# Magnetic, thermal, transport, and structural properties of $Sr_2RuO_{4+\delta}$ : Enhanced charge-carrier mass in a nearly metallic oxide

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Measurements of electrical resistivity, magnetic susceptibility, heat capacity, and powder neutron diffraction are presented on  $Sr_2RuO_{4+\delta}$ . Specimens with low-impurity levels allow magnetic susceptibility in the range 5 < T < 350 K to be measured; these measurements indicate a small effective magnetic moment of  $\mu_{eff} \approx 1\mu_B$  per Ru ion. Electrical resistivity displays nonmetallic behavior in the range 1.2 < T < 300 K with  $\rho(295 \text{ K}) = 51 \text{ m}\Omega \text{ cm}$ . A rather large linear heat-capacity coefficient of  $\gamma = 45.6$  mJ/mol K<sup>2</sup> is reported; speculation is made regarding its origin. Rietveld refinement of powder-neutron-diffraction data provide insight into the physical properties and reveal interesting differences to isostructural La<sub>2</sub>CuO<sub>4</sub>. Comparisons are drawn to other transition-metal oxides.

## I. INTRODUCTION

The discovery of superconductivity in copper-oxide systems, which now possess superconducting transition temperatures  $T_c$  above 150 K,<sup>1</sup> has posed many challenges to experimental and theoretical scientists. A major curiosity of results acquired during the past seven years is that superconductivity with  $T_c > 40$  K has not yet been observed in any material devoid of the element copper. This fact leads us to query the potentially unique role of copper in these oxides which allows the condensation of the superconducting state at such high temperatures. A possible route through which to approach this question is the study of transition-metal oxides that contain no copper, but possess exactly the same crystal structures as the superconducting copper oxides. Since crystal structure is known to be of central importance to physical properties, we may think of this as a constant in the experiment. To this end, ruthenium oxides have been chosen as the focus of the present study. Ruthenium oxides exhibit a rich variety of magnetic behavior while also possessing rather high electrical conductivity.<sup>2-5</sup> The

system  $Sr_2RuO_{4+\delta}$  is particularly interesting because it forms in the  $K_2NiF_4$  crystal structure, identical to the I4/mmm crystallographic space group of the La<sub>2</sub>CuO<sub>4</sub> system, but in this case contains RuO<sub>2</sub> planes. Although this particular chemical system has been known for almost 30 years, the magnetic susceptibility has never satisfactorily been measured below 160 K due to the presence of the impurity phase SrRuO<sub>3</sub> which is ferromagnetic below this temperature.<sup>5</sup> In this report measurements of the magnetic susceptibility of  $Sr_2RuO_{4+\delta}$  below 160 K along with low-temperature heat-capacity, electrical resistivity, and structural studies are presented.

## **II. EXPERIMENTAL DETAILS**

Polycrystalline specimens of  $Sr_2RuO_{4+\delta}$  were prepared by mixing the appropriate quantities of high-purity (better than 99.9% purity) SrCO<sub>3</sub> and RuO<sub>2</sub> followed by reaction in an Al<sub>2</sub>O<sub>3</sub> crucible at 1100 °C in air for 8 h. The SrCO<sub>3</sub> was dried for 14 h at 200 °C before use. Subsequently, the powder was reground for 5 min and reacted at 1200 °C for 40 h. This last step was repeated five

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times with a reaction temperature of 1300 °C for 24 h. Finally, the powder was pressed into pellets, reacted for 35 h at 1350 °C and cooled slowly to room temperature over a period of 20 h by turning off the furnace. The resulting specimens were bluish black in color. The oxygen concentration was determined by neutron diffraction for one of the specimens to be  $4+\delta=4.25\pm0.06$ ; it is noted that all specimens were prepared under identical conditions and therefore that their oxygen concentrations are expected to be similar. Annealing in argon gas at 875 °C seems to have little effect on the magnetic susceptibility, indicating that  $Sr_2RuO_{4+\delta}$  is not readily reduced as are some copper oxides.

