# Determination of Ru valence from x-ray absorption near-edge structure in RuSr$_2$GdCu$_2$O$_8$-type superconductors

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The Ru valence in the antiferromagnetic and ferromagnetic ruthenocuprate superconductors RuSr$_2R$Cu$_2$O$_8$ (Ru-1212), with $R =$ Eu, Gd, and Gd$_{0.6}$Dy$_{0.4}$, has been studied using Ru $L_{\text{III}}$-edge x-ray absorption near-edge structure spectroscopy. Comparison with reference materials Sr$_2$RuO$_4$ and Sr$_2$RuGdO$_6$ in which Ru is tetravalent and pentavalent, respectively, reveals the strong likelihood of mixed valence in Ru-1212 with 40–50% Ru$^{4+}$ and 60–50% Ru$^{5+}$, depending upon specific substitutions. This introduces several possibilities for the nature of the magnetic ordering in these compounds.

    

Coexisting ferromagnetism and superconductivity have recently been discovered in the 1212-type layered ruthenocuprates RuSr$_2R$Cu$_2$O$_8$ ($R =$ Eu and Gd).[1,2] The materials exhibit a Curie transition at $T_M \sim 132$ K and bulk superconductivity below 46 K depending on sample preparations.[1–3] Bauernfeind *et al.*[4] were the first to study these materials, though they discussed only superconductivity and not magnetism. These authors suggested that the Ru ion is pentavalent ($d^3$ or $t_{2g}^3 e_g^0$ configuration) in these compounds. If Ru is to be less than pentavalent in 1212 compounds, one would expect that the ''self-doping'' of the Cu-O planes should occur when the partially occupied $\pi$ ($t_{2g}$) bands of the perovskite Ru-O layer cross the $\sigma^*$ ($e_g$) Hubbard bands of the Cu-O planes. Therefore, it is important to determine the valence of the Ru ions in these newly discovered ruthenocuprates in order to understand the superconducting state. In addition, while early reports[1,2] showed a Curie-Weiss behavior in the paramagnetic susceptibility which was fully consistent with a ferromagnetic (FM) exchange field and $M$-$H$ loops below the Curie temperature exhibited FM hysteresis with a finite remanent magnetization, more recent neutron diffraction studies[5] show that the dominant low-temperature ordering is antiferromagnetic (AF). In view of the fact the RuO$_6$ octahedra possess both a twist and a tilt,[3] one possible scenario for the coexistence of FM and AF is canting of AF-ordered moments. However, an alternative possibility is that two different Ru moments are present due to mixed valency and that the ordering is ferrimagnetic. For these reasons, we sought to determine the Ru valence state.

X-ray absorption near-edge structure (XANES) spectroscopy is a useful tool for determining electronic states. XANES studies at the $L_{\text{II,III}}$ edges have been performed in order to understand the distribution of valence electrons and the valence of transition metal ions in a variety of compounds.[6–9] We have used this technique in an attempt to determine the valence of the Ru ions in several Ru-1212

compounds. Specific Ru-1212 samples investigated include RuSr$_2$EuCu$_2$O$_8$, RuSr$_2$GdCu$_2$O$_8$, RuSr$_2$(Gd$_{0.6}$Dy$_{0.4}$)Cu$_2$O$_8$, and Ru(Sr$_{1.6}$Ba$_{0.4}$)GdCu$_2$O$_8$, together with reference samples SrRuO$_3$ (Ru$^{4+}$), Sr$_2$RuO$_4$ (Ru$^{4+}$), and Sr$_2$GdRuO$_6$ (Ru$^{5+}$). These Ru-1212 samples were chosen because there is a strong variation in $T_c$ with rare-earth ion size and the Ba substitution significantly reduces (by about 40%) the size of the remanent magnetization. It is hoped that correlation of such properties with structure, transport, superconductivity, and Ru valence will provide clear guidelines as to the nature of the magnetic and superconducting states.

