Structure and magnetism of the layered ruthenocuprate $Pb_2RuSr_2Cu_2O_8Cl$

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The crystal structure and magnetism of the layered ruthenocuprate $Pb_2RuSr_2Cu_2O_8Cl$ have been studied. A powder neutron diffraction study reveals that the crystal structure is tetragonal (space group $P4/mmm$, $a = 3.86681(9)$ Å, $c = 15.3699(8)$ Å at 295 K) with disordered rotations and tilts of the RuO_6 octahedra with no structural transitions down to 10 K. A magnetic transition to a canted antiferromagnetic state occurs at $T_M = 117$ K, and the ordered Ru moment is $1.1(1)\mu_B$, at 10 K from Rietveld analysis of neutron data. A spin-flop or metamagnetic transition is observed above a field of 0.5 T, and the saturated ferromagnetic Ru moment is $0.5\mu_B - 0.8\mu_B$. The sample is not superconducting.

The coexistence of weak ferromagnetism and superconductivity has recently been observed in the 1212-type layered ruthenocuprate $RuSr_2GdCu_2O_8$ (Refs. 1–9) and in 1222-type analogs such as $RuSr_2Ce_{0.5}Gd_{1.5}Cu_2O_{10}$.[1] Bulk superconductivity originates in the CuO_2 planes below $T_c < 50$ K, and a magnetic transition ($T_M = 136$ K in $RuSr_2GdCu_2O_8$) results from the ordering of moments in the RuO_2 planes and persists through the onset of superconductivity to the lowest temperature investigated (1.9 K).[3] G-type antiferromagnetic order within the RuO_2 planes has been observed from neutron scattering experiments[6] on $RuSr_2GdCu_2O_8$ with an ordered moment of $1.18(6)\mu_B$, and an upper limit of $0.1\mu_B$ was obtained for the ferromagnetic component. The Ru moments are canted in $RuSr_2GdCu_2O_8$, yielding a small ferromagnetic moment in zero field, due to a Dzyaloshinsky-Moriya interaction between neighboring Ru moments which is nonzero due to the symmetry-breaking tilts and rotations of the RuO_6 octahedra. Upon the application of a magnetic field the Ru spins cant further away from the G-type magnetic structure until at 7 T there is no evidence of antiferromagnetic order.

In this paper, results from the ruthenocuprate $Pb_2RuSr_2Cu_2O_8Cl$ (Fig. 1) will be discussed. This material has a similar structure to $RuSr_2GdCu_2O_8$, but diamagnetic Pb_2Cl layers replace Gd, making the material an attractive candidate for neutron diffraction and magnetic measurements although it is difficult to prepare as a pure phase. The isostructural materials $Pb_2MSr_2Cu_2O_8Cl$ ($M = Nb, Ta, Sb$) have previously been reported;[10–12] they are insulating ($\rho \sim 10^6 \, \Omega$ cm, at 300 K) and are not ferromagnetic.

Samples were prepared by the solid-state reaction of RuO_2, $SrCO_3$, CuO, and PbO and at 550–700 °C. Details of the synthesis will be reported elsewhere. It has proved very difficult to prepare $Pb_2RuSr_2Cu_2O_8Cl$ free of other phases. The sample used here contained 73% (by mass) $Pb_2RuSr_2Cu_2O_8Cl$, 19% ''$SrRuO_3$,'' and 8% CuO; phase proportions were determined by Rietveld fitting of neutron data. Although this sample contains secondary phases, it has enabled the basic physical properties of the ruthenocuprate $Pb_2RuSr_2Cu_2O_8Cl$ to be determined as below.

