Magnetic and Magnetotransport Properties of the Lacunar La$_{0.67}$Sr$_{0.15}$MnO$_{3}$ Perovskite Manganite

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Abstract

Magnetic and magnetotransport properties of the lacunar perovskite manganite oxide La$_{0.67}$Sr$_{0.15}$MnO$_{3}$ have been investigated. X-ray diffraction patterns have been indexed in the rhombohedral structure with $R3c$ space group. Magnetic measurements show that our sample exhibits a paramagnetic-ferromagnetic transition at $T_C = 360K$, while electrical measurements show a semiconductor-metallic transition at $T_P = 210K$. Strontium deficiency does not destroy the electrical transition from semiconducting to metallic state with decreasing temperature obtained in the stoichiometric sample but leads to a strong decrease of the electrical transition temperature. At very low temperature (20K), a magnetic applied field of about 0.3T induces a decrease of the resistivity up to 85%. Also, the sample exhibits a magnetoresistance effect of about 30% at a magnetic applied field of about 4T.

Introduction

With the discovery of the very large negative magnetoresistance, great interest has been focused on the perovskite-type hole doped manganese oxides with general formula Ln$_{1-x}$M$_x$MnO$_3$ where Ln is a trivalent rare-earth and M is a divalent alkali-earth [1-8]. These systems have been given so much attention since they could possibly be used for sensor applications [9, 10], and especially to increase data storage by increasing the sensitivity of hard disk drive read heads [11]. Different substitutions in these systems lead to different crystal structures, spin states and transport properties. The substitution of the trivalent element by divalent or

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monovalent elements produces mixed valence Mn$^{3+}$-Mn$^{4+}$ ions to maintain charge neutrality and subsequently a modification of both magnetic and transport properties. Such modifications can be understood on the basis of double-exchange interactions between the spins of Mn$^{3+}$ and Mn$^{4+}$ ions [12, 13]. However, recent studies have shown that the double exchange can not alone explain the observed behaviors in these systems and suggested, that other effects play a crucial role; such as charge ordering, average A-site cationic radius $\langle r_A \rangle$ [14-16], the A-site cationic size mismatch [17, 18], the oxygen deficiency [19-21] and the polaron effect due to the strong electron-phonon interaction arising from the Jahn-Teller distortion [22].

Many studies are being performed on the magnetic and magneto-transport properties of these materials. Effects of divalent alkaline-earth elements have been extensively studied [7, 8-14]. These studies showed that the Curie temperature $T_C$ and the magnetoresistance effects are optimized for a Mn$^{4+}$ content of about 33%. However, only few studies have been carried on deficiency effects in lacunar systems [23-25]. Deficiencies in the A perovskite site leads to an increase in the Mn$^{4+}$ content. In order to study the strontium vacancy effects in La$_{0.67}$Sr$_{0.33}$MnO$_3$, we investigate the structural, magnetic and electrical properties in the La$_{0.67}$Sr$_{0.15}$O$_{0.18}$ MnO$_3$ lacunar system. In such sample, vacancy implies an increase of the Mn$^{4+}$ content beyond 33% and also a change in the average ionic radius $\langle r_A \rangle$ of the A-site.

2. Sample Preparation And Characterization:

Bulk polycrystalline powder of the nominal composition La$_{0.67}$Sr$_{0.15}$O$_{0.18}$MnO$_3$ was prepared by the conventional ceramic route. The precursors La$_2$O$_3$, SrCO$_3$ and MnO$_2$ of high purity (more than 99%) powders were fired in air at 700°C for 10h before being used. These materials were thoroughly mixed in an agate mortar, in stoichiometric proportions and heated in air at 900°C for 48h to achieve decarbonation. The resulting powder was then pressed into pellets form and fired at 1350°C for 36h in air with several periods of grinding and repelling. Finally, the pellets were rapidly quenched to room temperature. This final step was carried out in order to keep the structure obtained at the sintered temperature 1350°C.

Phase purity, structure and lattice parameters were checked by X ray powder diffraction using Guinier-Hagg cameras, with Cr ($K\alpha_1$) radiation, at room temperature. High purity silicon powder was used as an internal standard. Unit cell parameters were obtained by least squares calculations.

Magnetization measurements versus temperature were recorded by a home-made faraday balance, whereas the susceptibility under 0.05T was recorded with a vibrating sample magnetometer.
Magnetic and Magnetotransport Properties of the Lacunar La$_{0.67}$Sr$_{0.33}$MnO$_3$ Perovskite Manganite

Electrical measurements were performed by the conventional four-probe technique in the temperature range 20-300K.

3. Results And Discussion

X-ray analysis shows that our sample exhibits practically identical X-ray powder patterns as the stoichiometric La$_{0.67}$Sr$_{0.33}$MnO$_3$ sample. All the observed peaks are indexed in a perovskite structure with a distortion from the ideal cubic cell giving the rhombohedral symmetry with $R3c$ space group. We plot in figure 1 X-ray powder diffraction patterns at room temperature for both La$_{0.67}$Sr$_{0.33}$MnO$_3$ and La$_{0.67}$Sr$_{0.15}$Ti$_{0.15}$MnO$_3$ samples. Indexed in the classical hexagonal cell, our lacunar sample has the following parameters: $a_{\|}=5.4958\,\AA$ and $c_{\|}=13.3773\,\AA$.