A slight excess of Sr was found to inhibit the formation of the SrRuO<sub>3</sub> and Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub> phases which are always present in  $Sr_2RuO_{4+\delta}$ . For this reason a series of specimens were prepared with excess Sr at the level of y=0, 1%, 2%, 3%, 4%, 5%, 7%, and 8% in order to investigate the SrRuO<sub>3</sub> and Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub> impurity level as a function of excess Sr. Heating of SrCO<sub>3</sub> in the oven during reaction of the  $Sr_2RuO_{4+\delta}$  specimens showed nearly complete conversion to SrO with no weight loss. Thus it must be assumed that SrO is an impurity in the  $Sr_2RuO_{4+\delta}$  specimens for y > 0. X-ray diffraction reveals SrO impurity peaks for samples with y > 4%. An x-ray powder diffraction scan of  $Sr_2RuO_{4+\delta}$  with y = 4% is shown in Fig. 1. It showed no impurity phases and is consistent with earlier reports that  $Sr_2RuO_{4+\delta}$  possesses the  $K_2NiF_4$  structure;<sup>2-4</sup> presumably, the 4% SrO is below the resolution of the x-ray diffractometer. Lattice parameters of the tetragonal cell calculated with reference to the Si internal standard are a = 3.872(1) Å and c = 12.74(1) Å. Scanning electron microscopy on a  $Sr_2RuO_{4+\delta}$  specimen revealed a typical grain size ranging from 2 to 7  $\mu$ m. To measure the magnetic susceptibility and establish the amount of SrRuO<sub>3</sub> impurity, a commercially available superconducting quantum interference device (SQUID) magnetometer was utilized; this device is



FIG. 1. X-ray intensity (arbitrary units) vs two-theta angle of  $Sr_2RuO_{4+\delta}$  with y = 4%. The Si peaks are due to the silicon internal standard. Contributions to the intensity due to the  $K\beta$  line have been subtracted.

extremely sensitive in detecting the magnetic impurity phases  $SrRuO_3$  (a ferromagnetic with  $T_c \approx 160$  K) and Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub>, which are highly magnetic with effective magnetic moments  $\mu_{eff} \approx 2.7 \mu_B$  and  $2.3 \mu_B$  per Ru ion, respectively,<sup>2,5,6</sup> far more sensitive than x-ray or neutron diffraction. Measurement in high magnetic fields limits the influence of the SrRuO<sub>3</sub> impurity on the data since the magnetization of the ferromagnetic impurity saturates while that of the paramagnetic majority phase increases proportionally to the field. Comparison between low-field measurements (H = 500 Oe) on  $Sr_2RuO_{4+\delta}$  samples and susceptibility measurements on SrRuO<sub>3</sub> (Ref. 5) in the region around the ferromagnetic transition indicates that the level of SrRuO<sub>3</sub> impurity decreases monotonically from about 55 (y = 0) to 1.5 ppm (y = 4%), and values of y > 4% yield SrRuO<sub>3</sub> impurity levels scattered under 5.5 ppm. Two additional y = 0 and 4% specimens were prepared at a later date, and they followed the same SrRuO<sub>3</sub> impurity trend. From our observations the following information concerning the influence of excess Sr can be deduced: (1) a reduction of a small impurity level (53.5 ppm with 4% excess Sr) requires a large excess of Sr, (2) higher levels of Sr do not appear to influence the amount of SrRuO<sub>3</sub> impurity in a systematic manner; and (3) excess SrO apparently remains as an impurity if y > 0. This information shows that a reduction of the SrRuO<sub>3</sub> impurity to a level of 1.5 ppm is possible by simply adding a modest amount of excess Sr to the  $Sr_2RuO_{4+\delta}$  solid solution, thereby causing the SrRuO<sub>3</sub> phase to form  $Sr_2RuO_{4+\delta}$ . This result will become important below when addressing the magnetic-susceptibility measurements on  $Sr_2RuO_{4+\delta}$ .

Electrical resistivity was measured using a four-contact dc technique whereby the current direction is reversed at each temperature to compensate for thermoelectric voltages. Heat capacity was measured using a thermal timeconstant method.<sup>7</sup> Neutron-diffraction data were collected using the University of Missouri Research Reactor's position-sensitive detector diffractometer at a neutron wavelength of 1.4766 Å. The sample was contained in a thin-wall 3-mm-diameter vanadium can, and all data sets were taken with the sample in a closed-cycle refrigerator to maintain the relative position at all temperatures.