The polycrystalline Ru-1212 samples were prepared as described earlier,[1–3] including a final anneal at 1060 °C in oxygen for 7 days, in which the material densified and granularity was substantially reduced. This resulted in a significant increase in the zero-resistance $T_c$ value for the Gd compound from 20 to 38 K, but did not affect the thermodynamic transition at 47 K.[10] Moreover, the three standards of SrRuO$_3$, Sr$_2$RuO$_4$, and Sr$_2$GdRuO$_6$ were all prepared by solid-state synthesis at 1170 °C. X-ray diffraction showed that all the samples are of single phase. In Fig. 1 we show the resistivity as a function of temperature for the samples of the RuSr$_2$EuCu$_2$O$_8$, RuSr$_2$GdCu$_2$O$_8$, RuSr$_2$(Gd$_{0.6}$Dy$_{0.4}$)Cu$_2$O$_8$, and Ru(Sr$_{1.6}$Ba$_{0.4}$)GdCu$_2$O$_8$. The first three samples have superconducting onset transition temperatures ($T_c$) of 35, 48, and 58 K, respectively, which increase remarkably rapidly with reducing the ion size, while the Ba-substituted compound shows little change in its superconducting transition from the parent RuSr$_2$GdCu$_2$O$_8$ compound. The variation in superconducting transition temperature may arise from differences in doping state or from differences in magnetic pairbreaking, and it is an object of the present studies in combination with other transport, thermodynamic, magnetic, and structural studies to ultimately unravel the relative contributions of doping and pairbreaking.

XANES measurements were performed at the BL15B beamline of the Taiwan Synchrotron Radiation Research
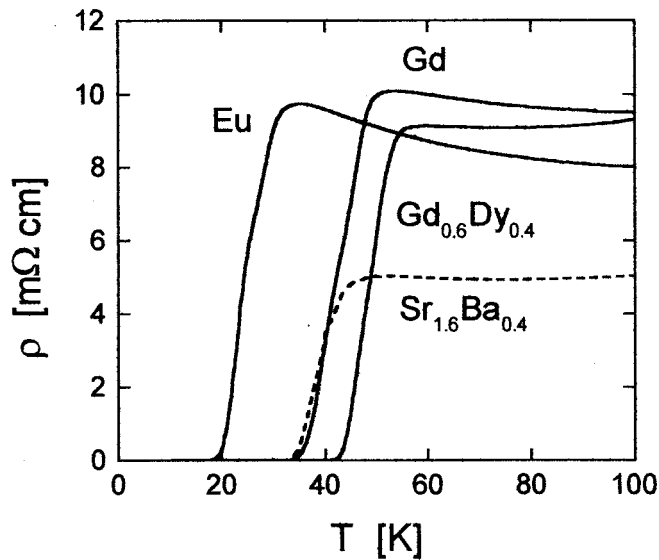
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FIG. 1. Resistivity as a function of temperature for $RuSr_2RCu_2O_8$ with $R=$Eu, Gd, and $Gd_{0.6}Dy_{0.4}$ and for $Ru(Sr_{1.6}Ba_{0.4})GdCu_2O_8$ (dashed curve).



FIG. 2. Ru $L_{III}$-edge x-ray absorption near-edge structure (XANES) spectra for $RuSr_2RCu_2O_8$ with $R=$Eu, Gd, and $Gd_{0.6}Dy_{0.4}$ and for $Ru(Sr_{1.6}Ba_{0.4})GdCu_2O_8$. Also shown are the spectra for reference samples $Sr_2RuO_4$ ($Ru^{4+}$) and $Sr_2GdRuO_6$ ($Ru^{5+}$). The dashed curve is a linear combination of these reference spectra in the proportion 0.4 ($Sr_2RuO_4$) and 0.6 ($Sr_2GdRuO_6$).

