EXTRAORDINARY COLOSSAL MAGNETORESISTANCE IN
La$_{0.67}$Ca$_{0.33}$Mn$_{0.9}$Cr$_{0.1}$O$_3$ COMPOUND

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Abstract: The magnetic and magnetotransport properties of La$_{0.67}$Ca$_{0.33}$Mn$_{0.9}$Cr$_{0.1}$O$_3$ compound have been investigated. The resistance of the sample strongly changes by magnetic field variation in lower temperature region of the metal-semiconductor transition temperature. The maximum magnetoresistance ratio \((\text{MR} = (R(0)-R(H))/R(0))\) of 12.5\% in the sample is obtained in a magnetic field of 4 kOe. It is found that the extraordinary colossal magnetoresistance behavior, characterized by double peaks on the curve of the magnetoresistance versus temperature, concerning broadened temperature range of CMR. The explanation of these results based on suppose of the existence of the ferromagnetic coupling between Cr and Mn ions.

1. Introduction

After the discovery of magnetoresistance effect in the neodymium manganite Nd$_{0.5}$Pb$_{0.5}$MnO$_3$ [1], a systematic exploration of the lanthanum perovskites, La$_{1-x}$Ba$_x$MnO$_3$ with \(B = \text{Ca, Sr, Ba, Pb}\) was performed, dealing either with thin films [2] or ceramics [3]. It was shown that two factors govern essentially the colossal magnetoresistance (CMR) properties of these compounds, the size of the interpolated cation and the hole carrier density characterized by the mixed valence Mn(III) : Mn(IV). Besides, it is now clear that lattice strain and deformations, which affect the Mn$^{3+}$-O-Mn$^{4+}$ bond angle and length, have dramatic consequences for the properties of these systems [4]. In terms of the crucial role of Mn site, it would be interesting and worthwhile to study the effects of doping the Mn-sites with a foreign cation, which may provide clues for both exploring novel CMR materials and concerning with mechanism of CMR. In the last years, there have been considerable reports on the effects of Mn-site substitution by foreign elements such as Fe, Ni, Co [5], Al [6], Cr [7], etc. Among these doping elements, Cr has a spectacular effect and attracts more attention. For instance, the doping on Mn site with 5\% of Cr in the charge ordered (CO) insulator Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ can destroy the CO antiferromagnetic state and induces an insulator-metal transition [7]. For this reason, we study the magnetic and magnetotransport properties of the La$_{0.67}$Ca$_{0.33}$Mn$_{0.9}$Cr$_{0.1}$O$_3$ compound.

2. Experimental

Sample with the nominal compositions of La$_{0.67}$Ca$_{0.33}$Mn$_{0.9}$Cr$_{0.1}$O$_3$ were prepared by using the solid-state reaction method. The structure and phase purity of as-prepared sample was checked by powder X-ray diffraction (XRD) using Cu \(K_a\) radiation at room temperature. The magnetization measurements were carried out using an extracted sample magnetometer (ESM). Resistance was measured by standard four-probe method.
3. Results and discussion

Fig. 1, XPD pattern prove that the sample was a single phase with orthorhombic perovskite structure.

The temperature dependence of magnetization of the sample registered in a magnetic field of 80 Oe in fig. 2 shows that there exists a magnetic ordering transition from paramagnetism to ferromagnetism at about 215 K as T decreases. Interestingly, when T<T_c, the magnetization decreases with cooling. This implies that the antiferromagnetic (AFM) component may develop at low temperature. It is also clear that the zero-field cooled (ZFC) magnetization data do not coincide with FC data below T_c, which is a characteristic of cluster glass [8].

The temperature dependence of the resistance under zero and 4 kOe magnetic field is demonstrated in fig. 3. From these curves, we have determined the transition from a ferromagnetic metallic (FMM) state to a paramagnetic semiconducting (PMS) state at about T_p = 145 K as T increases.

The corresponding temperature dependence of CMR is shown in fig. 4. The MR ratio is defined as MR = (R(0)-R(4 kOe))/R(0), where R(0) is the zero-field resistance and R(4 kOe) is the resistance under 4 kOe magnetic field. From fig. 4, one can see that Cr doping leads to extraordinary magnetoresistance behavior, characterized by double peaks on the MR(T) curve. It is contrast to the case in La_{0.67}Ca_{0.33}MnO_3 in which CMR occurs merely near T_f, the temperature range of CMR response is greatly broadened by Cr doping. This extraordinary CMR effect is beneficial to practical application in terms of the very broad temperature range of CMR response. Therefore, it suggested that Cr doping could be a potent way in tuning CMR. The explanation of these results based on suppose of the existence of the ferromagnetic coupling between Cr and Mn ions. One possible mechanism may be that a double exchange-like interaction could take place through Mn^{2+}-O-Cr^{3+} due to the identical electronic configuration between Cr^{3+} and Mn^{4+}. It is well known that double exchange correlates electrical transport to magnetic configuration and consequently plays a key role in the CMR phenomenon.
role in CMR. The appearance of an additional CMR peak in La_{0.67}Ca_{0.33}Mn_{0.9}Cr_{0.1}O_{3} implies that the interaction through Mn^{3+-O-Cr^{3+}} could be double exchange-like rather than super exchange because super exchange generally does not give rise to a CMR. Due to the different coupling constant between Mn^{3+-O-Mn^{4+}} and Mn^{3+-O-Cr^{3+}}, the delocalization of carriers by applied magnetic field may happen at separated temperature ranges, consequently resulting in two CMR peaks.

One another hand, the cluster glass nature of La_{0.67}Ca_{0.33}Mn_{0.9}Cr_{0.1}O_{3} also plays a key factor in the origin of low temperature magnetoresistance. Cr substitution induces AFM interaction between Cr^{3+-O-Cr^{3+}} and promotes the proportion of Mn^{4+-O-Mn^{4+}} AFM interaction. The random distribution of FM and AFM exchange interaction would favor the formation of cluster glass, as evidenced in the temperature dependence of magnetization of the sample. Due to the formation of FM clusters and their randomly frozen moment as well as the large spin fluctuation, there should be severe spatial magnetic disorder that may play a key role in electron localization and lead to high resistivity state at low temperature. Under an applied magnetic field, the whole moment of the frozen FM clusters expand and their orientation are forced to align uniformly so that the spatial magnetic disorder is reduced, which favors the electron delocalization and consequently results in a significant drop of the low temperature resistivity. This may be the reason that a low temperature CMR effect is usually observed in a cluster glass state.

In conclusion, our obtained results of La_{0.67}Ca_{0.33}Mn_{0.9}Cr_{0.1}O_{3} sample showed that the extraordinary CMR effect as well as cluster glass behaviors have been observed in the sample. CMR occurs near T_{C} and the temperature range of CMR response is greatly broadened by Cr-doping content. The double exchange interaction through Mn^{4+-O-Cr^{3+}} may be the major reason which is concerning with iso-electronic configuration between Cr^{3+} and Mn^{4+}. The formation of FM cluster and spatial magnetic disorder in the sample plays role to change the resistivity state at low temperature.


References