Studies of microstructure and ruthenium valence in the ruthenocuprates Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl and (Ru, $M$)Sr$_2$GdCu$_2$O$_8$ ($M$ = Sn, Nb)

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Abstract

Ruthenocuprate microstructures and Ru valences have been studied. Electron microscopy reveals short-range order of the RuO$_6$ octahedra rotations into a $\sqrt{2}a \times \sqrt{2}a \times c$ supercell in Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl. However, reanalysis of neutron diffraction data gives no significant difference between the populations of the rotation states, showing that the coherence length is very short (< 100 Å). The Ru valence estimated from the XANES spectrum of Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl is $\sim$ 5, in keeping with the physical properties of this material which show that there is essentially no Ru–Cu charge transfer. The Ru valence in doped Ru$_{1-x}M_x$Sr$_2$GdCu$_2$O$_8$ ($M$ = Sn, Nb) is $\sim$ 4.8 in all samples, verifying a previous rigid band analysis of the charge distribution in these materials.

Keywords: Ruthenocuprate; Superconductivity; Magnetism; HREM; XANES

1. Introduction

Since the discovery of coexisting superconductivity and weak ferromagnetism in the ruthenocuprates, the physical and magnetic properties of the materials RuSr$_2$GdCu$_2$O$_8$ and RE$_{2-x}$Ce$_x$RuSr$_2$Cu$_2$O$_{10-\delta}$ have been studied extensively [1–28]. The superconductivity originates in the CuO$_2$ planes with $T_c = 37$ K for the former material, and the weak ferromagnetism is associated with the ruthenate layers [3–5]. G-type antiferromagnetic order within the RuO$_2$ planes has been observed in neutron scattering experiments on RuSr$_2$GdCu$_2$O$_8$ below $T_M = 134$ K [12]. Variable field neutron diffraction studies of this material showed that the Ru spins cant into a ferromagnetic arrangement upon the application of a magnetic field and at 7 T the Ru spins are fully ferromagnetic. It is thought that the weak ferromagnetism arises via a canting of the Ru spins in RuSr$_2$GdCu$_2$O$_8$. This occurs due to the antisymmetric Dzyaloshinsky–Moriya interaction between neighbouring Ru moments, [29,30] which is non-zero due to the tilts and rotations of the RuO$_6$ octahedra observed in synchrotron X-ray and neutron diffraction studies [9–11]. Recent neutron and synchrotron X-ray powder diffraction studies have shown that rotations and tilts of the RuO$_6$ octahedra also occur in Gd$_{1.3}$Ce$_{0.7}$RuSr$_2$Cu$_2$O$_{10}$ [27,28] and it is thought that a similar magnetic mechanism occurs although there has been no evidence of this from neutron diffraction studies as yet.

A new ruthenocuprate Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl has recently been synthesized; this material is of similar structure to RuSr$_2$GdCu$_2$O$_8$ (Fig. 1(a)) but diamagnetic Pb$_2$Cl layers replace Gd [31,32] (Fig. 1(b)). Field dependent magnetism is observed in the ruthenate layers of Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl; G type antiferromagnetism is observed below $T_M = 117$ K but above $H = 0.5$ T the Ru
spins cant into a ferromagnetic arrangement yielding a saturated Ru moment of 0.5–0.8 μB. Despite the similarity of both crystal and magnetic structures to RuSr2GdCu2O8, Pb2RuSr2Cu2O8Cl is not superconducting and it is thought that the RuO2 planes contain Ru5+ with little or no electron doping to the Ru4+ state.

In order to investigate the charge distribution further we have performed X-ray absorption near-edge structure (XANES) spectroscopy to determine the Ru valence state. For comparison, we have also performed XANES studies on two sets of doped samples Ru1−xMxSr2GdCu2O8 (M = Nb, Sn) [33,34] to observe any change in Ru valence upon doping. The microstructures of the ruthenocuprate materials have also been of interest, and we report here high-resolution transmission electron microscopy (HRTEM) studies and selected area electron diffraction (SAED) experiments on Pb2RuSr2Cu2O8Cl.

