Structural analysis, magnetic and transport properties of the (Ru$_{1-x}$Co$_x$)Sr$_2$GdCu$_2$O$_8$ system

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Abstract
The effects of Co substitution on the structural and superconducting properties of the RuSr$_2$GdCu$_2$O$_8$ compound have been studied. Rietveld refinements of the x-ray diffraction patterns indicate that the cobalt ion progressively replaces ruthenium sites. This replacement induces significant changes on the crystal structure and on the magnetic and superconducting properties. The effects of Co substitution on the superconducting behaviour, and more particularly on the changes induced by the hole doping mechanism, were investigated in (Ru$_{1-x}$Co$_x$)Sr$_2$GdCu$_2$O$_8$ by a ‘bond valence sum’ analysis with Co content from $x = 0.0$ to $0.2$. The weak ferromagnetic transition at $T_M = 138.2$ K is shifted to lower temperature, and suppressed at higher Co content. From the crystallographic point of view the Ru–O(1)–Cu bond angle, associated to the rotation of the RuO$_6$ octahedra around the c-axis, remains essentially constant when Ru is substituted by Co. Furthermore, increasing Co content has the effect of increasing the weak ferromagnetic moment, which may be interpreted as the main feature responsible for breaking the delicate balance between magnetic and superconducting ordering.

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

1. Introduction
In the RuSr$_2$GdCu$_2$O$_8$ (Ru-1212) compound, both ferromagnetic and superconductivity phenomena coexist at the microscopic level [1, 2]. The ferromagnetic ordering appears at a rather high temperature, about 130–150 K [3, 4], whereas the superconducting transition occurs at low temperature, from about 15 to 45 K. The characteristics of the crystalline structure of this compound can be described based on the high transition temperature compound, YBa$_2$Cu$_3$O$_y$ (Y-123). Ru-1212 contains CuO$_2$ planes, which are separated by single oxygen-less Gd planes; RuO$_2$ planes replace the equivalent CuO chains as in Y-123. In the RuO$_2$ planes, the Ru atoms are six coordinated, and form RuO$_6$ octahedra. Additionally, the structure contains SrO planes which are localized between the CuO$_2$ and RuO$_2$ planes. The O(1) oxygen sites are localized in the SrO planes, whereas the oxygen sites O(2) and O(3) are localized in the CuO$_2$ and RuO$_2$ planes, respectively. These planes are connected via the apical oxygen O(1). The CuO$_2$ planes’ role may be similar to that in the high-$T_C$ cuprates, and directly related to the superconducting formation, whereas the RuO$_2$ planes are related to magnetic order. Several experimental studies have been carried out in order to determine the role of cationic substitutions in RuO$_2$ sites [5–7, 9]. For instance, studies of heterovalent substitutions in Ru$_{1-x}$M$_x$-1212 with (M = Nb$^{5+}$, Sn$^{4+}$) reveal a reduction of magnetism in the RuO$_2$ planes [8], whereas doping Ru sites with Cu$^{II}$ increases the superconducting transition and reduces the magnetic ordering [9]. Actually, the current understanding of the physical characteristics of this system is that superconductivity and ferromagnetic ordering originate in the CuO$_2$ and RuO$_2$ planes, respectively. However, the nature of the competition/coexistence of both
2. Experimental details

Polycrystalline samples of \((\text{Ru}_{1-x}\text{Co}_x)\)\text{Sr}_2\text{GdCu}_2\text{O}_8 (x = 0, 0.025, 0.05, 0.075, 0.1, 0.2) were synthesized by solid state reaction of oxides: \text{RuO}_2 (99%), \text{CoO} (99.999%), \text{Gd}_2\text{O}_3 (99.9%), \text{CuO} (99.99%) and \text{SrCO}_3 (98+%). After calcinations in air at 900°C, the samples were ground, pressed into pellets and annealed in oxygen at 1000°C. Phase identification was performed using a Siemens D5000 x-ray diffractometer, with Cu Kα radiation and Ni filter. Intensities were measured in steps of 0.02° for 14 s in the 2θ range from 5° to 120°, at room temperature. Crystallographic phases were identified by comparison with x-ray patterns in the JCPDS database. The crystalline structure was refined with the program Rietica [10] (Rietveld program for quantitative phase analysis of polycrystalline mixtures with multi-phase capability). The Bond Valence Sum program was used to distinguish the oxidation states of metals Ru and Cu [11]. The superconducting transition temperatures were determined with a closed-cycle helium refrigerator by measuring the resistance versus temperature characteristic by the standard four-probe technique, from 250 to 14 K. Measurements of ac susceptibility, dc susceptibility, and magnetization versus magnetic field were carried out using a superconducting Quantum Interference Device Magnetometer, (MPMS Quantum Design), from 2 to 300 K and applied field up to ±40 kOe.

