Strong Electron Hybridization and Fermi-to-Non-Fermi Liquid Transition in LaCu₃Ir₄O₁₂

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ABSTRACT: The AA′B₄O₁₂ type quadruple perovskite LaCu₃Ir₄O₁₂ prepared at high pressure (9 GPa) and temperature (1523 K) crystallizes in cubic symmetry (Im₃, a = 7.52418(3) Å) with square planar CuO₄ and octahedral IrO₆ coordination as established from synchrotron powder X-ray diffraction studies. Both crystal structure and X-ray absorption near edge spectroscopy analyses indicate formal oxidation states of LaCu²⁺Ir³⁻₇₅⁺O₁₂. The temperature dependence of resistivity of LaCu₃Ir₄O₁₂ is metallic down to 10 K with Fermi-liquid behavior above T* ∼ 15 K, and non-Fermi-liquid behavior below T*. The two-fluid behavior of magnetic susceptibility and the dramatic downturn of the resistivity below T* indicate strong Cu²⁺ 3d and Ir⁵⁻₇₅⁺ 5d orbital hybridization below T*, also supported by an enhanced electronic specific heat coefficient at low temperature. Theoretical calculations are in good agreement with the experimental results and show that the electronic structure of LaCu_3Ir_4O_12 is different from that of CaCu_2Ir_4O_12, which is also metallic down to 0.5 K, but presents non-Fermi-liquid behavior above T* ∼ 80 K and strong Cu3d-Ir5d orbital coupling at significantly lower temperature (T < T* ∼ 80 K).

1. INTRODUCTION

ABO₃ perovskites continue to attract much research, because of their wide variety of important physical properties such as superconductivity, ferroelectricity, magnetoresistance, and multiferroic behavior.¹⁻⁴ Interest in the quadruple perovskites AA′B₄O₁₂ (A = mono- or divalent cations or rare earths; A′ = Jahn–Teller (JT) cations; B = transition metals) has been renewed due to the low-field magnetoresistance properties in ACu₃Mn₂O₁₂,⁵ the giant dielectric constant of CaCu₃Ti₄O₁₂,⁶ the heavy Fermion behavior of CaCu₃Ru₂O₁₂,⁷ the magneto-electric properties of BiMn₂Mn₂O₁₂,⁸ and the charge transfer in LaCu₃Fe₄O₁₂.⁹ The crystal symmetry of AA′B₄O₁₂ perovskite-like phases is cubic (space group Im₃) with a doubling of the ideal perovskite cell, due to the ordering of the A and A′ ions and the distortion of the oxygen sublattice, which leads to a tilted three-dimensional (3D) network of corner-sharing BO₆ octahedra. The B–O–B angle is ∼142° instead of 180° as in the ideal perovskite. This large distortion of the 3D network is due to the ordering of the A and A′ cations, with two different coordination polyhedra: a slightly distorted 12 oxygen-coordinated A site and a highly distorted A′ site of a nearly square-planar coordination. The AA′B₄O₁₂ is mostly stable with A′ = Cu²⁺ (δ⁰) or Mn⁵⁺ (δ⁰), both JT distorted ions. Very recently CaPd₃B₄O₁₂ (B = Ti and V) was reported with Pd²⁺ (δ⁰, low spin) square planar coordination.¹⁰ Typically, a high pressure synthesis technique is required to stabilize the AA′B₄O₁₂ perovskite.

In the recent past, much attention has been focused on the chemistry of oxides containing 4d and 5d transition metal cations, since they exhibit interesting electronic and magnetic properties.¹¹ The increased spatial extent of 4d and 5d, compared to the more localized 3d orbitals of the first row transition metals, yields a weaker on-site Coulomb interaction and a greater level of splitting in the crystal field, increasing their sensitivity to lattice distortions, especially in layered oxides such as Sr₂RuO₄, Sr₂RhO₄, Sr₂IrO₄, and Na₃IrO₅.¹²⁻¹⁴ Moreover, the energy of the spin–orbit coupling approaches that of the on-site Coulomb interactions modifying the relative energy scale and showing up unusual electronic structures.¹⁵ Iridium can form oxides in different oxidation states, and its
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extended 5d orbitals together with spin–orbit coupling (SOC) can lead to a rich variety of interesting properties.

