Electron localization and magnetism in SrRuO$_3$ with non-magnetic cation substitution

W. Tong  
*Chinese Academy of Sciences*

F Q. Huang  
*Chinese Academy of Sciences*

I-Wei Chen  
*University of Pennsylvania, iweichen@seas.upenn.edu*

Follow this and additional works at: [https://repository.upenn.edu/mse_papers](https://repository.upenn.edu/mse_papers)

**Recommended Citation**
Tong, W., Huang, F. Q., & Chen, I. (2011). Electron localization and magnetism in SrRuO$_3$ with non-magnetic cation substitution. Retrieved from [https://repository.upenn.edu/mse_papers/211](https://repository.upenn.edu/mse_papers/211)

This is an author-created, un-copyedited version of an article accepted for publication in Journal of Physics: Condensed Matter. IOP Publishing Ltd is not responsible for any errors or omissions in this version of the manuscript or any version derived from it. The definitive publisher authenticated version is available online at http://dx.doi.org/10.1088/0953-8984/23/8/086005.

This paper is posted at ScholarlyCommons. [https://repository.upenn.edu/mse_papers/211](https://repository.upenn.edu/mse_papers/211)  
For more information, please contact repository@pobox.upenn.edu.
Electron localization and magnetism in SrRuO$_3$ with non-magnetic cation substitution

Abstract
The destruction of the ferromagnetism of alloyed SrRuO$_3$ can be caused by electron localization at the substitution sites. Among all the non-magnetic cations that enter the B site, Zr$^{4+}$ is the least disruptive to conductivity and ferromagnetism. This is because Zr$^{4+}$ does not cause any charge disorder, and its empty d electron states which are poorly matched in energy with the Ru t$_{2g}^4$ states cause the least resonance scattering of Ru’s d electrons. Conducting Sr(Ru, Zr)O$_3$ may be used as an electrode for perovskite-based thin film devices, while its insulating counterpart provides unprecedented magnetoresistance, seldom seen in other non-manganite and non-cobaltite perovskites.

(Some figures in this article are in colour only in the electronic version)

Comments
This is an author-created, un-copyedited version of an article accepted for publication in Journal of Physics: Condensed Matter. IOP Publishing Ltd is not responsible for any errors or omissions in this version of the manuscript or any version derived from it. The definitive publisher authenticated version is available online at http://dx.doi.org/10.1088/0953-8984/23/8/086005.

This journal article is available at ScholarlyCommons: https://repository.upenn.edu/mse_papers/211
Electron localization and magnetism in SrRuO$_3$ with non-magnetic cation substitution

W Tong$^{1,2}$, F-Q Huang$^1$ and I-W Chen$^3$

$^1$ Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People’s Republic of China
$^2$ High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei, Anhui 230031, People’s Republic of China
$^3$ Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104-6272, USA

E-mail: weitong@hmfl.ac.cn

Received 29 October 2010, in final form 24 December 2010
Published Online at stacks.iop.org/JPhysCM/23/000000

Abstract

The destruction of the ferromagnetism of alloyed SrRuO$_3$ can be caused by electron localization at the substitution sites. Among all the non-magnetic cations that enter the B site, Zr$^{4+}$ is the least disruptive to conductivity and ferromagnetism. This is because Zr$^{4+}$ does not cause any charge disorder, and its empty d electron states which are poorly matched in energy with the Ru t$_{2g}$ states cause the least resonance scattering of Ru’s d electrons. Conducting Sr$_{1-x}$Ca$_x$RuO$_3$ may be used as an electrode for perovskite-based thin film devices, while its insulating counterpart provides unprecedented magnetoresistance, seldom seen in other non-manganite and non-cobaltite perovskites.

