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Influence of Bi^{3+} doping on electronic transport properties of $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ 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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ABSTRACT

Electronic transport properties of $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ (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 $6s^2$ 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 $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ compounds is high sensitive to an external magnetic field, which could raise fresh opportunities for application in magnetic sensors.

1. Introduction

Perovskite manganites $Ln_{1-x}A_xMnO_3$ (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 $Ln_{1-x}A_xMnO_3$ family of compounds [11,12]. Wider e_g bandwidth, i.e., larger average A-site radius $\langle r_A \rangle$, 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 (~0.1300 nm) is almost identical to that of La^{3+} ion (~0.1302 nm). However, the CO temperature T_{CO} of $Bi_{0.5}Ca_{0.5}MnO_3$ is ~325 K (on warming) [13], which is much higher than that (~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 $6s^2$ lone pair of Bi^{3+} ions [15]. It is believed that the $6s^2$ lone pair can produce a local distortion or even hybridization between Bi–6s-orbitals and O–2p-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 $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ ($0 \le x \le 0.25$) system, the physical feature of CO is still unclear. In this work, we investigate this issue by examining the electronic transport properties of the $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ ($0 \le x \le 0.5$) system.

2. Experiment

Polycrystalline samples of $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ 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]. The

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[*] Corresponding author. Tel.: +86 5515595640; fax: +86 5515591149.
E-mail address: zhequ@hmfl.ac.cn (Z. Qu).

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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 crystallined in single phased perovskite orthorhombic structure. It is well known that around half doping, the physical properties of $La_{1-x}Ca_xMnO_3$ 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 $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ 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 (ρ) 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 $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ ($x=0\sim 1/2$). 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 replot 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 substation for La.

It is known that the average A-site radius $\langle r_A\rangle$ has a key effect on T_{CO} in $Ln_{1-x}A_xMnO_3$ 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 $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ 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 with the O:$2p_\sigma$ orbitals in the A-site, but also compete directly for the O:$2p_\pi$ electrons with the Mn:t_{2g} orbitals [16]. The hybridization between 6s lone pair of Bi^{3+} and O:$2p_\pi$ 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].

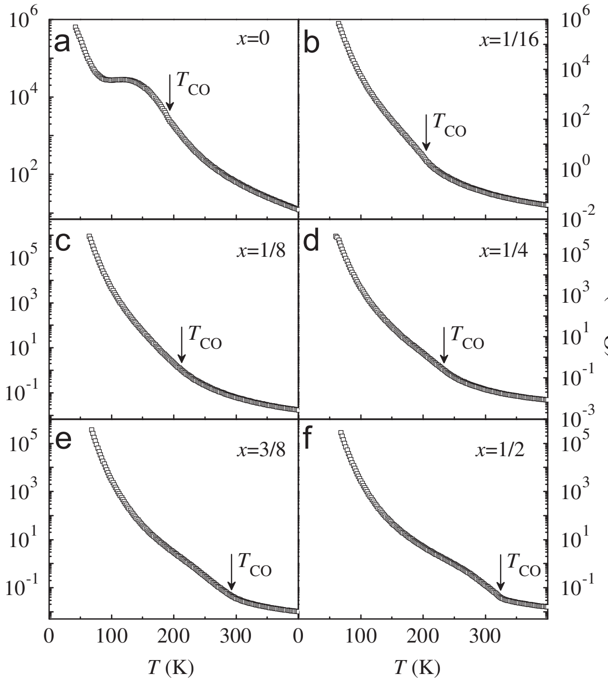

Fig. 1. (a)–(f) Temperature dependence of resistivity for samples $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ ($x=0$, 1/16, 1/8, 1/4, 3/8 and 1/2).

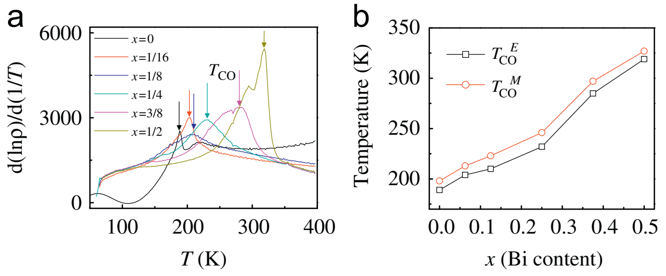

Fig. 2. (a) The variation of the logarithmic derivative $d(\ln\rho)/d(1/T)$ of the resistivity with temperature for all the samples. (b) The T_{CO} variation versus x of $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ samples. T_{CO}^E and T_{CO}^M are the CO temperature defined from $\rho(T)$ and $M(T)$ [24] curves, respectively.

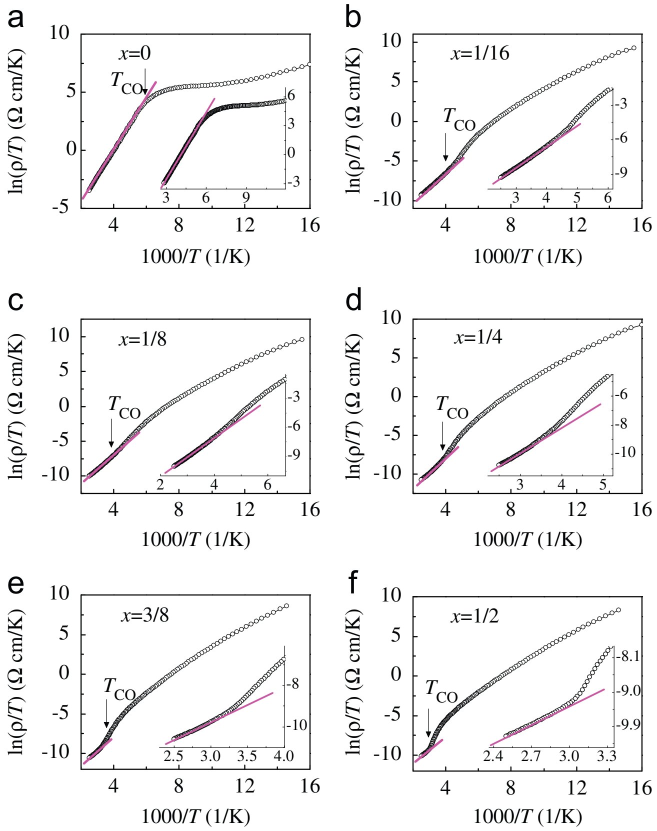

Fig. 3. The fitting curves of $\rho(T)$ by SPC mode, the insets show the enlarged views.

We further investigate the electronic transport mechanism for our studied samples. The $\rho(T)$ data are fitted by purely thermally activated conduction (TAC) model: $\rho=\rho_0\exp(E_a/k_BT)$, the adiabatic small polaronic conduction (SPC) model: $\rho=\rho_0T\exp(E_a/k_BT)$, and three-dimension (3D) Mott's variable range hopping (VRH) model: $\rho=\rho_0\exp[(T_0/T)^{1/4}]$. 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