3. Results and discussion

Figure 1(a) shows x-ray diffraction patterns for the \(\text{Ru}_{1-x}\text{Co}_x\)-1212 samples. The structural analysis indicate that all samples correspond to the Ru-1212 structure, with negligible content of impurities. In figure 1(b) we also show an amplification of the region on the x-ray data where impurities were detected at the 2θ position; these correspond to \text{Sr}_3(\text{Ru}, \text{Cu})\text{O}_7 (ICDD no 51-0307), and \text{SrRuO}_3 (ICDD no 28-1250). We can note that those are negligible, also at the maximum Co concentration. In the refinement process we took into account the presence of secondary phases and the substitution of Co ions in Ru and Cu sites. The superconducting transition temperatures were determined with a closed-cycle helium refrigerator by measuring the resistance versus temperature characteristic by the standard four-probe technique, from 250 to 14 K. Measurements of ac susceptibility, dc susceptibility, and magnetization versus magnetic field were carried out using a superconducting Quantum Interference Device Magnetometer, (MPMS Quantum Design), from 2 to 300 K and applied field up to ±40 kOe.

Figure 2. Rietveld refinement on the x-ray diffraction pattern for the \(x = 0.0\) sample. Experimental spectrum (dots), calculated pattern (continuous line), difference (middle line) and the calculated peak positions (bottom).
of the lattice parameters at room temperature with increased cobalt content. It is observed that as x is increased, the c-axis parameter decreases, mainly as a result of the decrease of the Ru/Co–O(1) average bond length. The bond valence sum (BVS) shows that the CoIII+ radius for coordination number six has a size of 0.565 Å [12].

On the other hand, the bond valence sum (BVS) shows that as x is increased, the valence of the Ru increases, whereas the Cu decreases; see table 2. For undoped samples the calculated Ru valence was 4.69. This result is in agreement with that obtained by NMR and XANES studies, which indicate mixed ionic states of about 40% RuIV+ and 60% RuV+ [14, 15]. Thus, the main effect of Co substitution is a strong increase of the unit-cell volume decreases slightly. This result may be explained considering the coordination numbers and the ionic radii of the CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+, CuII+ and RuV+ ions. It is noted that the CoIII+ radius with a size of 0.65 Å for coordination number five, and for coordination number six changes from 0.545 to 0.61 Å for CoIII+,

| x | 0.0 | 0.025 | 0.05 | 0.075 | 0.1 | 0.2 |
|---|---|---|---|---|---|---|
| a (Å) | 3.8367(3) | 3.8374(2) | 3.8382(2) | 3.8388(4) | 3.8393(4) | 3.8408(4) |
| c (Å) | 11.568(3) | 11.5622(2) | 11.5584(3) | 11.5544(3) | 11.5505(4) | 11.5417(4) |
| V (Å³) | 4.10 | 4.71 | 4.72 | 4.73 | 4.79 | 4.80 |
| p | 0.05 | 0.15 | 0.15 | 0.14 | 0.135 | 0.1 |
| N | 0.145 | 0.145 | 0.145 | 0.145 | 0.145 | 0.145 |
| Gd | 2.06(7) | 1.76(6) | 1.52(6) | 2.09(6) | 1.53(5) | 2.09(9) |
| Sr | 0.3067(4) | 0.3067(4) | 0.3066(2) | 0.3066(2) | 0.3066(2) | 0.3066(2) |
| Cu | 2.05 | 2.04 | 2.04 | 1.62 | 1.61 | 1.60 |
| p | 0.05 | 0.04 | 0.04 | 0.38 | 0.39 | 0.4 |
| B (Å³) | 5.84(8) | 5.4(7) | 3.9(6) | 7.2(7) | 6.9(7) | 8.5(1.3) |
| O(2) | 0.1295(1) | 0.1297(4) | 0.1293(5) | 0.1295(5) | 0.1295(4) | 0.1295(4) |
| B (Å³) | 2.9(4) | 2.1(3) | 0.7(2) | 1.0(3) | 2.0(3) | 1.9(5) |
| O(3) | 0.1139(1) | 0.114(1) | 0.1141(12) | 0.114(11) | 0.1140(1) | 0.1140(2) |
| B (Å³) | 5.86(6) | 5.6(5) | 5.7(4) | 5.6(4) | 5.6(4) | 5.6(4) |
| % Gd1212 | 94.92(1) | 95.83(1) | 95.43(1) | 93.28(2) | 86.16(3) | 83.40(6) |
| % SrRuO4 | 2.1(1) | 3.8(1) | 2.7(8) | 5.1(1) | 3.1(1) | 8.0(1) |
| % Sr3Ru2O7 | 2.9(4) | 0.3(2) | 1.9(2) | 1.6(3) | 3.3(3) | 6.7(8) |