Center (SRRC) in Hsinchu, using a Si(111) double-crystal monochromator. The energy resolution ($E/\Delta E$) of the beam-line is $\sim 6000$ (i.e., $\sim 0.47$ eV at $\sim 2.84$ keV). The beamline was optimized for x-ray photons in the 2–3 keV range (the Ru $L_{III}$ edge is at 2838 eV) for the XANES measurements. The Ru-$L_{III}$ x-ray absorption spectra of the polycrystalline samples were recorded in the fluorescence mode using a Lytle detector. Both the $L_{II}$ and $L_{III}$ edges of Mo and Pd foils were used to calibrate the photon energy before and after the measurements. The spectra were measured between energies $\sim 200$ eV before the edge and $\sim 130$ eV above the edge. The AUTOBK code[11] was used for background subtraction.

In Fig. 2 we show the Ru $L_{III}$-edge XANES spectra of $RuSr_2EuCu_2O_8$, $RuSr_2GdCu_2O_8$, $RuSr_2(Gd_{0.6}Dy_{0.4})Cu_2O_8$, $Ru(Sr_{1.6}Ba_{0.4})GdCu_2O_8$, $Sr_2GdRuO_6$ ($Ru^{5+}$), and $Sr_2RuO_4$ ($Ru^{4+}$). The Ru ions in each of these six compounds have an octahedral coordination and a crystal field with $O_h$ symmetry giving rise to a splitting of the $4d$ states into $t_{2g}$ and $e_g$ levels separated by $\Delta = 10$ Dq. The $L_{III}$ absorption spectrum of the Ru(IV) standard of $Sr_2RuO_4$ with $4d^4$ configuration exhibits two peaks (denoted as $A$ and $B$). The higher-energy peak $B$ (2842.0 eV) and a lower-energy peak (shoulder) $A$ (2839.6 eV) can be assigned to $2p \rightarrow e_g$ and $2p \rightarrow t_{2g}$ transitions, respectively. A very similar spectrum was obtained for $SrRuO_3$. The Ru(V) compound $Sr_2GdRuO_6$ with a $4d^3$ configuration also has two peaks (denoted as $A'$ and $B'$). The higher-energy peak $B'$ (2843.6 eV) and a lower-energy peak $A'$ (2840.6 eV) can be assigned to $2p \rightarrow e_g$ and $2p \rightarrow t_{2g}$ transitions, respectively, which is similar to that of Ru(IV) except with a larger $\Delta$ value. Moreover, with the increase in the valence of Ru from IV to V the double-peaked $L_{III}$ edge is shifted by $\sim 1.5$ eV to higher energy, which is consistent with the results reported by Hu *et al.*[9] using the standards of Ru(IV) of $RuO_2$ and $Sr_2RuO_4$ and Ru(V) of $Sr_4Ru_2O_9$.

