Physical properties of the novel ruthenate La$_{3.5}$Ru$_4$O$_{13}$: Possible mixed valence of Ru ions


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Structural, magnetization, heat capacity, and electrical resistivity measurements have been carried out on a new ruthenate compound La$_{3.5}$Ru$_4$O$_{13}$. This compound forms in the orthorhombic structure (Pnmm space group, #47). The coexistence of the triple-layered perovskite-type planes [quasi-two-dimensional (2D) structure] and the rutilelike slabs [one-dimensional (1D) structure] leads to interesting magnetic and electronic properties in this compound. The relatively short Ru–O bond distances or stronger 4d-2p hybridization of rutilelike slabs suggest an electronic delocalization feature along the slab axis (b-axis). In the high-temperature region, a Curie–Weiss behavior of the magnetic susceptibility is observed with an effective magnetic moment $\mu_{\text{eff}} = (2.44 \pm 0.02) \mu_B$ per Ru ion and a paramagnetic Curie temperature $\theta_p = -198 \pm 2$ K. The magnetic susceptibility of this compound shows a peak at $T \approx 47$ K typical of an antiferromagnetic (AFM) order which is confirmed by heat capacity measurements. This AFM order can be associated with the AFM coupling of Ru ions of the quasi-2D layers. The electronic specific heat coefficient $\gamma$ is found to be 12 mJ/mol$_{\text{Ru}}$ K$^2$, suggesting moderate carrier correlations. Resistivity and magnetic data suggest that the quasi-2D substructure shows semiconducting behavior, while a metallic behavior is expected for the 1D slabs. © 2009 American Institute of Physics. [DOI: 10.1063/1.3159647]

I. INTRODUCTION

The transition-metal oxides display a variety of physical phenomena related to the orbital degeneracy of the $d$-electrons. The orbital degeneracy depends strongly on the local environment of the transition-metal ion. The crystalline electric field (CEF) of octahedral symmetry causes the splitting of $d$ orbitals into two subgroups, $t_{2g}$ ($d_{3z^2}$, $d_{xz}$, and $d_{yz}$) and $e_g$ ($d^{2}_{z^2}$ and $d^{2}_{xy}$) orbitals, whose energy separation is determined by the CEF strength. The $t_{2g}$ orbitals are usually the ground state. The electronic occupation of $t_{2g}$ and $e_g$ orbitals is determined by the competition of the CEF and the intraionic Coulomb repulsion among the $e_g$ electrons of the transition-metal ion, and this in turn decides the magnetic ground state. In general, the magnetic behavior of the transition-metal oxides is governed by exchange interactions between metal ion spins. This interaction can occur either via the oxygen ion (superexchange) or by the direct metal-metal ion interaction (double exchange). On the other hand, the electrical and electronic properties of transition-metal oxides are commonly understood on the basis of the Mott–Hubbard model. Within the framework of this model, the ratio of the strength of the intraionic Coulomb repulsion between electrons ($U$) to the conduction band width ($W$), originating from the overlap of $d$ and $p$ orbitals, is a determinant parameter. For a system where $U/W \ll 1$, the splitting of the lower and upper Hubbard bands is large and an insulating behavior is expected. A metallic behavior is expected if $U/W \gg 1$, while the borderline between metal and insulator is expected when $U/W = 1$, which is strongly affected by small perturbations (such as strain, doping, etc.) promoting a metal-insulator transition.

