

Magnetotransport properties of $\text{Sm}_{0.864}\text{Pb}_{0.136}\text{MnO}_3$ single crystal

V. LOVCHINOV, A. APOSTOLOV, D. DIMITROV, P. SIMEONOVA, K. NENKOV^a

George Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria

^a*Leibniz-Institut für Festkörper und Werkstofforschung, 01171 Dresden, Germany*

Magnetic and electrical properties of $\text{Sm}_{0.864}\text{Pb}_{0.136}\text{MnO}_3$ single crystals have been studied. The sample is paramagnetic in the temperature range 150 - 300 K and has paramagnetic moment $5.3 \pm 0.3 \mu_B$ at room temperature. At 65 K antiferromagnetic ordering occurs as a second-order phase transition accompanied by a weak ferromagnetic moment along the Z direction ($f_z = 0.4 \mu_B$). At 8 K an additional low temperature antiferromagnetic transition occurs as a first order phase transition with spontaneous magnetization along the X direction ($f_x = 0.7 \mu_B$). A weak $M(H)$ curves hysteresis was observed only for the temperatures at which the ferromagnetic moments become reoriented from the Z direction (II order phase transition) to the X direction (I order phase transition). Resistivity measurements were fulfilled at zero and 5 T magnetic fields. They show that the $\text{Sm}_{0.864}\text{Pb}_{0.136}\text{MnO}_3$ single crystal is insulator in the temperature range 2 - 300 K and possesses a positive magnetoresistance (MR) only in the temperature range 129 - 142 K. The maximum value of MR reaches 154% around 141 K.

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1. Introduction

Substitution of rare-earth (RE) ions ($L = \text{La}, \text{Sm}, \text{Pr}$) in $\text{L}_{1-x}\text{A}_x\text{MnO}_3$ systems by alkaline-earth ions ($A = \text{Ca}, \text{Sr}, \text{Pb}$) results in significant variation of their magnetic, electrical and structural properties. Two different mechanisms to control this variation exists:

1. For Mn^{3+} rich manganites ($x < 0.5$), the double exchange (DE) $\text{Mn}^{3+} - \text{O} - \text{Mn}^{4+}$ ferromagnetic interactions predominate.

2. For Mn^{4+} rich ions ($x > 0.5$), there exist charge ordering (CO) phenomena of the Mn^{3+} and Mn^{4+} species together with anti-ferromagnetic insulating (AFMI) state, ferromagnetism (FM) or cluster glass (CG) appears concomitantly with charge delocalization.

The crystal lattice also plays a role in these mechanisms controlling magnetic coupling between neighboring Mn^{3+} and Mn^{4+} ions, through the Jahn-Teller distortion associated with the Mn^{3+} ion. The last one is static in the orbitally ordered end member LaMnO_3 and becomes dynamic in the ferromagnetic composition range where up to 40% of L is replaced by a divalent atom.

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Among different compositions, the $\text{Sm}_{1-x}\text{Pb}_x\text{MnO}_3$ compound is a system convenient for study of the variation between the wide band ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) [1] and narrow band ($\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$) [2] manganites. This system is especially suitable for investigation of the Jahn-Teller

distortion role in the mechanisms controlling the magnetic coupling between Mn^{3+} and Mn^{4+} ions. The reason for this is the fact that Sm is the smallest single rare-earth ion to form the compound with a small tolerance factor $t = (r_L + r_O) / \sqrt{2}(r_A + r_O)$, where r_L and r_A are the radii of the L and A – site cations and r_O is the oxygen radius. The small value of t results in a pronounced buckling of the array of MnO_6 octahedron in the structure, with reduced Mn-O-Mn bonds angles and a narrow e_g bandwidth. Unfortunately, $\text{Sm}_{1-x}\text{A}_x\text{MnO}_3$ (where $A = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Pb}^{2+} \dots$) system was studied insufficiently. Up to now, polycrystalline samples of few compositions, mainly in the ferromagnetic region ($0.3 \leq x \leq 0.45$) were investigated [3-10]. The entire concentration region was studied only for the $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$ system in Ref.[3] and for an $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$ single crystal from it in Ref.[10]. Recently, magnetic properties and spin excitations in SmMnO_3 single crystal was published in ref. [12].