2. Experimental

The preparation of the Pb2RuSr2Cu2O8Cl sample has been described previously [31,32]. This phase is very difficult to prepare in a pure form, and previous phase analysis has shown that the sample contains 73% (by mass) Pb2RuSr2Cu2O8Cl, 8% CuO and 19% SrRuO3, estimated by Rietveld fitting of time-of-flight powder neutron diffraction data. Preparation of ceramic samples of Ru1−xMxSr2GdCu2O8 (M = Sn: x = 0, 0.025, 0.05, 0.075; M = Nb: x = 0, 0.05, 0.1, 0.15, 0.2) has been reported previously [33,34]. All samples are >98% pure.

HRTEM studies of Pb2RuSr2Cu2O8Cl were performed on a JEOL JEM-2010 electron microscope operating at 200 kV. The lens parameter Cs is 0.5 mm and the corresponding point resolution is about 0.19 nm. The images were recorded by using a Gatan 794 CCD camera with original magnification of 800,000 × and the SAED patterns were recorded on film.

XANES measurements were performed on beamline BL15B at NSRRC in Hsinchu, Taiwan using a Si(111) double-crystal monochromator. The Ru L3-edge X-ray absorption spectra of the polycrystalline samples were recorded in the fluorescence mode using a modified Lytle detector [21,25]. Both the LII and LIII edges of Mo and Pd metallic foils were used to calibrate the photon energies and the AUTOBK code was used for background subtraction [35]. The fitting procedures have been described elsewhere [21,25].

3. Results

3.1. Pb2RuSr2Cu2O8Cl microstructure

A typical HRTEM image of Pb2RuSr2Cu2O8Cl is shown in Fig. 2. This confirms the layer stacking observed in the crystal structure with an 8-layer repeat sequence along the c-axis. However, many extended defects are also observed; the region in Fig. 2 shows a stacking fault (black arrow) and a dislocation defect (white arrow).

All of the main diffraction spots in the SAED pattern of Pb2RuSr2Cu2O8Cl could be indexed by the basic tetragonal cell (P4/mmm, a = 3.87 Å and c = 15.37 Å) as previously observed from neutron diffraction studies.
on the same sample [31,32]. However additional weak (h/2 k/2 0) spots in the [001] zone axis indicate the formation of a $\sqrt{2}a \times \sqrt{2}a \times c$ superstructure (Fig. 3). This superstructure has also been observed in SAED patterns of RuSr$_2$GdCu$_2$O$_8$ [9]. It results from rotations of the RuO$_6$ octahedra around c due to the bond length mismatch between the RuO$_2$ and CuO$_2$ layers. The rotations of the RuO$_6$ octahedra would give rise to a $\sqrt{2}a \times \sqrt{2}a \times c$ superstructure if long-range ordered, however only partial ordering has been observed from HRTEM and neutron diffraction studies of RuSr$_2$GdCu$_2$O$_8$ [9,11].

Rotations and tilts of the RuO$_6$ octahedra were observed in the previous neutron refinement of the Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl [31,32] structure in the basic $P4/mmm$ cell. The neutron refinement has been repeated using the approach reported to model the partial ordering of the RuO$_6$ octahedra in RuSr$_2$GdCu$_2$O$_8$ [11]. The structure is refined in the tetragonal, $P4/mmm$ symmetry, $\sqrt{2}a \times \sqrt{2}a \times c$ super-cell, and a second oxygen site within the RuO$_2$ layer, O(3)$'$, which represents the minority fraction of RuO$_6$ octahedra rotated in the opposite sense, is introduced. Using the GSAS program [36] to fit the principal and impurity phase structures gave an excellent Rietveld fit [37] to the 295K data. The co-ordinates are shown in Table 1. Unconstrained refinement of the fractional occupancies of O(3) and O(3)$'$ gave 0.47(3) and 0.51(3), respectively. This demonstrates that the coherence length for the octahedral rotations is very short (<100 Å) in Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl, and is consistent with the lack of any superstructure peaks in the neutron diffraction data.