The ruthenates ($4d$ transition-metal oxides) are one of the most intriguing systems and exhibit a variety of interesting properties ranging from unconventional superconducting behavior, as observed in Sr$_2$RuO$_4$ (Ref. 5), high $T_C$ itinerant metallic ferromagnetism in Sr$_3$Ru$_2$O$_{10}$ (Ref. 6) and in SrRuO$_3$ (Ref. 7). Fermi-liquid behavior in La$_3$Ru$_4$O$_{11}$ (Ref. 8), a non-Fermi-liquid behavior in La$_4$Ru$_6$O$_{19}$, and in Ca$_x$Sr$_{1-x}$RuO$_3$ system with $x > 0.75$, etc. Also there are ruthenates which exhibit metal-insulator transition induced by doping (such as Sr$_2$Ru$_2$O$_7$) or semiconductor-semiconductor transition, where the orbital ordering is expected to play a special role at low temperatures. The more extended nature of the $4d$ orbitals (relative to their $3d$ counterparts) is expected to considerably enhance the electron-lattice interaction, which may be the reason for the formation of a variety of structures for ruthenates (ranging from perovskites to pyrochlores) and also should be the source of structural phase transitions caused by metal ion substitutions. This higher degree of delocalization of $4d$ orbitals also tends to produce a greater overlap between them, leading to the increase in the intraionic Coulomb interaction in $4d$-metal oxides compared to that in their $3d$ counterparts.

In view of the interesting properties exhibited by the ruthenates, we have studied a novel Ru based compound, namely, La$_{3.5}$Ru$_4$O$_{13}$, the structure of which shows peculiar features. In this paper, we present the results of magnetic, heat capacity, and electrical resistivity measurements on this...
compound in order to understand the ruthenium spin state, magnetic interactions, and electronic properties. We find that this compound orders magnetically at about 47 K. It is either a poor metal or a small-gap insulator and the Ru ions seem to exist in more than one valence state in this compound.

II. EXPERIMENTAL DETAILS

The La$_{3.5}$Ru$_4$O$_{13}$ compound was synthesized from lanthanum hydroxide La(OH)$_3$ (Sigma-Aldrich, 99.9%) and RuO$_2$ (Alfa-Aesar, 99.95%) using conventional solid-state reaction technique. These reagents were previously preheated to ~200 °C to remove any absorbed water. Stoichiometric amounts of La(OH)$_3$ and RuO$_2$ were mixed intimately in isopropyl alcohol and dried at ~50 °C. The dried mixture was pressed into pellets under a pressure of ~4 × 10$^7$ kg/m$^2$ and fired in air at 1100 °C in an alumina crucible for 24–48 h. Intermediate grindings were performed in order to ensure homogeneity of the samples. Crystal-structure characterization and phase determination were carried out by x-ray diffraction (XRD) using Cu Kα radiation in the 2θ-range of 10°–100° with steps of 0.02°. Magnetic measurements in the temperature range of 2–300 K and in various applied magnetic fields were carried out using commercial superconducting quantum interference device (SQUID) magnetometer and vibrating sample magnetometer (VSM). Heat capacity measurements, using the relaxation method, and four-probe dc electrical resistance measurements were performed in a commercial system (PPMS, Quantum Design) in the range of temperature of 2–300 K with applied magnetic fields up to 9 T. For dc resistivity measurements, a piece of the sample cut in a rectangular shape with dimensions of 0.88 × 1.26 × 2.15 mm$^3$ was used. An excitation current of I~5 mA was chosen for these measurements in order to reduce any significant self-heating at low temperatures.

III. RESULTS AND DISCUSSION

A. Crystal structure

The XRD data of polycrystalline La$_{3.5}$Ru$_4$O$_{13}$ was analyzed using the Rietveld method. The analysis shows the formation of a single phase compound of an orthorhombic structure (space group: Pmmm, #47) and, within the resolution limits of XRD, no additional impurity phase was determined. A good fit to the x-ray data was obtained using the starting parameters taken from Ref. 19 (see Fig. 1). The structural information obtained from the refinement of atomic positions from our powder diffraction data is in agreement with that reported previously in Ref. 19 which also lists the atomic positions, interatomic bond distances, and bond angles.