## **III. RESULTS**

#### A. Electrical resistivity

Electrical resistivity measurements on a  $Sr_2RuO_{4+\delta}$ specimen with y = 0 will be discussed because the samples with y > 0 possessed higher resistivity values presumably due to SrO at the grain boundaries; on the other hand, the 55 ppm of metallic SrRuO<sub>3</sub> present in the y = 0 specimen should have essentially no influence. Electrical resistivity versus temperature is displayed in Fig. 2 for the Sr<sub>2</sub>RuO<sub>4+ $\delta$ </sub> specimen; it exhibits an increase with decreasing temperature. The absolute value of the electrical resistivity was determined by measurement of the sample dimensions. The electrical resistivity at 295 K is 51 m $\Omega$  cm which is similar to that found by others.<sup>4</sup> Mea-



FIG. 2. Electrical resistivity vs temperature of  $Sr_2RuO_{4+\delta}$  (y=0).

surements<sup>3,4</sup> on single crystals of  $Sr_2RuO_4$  grown by the floating-zone process showed that the electrical resistivity was highly anisotropic  $[\rho_c / \rho_{ab} \approx 300 \text{ at } T = 300 \text{ K},$  $\rho_c(300 \text{ K}) \approx 30 \text{ m}\Omega \text{ cm}$ , and  $\rho_{ab}(300 \text{ K}) \approx 90 \ \mu\Omega \text{ cm}$ ] and metallic in the *ab* direction (in the range 0 < T < 300 K) and in the c direction (in the range 0 < T < 100 K). This suggests that the polycrystalline material certainly should be metallic below 100 K, if not for all temperatures below 300 K. This temperature dependence is not observed here. This is probably due to poor intergranular conductivity of the sinter material, although it may indicate that the single crystals contain some other metallic impurities. Scanning electron microscopy shows poor contact between the grains, which indicates the root of the discrepancy between single-crystalline and polycrystalline resistivity behavior. This also suggests that the absolute value of the electrical resistivity obtained here may be reduced through variation of the sintering process.

#### B. Magnetic susceptibility

Magnetic susceptibility versus temperature of a  $Sr_2RuO_{4+\delta}$  sample with y = 4% at an applied magnetic field of 2 T is displayed in Fig. 3. Data obtained in fields of 2 and 5 T are essentially identical. Although it is difficult to prepare specimens completely devoid of the ferromagnetic impurity  $SrRuO_3$  ( $T_c \sim 160$  K), this specimen is quite clean. As mentioned above, comparison between low-field measurements (H = 500 Oe) on  $Sr_2RuO_{4+\delta}$  with y = 4% and susceptibility measurements on  $SrRuO_3$  (Ref. 5) in the region around the ferromagnetic transition suggest that the level of SrRuO<sub>3</sub> impurity is  $\sim 1.5$  ppm; this is about 35 times less than similarly prepared samples of  $Sr_2RuO_{4+\delta}$  with y=0. Measurements of the y = 0 Sr<sub>2</sub>RuO<sub>4+ $\delta$ </sub> sample were less meaningful due to a small bump in the data below T = 160 K (even in an applied field of 5 T) attributable to 55 ppm of SrRuO<sub>3</sub>. The Sr<sub>2</sub>RuO<sub>4+ $\delta$ </sub> y =4% specimen is discussed here in detail since it contains the lowest levels of both SrRuO<sub>3</sub> and excess Sr. Magnetic-susceptibility measurements of SrO were carried out to allow subtraction of its impurity contribution; an essentially temperature in-



FIG. 3. Magnetic susceptibility vs temperature of  $Sr_2RuO_{4+\delta}$ in an applied magnetic field of 2 T. Measurements were carried out on a sample of  $Sr_2RuO_{4+\delta}$  with y = 4% followed by subtraction of a small diamagnetic contribution due to 4% SrO impurity. The solid line is a fit to Eq. (1).