1. Introduction

Strontium ruthenate SrRuO$_3$ with its unusually high Curie temperature ($T_C$) of 160 K is practically the only ferromagnetic (FM) metal among 4d transition metal oxides [1]. It is generally believed that the magnetism in this ABO$_3$ perovskite is of the Stoner type, arising from a high density of state (DOS) at the Fermi level ($E_f$) due to a nearby van Hove singularity [2]. The DOS of SrRuO$_3$ indeed has a sharp peak that nearly coincides with $E_f$ according to the band structure calculation of Mazin and Singh [2]. A-site substituted Sr$_{1-x}$Ca$_x$RuO$_3$ is also metallic despite a substantial lattice contraction with Ca substitution [3, 4]. FM is maintained up to $x = 0.8$, but CaRuO$_3$ is paramagnetic—although its DOS is highly elevated at $E_f$, it has a relatively flat top which makes CaRuO$_3$ less susceptible to Stoner instability. On the other hand, nearly all alloying efforts attempting to fine tune the DOS by modifying lattice distortions severely suppress the FM [4–12]. This includes A-site substitution of either undersized cations (Ca, La/Na) or oversized cations (La/K, Pb) [4, 12]. In fact, Sr$_{1-x}$La$_{x/2}$Na$_{x/2}$RuO$_3$ loses FM faster than Sr$_{1-x}$Ca$_x$RuO$_3$ despite a smaller lattice contraction, indicating a strong FM-suppressing effect of A-site disorder [4]. However, a significantly higher $T_C$ is found in Sr(Ru$_{1-x}$Cr$_x$)O$_3$ [9], making this a rather exceptional case whose origin is still under investigation [13–20].

One consequence of a high DOS at $E_f$ is a large magnetic susceptibility, which causes a magnetic impurity to induce a giant magnetic moment around it. This effect, well known in nearly FM Pd in which 3d magnetic impurities induce a large host polarization [21, 22], was also theoretically predicted for SrRuO$_3$ and CaRuO$_3$ [2], the latter on the verge of FM. Experimental evidence of a giant magnetic moment was observed in SrRuO$_3$ doped with Fe and Co impurities, both causing an increase in magnetization [5, 6]. These impurities generate an especially strong effect because their empty orbitals at t$_{2g}$ levels are energetically close to Ru’s partially filled t$_{2g}$ level, allowing electron resonance between impurities and Ru$^{4+}$, hence spin polarization of the neighboring electrons.

In view of the complexity of these alloys, we believe that to fully understand the dopant effects in SrRuO$_3$ and CaRuO$_3$ it would be necessary to turn to simpler models...
focusing on non-magnetic impurities, i.e., impurities with a d⁰ electronic configuration. In the past, this has been rarely done except for A-site dopants. One reference point that may be used to view the effects of non-magnetic B-site dopants is the Jaccarino–Walker model [23], which was developed for metallic alloys that suffer a sudden loss of the FM moment when the FM site loses a critical number of FM neighbors. In the following it will be shown that this model does not apply to SrRuO₃; instead, the deterioration of FM upon B-site substitution proceeds by way of Anderson localization of itinerant electrons. The current work also reveals the best strategy to obtain highly conductive SrRuO₃ alloys that may be used as an electrode for perovskite-oxide-based devices [24–26].

2. Experimental procedures

Polycrystalline ceramic samples of the compositions SrRu₁₋ₓB′ₓO₃, with x up to 0.55 for Zr and Ti, 0.5 for Sc and Lu, 0.33 for Mg and Zn, 0.25 for Li and Nb, were prepared with starting materials of SrCO₃, RuO₂, and various oxides of B'. In the above B' (Li, Mg, Zn, Sc, Lu, Ti, Zr and Nb), none contains any d electron in its most common, ionized states.

The valences (z) and the Shannon cation radii in the six-fold coordination [27] of these B' are listed in table 1; they cover a very broad range of sizes and valences. (In table 1, the composition of metal/insulator transition is also listed, to be discussed later.) Certain combined A-site and B-site substitutions Sr₁₋ₓAₓRu₁₋ₓB′ₓO₃ (e.g., La₂Mg meaning the composition of Sr₁₋₂La₂(Ru₁₋₂MgₓO₃), using A = La and B' = Mg, Sc, Ti or Zr, were also investigated.

Sintering was performed in air at 1200–1500°C with samples embedded inside a powder pack to minimize Ru evaporation. Phase purity was monitored with x-ray powder diffraction (XRD) using Cu Kα radiation, with Si powder added as an internal standard, to ensure only single-phase perovskite samples were used for further studies. Additional verification of phase purity and compositional uniformity was provided by elemental mapping using an electron microprobe. Magnetization (M) and (four-point-probe) electrical conductivity (σ = ρ⁻¹) were measured using a Physical Property Measurement System (Quantum Design PPMS) at various magnetic fields (H) up to 90 kOe between 10 and 300 K. Other experimental details were similar to those described elsewhere [5, 6].