The crystal structure of La$_{3.5}$Ru$_4$O$_{13}$ is shown in Fig. 2. All the Ru atoms are in an octahedral environment. The corner-shared octahedra of Ru(1) and Ru(2) form a triple-layered perovskite-type structure along the [100] direction [i.e., parallel to the (100) plane] and the edge-shared octahedra of Ru(3) form the one-dimensional (1D) rutilelike slabs along the [010] direction. In agreement with Ref. 19, the bond distances of Ru(3)–Ru(3) of the 1D slabs are found to be smaller than the bond distances of Ru ions of the two-dimensional (2D) perovskite layers. This may result in different properties of the Ru ions in the two structures. The quasi-2D substructure of La$_{3.5}$Ru$_4$O$_{13}$ compound is closely related to those of the Ruddlesden–Popper (RP) ruthenate series, such as (Sr,Ca)$_{n+1}$Ru$_n$O$_{3n+1}$ where $n$ (=1, 2, 3, and ∞) is the number of layers of corner sharing RuO$_6$ octahedra. Since La$_{3.5}$Ru$_4$O$_{13}$ shows a triple-layered perovskite feature, it seems more related to the Sr$_3$Ru$_2$O$_{10}$ compound, which also shows a triple-layered structure. Despite the similarity between their structures, these two compounds show a remarkable difference related to the planar orientation and interconnectivity. The 2D planes of the $n=3$ member of RP are oriented along the [001] direction; whereas the 2D planes of the La$_{3.5}$Ru$_4$O$_{13}$ compound are oriented along the [100] direction. The RuO$_6$ octahedra of outer layers of the RP compound has corner-shared connections with five neighbor RuO$_6$, and the corresponding octahedra of La$_{3.5}$Ru$_4$O$_{13}$ have alternately four and six connections along the [001] direction where the two extra connections correspond to corner-shared connections with RuO$_6$ octahedra of the rutilelike slab (see Fig. 2). The inner layer of both compounds has the same features.
Two different values of Ru(3)–Ru(3) bond distances have been determined, which are alternately disposed along the 1D slab axis as shown in Fig. 3(a). In spite of the difference between Ru–Ru bond distances in the rutile chain of the La$_{3.5}$Ru$_4$O$_{13}$ compound, it seems not to be distinct enough to produce metal pairs (dimers) in a similar way that Ru–Ru pairs do in the La$_8$Ru$_6$O$_{19}$ compound. However, a change in crystal structure at low temperatures may lead to dimerization in La$_{3.5}$Ru$_4$O$_{13}$ compound as happens in the La$_4$Ru$_2$O$_{10}$ system, which can increase the difference of consecutive Ru–Ru bond lengths, thus modifying the structure of the 1D rutile chain from the edge-sharing octahedral sequence toward a line of dimers along the chain axis.

**B. Magnetic properties**

Figure 4(a) shows the temperature ($T$) dependence of the dc magnetic susceptibility ($\chi$) for La$_{3.5}$Ru$_4$O$_{13}$, obtained in a field of $H=5$ kOe, from 2 to 300 K. The $\chi$ versus $T$ curve shows some remarkable features in the low-temperature region: a cusp at 47 K, a shoulder centered at ~12 K, and a continuous increase when the temperature is further decreased below 12 K [see the inset at the bottom part of Fig. 4(a)]. In the high-temperature region, the experimental data are well described by the Curie–Weiss law ($\chi=\chi_0+C/(T-\theta)$) as indicated in the figure. The $\chi^{-1}$ versus $T$ curve shows a linear behavior for temperatures above 47 K as observed in the inset at the upper part of Fig. 4(a). From the fit carried out in the range of 60–300 K, we obtain an effective magnetic moment, $\mu_{\text{eff}}=(2.44 \pm 0.02)\mu_B$ per Ru ion (or $\mu_{\text{eff}}=4.88\mu_B$ per formula unit), a paramagnetic Curie temperature, $\theta_p=-198 \pm 2$ K, and a temperature-independent contribution to susceptibility $\chi_0=(1.0 \pm 0.2) \times 10^{-4}$ emu/mol of Ru. The negative value of $\theta_p$ is consistent with an antiferromagnetic (AFM) feature governing the magnetic interactions at low temperatures. At the lowest temperatures, the susceptibility shows an increasing tendency when the temperature is decreased and suggests the presence of a paramagnetic contribution. The fit of data below 7 K with a Curie–Weiss law provides a very small Curie constant ($C=9.4 \times 10^{-5}$ emu K/Oe mol of Ru) and a paramagnetic temperature $\theta_p=-1$ K. The value of $C$ remains approximately unchanged if one sets $\theta_p=0$. This Curie constant corresponds to a magnetic moment of 2.83$\mu_B$ residing on ~0.2% of the Ru ions present in the sample. This may represent some Ru ions not ordered magnetically or a small amount of extrinsic magnetic impurities below the threshold of XRD detection limit. The broad shoulder at $T_p \sim 12$ K which is also observed in sample prepared under O$_2$ flow (not shown here) may be associated with the magnetic transition of magnetic impurity phases such as La$_9$Ru$_6$O$_{18}$ ($T_N\sim10$ K), La$_4$Ru$_2$O$_{10}$ ($T_N \sim 18$ K), or any other unidentified magnetic compound which shows a magnetic transition at ~12 K.

