The superstructure and superconductivity of Ru1222 based
RuSr$_2$Gd$_{2-x-y}$Y$_y$Ce$_x$Cu$_2$O$_{10-\delta}$ compounds

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Abstract

For the first time, the local structure and physical properties of Ru1222 based compounds
(RuSr$_2$Gd$_{1.4}$Ce$_{0.6}$Cu$_2$O$_{10-\delta}$ and RuSr$_2$Gd$_{1.8-x}$Y$_{0.2}$Ce$_x$Cu$_2$O$_{10}$ ($x = 0.90–0.55$)) have been
investigated and analyzed together on the very same compounds. The Ru1222 superstructure
was confirmed by TEM at a local scale and was suggested to have an orthorhombic symmetry
with space group Aba2 and lattice parameters $a_s \approx \sqrt{2}a$, $b_s \approx \sqrt{2}a$ and $c_s = c$. This new
Ru1222 superstructure distortion from tetragonal symmetry is proposed to have a positive
correlation with the superconductivity variation of these compounds. The more the distortion
towards orthorhombic symmetry, the higher the critical superconducting temperature these
compounds can achieve. The $T_c(0)$ of RuSr$_2$Gd$_{1.8-x}$Y$_{0.2}$Ce$_x$Cu$_2$O$_{10-\delta}$ ($x = 0.85–0.55$)
increases monotonically from 4 to 16 K when $x$ decreases from 0.85 to 0.70, then
Ru$_2$Gd$_2$Cu$_2$O$_8$ defects emerge and the $T_c$ decreases with decreasing $x$. Ru1212 defects are
observed to intergrow epitaxially with the Ru1222 structure as lamellas along the $c$-axis in
RuSr$_2$Gd$_{1.4}$Ce$_{0.6}$Cu$_2$O$_{10-\delta}$. Although Ru1212 is a superconductor, the intergrowth severely
restrains its superconductivity.

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

1. Introduction

The ruthenocuprate Ru$_2$R$_{2-x}$Ce$_x$Cu$_2$O$_{8}$ (Ru1222) together with Ru$_2$RCu$_2$O$_8$ (Ru1212) ($R = Y$, Eu, Gd, Nd and Sm) has been more attention since the demonstration of the extremely unusual coexistence of ferromagnetism and bulk superconductivity within these materials [1, 2]. Ru1212 is a weak ferromagnetic or antiferromagnetic [3–5] and Ru1222 is frequently reported as a ferromagnetic [6–9]. This difference may be related to the weak interlayer exchange interactions of the RuO$_2$ layers [10]. Surprisingly, large bulk negative magnetoresistances (MR) have also been observed in the Ru1222 series Ru$_2$Nd$_{1.8-x}$Y$_{0.2}$Ce$_x$Cu$_2$O$_{10-\delta}$ ($x = 0.7–0.95$) at low temperatures [11]. The MR initially rises to ~2% below the Ru spin ordering temperature, $T_{Ru}$, as observed in other superconducting ruthenocuprates, but increases dramatically on cooling [11, 12].