dependent value of  $\chi_{\rm SrO} = -2.95 \times 10^{-7}$  emu/gm was observed. The data in Fig. 3 have been corrected for this small contribution, which amounted to a correction of 0.5% at 300 K, and therefore the ensuing discussion refers to the magnetic susceptibility of  $Sr_2RuO_{4+\delta}$ . Thus this method allows the magnetic susceptibility of  $Sr_2RuO_{4+\delta}$  to be measured below the Curie temperature of SrRuO<sub>3</sub>. Close inspection of the data in the region around 45 K reveals a small feature which indicates the occurrence of a weak antiferromagnetic transition. Neutron-scattering studies (to be discussed in detail below) do not yet support this interpretation. The possibility that this feature results from a small amount of oxygen adsorbed on the surface of the porous specimen cannot be ruled out. However, repeated measurements, where exceptional care was taken to flush out the sample chamber, did not alter this feature. Below 45 K an increase of the susceptibility occurs which is not altered by increased magnetic field; this feature may be the result of paramagnetic impurities at a ppm level.

Above  $T \sim 250$  K the susceptibility increases with temperature. Similar behavior is also seen in metallic RuO<sub>2</sub>,<sup>8</sup> although its magnetic susceptibility is about five times smaller at 300 K. Possible explanations for the increase with temperature is that two- or three-dimensional antiferromagnetic order has occurred at some temperature above 350 K, or that short-range antiferromagnetic correlations exist in this temperature range. Twodimensional antiferromagnetic order usually results in a broad maximum in the magnetic susceptibility,<sup>9</sup> whereas three-dimensional magnetic corder would result in a downward kink. It is interesting that  $La_{2-x}Sr_xCuO_4$ ,<sup>10,11</sup> as well as other Cu oxides,<sup>12,13</sup> in many instances also show an increase in their magnetic susceptibilities with temperature. In the copper oxides  $La_{2-x}Sr_xCuO_4$  and  $YBa_2Cu_3O_7$ , nuclear magnetic resonance results, <sup>14,15</sup> together with the phenomenological antiferromagnetic Fermi-liquid theory, <sup>16,17</sup> suggest that the charge carriers and the copper spins form a strongly correlated spin system in a single band.<sup>18</sup> Thus the spin

susceptibility in these systems consists of one component which should be regarded as a temperature-dependent Pauli susceptibility for metallic samples. As will be discussed in more detail below, it is not unreasonable to consider  $Sr_2RuO_{4+\delta}$  as a strongly correlated spin system. Therefore, we fit the data to the equation

$$\chi = \chi_{\rm spin} + \frac{C}{T + \Theta} , \qquad (1)$$

where

$$\chi_{\rm spin} = \chi_0 + \varepsilon T \ . \tag{2}$$

This equation is of standard Curie-Weiss form with the addition of a temperature-independent  $\chi_0$  term plus a term linear in T which fits the behavior of the data. In order to fit the data to Eq. (1), an initial fit was carried out in the region 50 K  $\leq T \leq 131$  K with  $\varepsilon = 0$ ; this is simply a standard Curie-Weiss fit. Here the parameters  $C = 0.135 \pm 0.011$  emu K/mole,  $\Theta = 219 \pm 12$  K, and  $\chi_0 = 5.29 \pm 0.17 \times 10^{-4}$  emu/mole were obtained. In this case the Curie constant provides an effective magnetic moment of  $1.04\pm0.04\mu_B$ . These parameters gave numbers to aid in the subsequent four-parameter fit. The magnitude of  $\varepsilon$  was first approximated by a linear fit to the data above 320 K. Then slight variations on the starting value of  $\varepsilon$  were tried, with the other three parameters varying freely until the best fit was found; this method proved to be more reliable than allowing free variation of all four parameters. Values of  $C = 0.127 \pm 0.001$  emu K/mole,  $\Theta = 153 \pm 2$  K,  $\chi_0 = 3.74$  $\pm 0.04 \times 10^{-4}$  emu/mole, and  $\epsilon = 7.03 \pm 0.05 \times 10^{-7}$ emu/K mole were obtained. The Curie constant C derived from this fit yields an effective magnetic moment of  $1.01\pm0.01\mu_{B}$ . Equation (1) provides a reasonable fit to the data in the range 50 K  $\leq T \leq$  350 K, as shown by the solid line in Fig. 3, and allows the reader the possibility of reconstructing the data. In a recent publication Cava et al.<sup>19</sup> obtained an effective magnetic moment for  $Sr_2RuO_4$  of  $\mu_{eff} \approx 0.5\mu_B$ . This small value, compared to that reported here, arises from the limited T > 160 K fitting region employed because of the comparatively large SrRuO<sub>3</sub> concentration in their samples. For example, a fit to the data in Fig. 3 using Eq. (2) in the region T > 160 K gives a value  $\mu_{\text{eff}} \approx 0.4 \mu_B$ , close to that reported by Cava et al. 19