The effective magnetic moment in La$_{3.5}$Ru$_4$O$_{13}$, obtained from the high-temperature region of susceptibility ($[\mu_{\text{eff}}=(2.44 \pm 0.02)\mu_B$ per Ru ion], reveals that the Ru ions are in the low-spin state, with spin $S=1/2$ or 1, since the expected values of the effective moments for these two spin states are 1.73$\mu_B$ and 2.83$\mu_B$, respectively. The experimental value of the effective moment strongly suggests the coexistence of Ru$^{3+}$ and Ru$^{3+}$ ions in this compound (whose electronic con-
The maximum in susceptibility in La$_{3.5}$Ru$_4$O$_{13}$ at 47 K is found to be field independent since essentially the same cusp position and a well-defined maximum is observed when a field as high as 50 kOe is applied, thus strongly suggesting a real AFM ordering. Figure 4(c) shows the ac susceptibility (at different excitation frequencies) versus $T$. Two cusps centered at $T_1 = 12$ and $T_2 = 49$ K are observed, both which show no shift of their positions when the excitation frequency is changed. These observations exclude the possibility of a spin-glass behavior in this sample and reinforce the occurrence of an AFM ordering below $\sim 50$ K, which is also corroborated by the linear behavior of $M$ versus $H$ curves [see Fig. 4(b)] in applied fields up to 90 kOe and by heat capacity measurements (see below).

The AFM ordering in La$_{3.5}$Ru$_4$O$_{13}$ may be associated with two possible sources: The AFM coupling of Ru spins along the 1D chains or the AFM ordering established in the quasi-2D layers. Neglecting the effect of next-nearest neighbors, the effective coupling constant for a magnetic ion along the chain axis with its nearest neighbors should be given by $-2J_1 + 2J_2$, where $J_1$ is the coupling constant between Ru ions along the chain (Ru(3)) and $J_2$ is the coupling constant between one Ru(3) ion and another Ru ion from the perovskite layers (Ru(2)). Based on bond distance values, the magnetic coupling along the 1D rutile chains should be determined by the strongest exchange interaction constant $J_1$. Moreover, the bond distances obtained at room temperature for Ru ions along the 1D chains (see Fig. 3) suggest that, if any low-temperature crystal symmetry change happens which leads to $J_1 > J_2$, then it would favor the magnetic interaction of Ru ions by pairs along the 1D chain. On the other hand, if the magnetic ordering below 47 K is related to the quasi-2D layers, the effective coupling constant of nearest neighbors should be given by $-6J_3$ for Ru(1) and $-4J_3 + 2J_2$ or $-4J_3$ for Ru(2); where $J_3$ is the average coupling constant between Ru ions inside the layers. It is known that the distortion (rotation and elongation or flattening) of octahedra of perovskite layers is related to the type of magnetic order. The triple-layered Sr$_3$Ru$_4$O$_{10}$ compound ($n = 3$ RP member) shows strongly 2D features with itinerant FM behavior, which has been assigned to the opposite rotation of RuO$_6$ octahedra of outer and central layers of each triple layer and to the elongation of RuO$_6$ in the outer layers at low temperatures. However, in La$_{3.5}$Ru$_4$O$_{13}$ which also has a triple-layered substructure, the octahedron of the central layer rotates by $\sim 11^\circ$ around the c-axis and shows flattened shape in a similar way as the Ca$_3$RuO$_4$ (a $n = 1$ RP member) does. The latter system is expected to show AFM ordering, which is associated with the delicate balance between the flattening, tilting, and rotation of the octahedra in the perovskite-type layers. A similar mechanism may be responsible for the AFM ordering observed in La$_{3.5}$Ru$_4$O$_{13}$.