The values of the magnetic and transport properties of the $\text{Sm}_{1-x}\text{A}_x\text{MnO}_3$ system when the doping element is Pb are placed between those for the compounds doped with Ca and Sr. According to [3] the $\text{Sm}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ polycrystalline sample exhibits an anti-ferromagnetic behaviour at temperatures lower than 180 K (which is the Neel temperature for the samples) and a ferromagnetic behaviour below 80 K. According to [10], where a monocrystalline $\text{Sm}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ sample was investigated, there exists only one temperature of anti-ferromagnetic (AF) transition at 75 K. Samples $\text{Sm}_{0.95}\text{Sr}_{0.05}\text{MnO}_3$ and $\text{Sm}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ also do not show second low temperature peculiarities. Polycrystalline samples with doping element Pb were investigated only in Ref. [7] earlier. There was reported only one transition at Curie temperature at 96 K.

The main purpose of this paper is an attempt to clarify the contradictory existing data for samples doped with a low percentage alkaline element. Moreover, our investigations on mono crystalline $\text{Sm}_{0.864}\text{Pb}_{0.136}\text{MnO}_3$ sample will help to fill up the lacking data for SmMnO_3 compounds doped with Pb^{2+} .

2. Sample preparation and properties

$\text{Sm}_{0.864}\text{Pb}_{0.136}\text{MnO}_3$ single crystal was grown by the High Temperature Solution Growth (HTSG) method. As a solvent we used a flux of $\text{PbO}:\text{PbF}_2:\text{B}_2\text{O}_3 = 75\%:24.5\%:0.5\%$. The synthesis of the main substance was carried out at 1280 °C for 72 hours. As a result, single phase ingots with orthorhombic structure were obtained. The stoichiometry of the crystal determined by electron microprobe analysis and chemical analysis was found to be $\text{Sm}_{0.864}\text{Pb}_{0.136}\text{MnO}_3$. The single crystal $\text{Sm}_{0.864}\text{Pb}_{0.136}\text{MnO}_3$ was XRD investigated both as a monocrystal and as a powder. The powder was obtained by grinding small parts of the monocrystal. In the XRD patterns obtained in this way no differences were observed. Fig. 1 shows only the data from the powder diffraction pattern. These studies demonstrate that $\text{Sm}_{0.864}\text{Pb}_{0.136}\text{MnO}_3$ crystallizes in an orthorhombic structure with space group $Pbnm$; $b = 5.671(3)$ Å; $a = 5.404(1)$ Å and $c = 7.569(2)$ Å, $(b > a > c/\sqrt{2})$ and cell volume/formula unit = 231.96 Å³.

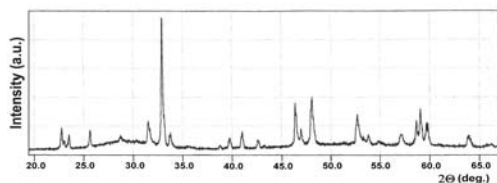


Fig. 1. X-ray diffraction pattern for $\text{Sm}_{0.864}\text{Pb}_{0.136}\text{MnO}_3$ single crystal.

The investigations were conducted on a crystal with dimensions $1.05 \times 0.75 \times 1.55$ mm. and weight of $g = 0.07081$ gr. Temperature dependent resistance was measured using four-probe technique by means of Physical Properties Measurements System (PPMS Quantum Design).

The sample was cooled from 300 K down to 4.2 K in zero fields and at 5T. The current used in $R(T)$ measurements was 1 μA. Magnetization and DC susceptibility were measured using SQUID-MPMS XL Quantum Design magnetometer at fields up to 8 T directed parallel to the c axis and temperatures from 2 K to 300 K.

3. Results and discussion

In Fig.2 the magnetization and DC susceptibility as a function of the temperature are presented. The magnetization at weak constant magnetic field (0.1 T)

remains practically unchanged between 300 K and 150 K and raises with the further lowering of the temperature. The curve shows two peculiarities which are separated by a profound minimum (see the insets of the Fig. 2).

