Polaron transport in $n = 3$ Ruddlesden–Popper phase $Sr_4Mn_{1.5}Fe_{1.5}O_{9.72}$ ceramics

WOO-HWAN JUNG
Department of Electronics, Howon University, 727 Wolha-Ri, Impi, Gunsan ChunBuk 573-930, Korea
E-mail: phdjung@sunny.howon.ac.kr

The discovery of high-T_C superconductivity in layered copper oxides containing perovskite-related intergrowth structures has intensified investigations during the past decade and research has primarily focused on the structure-property relationships of the 3d transition metal oxides [1]. Some of the perovskite-related 3d transition metal oxides exhibit interesting electrical and magnetic properties due to the existence of a small energy gap, either between the oxygen O: 2p and metal 3d levels or between the lower and upper Hubbard bands.

Recently, there has been a renewed interest in the properties of $LaMnO_3$, and related rare-earth orthomanganites that are doped by alkaline-earth ions, such as $La_{1-x}Ca_xMnO_3$ [1–4]. Other $3d^3/3d^4$ systems have been also studied to investigate whether double exchange and the properties observed in the CMR manganites can be replicated. Gundakaram *et al.* [5] synthesized the phase, $LaMn_{1-x}Cr_xO_3$, containg Mn^{3+} ($3d^4$) and Cr^{3+} ($3d^3$). Ferromagnetic coupling was preserved, but the compounds were insulators and CMR was not observed. Battle *et al.* [6] synthesized the $n = 3$ Ruddlesden–Popper phase (RP), $Ca_4Mn_2FeO_{9.75}$ and $Sr_4Mn_2FeO_{9.80}$, containing Mn^{4+} ($3d^3$) and Fe^{4+} ($3d^4$). Both compounds were shown to be insulators that ordered antiferromagnetically at 75 K (Ca) and 90 K (Sr) with a spin-glass transition at $\sim 11K$. d^3/d^4 coupling was achieved, but electron localization made it a super-exchange rather than a double-exchange interaction.

Fawcett *et al.* [7] synthesized $Sr_4Mn_{3-x}Fe_xO_{10-\delta}$ ($x = 1$, 1.5, and 2) compounds and measured several of their physical properties. They found that the Mn and Fe ions in the $Sr_4Mn_{3-x}Fe_xO_{10-\delta}$ bulk system are randomly distributed. In this case, however, they found that the Fe ions preferentially occupy the middle perovskite layer of Mn/Fe(1), and this effectively stabilizes the RP, in contrast to the $Sr_4Mn_3O_{10}$ structure. The $Sr_4Mn_{3-x}Fe_xO_{10-\delta}$ is oxygen deficient with both Fe^{3+} and possibly some Mn^{3+} present as evidenced by XANES. $Sr_4Mn_{3-x}Fe_xO_{10-\delta}$ are insulators and exhibit a spin glass-like transition at low temperature. The substitution of Fe for Mn increases the bandwidth (W_d) of the σ^* conduction band due to a strengthening of the (Fe, Mn)–O–(Fe, Mn) covalent interaction, and thereby decreases the coulomb gap. Fawcett *et al.* [7] found that the randomly distributed ions introduce a large number of potential interactions including antiferromagnetic Mn^{4+}–O–Mn^{4+}, and Fe^{3+}–O–Fe^{3+}, and both ferromagnetic and antiferromagnetic interactions between the Fe and Mn ions through the σ^* and π orbitals, respectively.

The basic transport process in $Sr_4Mn_{3-x}Fe_xO_{10-\delta}$ is the hopping of a d electron (and/or hole), d^4 to d^3 via oxygen, so that d^4 and d^3 ion exchange takes place. Therefore, the polaronic hopping conduction mechanism is responsible for the conduction behavior of this system. Since lattice interaction is also involved, there is a strong electron – lattice (phonon) interaction that leads to polaron formation. In order to gain insight into the nature of the transport mechanism in the insulating phase for the $Sr_4Mn_{3-x}Fe_xO_{10-\delta}$ system, we have performed electrical conductivity and magnetic measurements on $Sr_4Mn_{1.5}Fe_{1.5}O_{10-\delta}$ over a wide range of temperatures.