#### C. Heat capacity

Heat capacity was measured on a 35-mg portion of the  $Sr_2RuO_{4+\delta}$  sample with y = 0. The data are displayed in Fig. 4 as C/T vs  $T^2$ . The rather linear behavior of the heat capacity in the range  $5 \le T^2 < 400 \text{ K}^2$  suggests comparison to the behavior typical of a metal given by

$$C/T = \gamma + \beta T^2 , \qquad (3)$$

where  $\gamma$  is the Sommerfeld constant and  $\beta$  describes the phonon contribution and can be used to calculate the Debye temperature  $\Theta_D$ . Equation (3) is valid for  $T \ll \Theta_D$ . A fit to the data in the range  $T \leq 8$  K yields  $\gamma = 45.6$  mJ/mole K<sup>2</sup> and  $\beta = 0.192$  mJ/mole K<sup>4</sup> ( $\Theta_D = 414$  K).



FIG. 4. Heat capacity divided by temperature C/T vs  $T^2$  of  $Sr_2RuO_{4+\delta}$  (y=0). In the inset the low-temperature linear region is enlarged.

Similar results were obtained for a  $Sr_2RuO_{4+\delta}$  sample with y = 4%. The obtained value of  $\gamma$  is rather large; typical values for metals are under 10 mJ/mole K<sup>2</sup>, <sup>20</sup> while metallic RuO<sub>2</sub> exhibits<sup>21</sup>  $\gamma = 5.77$  mJ/mole K<sup>2</sup>. In conjunction with this study, the specific heat of SrRuO<sub>3</sub> has been measured; a value of  $\gamma \approx 30$  mJ/mole K<sup>2</sup> was deduced, which is also large for a metal. In part, ferromagnetic spin waves could contribute to this apparent " $\gamma$ ".<sup>22</sup> In any case, though, the contribution of 55 ppm of SrRuO<sub>3</sub> to the data in Fig. 4 is negligible. The large value of  $\gamma$  for Sr<sub>2</sub>RuO<sub>4+ $\delta$ </sub> suggests an enhanced chargecarrier effective mass  $m^*$  since  $\gamma$  is given by

$$\gamma = m^* \frac{Vk_B^2}{3\hbar^2} (3\pi^2 n)^{1/3} , \qquad (4)$$

where  $k_B$  is the Boltzmann constant,  $\hbar$  is Planck's constant divided by  $2\pi$ , V is the volume per mole, and n is the carrier concentration. Under the assumption of one charge carrier per unit cell, we obtain  $m^* \approx 14m_e$  ( $m_e$  is the electron's mass). Measurements of the Hall effect would be valuable to establish the value of n.

#### **D.** Neutron diffraction

Neutron-diffraction studies were carried out on a  $Sr_2RuO_{4+\delta}$  specimen with y = 0 to obtain a full Rietveld refinement in addition to searching for magnetic order. Full data sets were collected at 293 and 13 K, with measurements between 5° and 105° (2 $\Theta$ ) each taking approximately 24 h. In addition, data were collected for one span of the detector at 11 and 55 K for 48 h, each to search for evidence of additional magnetic intensity at low temperature. The difference between these two spectra revealed no peaks; it is therefore concluded that, if there is an ordered moment, it is too small to be observed with unpolarized neutrons.

Refinements of the full data sets were performed using the GSAS version<sup>23</sup> of the Rietveld code. They were car-

TABLE I. Neutron-diffraction Rietveld refinement results for  $Sr_2RuO_{4+\delta}$  (y=0) at T=293 and 13 K, and corresponding structural information for  $La_{1,8}Sr_{0,2}CuO_4$  at room temperature.