### 3.2. Ru valences

Recent X-ray Absorption Near Edge Spectroscopy (XANES) studies on RE$_{2-x}$Ce$_x$Ru$_2$Cu$_2$O$_{10}$ and RuSr$_2$GdCu$_2$O$_8$ have indicated that the average Ru valence state can vary significantly, with values of 4.6 [21] for RuSr$_2$RE$_2$Cu$_2$O$_{10}$ and between 5.0 and 4.95 [25] for RE$_{2-x}$Ce$_x$Ru$_2$Cu$_2$O$_{10}$ being determined. We have used this technique in an attempt to determine the Ru valence of the ruthenocuprates Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl and Ru$_{1-x}$M$_x$Sr$_2$Cu$_2$O$_8$ ($M$ = Nb, Sn). The L$_{III}$-edge XANES spectra of Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl and Ru$_{0.95}$M$_{0.05}$Sr$_2$Cu$_2$O$_8$ ($M$ = Nb, Sn) are shown in Figs. 4(a) and (b), respectively. The reference spectra of Sr$_2$GdRuO$_6$ (Ru$^{5+}$) and Sr$_2$RuO$_4$ (Ru$^{4+}$) are also shown. Ru is in octahedral co-ordination in each of these materials and hence the crystal field of $O_h$ symmetry leads to a splitting of the 4$d$ states into $t_{2g}$ and $e_g$ levels separated by $\Delta (=10$ Dq). The lower energy peak corresponds to a $2p \rightarrow t_{2g}$ transition and the higher

### Table 1

Refined cell parameters, agreement factors and atomic parameters for Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl at 295K in the $P4/mmm$ space group

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$ (Å$^2$)</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>4(f)</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0.3759(2)</td>
<td>0.0067(5)</td>
</tr>
<tr>
<td>Ru</td>
<td>2(a)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1436(2)</td>
<td>0.0053(7)</td>
</tr>
<tr>
<td>Sr</td>
<td>4(f)</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0.1255(3)</td>
<td>0.0092(8)</td>
</tr>
<tr>
<td>Cu</td>
<td>4(e)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.038(4)</td>
<td>0.0008(5)</td>
</tr>
<tr>
<td>O(1)</td>
<td>4(e)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.038(4)</td>
<td>0.0008(5)</td>
</tr>
<tr>
<td>O(2)</td>
<td>8(k)</td>
<td>0.2370(7)</td>
<td>0.2630(7)</td>
<td>0</td>
<td>0.0044(7)</td>
<td>0.47(3)</td>
</tr>
<tr>
<td>O(3)</td>
<td>4(g)</td>
<td>0.1902(7)</td>
<td>0.6902(7)</td>
<td>0</td>
<td>0.012(1)</td>
<td>0.51(3)</td>
</tr>
<tr>
<td>O(3)$'$</td>
<td>4(g)</td>
<td>0.6902(7)</td>
<td>0.1902(7)</td>
<td>0</td>
<td>0.013(1)</td>
<td>0.51(3)</td>
</tr>
<tr>
<td>Cl</td>
<td>2(b)</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.036(1)</td>
<td>1</td>
</tr>
</tbody>
</table>
The average Ru valence in each sample was obtained by fitting a linear combination of the Sr$_2$RuO$_4$ and Sr$_2$GdRuO$_6$ spectra to the XANES spectra of Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl and Ru$_{1-x}$M$_x$Sr$_2$Cu$_2$O$_8$ ($M = \text{Nb}, \text{Sn}$). This method was previously used to determine the Ru valence of RuSr$_2$RECu$_2$O$_8$ and RE$_2$Ce$_x$RuSr$_2$Cu$_2$O$_{10}$ [21,25].

The XANES spectra of Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl (Fig. 4(a)) and Ru$_{1-x}$M$_x$Sr$_2$GdCu$_2$O$_8$ ($M = \text{Nb}, \text{Sn}$) (Fig. 4(b)) are very similar and the average Ru valence estimated by the above method is 4.8 for all the samples. The separation of the two peaks gives the crystal field splitting as $\Delta = 2.2$ eV (18000 cm$^{-1}$) for Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl and $\Delta = 2.4$ eV (19000 cm$^{-1}$) for Ru$_{1-x}$M$_x$Sr$_2$GdCu$_2$O$_8$.

4. Discussion

The microscopy study of Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl demonstrates similar microstructural features to those found in the other (1212 and 2122) ruthenocuprate families. This was first observed in HRTEM images of RuSr$_2$GdCu$_2$O$_8$ that evidenced anti-phase boundaries at which the sense of rotation of the RuO$_6$ octahedra around $c$ is reversed but the rest of the structure is unaffected, dividing the structure into subdomains of 50–200 Å [9]. This was subsequently modelled from neutron diffraction data on an isotopically enriched sample of RuSr$_2$GdCu$_2$O$_8$ using the $P4/mmb$ supercell [11]. For this sample, neutron superstructure peaks were observed and the RuO$_2$-plane majority and minority oxygen site occupancies refined to 0.70(1) and 0.27(1), respectively. However, the analogous refinement of the Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl reported here (Table 1) gives O(3) and O(3') site occupancies that do not differ significantly, although the superstructure is observed by SAED (Fig. 3).

