Influence of Bi$^{3+}$ doping on electronic transport properties of La$_{0.5-x}$Bi$_x$Ca$_{0.5}$MnO$_3$ manganites

Renwen Li$^{a,b}$, Zhe Qu$^{a,*}$, Jun Fang$^a$

$^a$High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, People's Republic of China
$^b$Department of Physics and Electronic Engineering, Hefei Normal University, Hefei 230061, People's Republic of China

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Electronic transport properties of La$_{0.5-x}$Bi$_x$Ca$_{0.5}$MnO$_3$ ($x=0, 1/16, 1/8, 1/4, 3/8$ and $1/2$) compounds have been studied systematically to investigate their charge ordering (CO) behaviors. The results show that the CO temperature increases with the substitution of Bi$^{3+}$ ion for La$^{3+}$ ion, suggesting that the charge ordering is enhanced. This is attributed to the special role of the 6$s^2$ lone pair of Bi$^{3+}$. It is found that for all the samples the adiabatic small polaronic conduction mechanism is responsible for the transport behavior above CO transition, whereas Mott's variable range hopping mechanism dominates below the CO transition. In addition, the electronic transport behavior of La$_{0.5-x}$Bi$_x$Ca$_{0.5}$MnO$_3$ compounds is high sensitive to an external magnetic field, which could raise fresh opportunities for application in magnetic sensors.

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1. Introduction

Perovskite manganites Ln$_{1-x}$A$_x$MnO$_3$ (Ln=rare earth, A=alkaline earth) have been a subject of vivid interest in recent years because of their exotic electronic and magnetic properties [1–3]. The celebrated colossal magnetoresistance (CMR) effect has urged many theories, such as double exchange (DE) [4], polaronic effects [5] and phase separation combined with percolation [6], to explain its mechanism. It is widely believed that the properties of manganese oxides are mainly determined by the Mn$^{3+}$/Mn$^{4+}$ ratio and the Mn–O–Mn bond angle, which determine the orbital overlapping between neighboring ions and the direct space ordering of Mn$^{3+}$ and Mn$^{4+}$ ions [7]. Besides the CMR effect, charge ordering (CO) phenomenon [7] has also attracted a lot of attention. Previous studies show that CO state and the concomitant spin and/or orbital ordering (OO) are favored when the long-range Coulomb interaction and/or a strong electron–lattice interaction due to Jahn–Teller (J–T) distortion overcome the kinetic energy of $e_g$ electrons [8–10]. The one electron bandwidth has been widely believed to be a key parameter in determining the CO behavior in the Ln$_{1-x}$A$_x$MnO$_3$ family of compounds [11,12]. Wider $e_g$ bandwidth, i.e., larger average A-site radius $<r_A>$, favors lower $T_{CO}$ because the mobility of the itinerant electrons through the lattice is higher, while narrower bandwidth induces an opposite trend. Therefore, one may expect that Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ will exhibit physical properties similar to La$_{0.5}$Ca$_{0.5}$MnO$_3$ because the radium of Bi$^{3+}$ ion ($\sim 0.1300$ nm) is almost identical to that of La$^{3+}$ ion ($\sim 0.1302$ nm). However, the CO temperature $T_{CO}$ of Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ is $\sim 325$ K (on warming) [13], which is much higher than that ($\sim 200$ K on warming) of La$_{0.5}$Ca$_{0.5}$MnO$_3$ [14]. Moreover, Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ has a C-type AFM magnetic structure below $T_N=120$ K [13], which is also distinctly different from La$_{0.5}$Ca$_{0.5}$MnO$_3$ with CE-type AFM magnetic structure. The distinct differences between La$_{0.5}$Ca$_{0.5}$MnO$_3$ and Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ have been proposed to be associated with the unique role of the 6$s^2$ lone pair of Bi$^{3+}$ ions [15]. It is believed that the 6$s^2$ lone pair can produce a local distortion or even hybridization between Bi–6$s$-orbitals and O–2$p$-orbitals [16], leading to the block of the movement of $e_g$ electrons through the Mn–O–Mn bridges, which strongly favors the charge order. Therefore, bismuth based manganites may do not follow the dependency of $T_{CO}$ on the one electron bandwidth mechanism as the lanthanide ones. As we know, although several works have reported the Bi-doping effect on different manganites samples [17–20], and Wang et al. [21–23] have given some reports on the structural and spectroscopic study about La$_{0.5-x}$Bi$_x$Ca$_{0.5}$MnO$_3$ ($0 \leq x \leq 0.25$) system, the physical feature of CO is still unclear. In this work, we investigate this issue by examining the electronic transport properties of the La$_{0.5-x}$Bi$_x$Ca$_{0.5}$MnO$_3$ ($0 \leq x \leq 0.5$) system.