Recently, Cheng et al.\textsuperscript{16,17} prepared the first Ir containing quadruple perovskite, CaCu\textsubscript{3}Ir\textsubscript{3}O\textsubscript{12} (CCIO) at 9 GPa, which showed linear-T metallic behavior above \(T^*\) at \(\approx 80\) K, followed by a strong downward trend down to 0.5 K in the resistivity. The low-temperature (\(T < T^*\)) specific heat, magnetic susceptibility, and thermoelectric power show non-Fermi-liquid behavior suggestive of nearby quantum critical behavior. CCIO presents a large electronic specific-heat coefficient, \(\gamma\), with no magnetic ordering down to 0.35 K, and a magnetic contribution emerging at low temperature, which suggests a magnetic quantum critical point. The anomalous physical properties of CCIO suggest Kondo behavior of Cu\textsuperscript{2+} moments coupled to Ir\textsuperscript{3+/4+} moments emerging at low temperature, which suggests a magnetic magnetic ordering down to 0.35 K, and a magnetic contribution in the Brookhaven National Synchrotron Light Source (NSLS).

By increasing the temperature quenching and then released slowly in 8–12 h.

X-ray Diffraction, Absorption Fine-Structure, and Near Edge Absorption Spectroscopy. The product was initially characterized by laboratory powder X-ray diffraction (PXD, Bruker D8 ADVANCE, Cu Ka, \(\lambda = 1.5406\) Å) for phase identification and purity. Synchrotron powder X-ray diffraction (SPXD, \(\lambda = 0.779187\) Å, instrument resolution of 0.005Å) data were collected at RT at the X14A beamline in the Brookhaven National Synchrotron Light Source (NSLS). Rietveld refinements of the SPXD data were carried out with TOPAS program package.\textsuperscript{19,20} X-ray absorption fine-structure (XAFS) data were collected at beamline X3A (NSLS) and X-ray near edge absorption spectroscopy data (XANES) at X11A (NSLS). Layers of powder brushed onto Kapton tape were stacked to produce a uniform sample for transmission measurements with jump \(\mu \sim 1\). Measurements were made on a sample attached to the coldfinger of a cryostat. Three-to-six scans were taken at each temperature. At the Cu and Ir \(L_3\) edges, the corresponding metal foils were used for energy calibration. The reduction of the XAFS data was performed with standard procedures.\textsuperscript{21} For the Ir \(L_3\) edge and Cu \(K\) edge data, the \(k\)-ranges 1.53 < \(k\) < 19.53 Å\(^{-1}\) and 2.34 < \(k\) < 18.36 Å\(^{-1}\) were used, respectively (\(k = \left| (E - E_0)2\pi\right|^{1/2}/h\) and the ionization energy is \(E_0\)) to obtain the scattering coefficients.

Figure 1. Experimental, calculated, and difference of the RT SPXD patterns of LCIO. Inset shows the unit cell crystal structure. La, green spheres; CuO\(_2\) planes, blue; IrO\(_2\) octahedra, tan; O\(_2\) red spheres. Tick marks (|) indicate the index of LCIO (upper row) and IrO\(_2\) impurity (bottom row) phases, respectively.