It is difficult to overestimate the importance or the influence of local structure on the physical properties of a material. The Ru$_2$RCu$_2$O$_8$ (Ru1212) ($R = Y$, Eu, Gd, Nd and Sm) structure is closely related to the YBa$_2$Cu$_3$O$_{7-\delta}$ one, with Y, Ba, and Cu(1) being replaced by R, Sr, and Ru, respectively. Ru1212 contains corner-sharing RuO$_6$ octahedra substituting for the Cu(1)–O chains and has lattice parameters $a = 0.3838(4)$ nm, $c = 1.157(3)$ nm and space group (SG) $P4/mmm$ [13]. The crystal structure
of Ru$_{12}$Sr$_2$R$_{2-x}$Ce$_x$Cu$_2$O$_{10-δ}$ (Ru1222) can be derived from the Ru1212 structure by replacing its single R layer by a R$_2$...Ce$_x$O$_2$ fluoride layer. Metallic, semiconducting and superconducting behavior of Ru1222 can be achieved within the same mother structure through various changes in the R/8 ratio (R = Y, Eu, Nd, Sm and Sm) or oxygen deficiency [14–17]. Both cation substitution and oxygen deficiency can directly change the material’s fine structure and its CuO plane hole doping, thereby impacting its superconductivity [18–20]. The magnetotransport in Ru1222 is also very sensitive to lattice distortions. For Ru$_{12}$Sr$_{2}$Ce$_x$Cu$_2$O$_{10-δ}$ (R = Nd, Sm, Eu, and Gd with Y) where the hole doping level is constant, the high field MR does not correlate with the paramagnetic moment of the R cations. However it shows an unprecedented crossover from negative to positive MR values as ($p_A$), the mean A site (R$_1$)Ce$_{0.9}$ cation radius, decreases [12, 21]. By neutron diffraction (ND), Ru1222 structure was reported to have a superstructure which contains RuO$_6$ octahedra that are rotated [13, 17]. The long-range order superstructure or any impurity evidence of long-range order superstructure or any impurity (figure 1). The volume percentages of Ru$_{12}$Sr$_2$R$_{2-x}$Ce$_x$Cu$_2$O$_{10-δ}$-Ru1222 (δ = 0.90–0.55) samples Ru$_{12}$Sr$_2$Gd$_{1.8}$Y$_0.2$Ce$_x$Cu$_2$O$_{10-δ}$ (x = 0.90–0.55) samples were prepared by repeatedly sintering stoichiometric mixtures of Gd$_2$O$_3$, Y$_2$O$_3$, RuO$_2$, CuO, CeO$_2$ and SrCO$_3$ powders at 1025 °C. Samples were furnace cooled in air after the last heating.

Room temperature x-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer with twin Gobel mirrors using Cu K$_{α_1}$ radiation. Data were collected over the range 5° < 2θ < 100°, with a step size of 0.02° for the remaining samples. Neutron diffraction patterns were recorded at a wavelength of 2.41 Å and temperature of 200 K on the D20 equipment at ILL, Grenoble. A 1 g sample was inserted into a 7 mm vanadium can and neutron diffraction patterns were recorded with an acquisition time of 6 h.

The oxygen content of the samples was determined by thermogravimetric analysis in a 5% H$_2$/N$_2$ atmosphere using a Stanton Redcroft 780 thermal analyzer. Data were recorded at a rate of 3 °C min$^{-1}$ between temperatures of 20 and 800 °C. The samples decomposed to a mixture of Cu, Ru, SrO, CeO$_2$, Gd$_2$O$_3$ and Y$_2$O$_3$ in two steps between 300 and 750 °C, enabling δ to be determined from the mass loss. Magnetoresistance measurements were performed on sintered polycrystalline bars (approximate dimensions 4 × 4 × 12 mm$^3$) between 4 and 290 K using a standard four-probe ac technique on a Quantum Design Physical Property Measurement System in magnetic fields up to 7 T.

For electron microscopy, the bulk samples were crushed and deposited on holey carbon grids. Structural and chemical composition charaterizations were performed using a Philips CM20 with an Oxford Pentafet energy-dispersive x-ray spectrometer (EDX) system. A JEOL 4000EX with a point resolution of 0.17 nm was used for high resolution TEM (HRTEM). The HRTEM image simulations were performed using the Mactempas software.

### 3. Results

The XRD patterns of the Ru$_{12}$Sr$_2$Gd$_{1.8}$Y$_0.2$Ce$_x$Cu$_2$O$_{10-δ}$ (x = 0.90–0.55, y = 0 or 0.2) could be mainly indexed on a tetragonal I4/mmm symmetry SG as previously reported for Ru1222 [14]. All Gd$_{1.8}$Y$_0.2$Ce$_x$Ru1222 (x = 0.90–0.70) samples appear single phase but in the Gd$_{1.8}$Y$_0.2$Ce$_x$Ru1222 (x = 0.65–0.55) samples Ru1212 structure is clearly present (figure 1). The volume percentages of Ru1212 are determined by quantitative phase analysis using the Rietveld method and the results are summarized in table 1. Neutron diffraction was performed on isotopically enriched Gd$_{1.8}$Y$_0.2$Ce$_x$Ru1222 (x = 0.9). An excellent fit was obtained for the I4/mmm structural model (a = 0.38302(2) nm, c = 2.85076(8) nm) and there was no evidence of long-range order superstructure or any impurity phase (figure 1).

