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Magnetic Properties of Nonstoichiometric Perovskites $R_{1-x}MnO_{3+y}$ ($R = La, Eu$)

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Abstract. The crystal structure and magnetic properties of orthomanganites $R_{1-x}MnO_{3+y}$ ($R=La, Eu$; $x \leq 0.2$; $y \leq 0.13$) were investigated. It was shown that the increase of oxygen content leads to the transformation from the antiferromagnetic to the ferromagnetic state in these compounds. The Curie temperatures of $La_{1-x}MnO_{3+y}$ and freezing temperatures of magnetic clusters for $Eu_{1-x}MnO_{3+y}$ in the samples with deficit of A-cations are higher than those in parent compounds (with $x=0$). The magnetic data indicate that the mixed magnetic state involving ferro- and antiferromagnetic domains is realized in the intermediate range of x, y values.

1. INTRODUCTION

Orthomanganites on the base of $LaMnO_3$ have interesting magnetic and electric properties for their potential application [1]. The effect of the colossal magnetoresistance may approach 107 % in the field 6 T [2]. In these systems the ferromagnetic ground state arises by oxidation of $LaMnO_3$ or by substitution of the alkaline-earth ions for La-cations [3]. At present it has been shown that nonstoichiometry might arise due to the La-cations deficit [1]. The magnetic properties of samples with such a type of nonstoichiometry have not been studied yet.

2. EXPERIMENTAL

$LaMnO_{3+y}$ samples were prepared according to the phase diagram composition vs temperature and oxygen pressure, their composition was determined by chemical analysis. The specimens with cation deviation from stoichiometry were annealed in air or vacuum, quenched and cooled slowly with the furnace. Since X-ray diffraction patterns showed the presence of impurity phases for $x < 0.8$, the investigations were carried out on the samples $La_{0.8}MnO_{3+y}$ and $Eu_{0.8}MnO_{3+y}$.

3. RESULTS AND DISCUSSION

The ac-magnetic susceptibility of the $La_{0.8}MnO_{3+y}$ depends on the preparation conditions. A sharp peak at 120 K was revealed in the $\chi(T)$ curve for the specimens annealed in vacuum 10^{-4} Pa at 1073 K for 8 h (Fig.1, curve 1). The specimen quenched from 1400 K had the temperature of the magnetic ordering about 180 K (Fig. 1, curve 2). The anomalous behavior was observed near 120 K. The annealing in air at 1073 K for 20 h brings about of the Curie temperature up to 240 K (Fig.1, curve 4). The increasing oxygen content resulted in the magnetization rise. The saturation magnetization of the specimen annealed in air is estimated to be about 70 emu/g at 77 K. This value is close to that calculated for the case of ferromagnetic ordering of the Mn^{3+} , Mn^{4+} ions magnetic moments. The samples annealed at 1073 K for 20 h and cooled slowly from 1573 K had a rhombohedrally distorted unit cell in contrast to the specimen reduced in vacuum characterized by the O' -orthorhombic structure ($c/\sqrt{2} < a < b$, d_{z^2} -orbital ordered phase).

A sharp maximum of the susceptibility was observed for the $LaMnO_{3.02}$ at 120 K and the maximum is broadened with the increasing oxygen content. The temperature of the peak of susceptibility does not depend on a composition in a range $0 < y < 0.11$. The Curie temperature of the $LaMnO_{3.13}$ is measured to be about 160 K. The magnetization enhances with increasing oxygen content. The magnetization of the $LaMnO_{3.13}$ reaches the value of 70 emu/g at 77 K in the field 5 kOe. The X-ray patterns show the O' -orthorhombic structure of the $LaMnO_{3+y}$ system at $y < 0.05$, the O-orthorhombic structure at $0.07 \leq y \leq 0.11$ and the rhombohedral one at $y \geq 0.12$.