It has been suggested that the fractional population of the two domains in RuSr$_2$GdCu$_2$O$_8$ depends upon the annealing of the sample [9,11]. Upon cooling, domains with a particular sense of rotation nucleate and grow, and a well-annealed sample may approach a single domain in each crystallite although full ordering has not yet been observed. The Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl sample was prepared by firing the ceramic pellet for a relatively short time (10 h) at 700°C followed by quenching, to minimize the formation of secondary phases. This evidently does not allow long-range coherence of the RuO$_6$ rotations to develop, and in comparison to RuSr$_2$GdCu$_2$O$_8$, the domains are evidently small (<100 Å) in extent.

The intrinsic doping of the copper oxide planes that leads to superconductivity in RuSr$_2$GdCu$_2$O$_8$ results from Ru and Cu band overlap, which is represented by the formal oxidation states in the formula Ru$^{5-2p0}$Sr$_2$GdCu$_2^{2+p0}$O$_8$. The intrinsic hole doping $p_0$ is estimated to be 0.08. This was supported by substituting Ru in RuSr$_2$GdCu$_2$O$_8$ with fixed-valent cations Nb$^{5+}$ and Sn$^{4+}$ on the Ru site. The results were analyzed assuming a rigid band structure, i.e. that $p_0$ is fixed, so that the doping effects at the CuO$_2$ planes comes from the difference between the charge on Ru and $M^{2+}$ (= Nb$^{5+}$ or Sn$^{4+}$) according to the formula (Ru$_{1-x}$M$_x$)Sr$_2$GdCu$_2^{2+p0+x(p0+5-q)/2}$O$_8$. Hence, the Ru valence should not change with substitution. The present XANES results (Fig. 4(b)) provide an important corroboration of this, as no shift in the Ru edge is observed within the Ru$_{1-x}$M$_x$Sr$_2$GdCu$_2$O$_8$ solid solutions. This is in stark contrast to XANES results on Ru$_2$(Gd$_{1-x}$Dy$_x$)Cu$_2$O$_8$ and Ru(Sr$_{2-x}$Ba$_x$)GdCu$_2$O$_8$.

![Energy (eV)](Normalized Absorption (arb. units))

Fig. 4. Ru LIII-edge X-ray absorption near edge structure for (a) Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl and (b) RuSr$_2$GdCu$_2$O$_8$, Ru$_{0.95}$Nb$_{0.05}$Sr$_2$GdCu$_2$O$_8$ and Ru$_{0.95}$Sn$_{0.05}$Sr$_2$GdCu$_2$O$_8$. Also shown are spectra for the reference samples Sr$_2$GdRuO$_6$ and Sr$_2$RuO$_4$. 

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**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>O(3)</th>
<th>O(3')</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl</td>
<td>0.70</td>
<td>0.27</td>
</tr>
<tr>
<td>Ru$<em>2$(Gd$</em>{1-x}$Dy$_x$)Cu$_2$O$_8$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru(Sr$_{2-x}$Ba$_x$)GdCu$_2$O$_8$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where the Ru valence was found to decrease with Dy doping and increase with Ba doping [21]. In these materials, the intrinsic hole transfer $p_0$ is changed by the lattice effects resulting from the size of the substituted cation. Dy$^{3+}$ is smaller than Gd$^{3+}$ which tends to decrease the Cu–O distances in the adjacent CuO$_2$ planes, resulting in an increase in $p_0$ and so a decrease in the Ru valence. Replacing Sr$^{2+}$ by the larger Ba$^{2+}$ tends to expand the lattice by reducing the hole concentration in the CuO$_2$ planes, so the Ru valence increases.

The Ru valence of 4.8 in the Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl sample measured by XANES is a weighted average of the values for Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl and the SrRuO$_3$ impurity. The latter material may itself be doped, most probably by Pb$^{4+}$ substituting for Ru$^{4+}$, as evidenced previously [32]. Nevertheless, the Ru valence in this phase will be close to +4, so the average sample valence of 4.8 shows that Ru in Pb$_2$RuSr$_2$Cu$_2$O$_8$Cl is very close to Ru$^{5+}$. This is consistent with the physical properties [32] which showed that there is essentially no Ru–Cu charge transfer in this material.

Acknowledgments

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References