Neutron powder diffraction data were collected on the General Materials Diffractometer (GEM) at the Rutherford-Appleton laboratory. Neutron diffraction patterns were collected at 295 and 10 K from a 1 g sample in 1 h. The data from the 20, 60, 90, and 169.3° 2θ detector banks were analyzed simultaneously, giving a d space range of 0.42–12 Å, using the GSAS program.[13] The neutron diffraction pattern of the $Pb_2RuSr_2Cu_2O_8Cl$ sample showed it to contain a ''$SrRuO_3$'' perovskite phase and CuO. These secondary phases were included in the refinement and excellent Rietveld fits ($R_{WP} = 2.55\%$ and 2.61% at 295 and 10 K, respectively) were obtained (Fig. 2) with a tetragonal $P4/mmm$ symmetry structural model for $Pb_2RuSr_2Cu_2O_8Cl$ [$a = 3.86681(9)$ Å, $c = 15.3688(7)$ Å at 295 K; $a = 3.85804(8)$ Å, $c = 15.3094(7)$ Å at 10 K]. The atomic
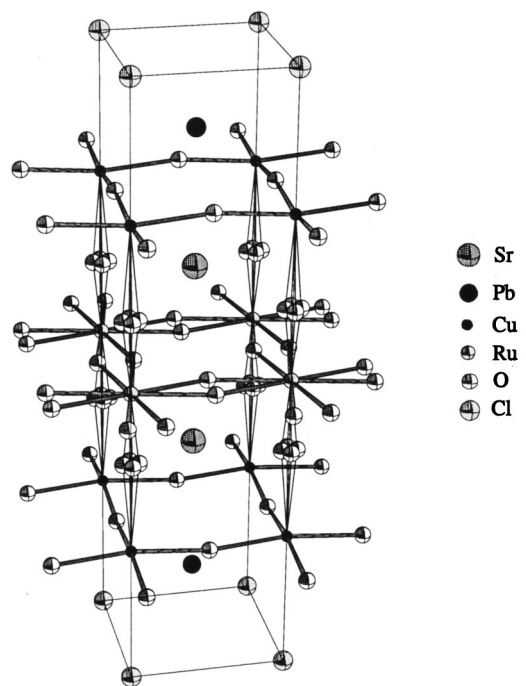

FIG. 1. Crystal structure of $Pb_2RuSr_2Cu_2O_8Cl$ showing the measured tilts and rotations of the RuO_6 octahedra.

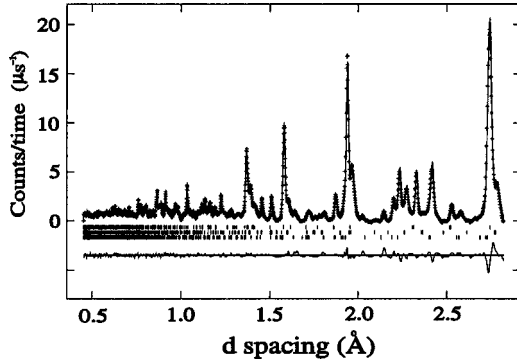FIG. 2. Rietveld fit to the $2\theta=90°$ detector neutron diffraction data for the $Pb_2RuSr_2Cu_2O_8Cl$ sample at 295 K. Lower, middle, and upper reflection markers correspond to $Pb_2RuSr_2Cu_2O_8Cl$, $SrRuO_3$, and CuO, respectively.

displacement factors for all sites in the $Pb_2RuSr_2Cu_2O_8Cl$ structure were refined, and displacive disorder of the oxygen atoms within the RuO_2 planes and those linking the CuO_5 units and RuO_6 octahedra was evidenced by large U values. This disorder was modeled in the same way as that in the 1212 and 1222-type ruthenocuprates.[6] The RuO_6 octahedra are rotated by 13.4° around the z axis and are tilted away from this axis by 7.1° at 295 K. These displacements were also observed at 10 K, showing that they are due to static disorder within the average structure rather than phonon motion. The metal and oxygen site occupancies did not yield any significant deviations from complete filling. The apical Cu-O distance [2.243(5) Å] is longer than that in $RuSrGdCu_2O_8$ [2.184(6) Å] at room temperature. A bond valence sum calculation shows that the hole transfer to the CuO_2 planes is ~0.1 less than that in $RuSr_2GdCu_2O_8$. Doping studies of the latter material have shown that the hole concentration per Cu is 0.08,[14,15] so we conclude that CuO_2 planes in $Pb_2RuSr_2Cu_2O_8Cl$ are essentially undoped.