The bulk sample was prepared by a standard ceramic process. Stoichiometric proportions of $SrCO_3$, Fe_2O_3, and Mn_2O_3 were mixed, ground, and calcined at 1273 K for 24 hr in air. The sample was then sintered at 1573 K for 7 days, also in an air atmosphere. The crystal structure and phase purity of the sample was examined by X-ray diffraction with Cu Kα radiation. The lattice parameters of the $Sr_4Mn_{1.5}Fe_{1.5}O_{10-\delta}$ phase were refined by the Rietveld method on the basics of the tetragonal space group *I4/mmm*. From the Rietveld method, we obtained the lattice parameters $a = 3.8424$ Å and $c = 27.8723$ Å. The oxidation state of (Fe, Mn) and the oxygen content of the sample was determined by iodometric titration [8]. The actual composition obtained was $Sr_4Mn_{1.5}Fe_{1.5}O_{9.72}$.

Dc magnetization measurements were performed using a SQUID magnetometer (Quantum Design MPMS). Susceptibility–temperature (χ–T) curves for each sample were measured under both the ZFC (zero field cooled) and FC (field-cooled) conditions. A Keithley 619 Resistance Bridge, an Advantest TR 6871 digital multi-meter

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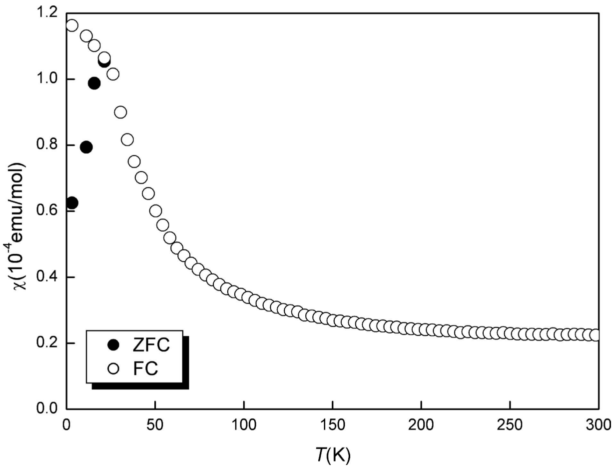

Figure 1 Molar magnetic susceptibility (χ) of $Sr_4Mn_{1.5}Fe_{1.5}O_{9.72}$ as a function of temperature, cooled in either a zero field (ZFC) or in a field of 1 T (FC).

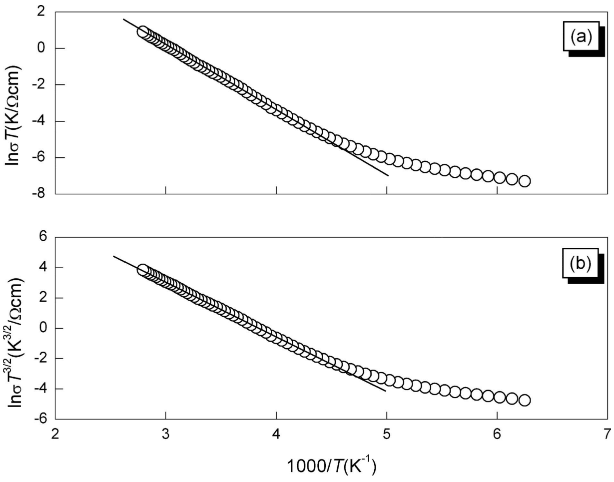

Figure 2 The dependence of conductivity on temperature (a) Arrhenius plot of σT vs. $1/T$, (b) Arrhenius plots of $\sigma T^{3/2}$ vs. $1/T$.

and an Advantest R6161 power supply were used for the conductivity-measurement using the four-probe method.

The temperature dependence of the molar magnetic susceptibility is shown in Fig. 1. The FC and ZFC susceptibilities diverge at low temperature with a maximum at 22 K (spin-glass transition temperature). The dc magnetic properties were in good agreement with the earlier reported values of a sample of similar composition [7].

Very recently, the experimental results of $Sr_3Fe_{2-x}Co_xO_{7-\delta}$ carried out by Prado *et al.* [9] shows that electronic transport in $Sr_3Fe_{2-x}Co_xO_{7-\delta}$ is activated over the entire temperature range, which they have analyzed in terms of polaron hopping. If the experimental results of Prado *et al.* [9] are employed, a similar hopping process of the polarons in $Sr_4Mn_{1.5}Fe_{1.5}O_{9.72}$ would be expected.

Small polaron hopping can be either adiabatic or nonadiabatic. In the former case, the temperature dependence of conductivity is given by [10–13].

$$\sigma T = \sigma_0 \exp\left(-\frac{\varepsilon_0 + W_H - J}{k_B T}\right) \tag{1}$$

where ε_0 is the energy difference between identical lattice distortions with and without a hole, J is the transfer integral (polaron bandwidth), $\sigma_0 = ne^2a_p^2\nu/k_B$, and W_H represents the activation energy. In Fig. 2a, ln (σT) and the adiabatic limit are plotted against $1000/T$. The straight line on the Arrhenius plot of $\ln(\sigma T)$ and $1000/T$ yields $\sigma_0 = ne^2a_p^2\nu/k_B = 4.44 \times 10^4$ K/Ω cm and $W_H = 0.3$ eV.