XANES studies have shown that the Ru valence remains at 4.95(5) as x increases from 0.5 to 1.0 in Gd$_{2-x}$Ce$_x$–Ru1222 [20]. It can therefore be deduced that Ru remains in

### 2. Experimental data

Ru$_{12}$Sr$_2$Gd$_{1.8}$Ce$_x$Cu$_2$O$_{10-δ}$ was prepared by solid state reaction of the stoichiometric oxides Gd$_2$O$_3$, CeO$_2$, SrCO$_3$, RuO$_2$ and CuO. These were ground, die-pressed into pellets and preheated for 24 h at 1000 °C. The sample was regrounded, repelleted and sintered for 24 h in air at 1064 °C and then furnace cooled to ambient temperature. This step was repeated and the sample was then annealed for 72 h at 1060 °C under flowing oxygen and finally furnace cooled. More details are available in [17]. Ru$_{12}$Sr$_2$Gd$_{1.8}$Y$_0.2$Ce$_x$Cu$_2$O$_{10-δ}$ (x = 0.90–0.55) samples were prepared by repeatedly sintering stoichiometric mixtures of Gd$_2$O$_3$, Y$_2$O$_3$, RuO$_2$, CuO, CeO$_2$ and SrCO$_3$ powders at 1025 °C. Samples were furnace cooled in air after the last heating.
Table 1. The oxygen deficiency (δ), superconducting temperature $T_c$ and percentage Ru1212 impurity of each RuSr$_2$Gd$_{1-x-y}$Y$_{0.5}$Ce$_x$Cu$_2$O$_{10-δ}$ $(x = 0.90–0.55)$. The Cu hole doping (p) is calculated by balancing the positive and negative charges in the compound.

<table>
<thead>
<tr>
<th>Ce concentration (x)</th>
<th>Cu hole doping (p)</th>
<th>O deficiency (δ)</th>
<th>$T_c$ (onset) (K)</th>
<th>$T_c$ (0) (K)</th>
<th>Volume % Ru1212 impurity</th>
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<tr>
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<tr>
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<tr>
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<tr>
<td>0.60</td>
<td>0.066</td>
<td>0.134(2)</td>
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<tr>
<td>0.55</td>
<td>0.069</td>
<td>0.156(2)</td>
<td>21</td>
<td>—</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 1. Rietveld refinement fit to the 200 K D20 neutron diffraction pattern of RuSr$_2$Gd$_{1-x-y}$Y$_{0.5}$Ce$_x$Cu$_2$O$_{10-δ}$ $(x = 0.9)$. The inset shows selected x-ray diffraction data for RuSr$_2$Gd$_{1-x}$Ce$_{0.6}$Cu$_2$O$_{10-δ}$ and RuSr$_2$Gd$_{1-x}$Y$_{0.5}$Ce$_x$Cu$_2$O$_{10}$ $(x = 0.9)$. The difference on top of the (110) structural peak shows evidence of the Ru1212 impurity in RuSr$_2$Gd$_{1-x}$Ce$_{0.6}$Cu$_2$O$_{10-δ}$.

The oxygen deficiency (δ), superconducting temperature $T_c$ and percentage Ru1212 impurity of each RuSr$_2$Gd$_{1-x-y}$Y$_{0.5}$Ce$_x$Cu$_2$O$_{10-δ}$ $(x = 0.90–0.55)$. The Cu hole doping (p) is calculated by balancing the positive and negative charges in the compound.

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Figure 2. (a) Superconducting transitions for RuSr$_2$Gd$_{1-x-y}$Y$_{0.5}$Ce$_x$Cu$_2$O$_{10}$ $(x = 0.85–0.55)$. (b) Variation of the onset superconducting transition and concentration of Ru1212 impurity with hole doping concentration (p).