### Table 1. Nominal valence and ionic radii of non-magnetic B-site cations, compared to Ru⁴⁺ with an ionic radius of 62 pm. Also listed are critical concentrations xₐ for the metal/insulator transition in substituted SrRu₁₋ₓB′ₓO₃ samples.

<table>
<thead>
<tr>
<th>B'</th>
<th>Li</th>
<th>Mg</th>
<th>Zn</th>
<th>Sc</th>
<th>Lu</th>
<th>Ti</th>
<th>Zr</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valence</td>
<td>+1</td>
<td>+2</td>
<td>+2</td>
<td>+3</td>
<td>+3</td>
<td>+4</td>
<td>+4</td>
<td>+5</td>
</tr>
<tr>
<td>Radii (pm)</td>
<td>76</td>
<td>72</td>
<td>74</td>
<td>74.5</td>
<td>86</td>
<td>60.5</td>
<td>72</td>
<td>64</td>
</tr>
<tr>
<td>xₐ</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.10</td>
<td>0.21</td>
<td>0.10</td>
<td>0.31</td>
<td>0.28</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Figure 1. X-ray diffraction patterns of (a) SrRu₁₋ₓZrₓO₃ and (b) SrRu₁₋ₓTiₓO₃ (x = 0.10, 0.20 and 0.50) ceramics, pulverized. The indexing is based on PDF card 79-735.

3. Results

3.1. Phase purity and structure

Since only single-phase perovskite samples are suitable for evaluating the dopant effects, we verified their phase purity using several techniques. Shown in figure 1 are the XRD patterns of Sr(Ru₁₋ₓZrₓO₃ and Sr(Ru₁₋ₓTiₓO₃, in which all the peaks can be indexed using perovskite reflections (orthorhombic, Pbnm GdFeO₃ structure in this case), indicating the absence of impurity phases. This example is chosen because Zr and Ti doping will prove to be the least disruptive to FM and electrical conductivity. Figure 2 shows the variation of unit cell volume versus x for Lu, Sc, Zr, Ti and Nb, all of which produced single-phase diffusion patterns at lower x (up to x = 0.5 for Lu and Sc, 0.55 for Zr and Ti, and 0.2 for Nb; data not shown). The systematic variation from undersized Ti⁴⁺, to oversized Zr⁴⁺ and Lu⁴⁺ is indicative of the incorporation of the dopants into the lattice. These data also provide evidence for the variation of Ru’s ionic state under z ≠ 4 doping: for slightly oversized Nb⁵⁺, the cell volume increases presumably because of Ru⁴⁺ reduction to the larger sized Ru⁴⁺; conversely, although Sc³⁺ is slightly larger than Zr⁴⁺, it causes less cell volume expansion presumably because of Ru⁴⁺ oxidation to the smaller sized Ru⁴⁺. In figure 3, the fractography, electron diffraction pattern and elemental mapping of a Sr(Ru₀.₅Zr₀.₅)O₃ sample are shown to illustrate
The magnetization is progressively suppressed with increasing $x$ at 0.5, which is well within the respective solubility limits. All the $M(T)$ measurements shown here were carried out during field-cooling. As extensively documented in previous studies of Sr$_{1-x}$La$_x$Ru$_{1-y}$Fe$_y$O$_3$ and Sr$_{1-x}$La$_x$Ru$_{1-y}$Co$_y$O$_3$ [5, 6], with increasing $x$ FM is replaced by magnetic characteristics reminiscent of cluster glass and spin glass. Similar property evolutions were also observed for all substitutions studied here, and they will not be elaborated further. However, it should be emphasized that different B-site dopants have rather different effects on FM despite their similar $d^x$ configuration. Some, such as Zr, Ti and Sc, cause a relatively small decrease in $M$ and $T_C$, while others, such as Li and Mg, strongly depress both $M$ and $T_C$ even at $x = 0.1$. This is at odds with the Jaccarino–Walker model [23].