between the observed and calculated patterns (\(R_p = 1.84\%\), \(R_wp = 2.65\%) and \(\sim 3.8\%\) IrO\(_2\) impurity. As observed in other similar materials, such as LaCu\(_2\)Cr\(_3\)O\(_8\) and LaCu\(_2\)Mn\(_3\)O\(_{12}\), the La atoms are located at \(2a\) (0, 0, 0) positions, Cu at \(6b\) (0, 1/2, 1/2), Ir at \(8c\) (1/4, 1/4, 1/4), and O atoms at 24g (\(x, y, 0\)) in LCIO. Table 1 summarizes the refined structural parameters at RT and Table 2 the main bond distances and angles. The inset of Figure 1 shows a schematic view of the crystal structure. The unit-cell parameter of LCIO (\(a = 7.52418(3)\) Å at RT) is twice the size of the simple perovskite and slightly larger than that of CCIO (7.47380(6) Å),\textsuperscript{17} which is consistent with the slightly larger size of La\textsuperscript{3+} (1.03 Å) than Ca\textsuperscript{2+} (1.00 Å), in 12-coordination,\textsuperscript{27,28} and also, considering the charge balance (required nominal Ir\textsuperscript{7+} in LCIO) with the presence of some Ir\textsuperscript{3+} (0.68 Å), which is larger than the all Ir\textsuperscript{8+} (0.625 Å) in the observed and calculated patterns (\(R_p = 1.84\%\), \(R_wp = 2.65\%) and \(\sim 3.8\%\) IrO\(_2\) impurity. As observed in other similar materials, such as LaCu\(_2\)Cr\(_3\)O\(_8\) and LaCu\(_2\)Mn\(_3\)O\(_{12}\)}, the La atoms are located at \(2a\) (0, 0, 0) positions, Cu at \(6b\) (0, 1/2, 1/2), Ir at \(8c\) (1/4, 1/4, 1/4), and O atoms at 24g (\(x, y, 0\)) in LCIO. Table 1 summarizes the refined structural parameters at RT and Table 2 the main bond distances and angles. The inset of Figure 1 shows a schematic view of the crystal structure. The unit-cell parameter of LCIO (\(a = 7.52418(3)\) Å at RT) is twice the size of the simple perovskite and slightly larger than that of CCIO (7.47380(6) Å),\textsuperscript{17} which is consistent with the slightly larger size of La\textsuperscript{3+} (1.03 Å) than Ca\textsuperscript{2+} (1.00 Å), in 12-coordination,\textsuperscript{27,28} and also, considering the charge balance (required nominal Ir\textsuperscript{7+} in LCIO) with the presence of some Ir\textsuperscript{3+} (0.68 Å), which is larger than the all Ir\textsuperscript{8+} (0.625 Å) in.
In addition, considering the cell parameter of LaCu$_3$Mn$_4$O$_{12}$ (a = 7.3272(4) Å), the replacement of Mn$^{4+}$/Mn$^{3+}$ (0.53/0.64 Å) by Ir$^{4+}$/Ir$^{3+}$ cations will increase the B$^-$O distances, expanding the unit cell of LCIO. La$^{3+}$ exhibits a regular dodecahedral environment, with 12 equal La$^-$O distances (2.665(11) Å) at RT. However, the Cu$^{2+}$ oxygen environment is highly distorted with four very long Cu$^-$O distances (2.828(11) Å) and an effective coordination number of four with a pseudosquare planar environment of Cu$^-$O bond lengths of 1.980(11) Å, consistent with JT Cu$^{2+}$. These CuO$_4$ units are not strictly coplanar since the values of O$^-$Cu$^-$O angles are $\sim$87°. The Ir$^{4+}$/Ir$^{3+}$ cations are at the center of corner-sharing IrO$_6$ octahedra with all Ir$^-$O bond lengths of 2.003(4) Å. The Ir$^-$O$^-$Ir bond angles are $\sim$140°, far away from 180° of the ideal cubic perovskite. The strong distortion of the structure occurs due to the small size of La and Cu cations forcing the Ir octahedra to tilt in order to optimize the A$^-$O distances. Bond valence sum (BVS) calculations of Mn$^{4+}$/Mn$^{3+}$ (0.53/0.64 Å) by Ir$^{4+}$/Ir$^{3+}$ cations will increase the B$^-$O distances, expanding the unit cell of LCIO.