Magnetoresistance measurements show that the $x = 0.9$ ($p = 0.030$) sample is semiconducting down to 4 K and there is no evidence of superconductivity at low temperature. A positive magnetoresistance is observed at low temperature (MR7T(5 K) = 11%) as previously reported [12]. Superconducting transitions are observed for Gd$_{1.4}$Ce$_{0.6}$Ru1222 ($T_c$ (onset) = 26 K) and Gd$_{1.8-x}$Y$_{0.2}$Ce$_x$Ru1222 ($x = 0.85–0.55$) (table 1, figure 2). As $x$ decreases from 0.85 to 0.70, the onset superconducting transition temperature increases from 19.4 to 28.0 K, and the Cu hole doping ($p$) increases from 0.041 to 0.06 as well (table 1, figure 2). However as the Ce concentration decreases further with a concomitant increase in $p$, $T_c$ starts to unexpectedly decrease. A small portion of Ru1212 impurity is present at the same time. The Ru1212 could be the reason for the decrease in $T_c$, depending on how it locally grows with Ru1222. TEM has been used to investigate the local structure and to analyze the chemical composition at a nanolevel of the following two compounds: Gd$_{1.4}$Ce$_{0.6}$Ru1222 ($p = 0.066$) and Gd$_{1.8-x}$Y$_{0.2}$Ce$_x$–Ru1222 ($x = 0.9$, $p = 0.030$), which have very different hole doping concentrations and superconductivities.

EDX analysis over a large number of crystals of Gd$_{1.4}$Ce$_{0.6}$–Ru1222 shows that the average elemental composition Ru: Sr: Gd: Ce is 1.0:1.85(1):1.35(2):0.58(9). The
composition of the elements was normalized with respect to Ru. The result is close to the expected value and proves that the material is fairly homogeneous. Figure 3 shows the ED patterns of Gd$_{1.4}$Ce$_{0.6}$–Ru1222 along the most informative zone axes: [001]*, [100]*, [110]* and [310]*. All main reflections can be indexed in a tetragonal structure with SG I$4/mmm$ and unit cell parameters $a = 0.384(4)$ nm and $c = 2.87(4)$ nm. In the [001]* pattern (figure 3(a)), the extra spots $h00$ ($h + k = 2n + 1$) (marked by black arrowheads) are forbidden for the SG I$4/mmm$ and their relative intensity varies from pattern to pattern. They may come from the Ru1222 superstructure or from the Ru1212 010 reflection spot. More extra reflections are observed at the location $\frac{1}{2}(h \pm k0)$ ($h$ integer) indicated by black triangles and $\frac{1}{2}(h \pm k0)$ ($h, k$ integer and $h \neq k$) indicated by a white arrowhead. In most cases, $\frac{1}{2}(110)$ and $\frac{1}{2}(110)$ have a similar intensity but in very few cases only one set is present. Since both of them have no relation to the presence of the $h00$ $(h + k = 2n + 1)$ extra spots, the origin of these families is different.

In order to investigate the origin of the extra spots such as 010, $\frac{1}{2}(1 \pm 10)$ and $\frac{1}{2}(130)$, diffraction patterns were taken along different zone axes: [100]* (figure 3(b)), [110]* (figure 3(c)) and [310]* (figure 3(d)). In the [100]* pattern, the absence of the 010 extra spots supports the assumption that these spots are not related to the Ru1222 structure but to the Ru1212 impurity structure. Very weak stripes are regularly observed between the basic spots 0kl and 0k(l + 2). This is most probably related to the presence of random stacking faults along the $c$-axis. Furthermore, weak periodic satellite reflections are also found in this pattern (figure 3(b)). These extra spots correspond to an ordered planar periodicity of 4.8 nm in real space. In the [110]* ED pattern (figure 3(c)), there is no extra spot at $\frac{1}{2}(110)$, indicating that the $\frac{1}{2}(110)$ extra spots in the [001]* pattern are induced by double diffraction. In the [310]* ED pattern (figure 3(d)), however, the $\frac{1}{2}(13)$ streaked reflections are always present, suggesting that the $\frac{1}{2}(130)$ extra reflections are from Ru1222’s superstructure. It also suggests that the stacking faults are nearly randomly distributed along the $c$-axis in most cases [26]. These phenomena have been observed by Yokosawa et al [24] but are found to be absent by Asthana et al [23].