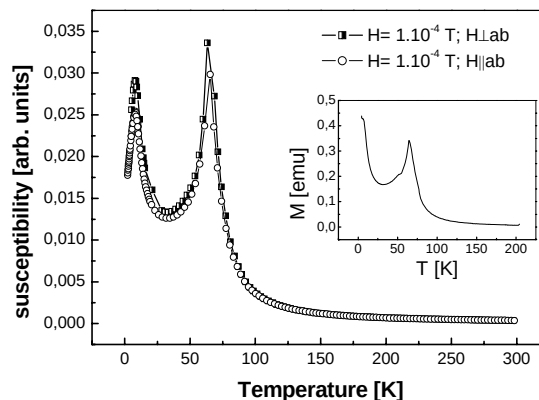


Fig. 2. Magnetization at $H=0.1$ T applied parallel to c axis (inset) and DC susceptibility, measured at $H=10^{-4}$ T magnetic field applied parallel (circles) and perpendicular (squares) to ab surface as a function of the temperature.

By susceptibility measurements in a DC field in two directions – parallel and perpendicular to ab the accurate places of the transitions can be determined. The high temperature one appears at 65.0 ± 0.5 K and the other one (low temperature) is at 8.0 ± 0.5 K. Above 65 K the sample is paramagnetic. In the temperature range 65 – 300 K χ values are obtained from $M(H)$ investigations performed at different temperatures (see Fig. 4).

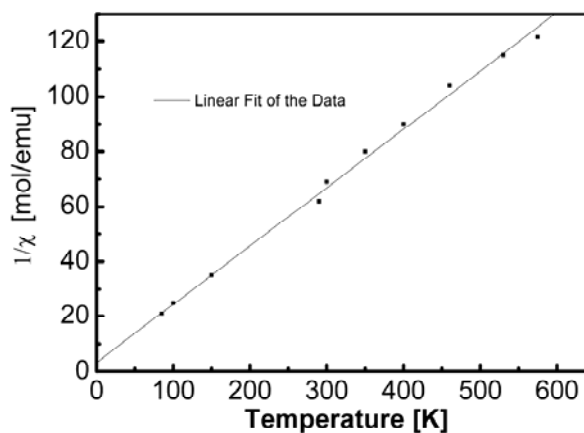


Fig. 3. The reciprocal susceptibility as a function of the temperature.

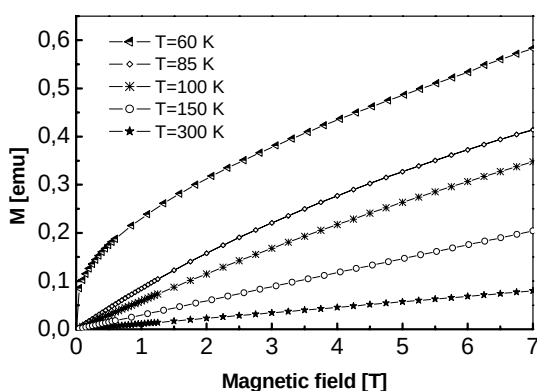


Fig. 4 Magnetization as a function of the magnetic field ($H \parallel c$) at different temperatures.

For a more precise determination of the paramagnetic moment at room temperature and the asymptotic temperature $\theta_{\text{paramagnetic}}$ some additional $M(H)$ measurements are conducted between 300 and 600 K using a magnetic balance. In Fig. 3 the Curie-Weiss dependence $1/\chi = f(T)$ is presented. The paramagnetic moment determined from this function at room temperatures is $5.3 \pm 0.3 \mu_B$ and the $\theta_{\text{paramagnetic}} = -15$ K.

The observed anisotropy of the magnetic susceptibility ($\chi_{ab} > \chi_c$) (see Fig. 2) indicates that the crystal is practically untwined. Recent investigations [12] on the pure single crystal SmMnO_3 by the quasi-optical sub-millimetre backward-wave-oscillator technique show two anti-ferromagnetic resonance modes in the Mn subsystem and $\chi_{ab} > \chi_c$ which is in good agreement with the results presented here.