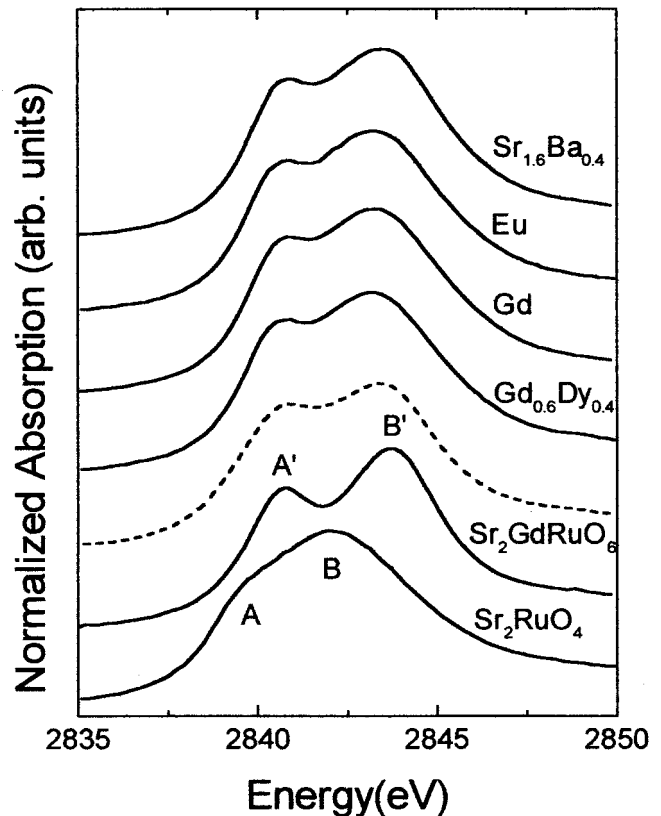Such a chemical shift is caused by changes in the electro-static energy at the Ru site driven by the variation of the ionic valence in the compounds. It is well established that the effective ionic valence of the compounds can be measured from the chemical shift in the core-level x-ray photoemission spectroscopy.[12] These chemical shifts in electron-energy-loss spectroscopy (EELS) have also been used to determine the valences of the transition-metal-based compounds.[13] We then adopt the same scheme to obtain the Ru valence in the present Ru-1212 samples. As demonstrated in Fig. 2, the main double-peaked $L_{III}$-edge positions of these four samples appear closer to those in $Sr_2GdRuO_6$ with $Ru^{5+}$. There is little obvious change in the Ru-1212 spectra irrespective of the chemical substitution at the $R$ sites of $RuSr_2RCu_2O_8$ ($R = $Gd, Eu, $Gd_{0.6}Dy_{0.4}$). However, it is clear that there is ad-ditional weight between these peaks that is attributable to the $B$ peak in the $Sr_2RuO_4$ (or $SrRuO_3$) spectrum. Indeed, the dashed curve shows the result of combining the two spectra in the ratio $0.4Sr_2RuO_4 + 0.6Sr_2GdRuO_6$. The result is a very close match to the spectrum for $RuSr_2GdCu_2O_8$. In this way, we conclude that the three Ba-free Ru-1212 samples are con-sistent with a combination comprising 0.4–0.5 Ru(IV) and 0.6–0.5 Ru(V), inasmuch as the linear combination of such spectra can be taken as a guide to the relative proportions of valence states. An almost identical apportionment of mixed valency was obtained by fitting the spectra using the $SrRuO_3$ reference spectrum. Because these compounds are highly

TABLE I. Best fits to the Ru-1212 XANES spectra from a linear combination of the spectra for $Sr_2RuO_4$ ($Ru^{4+}$) and $Sr_2GdRuO_6$ ($Ru^{5+}$). Also shown is the resultant inferred nominal hole concentration per copper atom, $p$, on the $CuO_2$ layers and the bond valence sum $V_- \equiv 2 + V_{Cu} - 2V_O$ determined from the copper and oxygen bond valence sums $V_{Cu}$ and $V_O$, respectively.

| Compound | $Ru^{4+}$ | $Ru^{5+}$ | $p$ | $V_-$ |
|---|---|---|---|---|
| $RuSr_2EuCu_2O_8$ | 0.38 | 0.62 | 0.19 | 0.46 |
| $RuSr_2GdCu_2O_8$ | 0.40 | 0.60 | 0.20 | 0.43 |
| $RuSr_2(Gd_{0.6}Dy_{0.4})Cu_2O_8$ | 0.47 | 0.53 | 0.23 | 0.45 |
| $Ru(Sr_{1.6}Ba_{0.4})GdCu_2O_8$ | 0.28 | 0.72 | 0.14 | 0.34 |

oxygen stoichiometric,[3,10] this mixed valence leads to a doped hole concentration on the $CuO_2$ planes of 0.2–0.25, values which are quite reasonable for the occurrence of superconductivity, but larger than the values (0.07–0.08) estimated from thermopower and superconducting properties.[1,2,10] The Ba-substituted sample appears to exhibit a slightly lower fraction of Ru(IV).