Diffraction patterns of Gd$_{1.8}$Ce$_{0.2}$–Ru1222 ($x = 0.9$) (figure 4) are recorded along the same zone axes as for Gd$_{1.4}$Ce$_{0.6}$–Ru1222 (figure 3). They reveal that this sample has the same basic I$4/mmm$ structure as Gd$_{1.4}$Ce$_{0.6}$–Ru1222 with lattice parameters $a = 0.384(7)$ nm and $c = 2.85(5)$ nm. The difference between both samples lies in the presence of the extra reflections. First, the relative intensities of the extra 010 spots in the [001]* ED pattern are almost absent compared with those of Gd$_{1.4}$Ce$_{0.6}$–Ru1222. This supports the idea that the relatively strong 010 spots in the Gd$_{1.4}$Ce$_{0.6}$–Ru1222 [001]* ED pattern are from some thin Ru1212 impurity; this will be further demonstrated later. Second, the intensities of the extra spots $\frac{1}{2}(130)$ and $\frac{1}{2}(130)$ are quite similar to those of Gd$_{1.4}$Ce$_{0.6}$–Ru1222 (figure 3(a)). However, for Gd$_{1.8}$Ce$_{0.2}$–Ru1222 ($x = 0.9$), the first ones are quite clear (indicated by white squares in figure 4(a)) while the latter are completely absent. This implies that the symmetry of the superlattice is no longer fourfold and the two types of reflections are twin related in different parts of

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**Figure 3.** ED patterns of RuSr$_2$Gd$_{1.4}$Ce$_{0.6}$Cu$_2$O$_{10-x}$ along the informative zone axes: (a) [001]*, (b) [100]*, (c) [110]* and (d) [310]*. The white long arrows with extra spots at their middle in (a) denote the directions where superstructure reflections are present. The inset in (b) is an enlargement of the rectangular region between two basic reflections.

**Figure 4.** ED patterns of RuSr$_2$Gd$_{1.8}$Ce$_{0.2}$Cu$_2$O$_{10-x}$ ($x = 0.9$) along the same zone axes as RuSr$_2$Gd$_{1.4}$Ce$_{0.6}$Cu$_2$O$_{10-x}$. In (a), the extra spots denoted by white squares are related to the crystal symmetry, while the other extra spots are induced by double diffraction. The white line in (a) and (d) indicates the same [130]* direction running through the superlattice spot $\frac{1}{2}(130)$. [Supplementary Material Files]
RuSr2Gd1.9(1):1.4(1):0.67(8), while the ideal chemical composition should be RuSr2GdCu2O8. The amount of Gd is around 1 and almost no Ce is present. Its chemical composition is RuSr2GdCu2O8.

HRTEM is applied to investigate the interface between Ru1212 and Ru1222 (figure 7). HRTEM image simulations prove that the lower part has the Ru1222 structure while the upper part has the Ru1212 structure. However, since both Ru1222 and Ru1212 have the same \((\text{CuO}_2)\)SrO(\(\text{RuO}_2\))SrO(\(\text{CuO}_2\)) atomic blocks at the interface, the interface is very smooth and it is quite hard and also meaningless to locate the exact boundary layer. For the image simulations the boundary layer is assumed to be the middle RuO2 layer. The simulated image (figure 7 inset) of this intergrowth model fits the experimental image. The cation layers are indicated on the image. It shows that the Ru1212 impurity always grows epitaxially with the Ru1222 structure as thin lamellas along the \(c\)-axis. More precisely, the Ru1212 impurity here should rather be termed Ru1212 defects in the Ru1222 structure.

4. Discussion

As we have shown in the [001]* ED patterns of Ru1222 (figures 3(a) and 4(a)), the presence of \(1\over{130}\) extra spots is not related to the presence of \(1\over{130}\) reflections. This implies that they have different origins and two different superstructures are involved. Figure 8(a) is a schematic representation of the [001]* ED pattern with basic spots indicated by black discs and superlattice spots by open circles. The pattern can be considered as the superposition of two 90° rotated patterns (figures 8(b) and (c)).

Figure 5. Four slightly different [310]* patterns of RuSr\(_{1.8}\)Gd1.8Y0.2Ce0.6Cu2O10 (\(x = 0.9\)). In (a) a complete diffuse streak is observed, in (b) clear spots are observed at the \(\overline{1}\)((13)) position with \(l = 4n\) (\(n\) is integer), in (c) clear maxima are observed for \(l = 4n + 2\) (\(n\) is integer), while in (d) maxima are observed for \(l = 2n\). At the top of each image an enlargement of the \(\overline{1}\)((13)) row is shown.

