

Communication

Electrical Resistivity Behavior and Small Polaron Conduction Transport Mechanism in Semiconducting $RMnO_3$ Manganites

Ashwini Kumar , Poorva Sharma* , Qiu Fujun, Hu Jiang, Cui Jin

School of Electrical and Electronics Engineering, Luzhou Vocational and Technical College, Luzhou, People's Republic of China

Abstract

Rare earth manganites, denoted by the chemical formula $RMnO_3$, where R signifies a rare earth element, have garnered significant interest in recent years. These perovskite oxides exhibit intriguing phenomena such as multiferroicity, ferroelectricity, and colossal magnetoresistance, primarily attributed to the role of polarons in conduction. The incorporation of rare earth ions imparts flexibility, making these compounds promising for applications in spintronics, sensors, and information storage devices. This study delves into the electrical resistivity behavior and Small Polaron Conduction (SPC) mechanisms of rare earth manganites, particularly $RMnO_3$. In this manuscript, electrical resistivity of the pristine $RMnO_3$ ($R = \text{Sm, Eu, Gd}$) manganites are analyzed within the framework of adiabatic nearest-neighbor hopping of SPC. The high temperature state of $RMnO_3$ within the SPC mechanism is influenced by polaron concentration, hopping distance, and resistivity coefficient. The localized charge carriers in undoped manganites enable one to estimate the activation energy for the electrical conduction. The activation energy decreases with the decrease in ionic radii from Sm to Gd. Deduced polaron activation energy is low for $GdMnO_3$ as compared to $SmMnO_3$ and is attributed to reducing disorder state in $GdMnO_3$ as compared to $SmMnO_3$. This work contributes to the fundamental understanding of condensed matter physics and the potential applications of rare earth manganites in emerging technologies. The interplay between electrical resistivity and Small Polaron Conduction offers insights for customizing these materials for specific technological needs.

Keywords

Manganites, Polaron, Small Polaron Conduction, Electrical Properties

1. Introduction

Rare earth manganites with their general chemical formula $RMnO_3$, where R represents a rare earth element, have been attracting attention in recent years due to the substantial role of polarons in conduction and various interesting physical phenomena such as multiferroicity, ferroelectricity and co-

lossal magnetoresistance [1-3]. These compounds belong to the family of perovskite oxides, a class known for its versatile and technologically relevant characteristics. The study of electrical resistivity behavior and Small Polaron Conduction (SPC) transport mechanisms in rare earth manganites, par-

*Corresponding author: poorva@lzy.edu.cn (Poorva Sharma)**Received:** 21 January 2024; **Accepted:** 3 February 2024; **Published:** 28 February 2024

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ticularly the $RMnO_3$ compounds, represents a captivating journey into the intricate realm of condensed matter physics. This class of materials has emerged as a focal point of extensive research, driven by its rich interplay of electronic, magnetic, and structural phenomena. The low temperature properties and doping effects at R -site in $RMnO_3$ are studied in detail but the high-temperature properties are less explored [4]. The high-temperature phase has shown the signatures of self-trapped small polarons as well the importance of Jahn-Teller coupling in transport. The incorporation of rare earth ions introduces a degree of flexibility, allowing for the manipulation of electronic configurations, magnetic ordering, and lattice structures. This inherent flexibility positions $RMnO_3$ compounds as intriguing candidates for a range of applications, including spintronics, sensors, and information storage devices [4-10].

The electrical resistivity behavior of $RMnO_3$ compounds is a pivotal aspect of their overall functionality. Understanding the intricacies of how these materials respond to an applied electric field is crucial for harnessing their potential in technological applications. The resistivity of $RMnO_3$ exhibits a diverse range of phenomena, from colossal magnetoresistance to charge ordering, metal-insulator transitions, and multiferroicity. Unraveling the underlying physics governing these phenomena requires a comprehensive investigation into the electronic and structural factors that influence the transport properties. One of the key transport mechanisms that often dominates the electrical behavior of $RMnO_3$ compounds is SPC. Small polarons, localized charge carriers formed by the interaction between charge carriers and lattice distortions, play a significant role in determining the resistivity and conductivity of these materials. The SPC mechanism involves the hopping of small polarons between lattice sites, influenced by factors such as temperature, doping, and external stimuli. This intricate dance of charges and lattice distortions not only governs the transport properties but also provides a window into the delicate balance between electronic correlations and structural degrees of freedom in these materials.