The field ($H$) dependence of magnetization at 10 K is depicted in figure 5 for all the Zr and Ti doped samples. The magnetization is progressively suppressed with $x$, which agrees with the $M$–$T$ results. At the lowest $x$ level (0.1), the saturation magnetization was decreased for Ti doping but not for Zr doping. At the highest $x$ levels (0.5 and 0.55), the magnetization under Ti doping— but not under Zr doping—becomes almost linear with $H$ indicating the complete destruction of the FM order. These data suggest that SrRu$_{1-x}$Zr$_x$O$_3$ retains more FM than SrRu$_{1-x}$Ti$_x$O$_3$ at the same $x$.

### 3.2. Magnetism

Both magnetic properties ($M$, $T_C$, etc.) and conductivity were found to monotonically decrease with increasing $x$. Examples of the suppression of magnetization by substitutions are provided in figure 4 for several substitutions at two fields and at $x = 0.1$ and 0.2, which are well within the respective solubility limits. All the $M(T)$ measurements shown here were carried out during field-cooling. As extensively documented in previous studies of Sr$_{1-x}$La$_x$Ru$_{1-y}$Fe$_y$O$_3$ and Sr$_{1-x}$La$_x$Ru$_{1-y}$Co$_y$O$_3$ [5, 6], with increasing $x$ FM is replaced by magnetic characteristics reminiscent of cluster glass and spin glass. Similar property evolutions were also observed for all substitutions studied here, and they will not be elaborated further. However, it should be emphasized that different B-site dopants have rather different effects on FM despite their similar $d^x$ configuration. Some, such as Zr, Ti and Sc, cause a relatively small decrease in $M$ and $T_C$, while others, such as Li and Mg, strongly depress both $M$ and $T_C$ even at $x = 0.1$. This is at odds with the Jaccarino–Walker model [23].

The field ($H$) dependence of magnetization at 10 K is depicted in figure 5 for all the Zr and Ti doped samples. The magnetization is progressively suppressed with $x$, which agrees with the $M$–$T$ results. At the lowest $x$ level (0.1), the saturation magnetization was decreased for Ti doping but not for Zr doping. At the highest $x$ levels (0.5 and 0.55), the magnetization under Ti doping— but not under Zr doping—becomes almost linear with $H$ indicating the complete destruction of the FM order. These data suggest that SrRu$_{1-x}$Zr$_x$O$_3$ retains more FM than SrRu$_{1-x}$Ti$_x$O$_3$ at the same $x$.

### 3.3. Conductivity

With increasing $x$, the metallic conductivity of SrRuO$_3$ gradually crossovers to a semiconducting/insulating behavior in substituted alloys. This is illustrated in figure 6 for several substitutions at $x = 0.1$ and 0.2. To aid comparison, the resistivity $\rho$ as a function of temperature ($T$) is normalized by its value at 300 K, $\rho_{300\text{ K}}$. Two features are noteworthy and illustrated for Sr(Ru$_{0.8}$Zr$_{0.2}$)O$_3$ in the inset of figure 6(b). First, there is a characteristic kink at the temperature that corresponds to the $T_C$ in figure 4. This was observed in figure 6 in the $\rho(T)/\rho_{300\text{ K}}$ plots for Zr, Ti, and Sc substitutions. Such kink is well known to be due to the scattering of itinerant electrons by enhanced critical spin fluctuations near $T_C$ [28]. Second, at $x = 0.1$, all except Li shows a minimum resistivity at an intermediate temperature before an upturn, as 0 K is approached. The temperature of the resistivity minimum is higher at $x = 0.2$ than at $x = 0.1$. This behavior, which has also been commonly seen in other studies of SrRuO$_3$ [29] and its alloys (e.g., [5, 6, 9]), is characteristic of Anderson disorder in metals, in which the resistivity rises at the low temperature due to a weak localization contribution. (At such low temperature, the mean free path of electrons exceeds Anderson’s localization length for electrons, triggering the localization effect.) A further manifestation of this behavior, illustrated in figure 7(a) for Sc substitution, is a crossover of the higher temperature slope from a positive $d\rho/dT$ (metal-like) at $x \ll 0.1$, to nearly zero at $x = 0.2$ (barely metal-like with a very slightly positive slope at higher temperature), then to a negative $d\rho/dT$ (insulator-like) at
$x = 0.3$, indicating a metal-to-insulator transition. A similar transition is seen in figure 7(b) for Nb substitution, occurring between $x = 0.1$ and 0.15. We have estimated the transition compositions $x_c$ (where $d\rho/dT = 0$) by interpolation and, as shown in table 1, this transition occurs at $x_c \sim 0.3$ for Zr and Ti, at $\sim 0.2$ for Sc, 0.13 for Nb, 0.1 for Zn and Lu, and <0.1 for Li and Mg. Again, as in their effects on $M$ and $T_C$, different substitutions have greatly different suppressing effects on metallicity. Some, such as Zr and Ti, cause a relatively small decrease in metallicity and has a relatively large $x_c$, while others, such as Li and Mg, strongly depress metallicity and $x_c$.