Magnetization measurements (figure 2) show that our sample exhibits a clear transition from a paramagnetic to a ferromagnetic state with decreasing temperature. The Curie temperature is found to be $T_C = 360K$. Strontium deficiency induces a slight decrease in $T_C$ which is found to be 370K for the stoichiometric sample.

Figure 3 shows the temperature dependence of the spontaneous magnetization ($M_{sp}$) and the inverse susceptibility ($\chi^{-1}$) for the studied sample. The $M_{sp}(T)$ curve drops rapidly near $T_C = 360K$ showing a better defined Curie temperature. The magnitude of the spontaneous magnetization $M_{sp}$ at 10K is about 2.8$\mu_B$/Mn. The theoretical $M_{th}$ value for full alignment of the Mn ion spins (using $S = \frac{4}{2}$ for Mn$^{3+}$ and $S = \frac{3}{2}$ for Mn$^{4+}$) is given by $M_{Sth} = 0.31 \times 4 + 0.69 \times 3 = 3.31 \mu_B$/Mn. The experimental value is smaller than the calculated one which may indicate a spin canting state at low temperature. The angle $\phi$ between the average magnetic moments of the Mn cations in our sample can be obtained using the following equation

$$\cos(\phi) = \frac{M_{sp}}{2 M_{Sth}} = \frac{2.8}{3.31} = 0.85.$$  

The angle $\phi$ is found to be 64°. The temperature dependence of the magnetic moment per mole $M_{sp}(T)$ can be described by the Brillouin-Weiss molecular field theory modeling the degree of spin collinearity.

In the paramagnetic phase, the inverse of the susceptibility evolution versus temperature exhibits the expected Curie-Weiss law $\chi = C/(T-\theta_p)$. From the linearity of $\chi^{-1}$-$T$ curve, a net transition between the paramagnetic and the ferromagnetic states is confirmed corresponding to a paramagnetic Curie temperature $\theta_p = 363.75K$. The obtained Curie constant $C$ is 0.4832 $K.\mu_B$/kOe. $\theta_p$ and $C$ are found to be 375.06K and 0.6536 $K.\mu_B$/kOe respectively for the stoichiometric sample La$_{0.67}$Sr$_{0.33}$MnO$_3$. Strontium deficiency leads to a decrease in the $T_C$ and $\theta_p$ values.
As a strontium vacancy induces an increase in the Mn$^{4+}$ content, the $T_C$ decrease observed in our sample can be explained by the increase of the Mn$^{4+}$ concentration which leads to a decrease of the double exchange interactions. This result is in concordance with previous work on La$_{1-x}$Sr$_x$MnO$_3$ which shows a parabolic behavior of $T_C$ versus Mn$^{4+}$ content with a maximum obtained at about 33% [26]. However, the double exchange mechanism based on the Mn$^{4+}$/Mn$^{3+}$ ratio can not alone explain the observed behaviors in the diluted manganese oxides. The average A-site cationic radius $\langle r_A \rangle$ of the perovskite ABO$_3$ may play a crucial role. As a vacancy must have an average radius $\langle r_V \rangle = 0$, the $T_C$ decrease due to the strontium deficiency in the lacunar La$_{0.67}$Sr$_{0.15}$Co$_{0.18}$MnO$_3$ sample can also be explained according to Hwang et al. [27] with a vacancy average radius $\langle r_V \rangle$ smaller than Sr$^{2+}$ (1.31 Å). Such behavior has been observed in strontium lacunar Pr$_{1-x}$Sr$_x$MnO$_3$ [25].

At zero applied field, resistivity measurements (figure 4) show a semiconductor-metallic transition with decreasing temperature. The maximum associated with the transition is at $T_p = 210K$. This value is far below Curie temperature $T_C = 360K$. Strontium deficiency leads to an increase of the resistivity values and a net decrease of the electrical transition temperature.

In the ferromagnetic range, the resistivity decrease does not drop to very small values as in good metallic samples. In fact we deal with a granular material, thus there is a possibility that more or less insulating barriers develop at the grains boundaries. These barriers will limit the residual resistivity. This mechanism is well known in ceramics, in ferrites as well as in high $T_C$ superconductors where insulating barriers cause the appearance of Josephson junctions below the transition temperature of the superconducting grains [28].

As illustrated in figure 5, the effect of the magnetic field is to lower the value of the resistivity and to weaken its temperature dependence. Meanwhile the resistivity maximum becomes broader.

In the semiconductor-like phase, the conduction is thermally activated indicating polaron conduction. Above $T_p$, the zero field resistivity data fit quite well the formula $\rho = \rho_0 \exp \left( \frac{E_a}{kT} \right)$ where $E_a$ is the activation energy (figure 6). At zero applied field, the activation energy is found to be 0.35eV. With applying magnetic field H, the activated energy decreases with increasing H. It decreases from 0.35eV at H = 0 to 0.31eV at 4T.