In the latter case, the nonadiabatic hopping conduction is determined by the following expression: [10–13]

$$\sigma T^{3/2} = \sigma_0 \exp\left(-\frac{W_P}{2k_B T}\right) \tag{2}$$

where W_P ($W_H \cong W_P/2$) is the polaron binding energy and $\sigma_0 = (ne^2a_p^2/k_B)(\pi J^2/h)(2\pi/W_P k_B)^{1/2}$, where e is the electron charge, n is the density of charge carriers determined by the number of the sub-stoichiometry oxygens, ν is the optical phonon frequency, a_p is the hopping distance of a polaron ($\approx$ polaron radius) which is taken as the distance in-plane spacing and h is Plank's constant. As opposed to the adiabatic model, the data should be fitted to a $\ln(\sigma T^{3/2})$ versus $1/T$ plot to obtain straight lines. Thus, the activation energy obtained from a nonadiabatic model will be higher than the adiabatic value, and the data interpretation will be quite different.

In Fig. 2b, $\ln\sigma T^{3/2}$ and the nonadiabatic limit are plotted against $1000/T$. The straight line on the Arrhenius plot of $\sigma T^{3/2} - 1000/T$ yields $W_H = 0.31$ eV and $\sigma_0 = 1.2 \times 10^6$ K$^{3/2}$/Ω cm. Using nonadiabatic conduction, in which $\sigma_0 = (ne^2a_p^2/k_B)(\pi J^2/h)(2\pi/W_P k_B)^{1/2}$, the magnitude of J is estimated to be ~ 0.03 eV.

The probability of an electron being able to adjust to the atomic fluctuations is proportional to the transfer integral J. For a large J, the electron transfer is fast enough to follow the lattice fluctuation and the electronic transport that occurs in the adiabatic regime. For a small J, the hopping is nonadiabatic. Quantitatively, these considerations can be expressed in terms of the parameter $\eta \equiv J^2/((h/2\pi)\nu(k_B W_H T)^{1/2})$; where $\eta > 1$ in the adiabatic limit, and for nonadiabatic transport, $\eta \ll 1$. For Holstein's nonadiabatic conduction theory, the transfer integral J should satisfy the inequality $J < \phi$ [14–16], where,

$$\phi = (2k_B T W_H/\pi)^{1/4}(h\nu/\pi)^{1/2} \tag{3}$$

Though the experimental value for ν of $Sr_4Mn_{1.5}Fe_{1.5}O_{9.72}$ is not available, the experimental values for similar transition metal compounds are $\sim 10^{13}$ Hz [15]. Employing $\nu \cong 10^{13}$ Hz, the value of ϕ calculated from Equation 3 at various temperatures, leads to ϕ (300 K) = 0.03 eV, ϕ (100 K) = 0.02. Since ϕ is lower than the nonadiabatic value over the temperature range studied, it may not necessarily be concluded that the polaron moves via nonadiabatic hopping mechanism.

An estimate for the small polaron coupling constant, γ_p, (which is a measure of the electron–phonon interaction in $Sr_4Mn_{1.5}Fe_{1.5}O_{9.72}$) was made from the relation $\gamma_p = 2W_H/h\nu$. The value of γ_p was found to be 14. The value of γ_p (>4) indicated a strong electron–phonon interaction in the present system [14–15]. Knowing γ_p, the effective mass m_p of a polaron may be calculated from the relation $m_p(h/2Ja2)$ exp $\gamma_p = m^*$ exp γ_p, where m^* is the rigid-lattice effective mass. The large value of m_p/m^* also indicated a strong electron–phonon interaction supportive of the formation of small polarons.

In summary, the electrical and magnetic properties in polycrystalline ceramics of Ruddlesden–Propper type $Sr_4Mn_{1.5}Fe_{1.5}O_{9.72}$ were investigated as a function of temperature. $Sr_4Mn_{1.5}Fe_{1.5}O_{9.72}$ showed a sudden transition to a complicated spin-glass state at 22 K. The temperature dependence of the electrical conductivity was characteristic of an insulator and the charge carriers responsible for conduction were strongly localized. The present electrical and magnetic study demonstrated that small polarons were formed in the layered perovskite.

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