Hopping conductivity of \( \text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3 \)

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Abstract. The resistivity, \( \rho \), is investigated in ceramic \( \text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3 \) samples with \( x = 0.3 \) and \( y = 0.03 \sim 0.25 \) at temperatures \( T \sim 5 \sim 310 \text{ K} \) in magnetic fields \( B \) up to 8 T. The metallic conductivity at \( y = 0.03 \) and the variable-range hopping (VRH) conductivity between \( y = 0.15 \sim 0.25 \) are observed. The Mott VRH conductivity takes place in all investigated samples with \( y \geq 0.15 \) in different temperature intervals. In addition, at \( y = 0.25 \) the interval of the Shklovskii-Efros VRH conductivity, characteristic of the Coulomb gap in the density of the localized states (DOS), is observed. Analysis of the VRH conductivity yields the values of the microscopic parameters, including the DOS features and the localization radii of charge carriers.

1. Introduction
The mixed-valence (\( \text{Mn}^{3+/4+} \)) hole-doped manganite perovskites attract a stable interest due to remarkable electronic and magnetic properties, including the colossal magnetoresistance (CMR) effect [1]. Such materials are characterized by coexistence of various microscopic phases, determined by interplay between ordering of the spin, the charge and the orbital degrees of freedom and the phase separation effect [2]. This leads to correlations of the macroscopic properties of the manganite perovskites, such as the resistivity, \( \rho \), and the magnetization, \( M \), including a similar behavior and close values of the ferromagnetic (FM) transition temperature, \( T_C \), and the metal-insulator transition (MIT) temperature, \( T_{\text{MI}} \) [1]. At \( T < T_{\text{MI}} \) the conductivity of manganites is metallic and above \( T_{\text{MI}} \) it is realized by hopping of small polarons [1]. The nearest-neighbor hopping (NNH) conductivity mechanism is observed usually above the room temperature, whereas with lowering \( T \) the microscopic disorder becomes important leading to the variable-range hopping (VRH) conduction [1, 3 \sim 6].

\( \text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3 \) (LSMFO) belongs to the family of the manganite perovskite compounds and is characterized by strong damping of the FM properties by doping with Fe [7 \sim 11, 12]. The latter leads to substantial decrease of \( T_C \) with \( y \) [12], which takes place along with the decay of \( T_{\text{MI}} \) stimulating the onset of the non-metallic character of \( \rho (T) \) at higher temperatures.

In this paper are presented investigations of the hopping conductivity of LSMFO. Mechanisms of the hopping charge transfer are identified and information about microscopic parameters of charge carries is obtained.
2. Results and discussion
Ceramic LSMFO samples with $x = 0.3$ and $y = 0.03$ (# 03), 0.15 (# 15), 0.20 (# 20) and # 25 (# 25), investigated in this work, were prepared and characterized in a same way as described in [12]. Measurements of the resistivity were made in the temperature interval of $T \sim 5 - 310$ K with the conventional four-probe technique in transversal magnetic field ($B$) configuration for $B = 0 - 8$ T.

![Figure 1. Temperature dependence of the resistivity in the investigated samples at $B = 0$ (solid lines) and $B = 8$ T (dashed lines). Inset: the plot of $\ln (\rho / T^{25/4})$ versus $T^{-1/4}$ at $B = 0$ for the interval HTM of # 15. The straight line is a linear fit. Open triangles mark $T_C$.](image)

As follows from figure 1 $\rho (T)$ depends strongly on $y$. Metallic conductivity in # 03 is changed eventually to activated one in # 25. The behavior of $\rho (T)$ in # 15 and # 20 is more complicated, exhibiting two extremes divided by the interval of the metallic behavior (downturn) in # 15, and two inflections of $\rho (T)$ in # 20 within similar intervals $\Delta T$ below $\sim 100$ K. It can be seen also the weak inflection of $\rho (T)$ in # 15 and # 20 near $T_C$, taken from [12] and shown by open triangles in figure 1. Large drop of the resistivity of LSMFO in the magnetic field, characteristic of CMR in manganites [1], is increased with increasing $y$ from 0.15 to 0.20. In addition, the CMR effect within the interval $\Delta T$, defined above, is stronger than at temperatures around $T_C$, which is enhanced in # 20, as well.