C. Heat capacity

Figure 5(a) shows the temperature dependence of the heat capacity ($C$) of La$_{3.5}$Ru$_4$O$_{13}$ in zero and 90 kOe magnetic fields. The magnetic field does not have any discernible effect on the heat capacity since both sets of data overlap in the whole range of temperature as shown. The heat capacity results have been analyzed in different temperature intervals in a manner described below:

1. Low-temperature region

The low-temperature region of the heat capacity [shown in Fig. 5(b)] was modeled considering the following contributions to the total heat capacity $C_{\text{total}}$:

$$C_{\text{total}} = C_{\text{hyp}} + C_{\text{ele}} + C_{\text{lat}} + C_{\text{sw}},$$

(1)

where $C_{\text{ele}}$ is the electronic contribution to the heat capacity given by $y\gamma T$ corresponding to the free charge carriers, $C_{\text{lat}}$ is the lattice contribution which can be expressed by $\beta_3 T^3 + \beta_2 T^2$, $C_{\text{sw}}$ is the spin-wave contribution to the heat capacity given by $\beta_n T^n$, where the value of the index $n$ depends on the nature of the magnetic excitations, and $C_{\text{hyp}}$ is the term representing the

\[ C_{\text{hyp}} = \alpha T\delta(x - T), \]

\[ C_{\text{ele}} = y\gamma T, \]

\[ C_{\text{lat}} = \beta_3 T^3 + \beta_2 T^2, \]

\[ C_{\text{sw}} = \beta_n T^n, \]

\[ C_{\text{total}} = C_{\text{hyp}} + C_{\text{ele}} + C_{\text{lat}} + C_{\text{sw}}. \]

FIG. 5. (Color online) Heat-capacity (c) data for La$_{3.5}$Ru$_4$O$_{13}$ obtained as a function of temperature ($t$) in different magnetic fields (b). (a) Polynomial fit in the range from 2 to 100 K to determine the magnetic contribution ($C_{\text{mag}}$) to the heat capacity at the magnetic transition. The upper inset shows the linear behavior of $C/T$ vs $T$ for $H=0$, 50, and 90 kOe; the lower inset shows the $C_{\text{mag}}/T$ vs $T$ curve for $H=0$ and 90 kOe. (b) Fitting of $C/T$ vs $T^2$ in the low-temperature region using Eq. (3). The different contributions are also depicted.
TABLE I. Summary of fitting results to heat capacity data of La$_{3.5}$Ru$_4$O$_{13}$ in the low-temperature region (from 2 to 15 K). $A_2$ is the hyperfine term coefficient, $\gamma$ is the electronic specific heat coefficient, $\beta_2$ is the spin-wave coefficient, $\beta_i$ and $\beta_j$ are the lattice contribution coefficients, and $\chi^2$ is the reduced chi-square. The numbers in parentheses are the errors determined from the fit and F means that parameter has been kept fixed during the fitting. F in parenthesis implies that the parameter was fixed.

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<th>$A_2$ (J K/mol)</th>
<th>$\gamma$ (J/mmol K$^2$)</th>
<th>$\beta_2$ (J/mmol K$^3$)</th>
<th>$\beta_i$ (mJ/mol K$^4$)</th>
<th>$\beta_j$ ($10^{-4}$ J/mol K$^6$)</th>
<th>$\chi^2$</th>
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<td>1.32(14)</td>
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<td>0.0212(10)</td>
<td>1.24(14)</td>
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<td>12.3 (1)</td>
<td>$-$87.5</td>
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This enhancement manifests itself by the increase in electron effective mass or, equivalently, by a large density of states (DOS) at the Fermi level. It is worth noting that similar values of Wilson ratio were reported for members of the RP series, e.g., $R_W \sim 1.3$ for the single-layered member Sr$_3$RuO$_4$ (Ref. 28). Values of $R_0=2.4$ and 0.08 were determined from magnetic and heat capacity measurements along the $c$ axis and basal plane, respectively, for the triple-layered Sr$_4$Ru$_3$O$_{10}$ single crystal, a system whose structure is closely related to the compound studied in this work, but magnetically different because the RP member shows FM ordering at $T < 105$ K.