3.4. Correlation between magnetic and transport properties

Comparing the effects on $M$, $T_C$, $\rho(T)/\rho_{300 \, \text{K}}$ and $x_c$, we find a new, broad picture to reveal itself: there is a strong correlation between the magnetic and transport properties. To illustrate this correlation, we first compare for various compositions the normalized conductivity ($\sigma_{20 \, \text{K}}/\sigma_{300 \, \text{K}}$ and $\sigma_{60 \, \text{K}}/\sigma_{300 \, \text{K}}$) with the ‘saturation’ magnetization $M_{90 \, \text{kOe}}$ (measured at 10 K) and the ‘weak-field’ magnetization $M_{100 \, \text{Oe}}$ (measured at either 10 K or $T_{\text{f}}$—the freezing temperature of spin-glass-like samples). They are strongly correlated as shown in figure 8 for both $x = 0.1$ and 0.2. Note that a small value of normalized $\sigma$ is indicative of Anderson localization as already illustrated in figures 6 and 7. Note further that in figure 8, the samples of the B-site substitution are arranged in the order of increasing nominal valence $z$ of the $B'$ cation, $\text{Li}^{+} < \text{Mg}^{2+} < \text{Zn}^{2+} < \text{Sc}^{3+} < \text{Lu}^{3+} < \text{Ti}^{4+} = \text{Zr}^{4+} < \text{Nb}^{5+}$. It is then seen that the $B'$ that is the least disruptive to FM and electron delocalization has $z = 4$ or 3, such as Zr$^{4+}$, Ti$^{4+}$ and Sc$^{3+}$, whereas the disruption increases when $z$ deviates from these values and is especially severe for Li$^{+}$ and Mg$^{2+}$. Since dopants other than Ti$^{4+}$ and Zr$^{4+}$ are likely to cause a change in the valence state of Ru$^{4+}$, this electronic (band filling/emptying) effect along with the charge disorder effect is apparently most deleterious to both FM and metallicity.

It is further found that simultaneous A- and B-site substitution often disrupts FM and causes more localization. For example, the (La, Sc), (La, Ti) and (La, Zr) combinations in figure 8 have a lower $M$ and a lower normalized $\sigma$ than the alloys substituted by Sc, Ti and Zr alone. This is reminiscent of the A-site disorder effect mentioned in section 1. On the other hand, there is no overriding correlation with the size of the cations, which affects lattice distortion. According to table 1, the cationic radii in six-fold coordination $\text{Li}^{+} < \text{Mg}^{2+} < \text{Zn}^{2+} < \text{Sc}^{3+} < \text{Lu}^{3+} < \text{Ti}^{4+} < \text{Zr}^{4+} < \text{Nb}^{5+}$; the data in figure 8 do not follow such a sequence.