2. Experiment

Polycrystalline samples of La$_{0.5-x}$Bi$_x$Ca$_{0.5}$MnO$_3$ with $x=0, 1/16, 1/8, 1/4, 3/8$ and $1/2$ were prepared by the conventional solid-state reaction method as described in Ref. [24].
structure and the phase purity of the samples were checked by powder X-ray diffraction (XRD, as shown in Ref. [24]) at room temperature. It shows that all samples crystallized in single phased perovskite orthorhombic structure. It is well known that around half doping, the physical properties of La$_{1-x}$Ca$_x$MnO$_3$ are rather sensitive to the oxygen content [14]. We performed energy-dispersive X-ray spectrometry (EDS) and ICP-AES measurements to check the chemical composition of the samples of La$_{0.5-x}$Bi$_x$Ca$_{0.5}$MnO$_3$ series. The results indicate that all samples have the correct oxygen content within experimental errors, suggesting that samples used here are of high quality. The resistivity ($\rho$) was measured by the standard four-probe method using the physical properties measurement system PPMS.

3. Results and discussion

Fig. 1(a)–(f) shows the temperature dependence of the resistivity $\rho(T)$ for La$_{0.5-x}$Bi$_x$Ca$_{0.5}$MnO$_3$ ($x=0$ to $1/2$). One can see that all samples show semiconductor-like transport behavior at the measured temperature range. The sharp increase of the resistivity at $\sim 200$ and $\sim 325$ K for $x=0$ and $1/2$, respectively, implying the appearance of CO. In order to clearly reflect the variation of the CO temperature $T_{CO}$ caused by Bi-doping, we replott the temperature dependence of the resistivity as $d(\ln \rho)/d(1/T)$ versus $T$ (as shown in Fig. 2(a)). It shows that there exists an abnormal peak which is suggested to correspond to the appearance of CO according to the viewpoint of Ramirez et al. [25]. Fig. 2(b) shows the dependence of $T_{CO}$ versus Bi-doping content $x$. It obviously indicates that $T_{CO}$ of the samples shifts to higher temperatures with increasing Bi-doping level. These results corroborate with our previous magnetic investigation [24], indicating the enhancement of the CO upon Bi substitution for La.

It is known that the average A-site radius $\langle r_A \rangle$ has a key effect on $T_{CO}$ in La$_{1-x}$A$_x$MnO$_3$ system [1,26,27]. However, while the $\langle r_A \rangle$ of La$^{3+}$ is almost identical to that of Bi$^{3+}$ ion, $T_{CO}$ in Bi-doped La$_{0.5-x}$Bi$_x$Ca$_{0.5}$MnO$_3$ system increases gradually with Bi content. Therefore the $\langle r_A \rangle$ could not be the main factor in determining the $T_{CO}$ in Bi-doped manganites. Instead, the enhancement of $T_{CO}$ with Bi-doping may be ascribed to the special role of the 6s$^2$ lone pair electrons of Bi ions [15,28]. The 6s$^2$ lone pair electrons of Bi ions not only couple directly for the O:2p$_\sigma$ electrons with the Mn:4s$_\sigma$ orbitals [16]. The hybridization between 6s lone pair of Bi$^{3+}$ and O:2p$_\sigma$ orbitals would block the movement of $e_g$ electrons through Mn–O–Mn bridges, which favors the localization of holes and results in the enhancement of $T_{CO}$ [29].

We further investigate the electronic transport mechanism for our studied samples. The $\rho(T)$ data are fitted by purely thermally activated conduction (TAC) model: $\rho = \rho_0 \exp(E_a/k_B T)$, the adiabatic small polaronic conduction (SPC) model: $\rho = \rho_0 T \exp(E_a/k_B T)$, and three-dimension (3D) Mott’s variable range hopping (VRH) model: $\rho = \rho_0 \exp(T_0/T)^{-\beta}$. It is found that for all the samples SPC model is responsible for the transport behavior above CO transition, whereas VRH mechanism dominates below CO transition. The fitting results are shown in Figs. 3 and 4. As one can see from the formula of these two models, the SPC model predicts a linear

![Fig. 1](image-url)  
*Fig. 1.* (a)–(f) Temperature dependence of resistivity for samples La$_{0.5-x}$Bi$_x$Ca$_{0.5}$MnO$_3$ ($x=0$, 1/16, 1/8, 1/4, 3/8 and 1/2).*

![Fig. 2](image-url)  
*Fig. 2.* (a) The variation of the logarithmic derivative $d(\ln \rho)/d(1/T)$ of the resistivity with temperature for all the samples. (b) The $T_{CO}$ variation versus $x$ of La$_{0.5-x}$Bi$_x$Ca$_{0.5}$MnO$_3$ samples. $T_{CO}$ and $T_{CO'}$ are the CO temperature defined from $\rho(T)$ and $M(T)$ [24] curves, respectively.

![Fig. 3](image-url)  
*Fig. 3.* The fitting curves of $\rho(T)$ by SPC mode, the insets show the enlarged views.
relation between \( \ln(\rho/T) \) and \( 1/T \), and \( E_0/k_B \) is the slope of the straight line, while the VRH model should have a linear dependence of \( \ln \rho \) on \( T^{-1/4} \).