The high temperature paramagnetic state of $RMnO_3$ records that the charge carriers are localized as small polarons. For insulating pristine $RMnO_3$, the adiabatic regime discerns that the charge carrier motion is large as compared to lattice vibrations. Small polaron conduction implies that the E_p that is the sum of the activation energy required for the carrier generation and activation of carrier hopping, must be larger than E_s , which is the energy required to activate carrier hopping. Acoustic and optical phonon frequencies can be derived by writing a Hamiltonian in the Hafemeister and Flygare method with long-range Coulomb, van der Waals interaction and short-range repulsive interaction to second neighboring ions [5, 6]. Our manuscript endeavors to provide an in-depth exploration of the nuanced electrical resistivity characteristics exhibited by $RMnO_3$, unraveling the complex mechanisms that underlie their transport properties. Therefore, we aimed to investigate the effectiveness of SPC on the electrical resistiv-

ity of pristine $RMnO_3$ manganites in the semiconducting state. Furthermore, obtaining the Debye temperatures of $RMnO_3$ ($R = Sm, Eu, Gd$) to support the lattice stiffening with enhanced ionic radii of R -ions, is another goal of studying semiconducting pristine $RMnO_3$ manganites. The significance of this research extends beyond the fundamental understanding of condensed matter physics. The intricate relationship between electrical resistivity and SPC in $RMnO_3$ compounds opens avenues for tailoring their properties for specific technological applications.

2. The Model

For the semiconducting $RMnO_3$, we analyze the electrical resistivity according to the SPC model. The small polaron model focuses on the coherent motion of charge carriers and involves relaxation due to low-lying optical phonon modes, and the conductivity in the paramagnetic phase is influenced by polaron concentration, hopping distance and resistivity coefficient. The residual resistivity is inversely proportional to the polaron diffusion constant, D , expressed as [7, 8]:

$$(\rho/T) = \frac{k_B}{n(1-x)e^2 D} \exp\left(\frac{E_p}{k_B T}\right) \quad (1)$$

$$(\rho/T) = \rho_0 \exp\left(\frac{E_p}{k_B T}\right) \quad (2)$$

where, n is the charge carrier density ($\sim 10^{20} \text{ cm}^{-3}$), x is the doping concentration, D is the polaron diffusion constant, and E_p the activation energy. The polaron diffusion constant for a cubic coordination can be given explicitly as $D = (1/6) a^2 \nu$ where a being the lattice constant and ν is the attempt frequency which corresponds to the optical phonon frequency.

We will now estimate the acoustic Debye branch characterized by the Debye temperature θ_D and the optical peak defined by the Einstein temperature θ_E . The Debye frequency is characterized as the cutoff frequency at the Brillouin zone boundary and can be expressed as effective value of ionic mass and elastic force constant for a crystal lattice with two different kinds of atoms such as Mn-O and R-O ($R = Sm, Eu, Gd$) [5], which we deal with. The acoustic-mode and optical-mode frequencies are estimated in an ionic model using a value of effective ion charge $Z_e = -2e$ [6, 9]. Small polarons move by hopping between trivalent atoms in real space due to the elastic stress introduced in the lattice by atomic size mismatch [10]. The number of sites available for hopping increases with the doping at R -site, so the mixing entropy remains constant.

3. Results and Discussion

The investigation into small polaron hopping conduction

within the framework of polaron concentration, hopping distance and resistivity coefficient successfully retraces the reported resistivity behavior as depicted in Figure 1. The comprehensive analysis of these parameters has provided valuable insight into the transport mechanism governing the studied materials. The resulting parameters are presented in Table 1. One noteworthy observation from our analysis is the discernible trend in polaron activation energy with respect to the ionic radii of R-ions, progressing from Sm to Eu and then Gd (*i.e.* Sm \rightarrow Eu \rightarrow Gd). Remarkably, an inverse correlation is evident, where the polaron activation energy decreases as the ionic radii of R-ions increase. These findings shed light on the influence of the size of the rare-earth ions on the energetics of polaron formation and migration within the manganite system. Specifically addressing the high resistivity observed in SmMnO₃, our analysis attributes this behavior to a correspondingly large polaron activation energy. Furthermore, for higher ionic radii of R-ions in pristine semiconducting manganites, the charge carrier density enhances and the polaron diffusion constant decreases slightly. This observation suggests that the larger ionic radii of R-ions contribute to a higher density of charge carriers, influencing the overall transport properties, while the polaron diffusion constant remains sensitive to changes in the ionic environment.

The fastest motion of small polaron occurs every time the carrier hops the configuration of vibrating atoms in an adjacent site coincides with that in the occupied site [11]. Thereafter, the charge carrier motion in the adiabatic state is faster than the lattice vibration in the semiconducting RMnO₃, resulting in the electrical resistivity induced by the conduction of small polarons [7, 11].