To further substantiate the correlation between magnetism and electron delocalization, we plot $M$ versus the normalized $\sigma$ in figure 9(a). The correlation is excellent for B-site substitutions (figure 9(a) for $x = 0.2$ and upper inset for $x = 0.1$); it is also quite good when combined A and B-site substitutions are considered (lower inset in figure 9(a)). A similar correlation between $T_C$ and normalized conductivity is found for B-site substitutions (figure 9(b)) as well as combined A and B-site substitutions (inset in figure 9(b)). Since all these substituting cations are non-magnetic, they should have the same effect on FM according to the Jaccarino–Walker picture. This is evidently not the case here. Instead, there is no doubt that FM is corrupted by the localization of itinerant electrons since both $M$ and $T_C$ decrease with
reduced conductivity, whereas FM can be largely sustained if metallicity is maintained. The retention of metallicity and its interplay with Stoner FM was further addressed by the temperature dependence and field dependence of resistivity. Recall that there is a characteristic kink at $T_C$ in magnetic metals due to the scattering of itinerant electrons by enhanced critical spin fluctuations. As shown in figure 10 for Sr$(\text{Ru}_{1-x}\text{Zr}_x)\text{O}_3$ this kink is suppressed by applying a large magnetic field (90 kOe), which suppresses spin fluctuations. This leads to a characteristic peak at $T_C$ in the (negative) magnetoresistance $(MR)$, defined as $\rho(T, H=90 \text{ kOe}) - \rho(T, H=0 \text{ kOe})$, in figure 10 inset, which may be used as sensitive signature of magnetism. For Sr$(\text{Ru}_{1-x}\text{Zr}_x)\text{O}_3$, this peak persists at $x=0.3$ ($T_C=108.5 \text{ K}$ in figure 9, versus the MR peak at 112 K in figure 10 inset), despite the fact that the temperature dependence of $\rho(T)$ is no longer the metallic type (figure 10 main panel). This indicates that there are still itinerant electrons and critical spin fluctuations in this nominally insulating composition, i.e., a coexistence of (FM) metallic and insulating regions in this sample. In contrast, while a MR peak was also seen in Sr$(\text{Ru}_{1-x}\text{Ti}_x)\text{O}_3$ at $x=0–0.2$, it disappeared from the $x = 0.3$ sample for Ti substitution and other non-Zr substitutions (data not shown). So the ability to sustain metallicity in heavily Zr substituted SrRuO$_3$ alloys is unmatched by any other non-magnetic dopant studied here. Incidentally, associated with the insulating behavior is another low temperature MR component that rises with decreasing temperature, as already reported in our previous work on Sr$_{1-x}$La$_x$Ru$_{1-x}$Fe$_x$O$_3$, Sr$_{1-x}$La$_x$Ru$_{1-x}$Co$_x$O$_3$, Ca$_{1-x}$La$_x$Ru$_{1-x}$Fe$_x$O$_3$, and Sr$_{2-x}$La$_x$Ru$_{1-x}$Fe$_x$O$_4$ [5–7]. This latter MR component dominates at larger $x$, e.g., $x = 0.5$ (inset of figure 10), and at 10 K it reaches $-70\%$ which is an unprecedented MR value for non-manganite and non-cobaltite perovskites. This phenomenon will be examined in more detail elsewhere.

4. Discussion

According to figures 8 and 9, Zr$^{4+}$ substitution is the least disruptive among the non-magnetic dopants studied here. This is quite unexpected since Zr$^{4+}$ is grossly oversized compared to Ru$^{4+}$, which should compel RuO$_6$ octahedron tilting—a highly unfavorable situation according to the first-principles calculation and the band structure theory of Mazin and Singh [2]. Indeed, according to their theory the substitution of undersized Ti$^{4+}$ should have been less disruptive to Stoner FM than Zr$^{4+}$. Yet contrary to the theoretical prediction, both $M$ and $T_C$ decrease faster upon Ti substitution than upon Zr substitution, as shown in figure 11.

To understand why Zr$^{4+}$ is less disruptive than Ti$^{4+}$, we propose an electronic explanation based on the fact that the d-electron $(t_{2g}^5)$ energy $(E)$ levels of Ru$^{4+}$ is closer to those $(d^9)$ of Ti$^{4+}$ (higher by $\Delta E = 2 \text{ eV}$) than Zr$^{4+}$ ($\Delta E = 4.5 \text{ eV}$) [30]. As a result, there should be a considerable

Figure 5. $M(H)$ loops at 10 K for (a) Zr and (b) Ti substituted SrRu$_{1-x}$B$^+_x$O$_3$ samples ($x = 0–0.55$).