Figure 6. [100]* ED patterns ((a), (b)) and bright field image (c) of RuSr\(_{1.4}\)Ce0.6Cu2O10. (a) shows a superposition of the [100]* ED patterns of Ru1212 and Ru1222. (b) is a [100]* pattern of a clean Ru1212 region. (c) shows two different periodicities on the left and right sides of the interface indicated by white arrows. The inset is an enlargement of the region marked by the rectangle at the interface. EDX data have been collected from the regions 1, 2 and 3.
An orthorhombic structure with lattice parameters \( a_s \simeq \sqrt{2}a \) and \( b_s \simeq \sqrt{2}a \) (suffix \( s \) indicates the superstructure and \( a_s > b_s \)) indeed allows us to index the patterns in figure 8. The new unit cell is orthorhombic and rotated 45° with respect to the basic one (figure 8(b)). Using this superlattice unit cell, the ED patterns in figures 3 and 4 can be re-indexed and new extinction conditions can be formulated (table 2). Yokosawa et al suggested a model of superlattice SG \( Aeam \) (standard symbol \( C_mce \)) with \((\vec{a}_s, \vec{b}_s, \vec{c}_s) = (\vec{a} + \vec{b}, \vec{a} − \vec{b}, \vec{c})\) [24]. However, since the \( 1/2(130) \) \((l = 4n, n \text{ integer})\) reflections are observed in the \([310]^*\) pattern (figure 4(d)), the \( 1/2(130) \) reflection \((120_s)\) in the \([001]^*\) ED pattern (figures 3(a) and 4(a)) should not be attributed to double diffraction. They cannot be indexed in \( Cmce \) because of contradicting its reflection condition \((hk0: h,k = 2n)\) [34]. Nevertheless, we found that the derived reflection conditions are compatible with the orthorhombic SG \( Aba2 \) (No. 41) [34] (table 2). In fact, if we switch the \( a \) and \( c \) axes of \( Cmce \), the symmetry difference between \( Cmce \) and \( Aba2 \) is that the former has \( mmm \) plane symmetry whereas the latter has \( mmm \) plane symmetry. Unfortunately they cannot be distinguished from SAED. In general, since the \( c \) axis of the original lattice is kept for the superlattice and the reflection condition suits the experimental data more, it is more reasonable to adopt SG \( Aba2 \) rather than \( Cmce \) for the superlattice structure.

This new superstructure allows us to interpret the variety of superlattice reflections appearing in the \([310]^*\) pattern (figure 5). In the basic tetragonal reciprocal lattice \([310]^*\) and \([130]^*\) zones are equivalent. However, \([310]^*\) and \([130]^*\) are no longer equivalent with the lower symmetry superstructure (figures 8(d) and (e)). The SG \( Aba2 \) allows for the super-reflections \( 1/2(130) \), but it forbids the \( 1/2(130) \) (figure 8(c)). The arrow in the [130] direction will cross the superlattice spot \( 1/2(130) \) (figure 8(c)) and therefore it is also observed in the \([310]^*\) pattern (figure 8(d)). The extra spot \( 1/2(310) \), however, is extinct in figure 8(c) and hence it is not observed in the \([130]^*\) pattern (figure 8(e)).

This superstructure originates from the basic one due to an ordering of the RuO₆ octahedra rotated along the \(c\)-axis [22], in order to compensate the different bond lengths of Cu–O in the CuO₂ plane and Ru–O in the RuO₂ plane [17, 24] (figure 9). In the \([001]\) plane, the RuO₆ octahedra rotate along the \(c\)-axis, alternating right (R) and left (L). A superlattice structure

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**Table 2. Extinction conditions of the superlattice structure derived from experimental results.** It only agrees with the extinction condition of the orthorhombic SG \( Aba2 \) (No. 41). Note that for the tetragonal structure with SG I\(4/mmm\), the ED patterns of \([\pm 1 \pm 30]^*\) and \([\pm 3 \pm 10]^*\) are identical.