From the $\beta_iT^3$ term of the lattice contribution to heat capacity, the Debye temperature ($\Theta_D$) can be calculated using the relation $\beta_i=12\pi^4/5N_Ak_B/\Theta_D^3$, where $N_A$ is the Avogadro number and $r$ is the number of atoms in each molecule ($r=20.5$). A $\Theta_D \sim 280$ K is obtained from the analysis of the low-temperature region. This value is comparable to the one obtained for La$_3$RuO$_5$ system ($\Theta_D = 255$ K). However, the analysis of the high-temperature heat capacity data gives a $\Theta_D \sim 500$ K. This finding suggests a temperature-dependent Debye parameter in agreement with common reports (see Ref. 29, for instance). Values of $\Theta_D$ in the range of 360–530 K are reported in other Ru-based systems.

As mentioned earlier, the heat capacity of La$_3$Ru$_4$O$_{13}$ is not affected by the applied magnetic field, which suggests that the low-temperature spin excitations are extremely stiff and survive in magnetic fields up to 90 kOe. However, if present, those spin waves should also contribute to the magnetic entropy change at $T_N$. The $T^2$ contribution to the heat capacity suggests the presence of long-wavelength spin excitations similar to those reported in the $A$-type antiferromagnet LaMnO$_3$ compound. Moreover, the Weiss temperature and other properties determined here are much more consistent with a regular AFM order ($G$-type). It is commonly known that the contribution to heat capacity coming from spin waves of three-dimensional (3D) AFM systems shows a $T^3$-dependence, but in La$_3$Ru$_4$O$_{13}$ compound a different temperature dependence is expected due to the lower dimensionality since parts of the structure are 1D and other quasi-2D. Depending on the dimensionality, spin waves are expected to show different temperature dependence, and
for lower dimensions a lower temperature dependence is expected. The $T^2$-dependence determined in this work should be related to the more complex structure of La$_{3.5}$Ru$_4$O$_{13}$ compound.

2. Intermediate- and high-temperature regions

As seen in the inset of Fig. 5(a), there is a broad weak peak in $C$ versus $T$ curve positioned at around 42 K—near to the temperature where the magnetic data show a peak. No discernible feature in heat capacity is seen around $T=12$ K where magnetic data show a shoulder and the ac susceptibility measurements a cusp. Considering our uncertainty level, there is no distinguishable variation in the peak position of the heat capacity under the application of magnetic field up to 90 kOe, which indicates that the AFM ordering is very stable for $T<T_N$ and supports the previous discussion of magnetization measurements. In order to quantify the contribution of this transition to the heat capacity, the experimental data were fitted following several trials. Attempts to fit the data using the Debye function over the whole temperature range were not successful, but when the data were analyzed using a polynomial function to represent the nonmagnetic contributions, a good fit was obtained. This strategy was carried out limiting the temperature region from 2 to 100 K and using polynomial functions (from fifth to seventh) to represent the nonmagnetic background. The curve depicted in Fig. 5(a) represents the best fit obtained using sixth order of polynomial and similar results can be obtained using other orders. On subtracting the nonmagnetic background from the experimental data, we obtain the magnetic contribution related to the transition which is shown in the inset of Fig. 5(a). The curve shows a weak peak centered at around 42 K the position of which is not affected by the strength of the magnetic field, since essentially the same value is obtained from the analysis of data under magnetic field up to 90 kOe. Even when the position of this peak is slightly below the expected value ($T_N \sim 47$ K), it seems to be consistent with the magnetic transition determined from magnetic measurements since the width of the peak is $\sim 30$ K.

