetic contribution to the magnetic susceptibility along the c-axis for temperatures lower than T_{SR} should be attributed to the moment of Ho^{3+} ions. The change of the magnetization at T = T_{SR} is an indication that at least some of the spins of Ho^{3+} ions are AFM ordered, and this ordering is linked with the transition with re-orientation of the spins of Mn^{3+} ions**.**

Reaching a temperature of T_{B1} = 5.2 K, a sharp increase in the magnetization is observed, and for temperatures lower than T_{B1}, a difference in the shape of the curves describing the magnetization in an external magnetic field applied parallel or perpendicular to the hexagonal plane is found.

At a temperature near to 1.8 K and a magnetic field of 0.5 T applied perpendicular to the hexagonal plane, again a peculiarity of the curve describing the sample magnetization is observed, showing an abrupt increase in its value. With increasing applied magnetic field, this change is shifted towards higher temperatures. Simultaneously, the magnitude of the transition decreases, and at fields above 1.3 T it changes its sign, i.e. it becomes negative and disappears near 1.8 T.

The results shown coincide with those obtained by experiments using neutron scattering [7, 11]. They support a picture in which the re-orientation of the spins of Mn^{3+} ions is accompanied by a partial c-axis AFM ordering of the moments of the Ho^{3+} ions. This results in a change not only in the magnetization but also in the dielectric constant and specific thermal capacity of the sample, creating in this way a relation between its dielectric and magnetic properties. To verify this assumption, we carried out a series of experiments on the temperature dependences of the specific heat and dielectric constant ε.

In Fig. 3, the temperature dependence of the specific heat of $HoMnO_3$ in zero magnetic field is given. Three specific parts of the curve are observed. The first is a λ – peak at a temperature of T_N = 76 K corresponding to the transition of second order to AFM ordering of the Mn^{3+} magnetic moments.

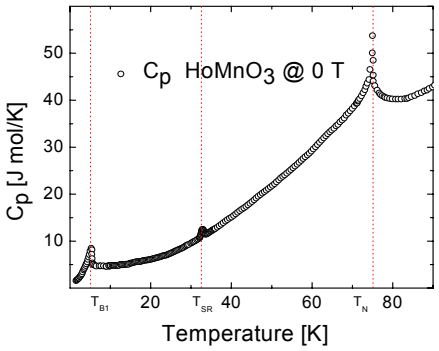

Fig. 3. Temperature dependence of the specific heat of the hexagonal $HoMnO_3$ sample.

This peak does not depend on the external magnetic field applied, which is an indication that the AFM ordering of the spins of Mn^{3+} ions is extremely insensitive to the external magnetic field. The second specificity is the appearance of a rather small peak at a temperature of T_{SR} = 32.8 K, which corresponds to the transition with re-orientation of the spins. The third peculiarity is a wide double peak at a temperature of T_{B1} = 5.2 K, which is transformed into a broad plateau when an external magnetic field perpendicular to the hexagonal plane is applied.

The results obtained correspond partially to those obtained for polycrystalline samples [7] and agree with those for single crystal samples of $HoMnO_3$ [8].

In Fig. 4, the temperature dependence of the dielectric constant ε, measured in the absence of external magnetic field, is presented. Using the plot of ε (T), one could clearly identify the three transition temperatures T_N, T_{SR} and T_{B1}, which were not visible in small magnetization measurements. The decrease in ε (T) at T_N is due to the transition to AFM ordering of far account of the spins of Mn^{3+} ions. At T_{SR} = 32.8 K, an extremely sharp peak in ε (T) is observed due to the spin re-orientation. At the start of the low temperature region at T_{B1} = 5.2 K, another clear peak in ε is found, probably as a result of the structural transition.

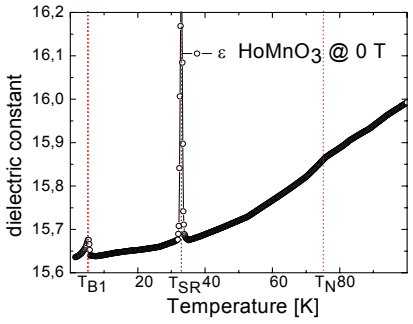

Fig. 4. Temperature dependence of the dielectric constant of the hexagonal $HoMnO_3$ sample.

The magnetic phase diagram of $HoMnO_3$ monocrystals was built and is presented in Fig. 5.

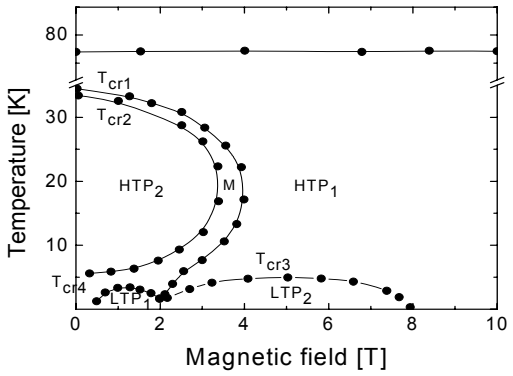

Fig. 5. Phase diagram of hexagonal $HoMnO_3$ for magnetic measurements in a field applied perpendicular to the hexagonal plane.

This was based on our measurements of the magnetization over a wide temperature range and in an external magnetic field applied perpendicular to the hexagonal plane of the crystal. The exact temperatures observed in the magnetisation transition were determined by the derivatives presented in Fig.2.

At temperatures higher than 76 K, where the reorientation of the Mn^{3+} ions took place, no peculiarities were observed, and this fact is represented by a straight line in the phase diagram. At temperatures lower than 76 K, two regions of well pronounced high temperature magnetic phases HTP_1 and HTP_2 were found. Between them, we determined the appearance of a new phase (called medial, M) which is stable at zero magnetic field and temperatures lower than 5.2 K.

Below this temperature, in the region 0.5 T to 8 T, the existence of two low temperature magnetic phases LTP_1 and LTP_2 were registered. Their boundary curves show that at 1.3 T, the sign of the magnetic anomaly was changed. The magnetic structure of the sample in these two phases, and also in the medial phase, it still remains unclear and needs additional structural investigations for their precise definition. Probably, the issue is the change in the symmetry during the phase transitions where the angle between the Mn^{3+} ions and the a-axis is turned smoothly from 90^0 to 0^0. Simultaneously, it is accomplished by partial AFM ordering of the Ho^{3+} ions parallel to the c-axis.

4. Conclusions

The main achievement of the present work is that we have demonstrated, experimentally, the existence of a closed relation between the magnetic ordering and the thermodynamic and dielectric properties of $HoMnO_3$ monocrystal samples. As can be seen from the presented

results, most of the peculiarities in the magnetic phase diagram of $HoMnO_3$ samples appear as peculiarities in the temperature dependences of the specific heat and the dielectric constant.

This physical phenomenon, as a relationship between magnetic ordering and the thermodynamic and dielectric properties, could be understood if all participating interactions are taken into account, such as the spins of Mn^{3+} ions and their AFM super exchange interaction, the magnetic moments of the Ho^{3+} ions and their relationship to the spins of Mn, as well as the magnetic interaction between the magnetic moments of Ho at low temperatures and, finally, the ferroelectric polarization including a non-direct interaction to the magnetic sub-system through spin-phonon interaction.

Obviously, the theoretical solution of the problem is quite complex, and additional experiments are necessary to determine the magnetic ordering in the different phases, and the nature of the observed phenomena.

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