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Magnetic Phase Transformation in the $\text{RE}(\text{Mn}_{0.5}\text{B}_{0.5})\text{O}_3$ Perovskites (RE is a Rare Earth Ion, B-Ni, Co)

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Abstract. A magnetic study of perovskites $\text{RE}(\text{Mn}_{1-x}\text{B}_x)\text{O}_3$ (RE=Eu, Gd, Tb, Dy, Y; B=Ni, Co) is reported. It is found that investigated perovskites are nonhomogenous ferromagnets with relatively high Curie temperatures. The magnetic anisotropy of Ni-containing perovskites is much lower than that of Co-containing ones. It is supposed that domains with different charge state of ions and magnetic structure coexist in a wide range of Co- and Mn- concentrations. The metamagnetic behavior has been observed for $\text{RE}(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_3$ perovskites (RE=Gd, Tb, Dy, Y).

1. INTRODUCTION

The structure and properties of the compounds on the base of LaMnO_3 were a subject of many investigations. In $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ the insulator-metal and antiferromagnetic-ferromagnetic transitions are brought about by doping charge carriers in a parent insulating LaMnO_3 . These compounds show a colossal magnetoresistance near their Curie temperatures. However, there is another class of compounds exhibiting substitutionally driven antiferromagnetic-ferromagnetic transition due to substitution of Co- or Ni-ions for manganese ions. According to [1,2] the compositions $\text{La}(\text{Mn}_{1-x}\text{B}_x)\text{O}_3$ (B=Co, Ni) exhibit the ferromagnetic ordering in the range $0.2 < x < 0.5$. There is no general agreement concerning the charge distribution and exchange interactions in $\text{La}(\text{Mn}_{1-x}\text{B}_x)\text{O}_3$ (B=Ni, Co) perovskite. The purpose of the present study is to clarify the mechanism of exchange interactions in mixed manganites and to show how the properties change with the replacement of La by Eu, Gd, Tb, Dy or Y.

2. EXPERIMENTAL

Our samples $\text{RE}(\text{Mn}_{1-x}\text{B}_x)\text{O}_3$ (RE=Eu, Gd, Tb, Dy, Y; B=Ni, Co) were synthesized by mixing in stoichiometric ratios of R_2O_3 , MnO_2 , NiO or Co_3O_4 and then heating under high pressure conditions ($P=4$ GPa, $T=1400$ °C). The powder X-ray diffraction study showed the samples to be clean single phase. All the samples have the perovskite structure with orthorhombic unit cell. The unit cell volume decreases gradually with decreasing rare-earth ionic radius.

3. RESULTS AND DISCUSSION

The results of measurements of ac- magnetic susceptibility are displayed in Fig.1 where the very sharp peaks are observed for $\text{RE}(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_3$. These anomalies are associated with the formation of magnetic order at temperatures below T_c . Results of ac-susceptibility measurements for $\text{RE}(\text{Mn}_{0.5}\text{Ni}_{0.5})\text{O}_3$ differ noticeably from those obtained for Co-containing perovskites (Fig.1). Ni-containing compounds are characterized with a much higher magnetic susceptibility below their Curie temperatures than Co-containing ones.

Magnetization vs field curve for $\text{Y}(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_3$ at 30 K measured after cooling in $H=300$ Oe is presented in Fig.2. At high fields a large magnetic hysteresis is observed. Magnetic hysteresis decreases with decreasing field. Such a behavior could be a consequence of the first order metamagnetic transition. The $\sigma(H)$ dependences for $\text{RE}(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_3$ (RE=Gd, Tb, Dy) are similar to those obtained for $\text{Y}(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_3$. It is interesting to note that the residual magnetization and coercive field for the heavy rare earth manganites are lower than those established for $\text{Eu}(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_3$ at 4.2 K. It is apparently caused by the fact that magnetic structure of the heavy rare earth compounds differs from that of $\text{Eu}(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_3$. The field H_T at which the metamagnetic transition takes place decreases with increasing temperature. The sharp peak of FC (field cooled) magnetization of $\text{Tb}(\text{Co}_{0.5}\text{Mn}_{0.5})\text{O}_3$ at $H \geq 400$ Oe appears near the Curie temperature. The temperature at which the FC magnetization maximum appears is

shifted to lower temperatures with increasing field value. We have observed no peak of FC magnetization near T_C for $\text{Eu}(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_3$ and $\text{RE}(\text{Mn}_{0.5}\text{Ni}_{0.5})\text{O}_3$ in different fields. The peak of FC magnetization near the Curie temperature is apparently due to the metamagnetic transition.