The behavior of the resistivity in figure 1 is attributable to the hopping conduction mechanism in # 20 and # 25 above $T_C$ and below it, and in # 15 at $T > T_C$. In the domain of the hopping charge transfer $\rho (T)$ is given by the universal expression,

$$\rho (T) = AT^m \exp \left[ (T_0 / T)^p \right], \tag{1}$$

where $A$ is the prefactor constant and $T_0$ is the characteristic temperature [13]. The exponents $m$ and $p$ in equation (1) are interrelated and depend on the type of the hopping conduction. The NNH conductivity is characterized by $m = p = 1$ [13]. The VRH conductivity takes place, when the hopping...
of charge carriers between the nearest sites becomes energetically unfavorable due to a microscopic disorder. The VRH conductivity is given by the values of $p = 1/4$ (the Mott mechanism) and $p = 1/2$ (the Shklovskii-Efros or SE mechanism). The Mott VRH conductivity sets in when the long-range Coulomb interactions between the carriers can be neglected. In the opposite case these interactions lead to a soft Coulomb gap with width $\Delta$ in the density of localized states (DOS) around the Fermi level, $\mu$, and to the SE VRH conductivity [13]. At any VRH conduction regime of manganite perovskites the relation $m = 8 - p (7 + q)$ has been predicted, where $q = 4$ or 0, depending on whether or not a fluctuating short-range potential is important for the disorder [3].

In equation (1) one has $T_0 = T_{0M}$ and $T_0 = T_{SE}$ for the Mott and the SE VRH conduction mechanisms, respectively, satisfying the expressions

$$T_{0M} = \beta_{M} / [k (\mu \alpha^3)] \text{ and } T_{SE} \approx [T^{-1/2}_{S} + (T_{S} + T_{SE})^{1/2}]^{2},$$

respectively [3, 13, 14]. Here $T_{S} = \delta_{V}^{-2} / (4k^{2}T_{SE})$, $\delta_{V}$ is width of the rigid gap, existing inside $\Delta$ due to polaron effects in manganites [3], $T_{SE}$ is the onset temperature of the SE VRH conductivity, $T_{0SE} = \beta_{SE} e^{2} / (k \kappa \alpha)$, $\beta_{M} = 21$ and $\beta_{SE} = 2.8$ are constants [13], $g (\mu)$ is the DOS value at $\mu$ in the Mott VRH model, $a$ is the localization radius and $\kappa$ is the dielectric permittivity [13]. The prefactor constant in equation (1) is given for the manganese perovskites by the equation

$$A = C_{0} \alpha^{11} T_{0}^{p (7 + q)},$$

where $T_{0} = T_{0M}$ and $T_{0} = T_{SE}$ for $p = 1/4$ and $1/2$, respectively, and $C_{0}$ is a constant [3]. The DOS outside the Coulomb gap, $g_{0}$, and $\Delta$ satisfy the expressions [3, 13]

$$g_{0} = (3/\pi) (\kappa^{3} / e^{6}) (\Delta - \delta_{V})^{2} \text{ and } \Delta \approx k (T_{SE} T_{SE})^{1/2}. \quad (4)$$

Identification of the hopping conduction mechanisms can be done by linearization of $\rho (T)$ in coordinates $\ln (\rho / T^{m})$ versus $T^{-p}$, taking into account equation (1), the relation between $m$ and $p$ and possible values of $m$ and $p$ as discussed above. In # 15 the best linearization of $\rho (T)$ above $T_{C}$ is achieved for $p = 1/4$ and $m = 25/4$ (inset to figure 1), giving evidence for the Mott VRH conductivity at high-temperature interval HTM ($T > T_{C}$) with $T_{0M} = 7.43 \times 10^{5}$ K and $q = 0$. As follows from the top panel of figure 2, the Mott VRH conductivity with $p = 1/4$ and $m = 25/4$ ($q = 0$) is observed in # 20, as well. This regime takes place in # 20 within three different temperature intervals HTM ($T > T_{C}$), ITM ($T$ around $T_{C}$) and LTM ($T < T_{C}$), given by different values of $T_{0M} = 9.43 \times 10^{5}$ K, $8.16 \times 10^{5}$ K and $3.19 \times 10^{3}$ K, respectively. In # 25 two intervals of the Mott VRH conductivity are observed, namely at high (interval HTM between $\approx 220$ K and $170$ K) and low (interval LTM with the onset near $T_{C} \approx 95$ K) temperatures, as follows from the bottom panel of figure 2. However, the intervals of the Mott VRH conductivity in # 25 are separated by the region of the SE VRH conductivity (interval SE in figure 2 between $T = T_{SE} \approx 150$ K and $T$ near $T_{C}$). The values of $m = 25/4$ in the intervals HTM and LTM, as well as $m = 9/2$ in the interval SE yield $q = 0$ in # 25, too. The value of $q = 0$ gives evidence for absence of the fluctuating short-range potential in LSMFO in the whole interval of $y = 0.15 - 0.25$. It is worth mentioning quite another situation ($q = 4$) in Li_{0.7}Ca_{0.3}Mn_{1-y}Fe_{y}O_{3}, indicating influence of the short-range potential on the microscopic disorder already at $y \geq 0.03$ [3].