The entropy associated with the magnetic transition can be estimated using the relation $\Delta S_{\text{mag}} = \int (C_{\text{mag}}/T)dT$. The data analysis provides the value $\sim 1.5$ J/mol K and similar value for data obtained with $H=90$ kOe. This entropy change is smaller than that expected from the AFM transition of Ru ions forming the 1D chain ($\sim 7.4$ J/mol K) or even much smaller for the AFM order of Ru ions forming the quasi-2D layers ($27.4$ J/mol K). There are some explanations for that apparent missing entropy. (1) Smaller entropy values in comparison with the expected one, $R \ln(25+1)$, were reported for the series Pr$_{1-x}$(Ca$_{1-x}$Sr$_x$)$_{10.4}$MnO$_3$ (Ref. 31). The missing entropy has been associated with the occurrence of short range magnetic correlations which can survive at temperatures well above the transition temperature. This may result in little magnetic contribution to the heat capacity within the temperature range considered and a considerable amount of entropy is given up at temperatures much higher than the transition temperature. (2) As discussed above (Secs. III A and III B), the formation of Ru dimers with resulting spin $S=0$, which can be favored by structural distortions happening at temperatures below 47 K, could be the responsible for that magnetic transition, in which case no entropy change is expected. (3) Although the formation of unexpected impurity phases such as LaRuO$_3$ (Ref. 33), La$_3$RuO$_5$ (Ref. 13), La$_4$Ru$_4$O$_{13}$, or La$_3$Ru$_4$O$_{11}$ (Ref. 8) does not show any magnetic transition in this range of temperature, the presence of an unknown impurity phase which should show a magnetic transition at $\sim 47$ K could be the responsible for the small entropy value.

D. Electrical resistivity

Figure 6(a) shows the temperature dependence of electrical resistivity, $\rho(T)$ of La$_{3.5}$Ru$_4$O$_{13}$, in applied field $H=0$, 10, and 50 kOe. No remarkable differences in $\rho$ versus $T$ curves in different magnetic fields are observed. The main features are the negative temperature coefficient of resistivity, $d\rho/dT$ vs $H=0$ [see inset in Fig. 6(a)], indicating nonmetallic behavior in the whole temperature range, and a decrease of $\sim 2$ orders of magnitude of the electrical resistivity from 2 to 300 K. The room-temperature value ($\rho_{300}$ K $\sim 26$ m$\Omega$cm) suggests a small-gap semiconductor or a weak metallic behavior (poor metal). The experimental data present a subtle anomaly at temperatures around 50 K, near to where a magnetic transition is observed. As is commonly reported for quasi-2D systems, such as RP series, an abrupt variation of $\rho$ is expected near the magnetic transition; which means that the weak signal at $T \sim 50$ K could be related to the polycrys-
talline nature of our sample. In accordance with our findings, a low room-temperature resistivity and almost temperature-independent value in the high-temperature range ($T > 300$ K) have been reported for a polycrystalline La$_3$SrRuO$_5$ sample. 35 Semiconducting behavior is in contrast with what has been determined from low-temperature heat capacity, since a metallic tendency ($dp/dT > 0$) is expected. This finding may be associated with the granular state of the sample (polycrystalline specimen), since a careful estimation of its mass density gives a value $\sim 60\% - 70\%$ that is expected from crystallographic results. Thus, it is likely that defects such as grain boundary and impurities intrinsically present in the specimen can produce the weak semiconducting behavior. However, the resistivity behavior may also be likely related to the competitive resistive contribution of the 1D and quasi-2D parts of the specimen, where one of them should behave as a metal and the other as a nonmetal.