The increasing Co-content above $x=0.5$ up to $x=0.7$ does not lead to the change of Curie temperature. The decreasing Co-content leads to the suppression of the long-range magnetic order. Below 64 K the FC magnetization of $\text{Gd}(\text{Co}_{0.25}\text{Mn}_{0.75})\text{O}_3$ is higher than ZFC (zero field cooled) one however no anomaly has been observed near 64 K. Both ZFC and FC magnetization have maxima at 52 and 33 K respectively. Below 18 K FC magnetization is directed antiparallel to the external field. The compensation temperature (when $M=0$) shifts towards the lower values with increasing external field. Such a behavior might arise from a system of ferrimagnetic clusters. Magnetic moments of clusters are gradually freezing below 64 K. At low temperatures magnetic moments of Gd ions are ordered due to f-d exchange interactions. Each Gd ion in the ferrimagnetic cluster is antiferromagnetically coupled to its nearest Co and Mn neighbors, what results in a decrease of magnetization with decreasing temperature. The external magnetic field should be higher than the internal anisotropy field necessary to reorient the magnetic moments at low temperatures. We have observed similar magnetic behavior for $\text{Tb}(\text{Mn}_{0.75}\text{Co}_{0.25})\text{O}_3$. It is worth to notice that we did not detect the compensation point for $\text{RE}(\text{Mn}_{0.5}\text{B}_{0.5})\text{O}_3$ ($\text{RE}=\text{Gd}, \text{Tb}, \text{Dy}$) compounds as it was earlier found for ferrites with the garnet structure. A minimum in the temperature dependence of magnetization was found for $\text{Tb}(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_3$ at 8 K, however the magnetization of $\text{Dy}(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_3$ increases strongly with decreasing temperature. It is possible that the rare earth ions sublattice is paramagnetic in the whole temperature range below the Curie temperature.

We assume that the samples of $\text{RE}(\text{Mn}_{1-x}\text{Co}_x)\text{O}_3$ with Co - content below $x=0.5$ contain an appreciable amount of Mn^{3+} and Co^{3+} ions. In the region $x \geq 0.5$ cobalt and manganese ions are in $2+$ and $4+$ valence states, respectively. It is reasonably to assume that the Co^{2+} and Mn^{4+} ions are ordered in considerable extent making up a rocksalt type lattice of the magnetic ions. The ionic ordering leads to the well defined Curie temperature (Fig.1). In the range $0 < x < 0.3$ the ferromagnetism arises due to $\text{Mn}^{3+}-\text{O}-\text{Mn}^{3+}$ superexchange interactions in agreement with Goodenough consideration [1]. For $x \geq 0.3$ ferromagnetism results from superexchange interactions between neighboring Co^{2+} and Mn^{4+} ions as it was suggested earlier by Blasse [2]. In the compositional range $0.5 < x < 0.8$ the chemical phase separation into phases consisting of Co^{2+} and Mn^{4+} ionic ordered domains and Co^{3+} ones seems to exist. The chemical phase separation leads to the sharp transition to magnetically ordered state for Co - rich compounds. The paramagnetic state of RE - sublattice for the ionic ordered phase can be understood if the supertransferred fields from Co^{2+} (Ni^{2+}) and Mn^{4+} ions at rare - earth ions have opposite signs.

The decrease of the size of rare earth ions leads to increase of crystal structure distortions and decrease of ferromagnetic $\text{Co}^{2+} - \text{O}^{2-} - \text{Mn}^{4+}$ superexchange interactions resulting in the noncollinear magnetic structure of $\text{RE}(\text{Co}_{0.5}\text{Mn}_{0.5})\text{O}_3$ ($\text{RE}=\text{Gd}, \text{Tb}, \text{Dy}, \text{Y}$). The noncollinear magnetic structure transforms into collinear one in the external magnetic field.

Figure 1: Ac susceptibility vs temperature for $\text{RE}(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_3$ ($\text{RE}=\text{Eu}$ - curve 1, Dy - 2) and $\text{RE}(\text{Mn}_{0.5}\text{Ni}_{0.5})\text{O}_3$ ($\text{RE}=\text{Eu}$ - curve 3, Tb - 4)

Figure 2: $\sigma(H)$ dependence for $\text{Y}(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_3$ at 30 K (1) and $\text{Tb}(\text{Mn}_{0.5}\text{Ni}_{0.5})\text{O}_3$ at 4.2 K (2)

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