The values of $T_{0M}$, found above, yield the localization radius $a$ of the charge carriers in the intervals of the Mott VRH regime. If $g (\mu)$ is known, evaluation of $a$ can be done with the first of equations (2). The DOS can be found with the expression $g (\mu) \approx N_{i} c (1 - c) / (2 W)$ [11], where $N_{i} \approx N_{0} (1 - y)$, $N_{0} = 1.42 \times 10^{22}$ cm$^{-3}$ is the concentration of Mn sites, $c \approx c_{0} - y$ is the relative concentration of Mn$^{4+}$ involved in the hopping, $c_{0} \approx 0.31$ and $W \approx 2.6$ eV is width of the electron band of LSMFO [12]. This gives $g (\mu) \approx 3.1, 2.1$ and 1.2 (in units of $10^{20}$ eV$^{-1}$ cm$^{-3}$) for # 15, # 20 and # 25, respectively.
Figure 2. The plots of $\ln (\rho / T^{25/4})$ versus $T^{-1/4}$ at $B = 0$ for the intervals HTM, ITM and LTM of #20 (top panel) and the plots of $\ln (\rho / T^{m})$ versus $T^{-1/2}$ and $T^{-1/4}$ for #25 (bottom panel). The lines are linear fits. $T_C$ is given by open triangles.
Eventually, the following values of the localization radius are found: \( a \approx 1.0 \text{ Å} \) in the interval HTM of \# 15, \( a \approx 1.1 \), \( 1.1 \) and \( 3.3 \text{ Å} \) in the intervals HTM, ITM and LTM of \# 20, respectively, and \( a \approx 1.2 \) and \( 1.0 \text{ Å} \) in the intervals HTM and LTM of \# 25, respectively.

In the interval SE of \# 25, corresponding to the SE VRH conductivity (the upper plot in the bottom panel of figure 2), one obtains the value of \( \Delta \approx 0.30 \text{ eV} \) with the second of equations (4) and the data of \( T_{SE} \) and \( T_{VSE} \) above. Then the value of \( \kappa \approx 3.6 \) is evaluated with the relation \( \Delta \approx U \), where \( U \approx e^2 / (\kappa R) \) is the mean energy of the Coulomb interactions and \( R \approx 2[4\pi N(0)(c_0 - y)/3]^{1/3} \) is the mean distance between the charge carriers or Mn\(^{4+}\) involved in the hopping. Finally, \( \delta_v \approx 0.07 \text{ eV} \) is found with the first of equations (4), whereas \( a \approx 2.0 \text{ Å} \) in the interval SE of \# 25 is obtained with the second of equations (2).

The value of \( \Delta \approx 0.3 \text{ eV} \) in \# 25 is smaller than \( \Delta \approx 0.4 - 0.5 \text{ eV} \) in \( \text{La}_1.4\text{Ca}_{0.6}\text{Mn}_{1.4}\text{O}_3 \) \([3]\), \( \text{La}_1.4\text{Ba}_{0.6}\text{MnO}_3 \) \([4]\) and \( \text{LaMnO}_3 \) \([5, 6]\). This is attributable to the smaller concentration of the holes or Mn\(^{4+}\), involved in the hopping, \( c \approx 0.061 \) in \# 25 versus \( c \approx 0.20 - 0.30 \) \([3, 4 - 6]\) in the aforementioned compounds, leading to weaker Coulomb interactions of charge carriers. The value of \( \kappa \approx 3.6 \) in LSMFO is close to those of \( \kappa \approx 3.0 - 3.7 \) \([3, 4 - 6]\), determined in other manganites from analysis of the hopping conductivity (the reason for smallness of \( \kappa \) in manganites is discussed in \([4]\)).

The value of \( \delta_v \approx 0.07 \text{ eV} \) in \# 25 is smaller, but quite comparable with the width of the rigid gap, \( \delta_v \approx 0.12 - 0.28 \text{ eV} \), whereas \( a \) is typical of the localization radius, \( a \approx 1.2 - 2.9 \text{ Å} \), of small polarons, found in the manganite perovskites mentioned above \([3, 4 - 6]\).