Rc (%) | 8.8 | 6.0 | 5.9 | 6.0 | 5.9 | 6.5 |
Rsp (%) | 11.5 | 8.3 | 8.2 | 8.7 | 8.0 | 9.1 |
Rsp (%) | 9.2 | 3.7 | 3.6 | 3.8 | 3.6 | 3.7 |
χ2 (%) | 1.2 | 2.2 | 2.3 | 2.4 | 2.2 | 2.5 |

* % of impurity in the phase.

Table 1. Structural parameters for Ru1−xCo2−x1212 at 295 K. (Note: space group: P4/mmm (no 123). Sj (vu) is the bond valence sum, p is the amount of charge transferred between the CuO6 and RuO6 plane, N is the cobalt occupancy factor. Atomic positions: Ru: 1b (0, 0, 1/2); Gd: 1c (1/2, 1/2, 1/2); Sr: 2h (1/2, 1/2, z); Cu: 2g (0, 0, z); O(1) in 8s (x, 0, z) × 1/4, O(2) in 4d (0, 1/2, 1/2, z) and O(3) in 4o (x, 1/2, 1/2, × 1/2 position.)

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rests on the assumption that the buckling of CuO$_2$ planes, and results reveal that as the shortening of the apical Cu–O bond, localize holes. Our

We determined the amount of charge (p) transferred between the CuO$_2$ and RuO$_2$ planes. We took into account the simple function of temperature at low magnetic field (15 Oe), in zero samples are structurally comparable to other samples produced and reported by other laboratories [3, 4].

In order to explain the $T_C$ degradation in our samples, we determined the amount of charge (p) transferred between the CuO$_2$ and RuO$_2$ planes. We took into account the simple model of valence (Ru: 5 – 2p, Cu: 2 + p) [6]. The p value comes from the structural data using BVS that make use of the sensitivity of Cu–O bond lengths at the hole concentration [18]. Our calculations show that with increasing p, p changes from 0.155 to 0.1, and from 0.05 to 0.0. Moreover, Jørgensen et al [19] propose that the highest $T_C$ is achieved in structures with flat and square CuO$_2$ planes and long apical Cu–O bond length. This fact rests on the assumption that the buckling of CuO$_2$ planes, and the shortening of the apical Cu–O bond, localize holes. Our results reveal that as p increases, the buckling of the CuO$_2$ plane increases, and the apical Cu–O bond length decreases. Therefore, the $T_C$ degradation may be associated with the increase of the buckling of the CuO$_2$ planes and the decrease of the apical Cu–O bond length, due to changes of charge (p) in the CuO$_2$ and RuO$_2$ planes.

We performed measurements of dc susceptibility as a function of temperature at low magnetic field (15 Oe), in zero superconducting ordering, as have been observed in rare earth intermetallic compounds [17]. These ac data show that our samples are structurally comparable to other samples produced and reported by other laboratories [3, 4].

Figure 3. Normalized resistances as a function of temperature in (Ru$_{1-x}$Co$_x$)$_2$1212 for different Co concentrations as indicated in the figure. The inset shows the ac susceptibility for $x = 0.0$ measured at 730 Hz and field amplitude of 3.0 Oe.

Figure 4. Measurements of dc susceptibility as a function of temperature for (Ru$_{1-x}$Co$_x$)$_2$1212. We show the ZFC and FC modes with an external magnetic field of 15 Oe. The inset shows $d\chi/dT$ versus $T$ for compositions $0 < x < 0.2$. Figure 4.