Antiferromagnetic order was detected in the 10 K diffraction pattern by the observation of the (1/2 1/2 1/2) magnetic diffraction peak which is not observed in the 295 K pattern [Fig. 3(a)]. This was fitted with a G-type antiferromagnetic model, as was used for $RuSr_2GdCu_2O_8$,[6] in which the spins are antiparallel to their neighbors in the ab plane and along c. Assuming the spins lie parallel to the c axis, this model gives a refined Ru moment of $1.1(1)\mu_B$ which is within error of the value $\mu_{Ru}=1.18(6)\mu_B$ in $RuSr_2GdCu_2O_8$.[8] There is no increase in the intensity of any of the (0 0 l) Bragg peaks between 295 and 10 K which would be expected from a ferromagnetic ordering in the xy plane. The temperature dependence of the (1/2 1/2 1/2) intensity [Fig. 3(b)] shows the magnetic ordering transition in $Pb_2RuSr_2Cu_2O_8Cl$ at 117 K.

Variable-field neutron diffraction measurements were recorded up to 3 T at 10 K using an Oxford Instruments 7.5-T cryomagnet. At fields higher than 0.5 T, the intensity of the (1/2 1/2 1/2) magnetic peak decreases while an increase of the (0 0 3) peak intensity is observed corresponding to the induced ferromagnetism in the xy plane [Fig. 4(a)]. There is no significant (1/2 1/2 1/2) intensity remaining at 1.1 T [Fig. 4(b)]. Returning to zero field, the (1/2 1/2 1/2) peak recovers its original intensity, indicating that the effect of the field is

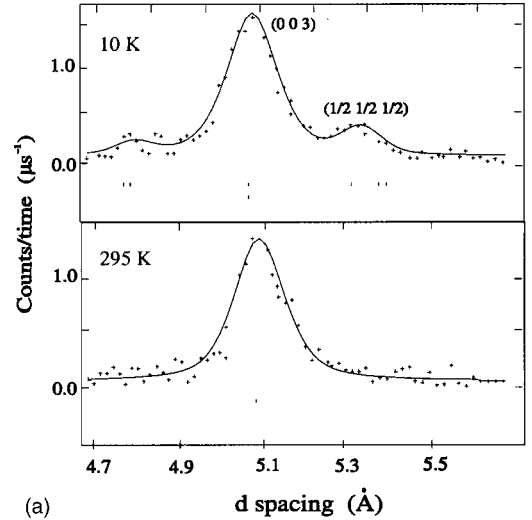FIG. 3. (a) Part of the diffraction pattern of the $Pb_2RuSr_2Cu_2O_8Cl$ sample showing the Rietveld fits to the nuclear (0 0 3) and the antiferromagnetic (1/2 1/2 1/2) Bragg peaks at 10 and 295 K. (b) shows the temperature variation of the (1/2 1/2 1/2) peak intensity.

reversible. Evidence of such a spin-flop or metamagnetic transition has been reported in $RuSr_2GdCu_2O_8$ at 0.4 T (Ref. 6) and $RuSr_2YCu_2O_8$ (Ref. 16). The similarity of the variable-field neutron diffraction data for $Pb_2RuSr_2Cu_2O_8Cl$ to those of the 1212 phases suggests that this field-dependent magnetic order is common to the ruthenocuprate structures, but more detailed neutron diffraction experiments on a phase pure sample of $Pb_2RuSr_2Cu_2O_8Cl$ will be necessary in order to confirm this.