The quasi-constant value of the magnetization between 150 K and 300 K shows that samarium and manganese magnetic moments are disordered in this region and that there exists only short range magnetic ordering which cannot be destroyed by fields of the order of 0.1 T. The observed short range ordering appears as a result of the competition between positive $\text{Mn}^{3+}\text{--O--Mn}^{4+}$ and negative $\text{Mn}^{3+}\text{--O--Mn}^{3+}$ magnetic interactions typical for this type of compounds where up to 10 % Mn^{4+} exists [11]. Similar data are reported in [6, 8, 10] for samarium manganite but doped with strontium.

The transition at 65.0 ± 0.5 K is anti-ferromagnetic II order phase transition for the manganese moments. These moments are arranged with anti-ferromagnetic configuration along the X axis and possess weak ferromagnetism along the Z direction. This behaviour is similar to that of other high temperature perovskite phases with the D_{16h}^{16} space group [6, 8, 10] and is connected with the Sm magnetic behaviour. The later remains magnetically disordered and is eventually slightly polarized from the weak magnetic moment of the manganese lattice. At temperatures below 2 K the Sm

magnetic moments should be arranged. The measured weak ferromagnetic moment at 60 K, i.e. just before the transition, is $f_z = 0.4 \mu_B$. The magnetic fields up to 8 T can not destroy it.

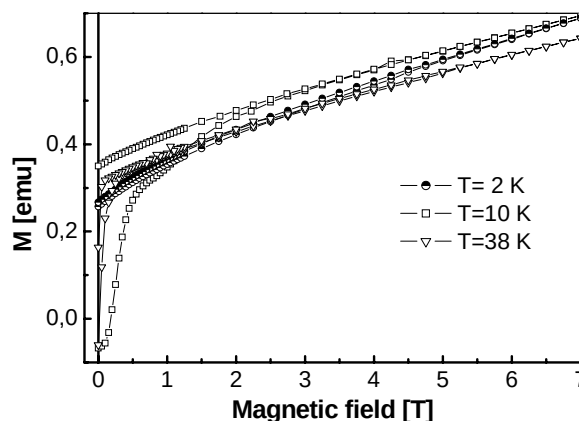


Fig. 5 Magnetization and hysteresis effect as a function of the magnetic field ($H \parallel c$) at the temperatures where the reorientation of the ferromagnetic moments occurs.

As can be concluded from the $M(H)$ curve at 10 K (see Fig.5), a meta-magnetic transition occurs which is without magnetic saturation of the sample at fields up to 8 T. Just around 8 K the structure destabilizes and the second transition (I order phase transition) is then observed. In contrast to the II order phase transition this I order phase transition makes reorientation towards an anti-ferromagnetic structure along the Z axis accompanied by weak ferromagnetism along the X axis due to the interaction between magnetic moments of manganese and samarium respectively. The maximal value of the weak ferromagnetic moment measured and calculated from $M(H)$ curve at 10 K is $f_x = 0.7 \mu_B$.

In Fig 4 and Fig.5 the magnetization curves as a function of the magnetic field at different temperatures are shown. The weak spontaneous ferro-magnetic moments measured and calculated from these curves vary from $0.07 \mu_B$ at 100 K to $0.7 \mu_B$ at 10 K and $0.62 \mu_B$ at 2K respectively. They were determined from the intersection of the tangent to the magnetization curves with the Y axis. The sample mass and the formula unit were taken into account in this procedure for calculation of f_x .

As can be seen on the magnetisation curves at 38K, 10K and 2K (see Fig.5) the weak hysteresis was observed. The origin of this hysteresis is probably connected with a weak ferromagnetic moment and its reorientation from Z direction for II order phase transition to X direction for I order phase transition. In fact, at the temperature range where the II order transition takes place and higher no hysteresis is observed (see Fig. 4).