In order to characterize the semiconducting behavior, we have analyzed the temperature dependence of the resistivity using various models. In the insulating state and at high temperatures, the electrons are excited above the mobility edge and the electronic conduction mechanism is governed by a simple thermal activation law: $\rho = \rho_o \exp(E_u/k_BT)$. From the plot of $\ln \rho$ versus $1/T$, an activation energy of $E_u = 15$ meV is estimated for the temperature range above 150 K. This value is small when compared to 170–200 meV reported for La$_3$RuO$_5$ single crystal or 230–300 meV for sintered pellets. 13,14 However, at lower temperatures, the conduction is driven by the hopping between localized states and the Mott’s variable range hopping model (VRH model) can be used, in which case the resistivity is given by $\rho(T) \propto \exp(T_0/T)^{1/n}$. A value of $n=2$ represents the 3D hopping of electrons under the influence of their correlations, while $n=4$ for 3D hopping without considering the correlation; 17,36–38 and $T_0$ depends on the carrier localization length and the DOS at the Fermi surface. This VRH mechanism has been also tested and the fits for $n=2$ and $n=4$ are shown in Fig. 6(b). Reasonable fits are obtained in the temperature range $70 < T < 230$ K, for both models, despite the tiny variation of the resistivity (less than a half decade). In the region of $T < 70$ K, the data remarkably deviate from the Mott’s VRH model, showing a weak tendency toward saturation near 2 K. The deviation from the VRH model suggests that the interacting mechanism that couples Ru moments below $T_g$ ($\sim 50$ K) involves conduction carriers.

Considering that in the temperature range $70 < T < 230$ K, the electronic correlations are overwhelmed by the thermal activation process (which means that the Coulomb gap created by the correlations is reduced), it seems reasonable to assume that the VRH model with $\rho \sim T^{-1/4}$ is the mechanism governing the electronic transport in this range. This characteristic temperature ($T_0$) obtained from the fitting procedure is $8.7 \times 10^4$ K. This parameter is given by $k_BT_0 = 18/(D(E_F)\xi^3)$. 36 Where $\xi$ is the carrier localization length and $D(E_F)$ is the DOS at the Fermi surface. An estimation of $D(E_F)$ can be obtained from the relation: $\gamma = 1/2\pi^2k_BT^2D(E_F)$. By using the electronic specific heat coefficient value determined in Sec. III C, we get a $D(E_F) \approx 7.9 \times 10^{22}$ eV$^{-1}$cm$^{-3}$. From these values, a localization length of $\xi \sim 3.1$ Å is estimated, which is larger than the distance among nearest-neighbor Ru ions ($\sim 2.80$ Å) along the 1D rutilelike slabs and smaller than the Ru(1)–Ru(2) distance ($\sim 3.88$ Å) in the quasi-2D perovskite-like layers. Because of the electronic delocalization expected along the slabs and caused by the stronger degree of 4d–2p hybridization (smaller Ru–O bond distance), it is expected that the 1D slabs formed by the edge-sharing Ru(3)O$_6$ octahedra provide an effective carrier conduction along the $b$-axis. However, the AFM ordering of the 2D perovskite-like layers must be related to an insulating behavior below the transition, in a similar way as other AFM layered systems such as the RP $n=1$ series Ca$_{2-x}$Sr$_x$RuO$_4$ behave. 2,23 This assumption is in agreement with the no electronic delocalization expected for this quasi-2D substructure due to the weaker hybridization determined for these layers.

IV. CONCLUSIONS

A study of structural, magnetic, heat capacity, and electrical resistivity of polycrystalline La$_3$SrRuO$_5$ compound has been carried out to understand the spin state of ruthenium ions, magnetic ordering transition, fundamental electronic parameters, and transport properties of this compound. An electronic delocalization feature is suggested due to the relatively short Ru–O bond distances (stronger orbital hybridization) along the rutilelike slabs axis ($b$-axis). From the Curie–Weiss behavior of $\chi$ magnetic susceptibility, an effective magnetic moment of $\mu_{eff}=(2.44 \pm 0.02)\mu_B$ per Ru ion is determined, which indicates a low-spin state ($S=1/2$ and $S=1$) for ruthenium ions (Ru$^{4+}$ and Ru$^{4+}$, respectively). While the magnetic transition at $T \sim 47$ K may be associated with the AFM ordering of Ru ions forming the quasi-2D perovskite layers, the tiny transition determined at $T \sim 12$ K may be related to the magnetic ordering of Ru ions forming the 1D slabs or to extrinsic impurities. The electronic specific heat coefficient $\gamma \sim 12$ mJ/molRuK$^2$ reflects the moderate electronic correlations in this ruthenate. The analysis of the electrical resistance and magnetic data suggest a semiconducting behavior for the quase-2D part and a metallic behavior for the 1D slabs.

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