Effect of Dy doping on magnetism of La$_{0.7}$Sr$_{0.3}$CoO$_3$ system

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Abstract

The effect of Dy doping on magnetism of La$_{0.7}$Sr$_{0.3}$CoO$_3$ system was studied through the measurements of $M$-$T$ curves and $M$-$H$ curves. The results show that with Dy content increasing, $T_C$ decreases, $M$ weakens, the coercive force strengthens, and the samples exhibit the abnormal phenomenon that $M$ increases continuously with $T$ decreasing in low temperature range. Research indicates that the variation of magnetism in the system comes from the changes of lattice parameters and magnetic environment caused by Dy doping and from the spin-state transition of Co ions induced by Dy ions.

Keywords: magnetic structure; cluster glass state; spin-state transition

1 Introduction

Perovskite manganite RE$_{1-x}$A$_x$MnO$_3$ (RE is trivalent rare-earth ion and A is divalent alkaline-earth ion) exhibits colossal magnetoresistance (CMR) effect near Curie temperature $T_C$ and contains plentiful physical transition content, so it has drawn people’s widespread research interest and becomes one of the forefront research objects in the areas of condensed matter physics and materials science.

The research emphasis is mostly focused on RE$_{1-x}$A$_x$MnO$_3$ system at present, but CMR effect has also been found in cobalt-based oxide RE$_{1-x}$A$_x$CoO$_3$[1], and a typical one is La$_{1-x}$Sr$_x$CoO$_3$ system [2–9]. Research shows that the trivalent Co ion in LaCoO$_3$ can exhibit spin-state transition through thermal excitation [10–11]. The crystal field splitting energy is slightly larger than the Hund coupling energy, and then Co$^{3+}$ ion is in low spin state (LS, $t^{5s}_{2g}$, $S$=0) at extremely low temperature; as the energy difference between low energy state and high energy states is very small, Co$^{3+}$ can be thermally excited into high spin state (HS, $t^{4g}_{2g}$ $\epsilon^2_{g}$, $S$=2) or intermediate spin state (IS, $t^{4g}_{2g} \epsilon^1_{g}$, $S$=1) with temperature increasing. In addition, Co$^{3+}$ ion can change its valence, a part of Co$^{3+}$ ions transform into Co$^{4+}$ when Sr partly substitutes La in LaCoO$_3$, and Co$^{4+}$ also exhibits low spin state ($t^{5s}_{2g}$, $S$=1/2), high spin state ($t^{3g}_{2g} \epsilon^2_{g}$, $S$=5/2), or intermediate spin state ($t^{3g}_{2g} \epsilon^1_{g}$, $S$=3/2) at different temperatures. Because Co ion exhibits spin-state transition and its valence is variable, magnetic and electric characteristics of La$_{1-x}$Sr$_x$CoO$_3$ system show complicated and interesting phenomena. The samples La$_{0.7-x}$Dy$_x$Sr$_{0.3}$CoO$_3$ ($x$=0.05, 0.10, 0.15, 0.20, and 0.25) were prepared, and the effect of Dy doping on magnetism of La$_{0.7}$Sr$_{0.3}$CoO$_3$ system was studied. The results show that, with Dy content increasing, $T_C$ decreases, $M$ weakens, the coercive force strengthens, and the samples exhibit the abnormal phenomenon that $M$ increases continuously with $T$ decreasing on low temperature range. Research indicates that the variation of magnetism in the system comes from the changes of lattice parameters and magnetic environment caused by Dy doping and from the spin-state transition of Co ions induced by Dy ions.

2 Experimental

La$_{0.7-x}$Dy$_x$Sr$_{0.3}$CoO$_3$ ($x$=0.05, 0.10, 0.15, 0.20, and 0.25) samples were fabricated by the solid-state reaction method. High-purity raw materials La$_2$O$_3$ (first dewatered at 400 °C for 4 h), Dy$_2$O$_3$, SrCO$_3$, and Co$_2$O$_3$ were weighed in proportion and mixed homogeneously and then were heated at 800°C for 14 h. The material was taken out and ground carefully and then sintered at 1000 °C for 12 h. It was ground again and sintered at 1200 °C for 24 h. Finally, it was ground, pressed into pellets, sintered at 1300 °C for 24 h, and cooled to room temperature in the furnace. Thus, the samples were prepared.
Powder X-ray diffraction of the samples was carried out by a Japanese 18 kW diffractometer (MXP18AHF) with Cu-Kα radiation (λ=0.1542 nm). Magnetization-temperature (M-T) curves of the samples were measured by a Lake Shore vibrating sample magnetometer (VSM), and the samples were cooled to 5 K in zero field and in 0.01 T magnetic field, respectively, and measured in warming condition. Magnetization-magnetic field (M-H) curves of the samples were also measured by the VSM.

3 Results and discussion

Figure 1 shows the powder X-ray diffraction patterns of the samples. It can be seen that all the samples are in rhombohedral structure and keep in good single phase.

Figure 2 gives field-cooling (FC) and zero field-cooling (ZFC) M-T curves of the La$_{0.7-x}$Dy$_x$Sr$_{0.3}$CoO$_3$ (0.05 ≤ x ≤ 0.25) samples. It exhibits that (1) Dy doping causes Curie temperature $T_C$ (defined as the temperature at which the absolute value of $dM/dT$ is the maximum for M-T curves) to decrease and magnetization $M$ to weaken. (2) ZFC and FC curves of the samples are irreversible, and they form typical $\lambda$ shape, so ferromagnetic clusters in the system are disorderly frozen at low temperature. (3) FC curves of the samples are not saturated at low temperature and turn up on the extremely low temperature range, which have been rarely seen in CMR manganite materials.

3.1 Changes of lattice parameters induced by Dy doping

Dy doping causes the lattice parameters of the samples to change. The ion radius of Dy$^{3+}$ (0.107 nm) is smaller than that of La$^{3+}$ (0.122 nm), so the average radius of A site decreases after La is substituted by Dy, then the Co-O-Co bond shows larger distortion, and its bond angle becomes smaller, which weaken the exchange coupling between Co ions. Thus, Dy doping causes $T_C$ to decrease and $M$ to weaken. The relation between Dy doping content $x$ and $T_C$ is shown in Table 1.

3.2 Coercive force changes induced by Dy doping

To make a detailed research on the magnetic behavior of