### Table 2. Bond lengths (Å), bond angles (deg) and octahedral distortion (Δoct) for Ru$_{1-x}$Co$_x$1212.

| $x$   | 0.0    | 0.025 | 0.05  | 0.075 | 0.1   | 0.2   |
|-------|--------|-------|-------|-------|-------|-------|
| Ru–O(1) | 2.13(6) | 2.13(6) | 2.13(6) | 2.13(6) | 2.13(6) | 2.13(6) |
| Cu–O(1) | 2.13(6) | 2.13(6) | 2.13(6) | 2.13(6) | 2.13(6) | 2.13(6) |
| Cu–O(2) | 2.13(6) | 2.13(6) | 2.13(6) | 2.13(6) | 2.13(6) | 2.13(6) |

The graph shows the resistivity as a function of temperature for different Co concentrations (0, 0.025, 0.05, 0.075, 0.1, 0.2) at a frequency of 730 Hz and a field amplitude of 3.0 Oe. The inset displays the ac susceptibility for $x = 0.0$. The ac data reveal that as the Co concentration increases, the buckling of the CuO$_2$ planes and the decrease in the apical Cu–O bond length are observed.

The results indicate that as the Co concentration is increased, the magnetic transition $T_M$ decreases at a Co concentration of $x = 0.200$. Moreover, in the range of compositions for $x < 0.10$ we observed a clear splitting of the ZFC and FC measurements close to $T_M$, which disappears for $x = 0.200$ (the inset presents only ZFC measurements). It is important to note that not only does the Co concentration have an effect on $T_M$, but also the external magnetic field; as an example of this behaviour, we show in figure 5 measurements of $\chi$–$T$ for the Co composition $x = 0.10$. These measurements were performed at ZFC and FC. The splitting of the data is clearly observed at low fields with two branches (note that the high susceptibility branch is FC). However, as the field is higher the splitting is small and it disappears at 10 and 20 kOe. The extended extracted data for measurements in other Co compositions are illustrated in figure 6(a). There, it seems that as the Co concentration is increased, the magnetic transition $T_M$ is shifted to low temperature, but depending also on the applied field. Furthermore, increasing the magnetic field shifts $T_M$ to high temperature (this also depends on...
the Co concentration); for example, at 1 kOe $T_M$ is about 133 K when $x = 0.025$, but when the field is 30 kOe, $T_M$ is shifted to about 155 K. $T_M$ disappears for the composition with $x = 0.10$ when the field is 30 kOe. Thus, both the Co concentration and the magnetic field may destroy $T_M$. On the other hand, in figure 6(b) we show that $T_N$ is noticeably affected by the intensity of the magnetic field, with no effect in Co concentration. In this figure it is observed that $T_N$ is shifted from 8 K at 1 kOe to about 2.6 K at 30 kOe. This behaviour is quite typical of layered structures; the external magnetic field tends to saturate the paramagnetic moment of the Gd sublattice [20]. Thus, the susceptibility results suggest that the dominant magnetic character is antiferromagnetic (AFM) order at low temperatures, and canted ferromagnetism at high temperature since the transverse components of spins differ from one crystallographic site to another and the equilibrium angles depend on both the external magnetic field and dopant content. These experimental evidences have been well documented in doped manganites, cuprates and intermetallic compounds [20–22]. In order to understand this susceptibility behaviour we can assume that two independent contributions exist: one for each Gd and Ru sublattices. The Ru sublattice orders as a weak ferromagnet at $T_M$, while the Gd one remains paramagnetic and orders antiferromagnetically at lower temperature. To separate the two contributions and to observe the behaviour as a function of Co content, we estimated, at high-temperature, the Ru moments by fitting the susceptibility data considering two contributions, i.e. $\chi^{-1} = [(C/(T - \Theta))_{\text{Gd}} + (C/(T - \Theta) + \chi_0)_{\text{Ru}}]^{-1}$. In the first term the Curie constant $C_{\text{Gd}}$ was taken as the theoretical value of 7.9 emu K mol$^{-1}$ and the Curie temperature as $\Theta_{\text{Gd}} = -9$ K. This value for $\Theta_{\text{Gd}}$ was used by Butera et al [23, 24], and was obtained performing EPR measurements. In the second term we included the Curie constant $C_{\text{Ru}}$, the Curie temperature ($\Theta_{\text{Ru}}$), and the susceptibility $\chi_0$ which is temperature independent because of the nonlinearity of the inverse susceptibility data in the measured range (170–300 K) as seen in figure 7. In this fitting process both $C_{\text{Gd}}$ and $\Theta_{\text{Gd}}$ were kept fixed in order to observe the Ru effective moment behaviour; these are plotted in the inset of figure 7.