Figure 6. Normalized $\rho(T)$ curves for Li, Mg, Sc, Ti and Zr substituted SrRu$_{1-x}$B$^+_x$O$_3$ samples, at $x = 0.1$ (a) and 0.2 (b). Inset in (b) shows detail near $T_C$ and minimal resistivity for SrRu$_{0.8}$Zr$_{0.2}$O$_3$.

Figure 7. $\rho(T)$ curves for (a) SrRu$_{1-x}$Zr$_x$O$_3$ at $x = 0$ (a) and 0.55 (b).
probability of resonance scattering of (Ru^{4+}) electrons by Ti^{4+}

Figure 7. $\rho(T)$ curves for (a) SrRu$_{1-x}$Sc$_x$O$_3$ samples, from $x = 0.1$ to 0.4, showing a sign change in the (high temperature) slope at about $x = 0.2$; and (b) SrRu$_{1-x}$Nb$_x$O$_3$ samples, from $x = 0.05$ to 0.2, showing a sign change between $x = 0.1$ and 0.15.

Figure 8. Variation of magnetization at strong field (90 kOe) and weak field (100 Oe) is strongly correlated to normalized conductivity at 20 and 60 K in SrRuO$_3$, with various cation substitutions, listed in the order of nominal valence of the B$^+/A'B'$ cation. Same symbols are used in (a) $x = 0.1$ and (b) $x = 0.2$. The data of Cr substitution is shown on the far right for comparison. (See text for the effect of Cr, which is magnetic unlike other dopants shown here.)

The work thus indicates that the Stoner FM in SrRuO$_3$ is quite robust and may withstand considerable B-site substitution (up to 30%) provided the itinerancy of electrons is not severely disrupted. This is despite a myriad of electronic transitions, including superconductivity, observed at low temperatures in perovskite-based ruthenates which suggest an apparent sensitivity of electronic properties to structure variations [32]. Our results are consistent with the literature of A-site substituted SrRuO$_3$ which does not disrupt the Ru–O network; for example, the fact that Sr$_{1-x}$Ca$_x$RuO$_3$ is metallic throughout the entire range indicates that Ca hardly disrupts metallicity; therefore, FM is maintained up to $x = 0.8$ in Ca substitution [3]. The finding also sheds light to the effect of magnetic dopants, including Cr. Such dopants are expected to cause spin polarization of electrons to various extent, thus they are intrinsically disruptive to metallicity, hence unfavorable for FM unless there is a strong dopant–Ru or dopant–dopant exchange interaction that is FM. Even for SrRu$_{1-x}$Cr$_x$O$_3$, despite its enhanced $T_C$, it is found SrRu$_{1-x}$Cr$_x$O$_3$ ceramics at both $x = 0.1$ and 0.2 actually have a lower normalized conductivity than SrRu$_{1-x}$Zr$_x$O$_3$. These data have been included in figure 8 on the far right. (It is also confirmed that $M$ decreases with $x$ in SrRu$_{1-x}$Cr$_x$O$_3$, despite the $T_C$ increase, consistent with the finding in the literature [9, 13–20].) Therefore, Cr does cause a disruption to
Figure 9. (a) Magnetization at strong field (90 kOe) and weak field (100 Oe) is strongly dependent on normalized conductivity in SrRuO$_3$ alloys, both for B-site substitution at $x=0.2$ (main panel) and $x=0.1$ (upper inset), and for mixed A/B-site substitution at $x=0.2$ (lower inset). (b) Curie temperature $T_C$ versus normalized conductivity at $x=0.2$, main panel for B-site substitution and inset for mixed A/B-site substitution. Same symbols used in main panel and insets.

metalllicity, as expected for any magnetic dopant, even though a presumably strong FM exchange interaction of the Cr–Ru pair or the Cr–Cr pair can overcome this disadvantage to raise $T_C$ (but not $M$).