Defining the magnetoresistance MR as $[(\rho(H,T) - \rho(0,T))/\rho(0,T)]*100$ where $\rho(H,T)$ and $\rho(0,T)$ are the resistivities at an applied magnetic field H and at zero field. 

888
Magnetic and Magnetotransport Properties of the Lacunar La$_{0.67}$Sr$_{0.15}$La$_{0.18}$MnO$_3$ Perovskite Manganese

respectively, we have plotted in figure 7 the magnetoresistance versus applied magnetic field for several temperatures. Below $T_C$, two regions in the field-dependence of the resistivity can be distinguished, which are seen better for the 20K isotherm: an initial rapid drop in the region where the magnetization saturates, and a gentle decrease for larger fields. The first rapid drop of the resistivity that coincides with the saturation of the magnetization is due to domain wall motion, which occurs below 3kOe in the ferromagnetic range. This MR is maximum at low temperature where $ρ(0,T)$ is minimum. The amplitude of this term, is about 15% of the total resistivity at 20K. The second regime situated above 3kOe corresponds to a slower decrease of the resistivity, with a larger slope near the electrical transition temperature $T_P=210K$. This behavior is similar to the spin–disorder resistivity of ferromagnetic materials [29], but with a carrier density modified by the semiconductor/metal transition. Our sample exhibits a magnetoresistance behavior at low temperature of about 30% for a magnetic applied field of about 4T (figure 8).

4. Conclusion

We have investigated magnetic and magneto-transport properties of the lacunar La$_{0.67}$Sr$_{0.15}$La$_{0.18}$MnO$_3$ powder sample. X-ray diffraction studies show that our sample crystallizes in the rhomboedral structure with $R$3$C$ space group. Our sample exhibits a ferromagnetic-paramagnetic transition at $T_C=360K$ and a semiconducting-metallic one at $T_P=210K$. At very low temperature, a magnetic applied field of about 0.3T induces a decrease of the resistivity up to 85%. Also, the sample exhibits a magnetoresistance effect of about 30% at a magnetic applied field of about 4T.

الخصائص المغناطيسية والانتقالية المغناطيسية للفيتوبروفيسكايت العميق

La$_{0.67}$Sr$_{0.15}$La$_{0.18}$MnO$_3$

لاروى ويخو روحو ويبن

ملخص

لقد تمت دراسة الخصائص المغناطيسية والانتقالية - المغناطيسية للكسيد المغنيت العميق البروفيسكايت. ان النماذج التي تم استخدامها في الدراسة البينية ذات الأطوال من المجموعة الفضائية R3C توضح أن المكانتا تمثل الناقل بالكيميائي فرومغناطيسية عند Tp=210K بينما القياسات الكوبيرانية توضح أن الانتقال هو جه موصلي قلسي عند Tk=360K لذا، يمكن القول أن نقصان الستريتيمو لا يدمر الانتقال الكوريتي من شبه الموصل إلى الحالة الفلزية مع تقصان

889
References


Figure 1. X-ray diffraction patterns at room temperature for La$_{0.67}$Sr$_{0.15}$Ca$_{0.18}$MnO$_3$ and La$_{0.67}$Sr$_{0.33}$MnO$_3$.

Figure 2. Temperature dependence of the magnetization for La$_{0.67}$Sr$_{0.15}$Ca$_{0.18}$MnO$_3$ and La$_{0.67}$Sr$_{0.33}$MnO$_3$. 

892
Magnetic and Magnetotransport Properties of the Lacunar La$_{0.67}$Sr$_{0.15}$Co$_{0.18}$MnO$_3$ Perovskite Manganite

Figure 3. Spontaneous magnetization and reciprocal susceptibility data versus temperature for La$_{0.67}$Sr$_{0.15}$Co$_{0.18}$MnO$_3$

Figure 4. Temperature dependence of the resistivity for both La$_{0.67}$Sr$_{0.15}$Co$_{0.18}$MnO$_3$ and La$_{0.67}$Sr$_{0.31}$MnO$_3$
Figure 5. Temperature dependence of the resistivity for $\text{La}_{0.67}\text{Sr}_{0.13}\text{MnO}_3$ at different applied magnetic fields.

Figure 6. Evolution of $\ln(\rho)$ as function of $1/T$ for $\text{La}_{0.67}\text{Sr}_{0.13}\text{MnO}_3$. 
Magnetic and Magnetotransport Properties of the Lacunar $\text{La}_{0.67}\text{Sr}_{0.13}\text{Co}_{0.18}\text{MnO}_3$ Perovskite Manganese

Figure 7. Isotherms of MR $\text{La}_{0.67}\text{Sr}_{0.13}\text{Co}_{0.18}\text{MnO}_3$ from 20 to 300K

Figure 8. Temperature dependence of the magnetoresistance for $\text{La}_{0.67}\text{Sr}_{0.13}\text{Co}_{0.18}\text{MnO}_3$ at different applied magnetic fields