An appreciable difference between the values of \( a \) in the intervals HTM at \( T > T_C \) \((1.1 \text{ Å}) \) and LTM at \( T < T_C \) \((3.3 \text{ Å}) \) of \# 20 is attributable to the narrow FM transition and well-defined FM properties of \# 20 below \( T_C \) \([12]\). At this point, the FM transition in \# 25 is considerably expanded and FM properties of \# 25 are damped \([12]\). This correlates well with close values of \( a \approx 1.2 \) and \( 1.0 \text{ Å} \) in the HTM and LTM intervals of \# 25, respectively. One can also see that the value of \( a \approx 2.0 \text{ Å} \) in the SE interval of \# 25 above \( T_C \) is enhanced with respect to \( a \approx 1.0 - 1.2 \text{ Å} \) in \# 15 and \# 20 at \( T > T_C \). Such enhancement suggests proximity to the metal-insulator transition, induced by doping with Fe \((\gamma\text{-MIT})\). Indeed, the SE interval of \# 25 can be treated as a result of transformation of the interval of the metallic behavior of \( \rho (T) \) in \# 15 via the intermediate interval between two inflections of \( \rho (T) \) in \# 20 (these intervals are defined as \( \Delta T \) above). Therefore, a critical behavior of \( a \\approx a' \left( 1 - c/c_{cr} \right)^{1/3} \) alike that near the Anderson transition \([14, 15]\), is expected inside \( \Delta T \). Here \( c_{cr} = c_0 - y_{cr} \), \( y_{cr} \) is the value at \( \gamma\text{-MIT} \), \( v \approx 1 \) and \( a' \) is the localization radius far from \( \gamma\text{-MIT} \). Taking into account the universal Mott criterion, \( N(0)^{1/3} a' \approx 0.25 [14, 15] \), where \( N_{cr} = N_0(1 - y_{cr}) \), the equation \( a(y) \approx 0.25 \left[ N_0(1 - y_{cr}) \right]^{1/3} \left[(c_0 - y_{cr})(y - y_{cr}) \right]^{1/3} \) can be obtained. Then, putting \( a(0.25) \approx 2.0 \text{ Å} \), one finds with this equation \( y_{cr} \approx 0.18 \), lying between \( y \approx 0.15 \) in \# 15 and \( y \approx 0.20 \) in \# 20. This means proximity of \# 15 to \( \gamma\text{-MIT} \) from the metallic side and closeness of \# 20 to \( \gamma\text{-MIT} \) from the insulating side. Such relations are in a complete agreement with metallic behavior of \( \rho (T) \) in \# 15 and activated behavior, accompanied with two inflections, of \( \rho (T) \) in \# 20 in the interval \( \Delta T \). In addition, the value of \( a' \approx 0.25 [(1 - y_{cr}) N_0]^{1/3} \approx 1.1 \text{ Å} \) is quite close to \( a \approx 1.0 - 1.2 \text{ Å} \), characterizing the temperature intervals \( T > T_C \) outside \( \Delta T \), where the \( \gamma\text{-MIT} \) does not take place.

The magnetic field dependence of the microscopic parameters \( a \) and \( g (\mu) \) for \# 15 and \# 20 can be obtained with the linearization of \( \rho (T) \) in non-zero field, similar to that in the inset to figure 1 and in the top panel of figure 2 at \( B = 0 \), and using equations (2) and (3). The general tendency is increase of \( a \) and decrease of \( g (\mu) \), when \( B \) is increased. Decrease of DOS with \( B \) can be expected due to the increase of the effective electron bandwidth. This is the broader the smaller is the angle between the spins in the \( \text{Mn}^{3+} - \text{Mn}^{4+} \) pairs \([1]\), decreasing by alignment of these spins in the applied magnetic field. The increase of \( W \) with \( B \) stimulates increase of \( a (B) \), as well, making the hopping of electrons between \( \text{Mn}^{3+,4+} \) sites easier, when the localized magnetic moments of the neighboring ions are aligned better \([1]\). In addition, different dependences of \( a \) and \( g (\mu) \) on \( B \) in various temperature intervals are observed, indicating different sensitivity of the Mn ion spins to the magnetic field.
3. Conclusions
We have investigated resistivity of La$_{1-x}$Sr$_x$Mn$_{1-y}$Fe$_y$O$_3$ with $x = 0.3$ and $y = 0.03 - 0.25$, paying major attention to the mechanisms of the hopping charge transfer. The transformation of the metallic conduction at $y = 0.03$ into the activated conductivity at $y = 0.25$, accompanied with strong overall increase of the resistivity with increasing $y$, is observed between $T \approx 5 - 310$ K. The Mott and the Shklovskii-Efros variable-range hopping conductivity regimes have been identified. The values of the microscopic parameters such as the localization radius, the density of the localized states and the width of the soft Coulomb gap and of the rigid gap have been obtained and analyzed.

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