<table>
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<tr>
<th>Basic structure zone axis (tetragonal)</th>
<th>Superlattice zone axis (orthorhombic)</th>
<th>Present superlattice spots</th>
<th>Extinction condition</th>
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<td>[001]⁺</td>
<td>(hk0)</td>
<td>(k) = (2n + 1)</td>
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<tr>
<td>[001]⁺</td>
<td>[001]⁺</td>
<td>(ho0)</td>
<td>(h) = (2n + 1)</td>
</tr>
<tr>
<td>[110]⁺</td>
<td>[110]⁺</td>
<td>(0k0)</td>
<td>(k) = (2n + 1)</td>
</tr>
<tr>
<td>[110]⁺</td>
<td>[110]⁺</td>
<td>(0kl)</td>
<td>(k) = (2n + 1)</td>
</tr>
<tr>
<td>[110]⁺</td>
<td>[110]⁺</td>
<td>(hk0)</td>
<td>(h) = (2n + 1)</td>
</tr>
<tr>
<td>[310]⁺</td>
<td>[210]⁺</td>
<td>(hk\tilde{l}) ((h = k))</td>
<td>(k) + (l) = (2n + 1)</td>
</tr>
</tbody>
</table>

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**Figure 7.** [100] HRTEM image of the intergrowth of Ru1222 and Ru1212 structures in RuSr₂Gd₁₋₅Ce₀₆₋₅Cu₂O₁₀₋₄. The interface is indicated by black arrows. The unit cells with height 1.1 nm and 2.86 nm are outlined respectively. The simulated image at the interface is inserted and the cation layers are marked.

**Figure 8.** Schematic diagrams of the [001]⁺ ED pattern of the Ru1222 structure. Solid and open discs are the basic and superlattice reflections, respectively. The pattern in (a) can be interpreted as a superposition of the patterns (b) and (c). (d) and (e) are the ED patterns along the [310]⁺ and [130]⁺ directions respectively with different superlattice reflection spots at \(l\) = \(2n\) and \(2n + 1\).
squares represent left rotated RuO$_6$ and darker ones represent right rotated RuO$_6$. The basic and superlattice unit cell are denoted by a (figure 9(b)). NDP proves that the RuO$_6$ octahedra rotate 13.4$^\circ$ compared to the basic Ru$_{12}22$ cell (dashed line square) superstructure induced by a rotation of the RuO$_6$ octahedra along the dashed line and a solid line respectively.

I basic tetragonal lattice (occasionally we observed a very different intensity between basic reflections do not show the spot splitting. However, around the small Ru$_{12}22$ superstructure [13, 24, 26–28].

Such a 6$^\circ$ tilt theoretically makes the $b_s$ parameter 0.5% smaller than the $a_s$ parameter and therefore deforms the basic tetragonal lattice (14/mmm) into an orthorhombic one (Aba2) (figure 9(c)). A tilt along $a_s$ or $b_s$ is equivalent but they are rotated 90$^\circ$ with respect to each other. Mostly both tilting modes occur on a small scale and they are arranged almost randomly. The NDP analysis also chooses a model of 6$^\circ$ random tilt of RuO$_6$ octahedra to best fit the experimental spectrum [22]. We usually see the superposition of both deformations on the ED patterns (figure 3(a)). Because the difference between $a_s$ and $b_s$ is very small, their basic reflections do not show the spot splitting. However, occasionally we observed a very different intensity between the $\frac{1}{2}(110)$ and the $\frac{1}{4}(110)$ reflections on the same ED pattern (figure 4(a)). It indicates that one tilt dominates in these areas. The alternation of the RuO$_6$ octahedra tilt around either $a_s$ or $b_s$ creates superstructure disordering along the c direction. These different tilt combinations are at the origin of the various extra spot arrangements at $\frac{1}{2}(13\bar{1})$ in the [310]$^*$ pattern (figures 5, 8(d) and (e)). More details can be found in [26].

Asthana et al [23] reported that no extra spots are found in the [001]$^*$, [100]$^*$ and [310]$^*$ ED patterns of RuSr$_2$Eu$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10−δ}$ and therefore no superstructure is formed. The authors explain that their material is oxygen deficient and hence no rotation of the RuO$_6$ octahedra takes place. Their sample was furnace cooled to ambient temperature, while our Gd$_{1.4}$Ce$_{0.6}$–Ru$_{12}22$ sample is annealed in floating oxygen for 72 h to compensate the oxygen deficiency to some extent. Although our samples still have oxygen vacancies (table 1), the annealing seems to be sufficient to suppress the oxygen deficiency [29] and to form a superstructure.