Table 1. Calculated parameters of SmMnO₃, EuMnO₃, and GdMnO₃ systems.

Compounds	D (cm ² s ⁻¹)	ν (10 ¹³ s ⁻¹)	E_s (meV)
SmMnO ₃	4.047	0.208	193
EuMnO ₃	4.039	0.204	156
Gd MnO ₃	4.016	0.199	150

Table 2. Debye and Einstein temperatures of SmMnO₃, EuMnO₃, and GdMnO₃ systems.

Compounds	θ_D	θ_E
SmMnO ₃	339	392
EuMnO ₃	372	378
Gd MnO ₃	395	392

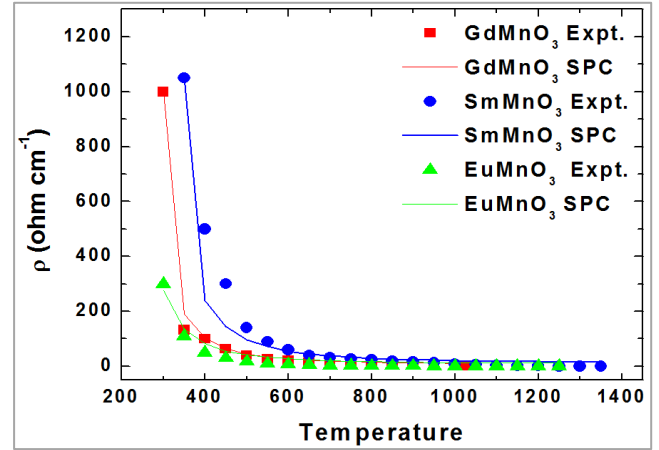


Figure 1. Variation of resistivity with temperature, solid symbols represent the experimental data [9], and solid line represent fitting with SPC model.

We address the possible reason for elastic stress in terms of the contribution from the hopping due to disorder. We note that doping at R-site creates variations in resistivity coefficients due to variation in polaron concentration or polaron hopping distance. Henceforth, the electrical resistivity behavior indicates that the small polaron conduction mechanism is effective in the paramagnetic insulating regions of parent manganites. Deduced values of Debye temperatures essentially point to the lattice hardening with increased ionic size of R-ions [12, 13]. The values of θ_D are documented below in Table 2. It can be seen from the table that θ_D values increase with enhanced ionic radii of rare earth ions. Lattice stiffening as evident from behavior of Debye temperature is earlier observed in ferrites and manganites [14, 15].

4. Conclusions

In summary, our investigation into the behavior of manganites highlights the significant impact of Jahn-Teller distortion on the electronic and structural properties of these materials. The manifestation of Jahn-Teller distortion introduces the intriguing possibility of strong electron-phonon coupling, culminating in the formation of polarons.

In the insulating region, we have observed that the charge carriers are not itinerant. Instead, the transport properties are predominantly governed by thermally activated carriers. This implies that the charge carriers in this regime exhibit localized behavior, and their movement is facilitated by thermal activation processes.

Moreover, our findings underscore the pivotal role of Jahn-Teller distortion in inducing elastic stress and lattice stiffening within manganite structures. This phenomenon has important ramifications for the overall material properties. The elastic stress and lattice stiffening contribute to the modification of the electronic structure, affecting the charge car-

rier dynamics and transport characteristics. It is noteworthy that the Small Polaron Conduction (SPC) mechanism appears to be a viable explanation for the transport properties observed in pristine RMnO₃. The formation and migration of small polarons seem to be consistent with the experimental observations for this specific composition.

However, it becomes evident that the SPC mechanism may not be as satisfactory for doped manganites. The introduction of dopants appears to alter the delicate balance between electron-phonon interactions, Jahn-Teller distortion, and charge carrier dynamics. This suggests that the interplay of these factors in doped manganites could give rise to different transport mechanisms, possibly deviating from the SPC model. Further investigations into the transport mechanisms of doped manganites are warranted to unravel the specific factors that govern their behavior and to elucidate potential applications in the realm of functional materials.

Data Availability

The data used to support the findings of this study are included within the article and is available from the corresponding author upon request.

Acknowledgments

This research was funded by the High-end Foreign Experts Introduction Program of Ministry of Science and Technology of China Project (grant number: G2022036014L), Luzhou Municipal Science and Technology Plan Project (grant numbers: 2021-JYJ-98, 2021-JYJ-99), and Department of Science and Technology of Sichuan province Key R&D research Program (grant number 2022YFWZ0005).

Abbreviations

SPC: Small Polaron Conduction

Conflicts of Interest

The authors declare no competing interests.

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