The occurrence of mixed Ru valency in accordance with two quite different moments within the $RuO_2$ layer allows the possibility of ferrimagnetic ordering in these compounds—namely, AF ordering of moments such that adjacent spins are antiparallel, but sum to a net moment because of their two different magnitudes. A scenario such as this could explain the different size[14] of the high-temperature effective moment ($3.15\mu_B$) and the low-temperature saturation moment ($1.1\mu_B$), which, below 30 K, requires only ~1 T to saturate. It could also implicate a double-exchange interaction, explaining the sharp reduction in the Hall coefficient[15] observed at the onset of the magnetic transition at 132 K.

By comparing the measured spectra, it is also clear that they exhibit subtle changes induced by the variation in rare-earth element or by Ba substitution for Sr. In particular, the apparent proportion of $Ru^{4+}$ and $Ru^{5+}$ changes with such a substitution. The difference spectra between $Ru(Sr_{1.6}Ba_{0.4})GdCu_2O_8$ and $RuSr_2GdCu_2O_8$ can be well modeled by 0.12 Ru(V)–0.11 Ru(IV), suggesting that the Ba compound has 0.72 Ru(V) and 0.28 Ru(IV), while the pure compound has 0.6 Ru(V) and 0.4 Ru(IV). In support of this scenario, we note that the remanent magnetization for $Ru(Sr_{1.6}Ba_{0.4})GdCu_2O_8$ is reduced to half that of the Ba-free compound,[16] reflecting the substantially reduced fraction of $Ru^{4+}$. The best-fit proportions for each Ru-1212 compound are summarized in Table I together with the resultant esti-

mates of the hole concentration $p$, assuming charge balance and fully stoichiometric oxygen content. Also shown are the values of the bond valence parameter for the $CuO_2$ planes $V_- \equiv 2 + V_{Cu} - 2V_O$, which has been used to estimate hole concentrations in the cuprates.[17] Values of $V_-$ are calculated, as described previously,[17] from bond lengths determined from synchrotron x-ray diffraction measurements on these samples.[18] The numbers presented in Table I probably cannot be taken too literally, but the qualitative trends are likely to be real. Both estimates of hole concentration well exceed values estimated from transport properties.[1,2,10]

Recently, Felner *et al.*[19] have reported that Ru is pentavalent in $RuSr_2(Eu_{1.5}Ce_{0.5})Cu_2O_{10}$ (Ru-1222) by Ru $K$-edge XANES spectroscopy. The Ru-1222 compounds, which also exhibit similar superconductivity and weak ferromagnetism, have a bilayer fluorite-type $Eu_{1.5}Ce_{0.5}O_2$ block separating the adjacent $CuO_2$ layers unlike the 1212 compounds, which have a single rare-earth layer.[3] Because of the similarity of the superconducting and magnetic properties of Ru-1222 and Ru-1212, one might expect that Ru-1222 also exhibits mixed Ru valency. However, this compound is not oxygen stoichiometric, and this, in combination with the Eu/Ce substitutional chemistry, could accommodate a rigid $Ru^{5+}$ valency while still allowing charge transfer of carriers into the superconducting $CuO_2$ layers. Clearly, a close comparison of the magnetic properties of these two compounds is called for.

In summary, our study using Ru $L_{III}$-edge x-ray absorption near-edge structure spectra has shown that the Ru valence in the Ru-1212 ruthenocuprate superconductors is a mixture of 0.4–0.5 $Ru^{4+}$ and 0.6–0.5 $Ru^{5+}$, thus raising the possibility of ferrimagnetic ordering or possible double-exchange interaction. This deduced valency admixture is consistent with recent high-temperature susceptibility measurements of the effective moment.[14] It is, moreover, consistent with the observation that substitution of $Sn^{4+}$ for Ru causes an increase in $T_c$ and a decrease in room-temperature thermoelectric power consistent with hole doping in the $CuO_2$ planes. On the other hand, substitution of $Nb^{5+}$ for Ru results in the opposite effect—namely, a decease in $T_c$ and an increase in the room-temperature thermoelectric power consistent with electron doping.[20] These substitutional effects suggest that the mean Ru valence is neither 4+ nor 5+, but takes an intermediate value.

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