It is well known that the superconductivity and crystal symmetry of YBa$_2$Cu$_3$O$_{7−δ}$ vary with its oxygen stoichiometry [30]. As $δ$ decreases its symmetry transforms from tetragonal to orthorhombic and superconductivity arises with increasing $T_c$ [31, 32]. In the Ru$_{12}22$ compounds, the oxygen deficiency could affect the symmetry and superconductivity in a similar way. When the oxygen deficiency decreases, the Ru$_{12}22$ tetragonal symmetry reduces to orthorhombic because of the RuO$_6$ rotation and tilt. Simultaneously, superconductivity arises with increasing $T_c$. Felner et al reported that with annealing under higher oxygen pressures up to 150 atm, the $T_c$ of RuSr$_2$Eu$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10−δ}$ increases monotonically from 32 to 49 K [33]. In our samples, Gd$_{1.4}$Ce$_{0.6}$–Ru$_{12}22$ is superconducting with a clear orthorhombic deformation (table 1, figure 1), whereas Gd$_{1.8}$–Y$_0.2$Ce$_{0.8}$–Ru$_{12}22$ ($x = 0.9$) is not superconducting and its superstructure distortion is much less obvious (table 1, figure 2). Unfortunately, no further data correlating superconductivity and superstructure formation can be found for exactly the same Ru$_{12}22$ compounds in the literature, which also attests the importance of such work.

The presence of the thin Ru$_{12}22$ lamellas deserves special notice in the Ru$_{12}22$ compound (figures 6 and 7). Although RuSr$_2$RCu$_2$O$_8$ itself is superconducting, the lamellas which intergrow with Ru$_{12}22$ may deform both structures because of their slight lattice mismatch and change the hole doping in the CuO planes. Therefore they could seriously decrease the $T_c$ of this compound (table 1). So their presence and impact could be as important as the Ce substitution to study the Ru$_{12}22$ superconductivity. Why does the intergrowth of Ru$_{12}12$ superconductivity arising with increasing $T_c$? Combining all information, we may conclude the following: under the present synthesis conditions, the samples need more Gd (Gd/Ru > 1) to have a considerable probability to form Ru$_{12}12$. When the Gd/Ru ratio is above 1.15 (table 1), which means $x < 0.65$, XRD shows the presence of Ru$_{12}12$ lamellas. The higher the Gd/Ru ratio, the more Ru$_{12}12$ lamellas are found. When the Gd/Ru ratio is below 1.15, the probability of

Figure 9. Schematic diagrams of the Ru$_{12}22$ superstructure. The RuO$_6$ octahedra are projected as square blocks and CuO$_2$ pyramids as triangular blocks. (a) The basic undistorted lattice. (b) The superstructure induced by a rotation of the RuO$_6$ octahedra along the c-axis. (c) Superstructure resulting from a rotation of the RuO$_6$ octahedra along the c-axis and a tilting along the $a_s$-axis. The lighter squares represent left rotated RuO$_6$ and darker ones represent right rotated RuO$_6$. The basic and superlattice unit cell are denoted by a dashed line and a solid line respectively. With a $\sqrt{2}$ times bigger super-unit-cell (solid line square) is created compared to the basic Ru$_{12}22$ cell (dashed line square) (figure 9(b)).
Ru1212 lamella formation is highly suppressed. The presence of both phases in RuSr2Eu1.6Ce0.4Cu2O10−δ, where Ru/Ru = 1.6, also supports this explanation [23].

5. Conclusions

The local structure and the corresponding physical properties of RuSr2Gd1.4Ce0.6Cu2O10−δ and RuSr2Gd1.8−xY0.2Ce1−xCu2O10 (x = 0.90–0.55) have been investigated. The rotation and tilt of the RuO6 octahedra of Ru1222 is confirmed by TEM. The resulting superstructure is proved to have an orthorhombic symmetry with space group Aba2 and lattice parameters \( a_s \approx \sqrt{2}a, b_s \approx \sqrt{2}a \) and \( c_s = c \). This structure distortion is proposed to be associated with the superconducting properties of these compounds. The critical superconducting temperature of RuSr2Gd1.8−xY0.2Ce1−xCu2O10 (x = 0.85–0.55) increases with decreasing x until Ru1212 impurities are formed at x = 0.65. Ru1212 lamellas are observed to intergrow epitaxially with RuSr2Gd1.8−xY0.2Ce1−xCu2O10 (x = 0.65–0.55) along the c-axis in RuSr2Gd1.4Ce0.6Cu2O10−δ.

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