As shown in the insets of Fig. 3(a)–(f), the resistivity can be well fitted using SPC model for \( T > T_{CO} \), but there are more marked deviations at low temperature, indicating the SPC model is not applicable once the CO transition occurs. In fact, below \( T_{CO} \), \( \rho(T) \) curves are best described in terms of three-dimension (3D) Mott’s variable range hopping (VRH) model. The fitting results to the VRH model are shown in Fig. 4(a)–(f). It is clear that the linear behavior is only seen below \( T_{CO} \). These results clearly indicate that there is a crossover from SPC-type behavior for \( T > T_{CO} \) to VRH-type behavior for \( T < T_{CO} \). It is known that the VRH-type transport behavior requires the appearance of random potentials. This could be attributed to the charge ordering transition. Below \( T_{CO} \), the charge ordered state occurs and will trap the electron carriers. Also, the hopping across the grain boundaries is the variable-range case and will contribute to the whole transport process at low temperature. Therefore, with decreasing temperature, the transport mechanism changes from SPC to VRH.

The fitting parameters, i.e. \( E_s \) and \( T_0 \), are summarized in Table 1. Interestingly, for \( x=3/8 \) and 1/2, the slopes of \( \ln \rho - (1/T)^{1/4} \) curves show visible change around \( T_N \), and the resistivity increases very quickly when temperature decreases from \( T_N \). In the AFM phase, the magnetic moments of neighboring Mn ions are anti parallel, while in the PM phase, the orientation of the magnetic moment of Mn ions is random. As a result, the carriers hopping in the AFM phase may be more difficult than that in the PM phase, leading to the increase of \( T_0 \) below \( T_N \).

Fig. 5(a)–(f) shows the temperature dependence of resistivity \( \rho \) measured in various fields for our studied samples. For \( x \leq 1/8 \), the resistivity of the samples shows insulating behavior at zero field, but exhibits a metal–insulator (M–I) transition upon an application of a magnetic field. It is noticed that, with Bi-doping, the magnetic field needed to drive an M–I transition increases. It has been known that an applied magnetic field enhance FM spins alignment and drive the system to metallic state by actuating the double exchange mechanism and destroying the charge ordering. As the magnetic results shown in Ref. [24], in Bi-doped compound, Bi-doping strongly suppresses FM and enhances CO AFM, so the magnetic field to enforce FM spins alignment and to destroy CO increases with Bi content. As shown in Fig. 5, when a magnetic field is applied, the peak temperature (\( T_{N} \)) shifts to a higher temperature region with decreasing resistivity \( \rho \), which results in a negative magnetoresistance (MR) effect. Defining the relative negative magnetoresistance as

\[
MR = \frac{\rho(T,H) - \rho(T,H=0)}{\rho(T,H=0)} \times 100\%,
\]

where the \( \rho(T,H) \) and \( \rho(T,H=0) \) are the resistivity measured in a static and a zero field, respectively. The measured magnetoresistances for all samples are shown in the insets of Fig. 5. It can be seen that: (1) all the samples show typical features of CMR in the low temperature regions. The low temperature magnetoresistance monotonically increases on cooling. Meanwhile, with increasing the applied magnetic field, the MR increases. (2) The value of the low temperature MR of Bi doped \( \text{La}_{0.5-x}\text{Bi}_x\text{Ca}_{0.5}\text{MnO}_3 \) is obviously lower than that of pure \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \). For example, in a lower magnetic field, such as 3 T, the MR values of \( \text{La}_{0.5-x}\text{Bi}_x\text{Ca}_{0.5}\text{MnO}_3 \) are much lower than that of pure \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \). This high sensitivity to an external field of \( \text{La}_{0.5-x}\text{Bi}_x\text{Ca}_{0.5}\text{MnO}_3 \) compounds could raise fresh opportunities for application in magnetic sensors.

### 4. Conclusion

In summary, we have systematically investigated the electronic transport properties of perovskites \( \text{La}_{0.5-x}\text{Bi}_x\text{Ca}_{0.5}\text{MnO}_3 \) \((x=0, 1/16, 1/8, 1/4, 3/8 \) and \( 1/2 \)) with Bi substitution for La, the charge ordering transition temperature is systematically enhanced, while the MR effect is suppressed, which can be attributed to the special polarized \( 6\overline{2\overline{1}} \) lone pairs of \( \text{Bi}^{3+} \). Below and above the CO transition, the transport behavior is dominated by the Mott’s variable range hopping (VRH) mechanism and the adiabatic small polaronic conduction (SPC) mechanism, respectively. The high

### Table 1

<table>
<thead>
<tr>
<th>( x )</th>
<th>( E_s ) (eV) ( (T &gt; T_{CO}) )</th>
<th>( T_0 ) ( (10^5) ) ( (T_0 &lt; T &lt; T_{CO}) )</th>
<th>( T_4 ) ( (10^5) ) ( (T &lt; T_N) )</th>
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<td>0.127402</td>
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<td>4.76939</td>
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sensitivity to an external field of La$_{0.5}$Bi$_x$Ca$_{0.5}$MnO$_3$ compounds could raise fresh opportunities for application in magnetic sensors.

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