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Table 1. Comparison of the Structure Parameters of LCIO and CCIO at RT (space group Im$\bar{3}$ (No. 204), Z = 2)

<table>
<thead>
<tr>
<th></th>
<th>A = La</th>
<th>A = Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, Å</td>
<td>7.524183(3)</td>
<td>7.47380(6)</td>
</tr>
<tr>
<td>V, Å$^3$</td>
<td>425.97(1)</td>
<td>417.47(1)</td>
</tr>
<tr>
<td>A (2a, 0 0 0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B$_{iso}$ Å$^2$</td>
<td>0.58(8)</td>
<td>0.37(7)</td>
</tr>
<tr>
<td>MM, μ$_B$</td>
<td>-0.01</td>
<td>-0.01</td>
</tr>
<tr>
<td>Cu (6b, 0 1/2 1/2)</td>
<td>0.76(6)</td>
<td>0.90(2)</td>
</tr>
<tr>
<td>B$_{iso}$ Å$^2$</td>
<td>0.65</td>
<td>0.65</td>
</tr>
<tr>
<td>Ir (8c, 1/4 1/4 1/4)</td>
<td>0.72(1)</td>
<td>0.30(1)</td>
</tr>
<tr>
<td>B$_{iso}$ Å$^2$</td>
<td>0.54</td>
<td>0.70</td>
</tr>
<tr>
<td>O (24g, x y 0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>0.306(1)</td>
<td>0.3040(1)</td>
</tr>
<tr>
<td>y</td>
<td>0.178(1)</td>
<td>0.1719(10)</td>
</tr>
<tr>
<td>B$_{iso}$ Å$^2$</td>
<td>1.0(2)</td>
<td>0.04(4)</td>
</tr>
<tr>
<td>MM, μ$_B$</td>
<td>0.15</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Table 2. Comparison of Selected Interatomic Distances (Å), Bond Valence Sums (BVS), and Bond Angles (deg) in LCIO and CCIO at RT

<table>
<thead>
<tr>
<th></th>
<th>A = La</th>
<th>A = Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>bond lengths</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A$^-$O ($\times$12)</td>
<td>2.665(11)</td>
<td>2.610(7)</td>
</tr>
<tr>
<td>Cu$^-$O ($\times$4)</td>
<td>1.980(11)</td>
<td>1.948(8)</td>
</tr>
<tr>
<td>Cu$^-$O ($\times$4)</td>
<td>2.826(11)</td>
<td>2.856(4)</td>
</tr>
<tr>
<td>Ir$^-$O ($\times$6)</td>
<td>2.003(4)</td>
<td>1.999(3)</td>
</tr>
<tr>
<td>bond angles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$^-$Cu$^-$O</td>
<td>84.9(5)</td>
<td>82.5(5)</td>
</tr>
<tr>
<td>O$^-$Ir$^-$O</td>
<td>90.1(4)</td>
<td>88.6(3)</td>
</tr>
<tr>
<td>Ir$^-$O$^-$Ir</td>
<td>139.9(0)</td>
<td>138.4(1)</td>
</tr>
<tr>
<td>Cu$^-$O$^-$Ir</td>
<td>109.7(3)</td>
<td>110.1(2)</td>
</tr>
</tbody>
</table>

By comparing the data collected at 300 and 22 K, it is found that while the Cu sites exhibit the typical temperature dependence of other transition metal oxides such as manganites, by contrast, the Ir polyhedra exhibit negligible temperature dependence and indicate that these systems possess extremely rigid IrO$_6$ octahedra. This rigid behavior of the polyhedra will support strong coupling between adjacent Ir sites.

XANES is a useful tool for locally probing the valence states at atomic sites in solids. The near edge features at the K edges of 3d row transition metal, T(3d), compounds are due to transitions from the 1s to 4p states of the transition metal, combined with a step feature for the continuum onset. Multiple
structure and the chemical shifts of the near edge structure are sensitive to the valence and local atomic environment. Figure 3a compares the Cu−K edge of LCIO to those of a series of Cu compounds with varying formal valences and Cu−O coordination: Cu$^{1+}$, Cu$_2$O with linear 2-fold coordination; Cu$^{2+}$, CuO with square planar coordination; and Cu$^{3+}$, KCuO$_2$ with square distortions. Considering these cases, the formal valences have been interpreted in terms of hybridized superpositions of differing 3d configurations.