Magnetizations were measured between 10 and 300 K on a Quantum Design superconducting quantum interference device (SQUID) magnetometer in an applied field of 0.1 T after zero-field and field cooling. A ferromagnetic transition at a Curie temperature of $T_M=117(1)$ K is evidenced from the rise in magnetism and the divergence of the field-cooled and zero-field-cooled magnetizations (Fig. 5). This coincides with the appearance of the (1/2 1/2 1/2) neutron peak that characterises long-range antiferromagnetic order [Fig. 3(b)], showing that the magnetic order in fields $0 \leq H < 0.5$ T has a mixed ferromagnetic-antiferromagnetic character as expected for a canted antiferromagnet (weak ferromagnet). No sepa-
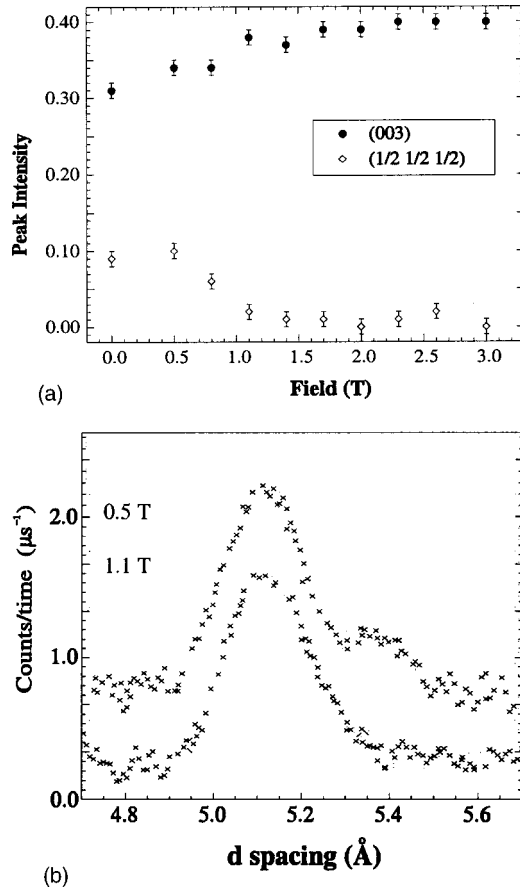
(a)

(b)

FIG. 4. (a) Field dependence of the intensity of the magnetic (1/2 1/2 1/2) and nuclear (0 0 3) neutron diffraction peaks at 10 K. The diffraction data at fields of 0.5 and 1.1 T are shown in (b); the former data are offset by 0.5 counts μs^{-1}.

FIG. 5. Variable-temperature magnetization data (zero-field and field cooled) for the $Pb_2RuSr_2Cu_2O_8Cl$ sample. The inset shows the hysteresis loop for the $Pb_2RuSr_2Cu_2O_8Cl$ sample at 10 K.

rate ferromagnetic transition is observed for the ''SrRuO$_3$'' secondary phase. This suggests that nonstoichiometry or chemical substitutions have either suppressed the ferromagnetism found in pure SrRuO$_3$ ($T_M = 165$ K) or reduced the Curie temperature until it is coincident with that of the main $Pb_2RuSr_2Cu_2O_8Cl$ phase. The former scenario seems most probable as there is no observable ferromagnetic contribution to the ''SrRuO$_3$'' peaks in the 10-K neutron profile. The magnetic properties of SrRuO$_3$ are known to be sensitive to substitutions at the Sr (Ref. 17) or Ru sites [e.g., in $SrRu_{1-x}Pb_xO_3$ (Ref. 18)] and to the synthesis conditions,[19] so the present ''SrRuO$_3$'' phase is likely to be a complex $(Sr,Pb)(Ru,Pb,Cu)O_{3\pm x}$ composition. This is corroborated by the difference between the lattice parameters of SrRuO$_3$ (Ref. 20) [$a = 5.5328(1)$ Å, $b = 7.8471(1)$ Å, $c = 5.5693(1)$ Å] and those of the ''SrRuO$_3$'' phase derived from our Rietveld refinement [$a = 5.5589(1)$ Å, $b = 7.8250(1)$ Å, $c = 5.5646(1)$ Å].