A continuous increase of the effective moment $\mu_{\text{eff}}$ is seen from $\sim 1.06 \; \mu_B$, for $x = 0–2.17 \; \mu_B$ at $x = 0.075$. Increasing the concentration of Co atoms affects $\mu_{\text{eff}}$, reducing it to a value of about 1.28 $\mu_B$. On the other hand, the Curie temperature, $\Theta_{\text{Ru}}$ changes from 153.9 ± 0.5 K to 112 ± 2.5 K, for $0.025 < x < 0.10$ and then increases again from $x > 0.10$ to a value of about 157.7 ± 1.2 K. To have a better understanding of this magnetic behaviour, we performed magnetization versus applied magnetic field ($M$ vs $H$) measurements at $T = 2$ K (see figure 8). The hysteresis loops at low field (main panel) is attributed to the weak magnetism of the Ru/Co sublattice, and the dependence of the magnetization in the high field region (inset (b)) to the antiferromagnetic order of the Gd ion. A trend to saturation is observed with a value at about 7.8 $\mu_B$ emu$^{-1}$, which corresponds to the Gd moment, as obtained by neutron diffraction studies ($\sim 7.0 \; \mu_B$) [25]. This experimental value confirms the two expected contributions: the Gd moment, plus 0.8 $\mu_B$ emu$^{-1}$ due to the ruthenium sublattice in the low spin state (1 $\mu_B$ for 3d$^5$, $S = 1/2$). On the other hand, the behaviour of the remanent magnetization ($M_R$) associated to the Ru sublattice as a function of Co content is plotted in inset (a). $M_R$ increases from 0.14 $\mu_B$ emu$^{-1}$ for $x = 0$ to 0.49 $\mu_B$ emu$^{-1}$ for $x = 0.05$, and then decreases to 0.05 $\mu_B$ emu$^{-1}$ at a concentration about $x = 0.2$. The small value of $M_R$ for $x = 0$ is consistent with the analysis of neutron diffraction measurements by Lynn et al [25], where an upper limit of about 0.1 $\mu_B$ was obtained for the ferromagnetic peaks below $T_M$. Again, it is worthwhile noting that both $M_R$ and $\mu_{\text{eff}}$ extracted from the Ru sublattice (inset of figure 7) increase as Co is introduced in the Ru sublattice (for $x < 0.10$). This behaviour is contrary to Sn.
and Nb as in Eu-1212 [26]. However, these characteristics are still more intriguing in the Ce, Eu-1222 [27] and Gd-1212 [28] compounds doped with iron where a decreasing of the magnetic moment in the Ru sublattice was observed. It is possible that this increase of the magnetic moment in the Ru/Co site may be due to an enhancement of the antisymmetric exchange, causing the effect that the spins are canting in the ab-plane as has been argued in several intermetallic and ruthenocuprate compounds [20, 22, 29, 30], where a delicate balance among the subtle variations in composition, magnetic structure, and superconducting state may exist. Furthermore, recent studies [31] have shown that complete substitution of Ru by Co gives a paramagnetic material which is accomplished by depleting oxygen in the structure. The drastic reduction of magnetic moment, \( \mu \) increases, the octahedral distortion observed here could be related to this fact.

4. Conclusions

In summary, we have presented a detailed crystallographic and magnetic study of the (Ru\(_{1-x}\),Co\(_x\))\(_2\)Sr\(_2\)GdCu\(_2\)O\(_8\) system by x-ray diffraction at room temperature and magnetization measurements. The x-ray diffraction results indicate that Co ions occupy the Ru sites. This replacement causes significant changes in the Ru–O(1) bond length, inducing an increase in the octahedral distortion. In contrast to previous reports, we found that the bond angle associated with the rotation around the c-axis remains essentially constant. From the BVS analysis, we demonstrate that as \( x \) increases, the amount of charge (\( p \)) decreases in the CuO\(_2\) and RuO\(_2\) planes; this could explain the observed \( T_c \) reduction with Co content. Finally, we found from magnetic measurements that a gradual introduction of Co ions into the structure enhances the magnetic moment, \( \mu_{\text{eff}} \), and \( M_R \) via the ferromagnetic component. Thus we believe that this increase of the magnetic moment might be responsible for the delicate balance between weak ferromagnetism and superconductivity via pair breaking or trapping holes in the CuO\(_2\) planes.

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