Indeed varying the formal Cu valence around 2+ typically involves strong covalency effects and subtle changes in the Cu−K edge best discerned by differential spectral comparisons. With such complications in mind the chemical shifts of the LCIO spectrum (see green boxed region in figure) appears consistent with a formal Cu$^{2+}$ state in this compound. As it will be shown below, this is in line with the Ir−L$_3$ edge results and the formal charge balance in the compound.

The L$_3$ edges of 5d transition metal compounds manifest very intense “white line” (WL) features due to dipole transitions into localized final d states. In an octahedral ligand field (LF) the d-states are split into lower, $t_2g$ (6X degenerate), and a higher, $e_g$ (4X), multiplets. In many high-hole (low-electron) count octahedral T-4d/5d compounds, separate $t_2g$ and $e_g$ related features can be discerned in their L$_3$ edge spectra. This structure is best illustrated in Figure 3b by the prominent $t_2g$-related shoulder on the low energy side of the WL-feature of the Sr$_2$CaIrO$_6$ spectrum. Figure 3b (top spectra) also shows the Ir−L$_3$ edges of formal valence standard compounds: Ir$^{6+}$, Sr$_2$CaIrO$_6$; Ir$^{5+}$, Sr$_2$SrIrO$_6$; Ir$^{4+}$, IrO$_2$ and La$_2$CuIrO$_6$. With decreasing Ir valence (decreasing $t_2g$-hole count) two spectral changes occur: the shoulder $t_2g$ feature decreases in intensity becoming less discernible and the centroid energy of the WL feature manifests a chemical shift to lower energy. In Figure 3b (bottom spectra) the Ir−L$_3$ edge of LCIO is compared to that of IrO$_2$ (scaled to equal peak intensity). The vertical line indicates the peak positions of IrO$_2$, and La$_2$CuIrO$_6$ standards and the LCIO spectrum can be seen to be slightly chemically shifted to lower energy relative to these Ir$^{4+}$ standards. With a formal Cu valence of 2+ the Ir valence would indeed be expected to be pulled somewhat lower than 4+ which is generally in line with the Ir−L$_3$ edge results.

3.3. Magnetic and Resistivity Properties. Figure 4a shows the ZFC magnetic susceptibility ($\chi$) vs temperature ($) plot of LaCu$_3$IrO$_{12}$ measured at 0.1 T. The FC plot overlaps with the ZFC data and thus it is not shown for clarity. The signal of the IrO$_2$ impurity has been subtracted according to the weight fraction from Rietveld refinement. No signature of magnetic ordering transition can be found in the whole temperature region of $\chi$(T) or $1/\chi$(T). Above a specific temperature $T^*$ around 155 K, the data can be fitted to the Curie−Weiss (CW) law, while a deviation from CW law is clearly seen below 155 K. The effective moment ($\mu_{eff}$) and paramagnetic temperature ($\theta$) obtained from the fit are 5.55 $\mu_B$/f.u. and $-397.9$ K, respectively. The experimental value of $\mu_{eff}$ is much larger than what is expected based on the contribution by three Cu$^{2+}$ (3 $\mu_B$/f.u.), as Ir$^{4+}$/Ir$^{3+}$ are expected to be itinerant with negligible local moments. This deviation may be attributed to orbital contribution from Ir.