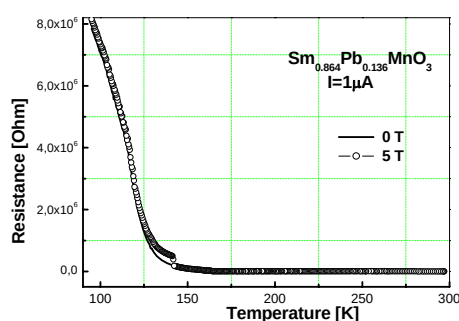


Fig. 6. Resistivity as a function of temperature under zero and 5 T magnetic field.

In Fig. 6 are shown measured values of the resistivity as functions of the temperature at two different magnetic fields (0 T and 5 T). Over the whole investigated temperature region the $\text{Sm}_{0.864}\text{Pb}_{0.136}\text{MnO}_3$ single crystal remains an insulator. No insulator-metal transition was observed. In the paramagnetic and short range order regions (from 300 to 150 K) the resistivity monotonically increases from 100 Ohm.m to 179 KOhm.m. In this region, the 5 T magnetic fields applied to the monocystal do not induce changes in the resistance. However, below 142 K is observed quite a large positive magnetoresistance (MR). MR is defined by the equation $\text{MR} = [R(H) - R(0)] / R(0)$ where $R(H)$ and $R(0)$ are the resistance at a given temperature in the applied and zero magnetic fields, respectively. The maximum value of MR is up to 154 % around 142 K. With the decrease of the temperature the value of this colossal magnetoresistance (CMR) slightly decreases and practically vanishes around 129 K. Further decrease of the temperature to the lowest value at which the resistivity could still be measured leads to further increase in the resistivity. No influence of the magnetic field in this region was observed. It the drastic difference between the properties of Pr- Nd- and Sm- based manganites compared to the La- based ones is pointed out in the review [11]. The doping of these systems with one and the same divalent element does not lead to the appearance of conductivity. Some specificity can be expected in the magnetic properties of these manganites too. These peculiarities can be explained with the forming of holes in the inner shell of the Pr- Nd- or Sm- ions instead of the d-shell of the Mn ions, or with the diminishing of the charge carrier density in magnetic field. Changes in the transport and magnetic properties sometimes are related to a change in the atomic structure or structural transition of the compounds [11].

We associate the appearance of a positive CMR effect in our case with some weak variations of the crystal lattice caused by the applied magnetic field which variations do not affect the magnetic properties of the $\text{Sm}_{0.864}\text{Pb}_{0.136}\text{MnO}_3$ single crystal but lead to changes in its conductivity.

4. Conclusions

In the present paper we have shown for the first time results of the magnetic and resistivity measurements on the monocrystalline SmMnO_3 doped with a small quantity of Pb^{2+} . Contrary to the results for polycrystalline samples of the same system doped with different divalent elements [3-12], our data for single crystal $\text{Sm}_{0.864}\text{Pb}_{0.136}\text{MnO}_3$ clearly show that the sample is paramagnetic down to 150 K and possesses two anti-ferromagnetic transitions – one at the high temperature ($65,0 \pm 0,5$ K) and another one at low temperature ($8,0 \pm 0,5$ K) with out registration of a pure ferromagnetic or counterpoise transition.

Over the whole investigated temperature region (2-300 K) the single crystal $\text{Sm}_{0.864}\text{Pb}_{0.136}\text{MnO}_3$ remains an insulator. No insulator-metal transition is observed. The resistivity measurements at 0 T and 5 T magnetic fields unexpectedly showed a positive CMR effect in the vicinity of PM – AFM transition. We associate the appearance of this effect with some weak variations of the crystal lattice caused by the applied magnetic field which variations do not affect the magnetic properties of the $\text{Sm}_{0.864}\text{Pb}_{0.136}\text{MnO}_3$ single crystal but lead to changes in its conductivity.

The wide disparity of critical properties reported in the literature for manganites calls for further experimental studies on high purity samples, in particular single crystal investigations with different compositions. The present study fill up the lacking data for SmMnO_3 compounds doped with Pb^{2+} .

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*Corresponding author: lovcinov@issp.bas.bg