The results of magnetization measurements for the $EuMnO_{3.02}$ in the field 20 Oe are shown in Fig.2. Curve 1 (ZFC (zero field cooled)) and curve 2 (FC (field cooled)) do not coincide below 48 K. At 4.2 K the ratio between the FC and ZFC

magnetizations is more than three orders of magnitude. A sharp alteration of magnetization near 40 K seems to be due to the antiferromagnetic ordering in Mn-sublattice. The magnetization of the $\text{EuMnO}_{3.02}$ depends linearly on the field up to 25 kOe at 4.2 K. The magnetic moments reorientation occurs in fields higher than the magnetic anisotropy field (25 kOe at 4.2 K). The spontaneous magnetization is estimated to be 2.5 emu/g. From these data it follows that the magnetic anisotropy is large at 4.2 K and $\text{EuMnO}_{3.02}$ is inhomogeneous antiferromagnetic. The decrease of Eu content leads to the abrupt fall of magnetic anisotropy and increase of both magnetization and freezing temperature of magnetic moments inside ferromagnetic clusters. The (ZFC) and (FC) magnetizations of $\text{Eu}_{0.8}\text{MnO}_{3+y}$ (the specimen was cooled slowly from 1573 K with the furnace) do not coincide below 60 K and have maxima near 40 K (Fig.2).

These data show the nonstoichiometric manganites to be inhomogeneous magnetics. Magnetic properties of most of the samples are due to microdomains of ferromagnetic and antiferromagnetic phases. The temperatures of magnetic ordering for antiferromagnetic phase depend weakly on conditions of the sample preparation (Figs.1,2). The ratio between ferromagnetic and antiferromagnetic phases depends on the oxygen content. The magnetic moments of the microdomains of both the phases interact through the interphase boundary as seen from the dependence of magnetic properties on the magnetic prehistory and from the considerable decrease of the ac-magnetic susceptibility below the temperature of antiferromagnetic phase ordering (Figs.1,2).

We suppose that the antiferromagnetism of La-manganite results from the orbital ordered phase while the ferromagnetism - from the orbital disordered phase. The magnetic anisotropy of the $\text{EuMnO}_{3.02}$ is much higher than that for LaMnO_{3+y} . The orbital state of Mn^{3+} inside ferromagnetic clusters in the $\text{EuMnO}_{3.02}$ is apparently characterized by a slow reorientation of the d_{z^2} orbitals (the static Jahn-Teller effect) while such a process for the $\text{La}_{1-x}\text{MnO}_{3+y}$ proceeds much faster (the dynamic Jahn-Teller effect).

It is believed that the double exchange interactions between pairs of Mn^{3+} and Mn^{4+} ions are responsible for the ferromagnetic and transport properties in manganites [2,3]. However for a slightly doped insulating regime in $\text{La}_{1-x}\text{MnO}_{3+y}$ the double exchange model suggested a canted or spiral antiferromagnetism [3-5]. This theory suggests also that the canted state continuously changes to the ferromagnetic one as a function of hole (Mn^{4+}) doping. It seems that the ferromagnetic ordering is governed by superexchange interactions via oxygen. The superexchange interactions between Mn^{3+} - Mn^{3+} and Mn^{3+} - Mn^{4+} ions via oxygen in octahedral surroundings and with the bond angle of 180° have been discussed earlier by many authors. According to [4,5] the dominant exchange interaction is ferromagnetic. Orbital or charge ordering in the perovskite lattice leads to antiferromagnetism [3]. Ferromagnetic part of superexchange interactions abruptly decreases with decreasing Mn-O-Mn angle [5].

Figure 1: Ac magnetic susceptibility vs temperature for $\text{La}_{0.8}\text{MnO}_{3+y}$: 1- sample annealed in vacuum; 2- sample quenched from 1400 K; 3- sample cooled slowly from 1573 K and 4- sample annealed in air at 1073 K

Figure 2: Magnetization vs temperature at $H=20$ Oe for $\text{EuMnO}_{3.02}$: 1- ZFC, 2- FC, and $\text{Eu}_{0.8}\text{MnO}_{3+y}$: 3- ZFC, 4-FC

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