The $\chi(T)$ below $T^*$ was fitted by a two fluid model for heavy Fermion materials. In this scenario, the local Cu$^{2+}$ 3d orbitals hybridize with the 5d conduction electrons of Ir$^{4+}$/Ir$^{3+}$ to reduce their entropy. The increased 3d−5d orbital interaction is also seen in the resistivity data in Figure 4b. The compound is metallic down to 10 K, while different types of electron correlations are observed in regions of $\rho(T)$ divided by $T^*$. Above $T^*$ (155 K), $\rho(T)$ fits Fermi liquid behavior, perfectly described by $\rho(T) = \rho_0 + A \times T^3$, where $\rho_0 = 0.539$ $\Omega$ cm and $A = 1.46 \times 10^{-6}$ $\Omega$ cm−K−3. It should be noted that $\rho(T)$ of CCIO follows a linear non-Fermi-liquid behavior above its own characteristic temperature ($T^* \sim 80$ K), indicating that electron correlations of the normal state in LCIO and CCIO are fundamentally different. For LCIO below $T^*$, $\rho(T)$ shows two
types of non-Fermi-liquid behavior: for 58 K < \( T \) < \( T^* \), the resistivity fits \( \rho(T) = \rho_0 + B \times T \), with \( \rho_0 = 0.502 \ \Omega \cdot \text{cm} \), and \( B = 4.62 \times 10^{-4} \ \Omega \cdot \text{cm} \cdot \text{K}^{-1} \). At the lower temperature regime (\( T < 58 \) K), the resistivity drop suggests heavy-Fermion behavior. To further understand the complex physics of this material, specific heat as well as theoretical calculations were investigated.

### 3.4. Specific Heat

Figure 5 shows the temperature dependence of specific heat (\( C_p \)) on cooling from 400 down to 2 K for LCIO. Figure 5a and its inset are the plots of \( C_p/T \) vs \( T \) between 2 and 390 K and \( C_p/T \) vs \( T^2 \) between 2 and 20 K, respectively. In the absence of any anomaly around \( T^* \), the possibility of a second- or first-order structural phase transition at \( T^* \) can be ruled out. An anomalous rise below 7 K is notable (Figure 5a). Data between 3.6 and 20 K were fitted by considering three contributions: \( C(T) = C_{\text{electron}} + C_{\text{lattice}} + C_{\text{magnetism}} \) where \( C_{\text{electron}} = \gamma T \) is the electronic contribution, \( C_{\text{lattice}} = \beta T^3 \) is the lattice part, and \( C_{\text{magnetism}} = \delta T \exp(-T/\Delta) \) is the magnetic contribution. The obtained value of \( \gamma = 336 \ \text{mJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-2} \) is almost twice as large as that of CCIO, which indicates a much stronger hybridization of Cu 3d and Ir 5d in LCIO. \( C_{\text{magnetism}} \) is responsible for the low-temperature rise in the susceptibility, which suggests that LCIO is close to a magnetic ordering phase or quantum criticality. The Debye temperature \( \Theta_D = 395 \) K obtained from \( \beta \) (\( \beta = 0.629 \ \text{mJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-4} \)) is very close to that of CCIO (0.608 mJ·mol⁻¹·K⁻⁴). The upturn below \( \sim 7 \) K exhibits no hysteresis (magnetic order change or continuous structural change), future low temperature x-ray and neutron scattering measurements will explore this region in detail. The spin on the magnetic sites is estimated from theoretical DFT simulations as discussed below.

### 3.5. Theoretical Calculations

The crystal structure of LCIO was calculated theoretically by optimization of the crystal structure of CCIO and replacing Ca by La. The calculated cell volume of LCIO is estimated to increase by \( \sim 1.8\% \) compared to that of CCIO due to the differences in ionic sizes (La³⁺ vs Ca²⁺) and changes of Ir oxidation states (Ir³⁺ vs Ir⁴⁺) from calculations, which is in good agreement with the observed value (\( \sim 2.0\% \)) as shown in Table 1. Density of state (DOS, Figure 6 upper panels) from GGA+U calculations indicated a rigid band like shift of DOS between LCIO and CCIO retaining more or less the same basic structures. Note, even though the compound does not order magnetically, in order to describe the correct spin and charge states of the various metal ions of the compound, it is necessary to carry out spin-polarized calculations.

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Figure 4. Temperature dependence of (a) magnetic susceptibility \( \chi(T) \) and \( 1/\chi(T) \) measured under \( H = 0.1 \) T in ZFC procedure, (b) resistivity \( \rho(T) \) response of LCIO between 10 and 350 K. The dashed lines show the transition point around the specific temperature \( T^* = 155 \) K. The temperature \( T^* \) separates the two-fluid model and Curie–Weiss fitting, respectively in (a), and non-Fermi-liquid behavior and Fermi-liquid behavior fitting in (b).