The strong correlation between FM and electron localization provides a new insight to the dopant effects of SrRuO$_3$. In the past, alloying efforts aiming to enhance the FM of SrRuO$_3$ were mainly designed based on (a) electronic doping considerations attempting to alter the valence of Ru, and (b) lattice distortion considerations attempting to alter the bandwidth, hence DOS, at the $E_f$. As already mentioned in the section 1, nearly all such efforts instead led to a severe suppression of the FM. We believe one reason for this outcome is electron localization, which depletes the DOS at the $E_f$, thus suppressing the Stoner instability. The current study of normalized conductivity of itinerant electrons is a sensitive, though non-specific probe of the DOS changes at the $E_f$. (Normalized conductivity reflects not only carrier concentrations, which may be depleted by electron localization, but also mobility which may be altered without necessarily causing localization.) Direct evidence of the depletion of DOS at the $E_f$ as a result of doping was obtained by photoemission spectroscopy in Sr(Ru$_{1-x}$Ti$_x$)O$_3$ [33]. Direct evidence of the depletion of carrier concentrations was also obtained in the same system by optical conductivity, which shows that both Drude-like electron contributions and the plasma edge decrease and eventually vanish as the Ti amount increases [8]. These results are consistent with ours and together they support our finding that the FM of SrRuO$_3$ is strongly correlated to electron itinerancy, just as the metal-to-insulator transition that occurs in all the doped SrRuO$_3$ systems studied here.

As mentioned in [8] and [33], the dopant effects on SrRuO$_3$ can be understood to some extent within the context of the Anderson–Hubbard Hamiltonian which considers a hopping integral $t$ between neighboring sites, an on-site Coulomb energy $U$, and a random site potential $\epsilon$. Such a model can explain the decrease of DOS at the $E_f$ due to the destruction of coherent scattering and the quasiparticle peak, hence the suppression of FM in SrRuO$_3$. As the concentration
of dopants increases, there is also an attendant decrease in the normalized $I/U$ due to disorder, which results in a metal-to-insulator transition. A similar argument can be used to rationalize the crossover from the metallic behavior to the correlation insulator behavior as structural disorder increases in SrRuO$_3$, which manifests itself both in magnetism and in low temperature conductivity [29, 34]. The above model is incomplete, however. In the case of Zr/Ti doping, Zr doping creates more randomness in the site potential than Ti doping, yet there is less localization and magnetism disruption caused by Zr doping. This points to a clear need to include resonance scattering into the model: resonance scattering occurs when the (electronic) site potential is well matched, and it has the effect of increasing $U/t$.

Since SrRuO$_3$ is a common electrode for perovskite-oxide-based thin film devices, the finding that Zr substitution causes the least disruption to conductivity is also of practical utility. In this regard, the simultaneous (oversized) Zr substitution on B site and (undersized) Ca substitution on A site could be advantageous since it can best maintain conductivity and the average unit cell volume at the same time. Our lab experience additionally indicated that spattering targets of Zr substituted SrRuO$_3$ can be readily sintered to full density whereas SrRuO$_3$ cannot, due to another beneficial effect of Zr on suppressing grain growth and Ru volatility.

4.1. Conclusions

This work demonstrated a strong correlation between the conductivity and Stoner FM in SrRuO$_3$, and that the destruction of FM by non-magnetic cation substitution of Ru is due to electron localization. Among all the non-magnetic cations that enter the B site, Zr$^{4+}$ is the least disruptive to conductivity and FM, because it causes no charge disorder and the least resonance scattering of the d electrons of Ru$^{4+}$. Such SrRuO$_3$ alloys may be used as conducting electrode for perovskite-oxide-based devices.

Acknowledgments

This work was supported by National Science Foundation of China (Grant No. B010504-20471068), Chinese Postdoctoral Science Foundation and the US National Science Foundation (Grant No. DMRO5-20020, 07-05054 and 09-07523).

References

[40] For a review, see Lichtenberg F 2002 Prog. Solid State Chem. 30 103
Queries for IOP paper 373761

Journal: JPhysCM
Author: W Tong et al
Short title: Electron localization and magnetism in SrRuO$_3$
with non-magnetic cation substitution

Page 1

Query 1:
Author: Please check the author names and affiliations carefully.

Query 2:
Author: Amended wording in the abstract and title OK?

Query 3:
Author: Please be aware that the colour figures in this article will only appear in colour in the Web version. If you require colour in the printed journal and have not previously arranged it, please contact the Production Editor now.

Page 8

Query 4:-
Author: Please check the details for any journal references that do not have a blue link as they may contain some incorrect information. Pale purple links are used for references to arXiv e-prints.