Magnetic hysteresis loops recorded at 10 K with the field swept between ± 5 T confirm the ferromagnetic order and yield a moment of $0.8(1)\mu_B$ per Ru atom in the sample; a typical loop is displayed in the inset of Fig. 5. The maximum possible contribution of the 19% ''SrRuO$_3$'' secondary phase is ~ 0.3 μ_B per Ru [if it were stoichiometric SrRuO$_3$
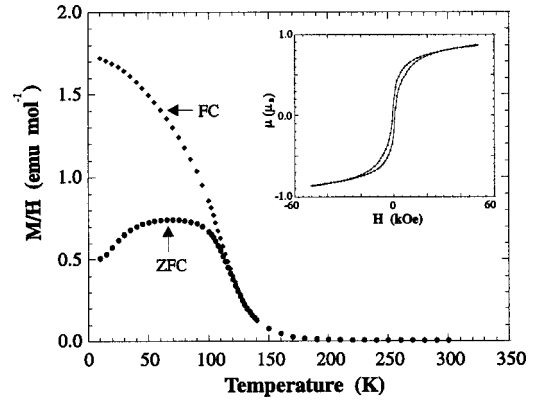
which has $\mu_{Ru} = 1.4$ μ_B at 5 T (Ref. 18)]. Hence we conclude that the principal ferromagnetic phase at high fields is $Pb_2RuSr_2Cu_2O_8Cl$ for which the saturated Ru moment of $0.5\mu_B - 0.8\mu_B$ is comparable to the value of $1.09\mu_B$ for $RuSr_2GdCu_2O_8$.[14,15] The narrowing of the hysteresis loop for $Pb_2Sr_2RuCu_2O_8Cl$ at low fields is consistent with the transition from weak ferromagnetism to full ferromagnetism above 0.5 T. The Ru magnetism in $Pb_2RuSr_2Cu_2O_8Cl$ is thus similar to that of the ruthenocuprates $RuSr_2GdCu_2O_8$ (Ref. 6) and $RuSr_2Ce_{0.5}Gd_{1.5}Cu_2O_{10}$ (Ref. 1).

The resistivity of a sintered polycrystalline bar was measured between 10 and 300 K using the standard four-probe ac technique. Resistivity measurements show that the sample is semiconducting with a room-temperature resistivity of 160 Ω cm. There is no evidence for a superconducting transition at low temperatures. This is consistent with the copper oxide planes being too underdoped to superconduct as the apical Cu-O bond length is longer for $Pb_2RuSr_2Cu_2O_8Cl$ than that in $RuSr_2GdCu_2O_8$.

In conclusion, the ruthenocuprate $Pb_2RuSr_2Cu_2O_8Cl$ has a crystal structure (including rotations and tilts of the RuO$_6$ octahedra) and magnetic properties that are very similar to the previously reported Ru-1212 and -1222 phases, although the sample is not superconducting. $Pb_2RuSr_2Cu_2O_8Cl$ is a canted antiferromagnet in zero field with a Curie temperature of $T_M = 117$ K and an ordered moment of $1.1\mu_B$ per Ru. The Ru spins undergo a spin-flop or metamagnetic transition above $H = 0.5$ T, giving a saturated Ru moment of $0.5\mu_B - 0.8\mu_B$. Despite the similarity to the Ru-1212 and -1222 phases, the carrier distribution in $Pb_2RuSr_2Cu_2O_8Cl$ appears to be different, as the lack of superconductivity and the longer apical Cu-O distance suggest that the CuO$_2$ planes are essentially undoped. The RuO$_2$ planes thus contain Ru^{5+} with little or no electron doping to the Ru^{4+} state. This confirms that the weak ferromagnetism in the layered ruthenocuprates arises from the local symmetry-breaking structural distortions rather than a mixed Ru^{4+}/Ru^{5+} electronic state.

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