Figure 5. (a) Specific heat \( C_p(T) \) and inset showing low-temperature (0–20 K) upturn and the leap of \( C_p(T) \) vs \( T^2 \) plot. (b) Three parts of specific heat at low-temperature region.
4. CONCLUSION

The second Ir-containing quadruple perovskite LaCu$_3$Ir$_4$O$_{12}$ was prepared at high pressure and temperature. It adopts the typical AA’B$_2$O$_6$ structure with square planar coordination of Jahn–Teller A’–Cu$^{2+}$ cation. Both the magnetism and resistivity of LaCu$_3$Ir$_4$O$_{12}$ show different behavior above and below a characteristic temperature ($T^*$ = 155 K). The magnetic susceptibility follows the Curie–Weiss Law above $T^*$ but can only be fitted by a two fluid model for heavy-electron materials below $T^*$, while the resistivity can be fitted to Fermi liquid and non-Fermi liquid behavior above and below $T^*$ respectively, indicating strong electron hybridization as evidenced by the specific heat data. Compared with the isostructural CaCu$_3$Ir$_4$O$_{12}$, the replacement of Ca by La yields a slightly larger unit cell and drives Ir$^{4+}$ ($d^7$) to mixed-valence state of Ir$^{5+}$ (formally 3Ir$^{4+}$ ($d^7$) + Ir$^{3+}$ ($d^8$)) in LaCu$_3$Ir$_4$O$_{12}$. First principle calculations are in good agreement with the experimental results and indicate that spin orbit coupling (SOC) destroys the half metallic character of CCIO, making it metallic on both spin channels, while in LCIO the half-metallic character is marginally retained with SOC (Figure 6). Although both CaCu$_3$Ir$_4$O$_{12}$ and LaCu$_3$Ir$_4$O$_{12}$ are metallic, the La compound is a Fermi liquid above $T^*$ ($\sim$155 K), while the Ca analogue is a non-Fermi liquid above $T^*$ ($\sim$80 K), which indicate that electron correlations of the normal state in LCIO and CCIO are fundamentally different. This is corroborated by a very large value of $γ = 336$ mJ·mol$^{-1}$·K$^{-2}$, which is almost twice as large as that of CCIO, and indicates a much stronger hybridization of Cu 3d and Ir 5d in LCIO.

The discoveries in CaCu$_3$Ir$_4$O$_{12}$ and LaCu$_3$Ir$_4$O$_{12}$ suggest an interesting materials design platform, as the chemical potential variation of the A- and A’-site cations can be used to tune the physical properties by inducing valence changes at the B-site Ir in A A’Ir$_4$O$_{12}$. For example, non-Fermi liquid-to-Fermi liquid transition at higher temperature could be expected in Ca$_{1-x}$La$_x$Cu$_3$Ir$_4$O$_{12}$ ($0 < x < 1$) solid solution at a critical $x$ value, and it is worthy of further exploration. Moreover, a monovalent cation at the A-site of ACu$_3$Ir$_4$O$_{12}$ could result in some Ir$^{5+}$ ($d^7$) at the B-site as in NaCu$_3$Ir$_4$O$_{12}$ and Ca$_{1-x}$Na$_x$Cu$_3$Ir$_4$O$_{12}$. Thus, to draw a clear map of the electronic behavior of Ir-perovskite-related compounds, analogous phases should be investigated.

**ASSOCIATED CONTENT**

Supporting Information

The crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the ARO-434603-DOD-VV911NF-12-1-0172 grant. Work at NJIT (T.A.T.) is supported by DOE Grant DE-FG02-07ER46402. The work of J.S.-B. is supported by the Spanish grants MAT2013-41099-R and RyC-2010-06276. The Physical Properties Measurements System used in the heat capacity measurements was acquired under NSF MRI Grant DMR-0923032 (ARPA).
award). We thank Ms. J. Hanley at LDEO in Columbia University for making the high pressure assemblies and Dr. F. Mompean for his help in the conductivity measurements.

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