Parameter	T = 293  K	T = 13 K	$La_{1.8}Sr_{0.2}CuO_4$
a	3.8669(1)	3.8624(1)	3.784 46(14)
с	12.7290(4)	12.7229(6)	13.264 68(47)
Volume	190.34(1)	189.81(2)	189.979(20)
Sr $z(x=y=0)$	0.3533(2)	0.3534(3)	0.360 56(13)
O1 $y(x = z = 0)$	0.5	0.5	0.5
O1 occup.	1.058(14)	1.067(19)	
O2 $z(x = y = 0)$	0.1617(2)	0.1613(3)	0.181 95(20)
O2 occup.	1.067(15)	1.037(20)	
Sr-O1 $(\times 4)$	2.6877(22)	2.68477(9)	2.6461(12)
Sr-O2 (×1)	2.4390(50)	2.4441(1)	2.3690(40)
Sr-O2 (×4)	2.7411(3)	2.7376(1)	2.7348(6)
Ru-O1 $(\times 4)$	1.93348(5)	1.931 22(8)	1.89223(7)
(Cu-O1)			
Ru-O2 $(\times 2)$	2.0587(34)	2.0523(1)	2.4135(28)
(Cu-O2)			
$\chi^2$	2.134	1.455	
R <sub>wp</sub>	10.29	13.12	

ried out assuming the same 14/mmm symmetry reported for  $La_2CuO_4$  at room temperature, which was found to be satisfactory. Except for one small peak observed at low angle, which was temperature independent, all the reflections could be indexed, and the peak widths indicated no orthorhombic distortion of the unit cell. The refined parameters are given in Table I along with the lengths for the metal-oxygen bonds. Also given in Table I are results for a  $La_{2-x}Sr_xCuO_4$  sample measured at room temperature with the same apparatus.<sup>24</sup> The refinement indicated a 6% oxygen excess relative to the fixed metal ratio of 2:1. Little change in bond lengths is seen upon cooling, but it is noted that the single Sr-O2 bond expands while all others contract with the reduced cell volume. Comparison of this sample with the Cu system shows one striking difference. The oxygen bonds around the Ru atoms are much more nearly symmetric than around the Cu atoms. In the Ru system the difference between in-plane and out-of plane oxygen bond lengths is only 0.12 Å, while in the Cu system the difference is more than 0.5 Å. Thus the former can be described as octahedrally coordinated, while the latter is more nearly square planar. This difference manifests itself through the shift in the O2 z parameter from 0.162 to 0.182 as well as the longer c axis.

# **IV. DISCUSSION**

The large Sommerfeld constant  $\gamma$  in Sr<sub>2</sub>RuO<sub>4+ $\delta$ </sub> is in strong contrast to that of La<sub>2</sub>CuO<sub>4</sub>, where  $\gamma \approx 1$ mJ/mole K<sup>2,25</sup> Large values of  $\gamma$ , which can reflect a high density of electronic states at the Fermi level, may have several origins. They may arise from electronelectron interactions or through electron-phonon interactions. In addition to the large  $\gamma$ , the magnetic susceptibility is also rather large. Correction for the core diamagnetism using the values  $-15 \times 10^{-6}$ ,  $-18 \times 10^{-6}$ , and  $-12 \times 10^{-6}$  emu/mole for Sr, Ru, and O, respective-

ly,<sup>26</sup> yields  $\chi(300 \text{ K}) = 9.674 \times 10^{-4}$  emu/mole and  $\chi_0 = 4.73 \times 10^{-4}$  emu/mole. These values, compared to  $\chi(300 \text{ K}) = 1.5 \times 10^{-4}$  emu/mole for RuO<sub>2</sub> (Ref. 8) and  $\chi_{\text{Pauli}} < 3.7 \times 10^{-4}$  emu/mole for the copper-oxide superconductors,<sup>13</sup> also indicate an enhanced density of states at the Fermi level, as was suggested by Cava et al.<sup>19</sup> from their magnetic-susceptibility data on  $Sr_2RuO_4$ . The Wilson ratio  $\chi_0/\gamma$  (in units of  $3\mu_B^2/\pi^2 k_B^2$ ) is approximately 0.76, which is comparable to the value of unity typically found in heavy-fermion materials.<sup>27</sup> Variation in the fitting procedure to obtain  $\chi_0$  can influence this value. In addition to the large values of  $\chi_0$  and  $\gamma$ , the electrical resistivity is fairly small with a weak temperature dependence  $[\rho(1.2 \text{ K})/\rho(295 \text{ K})=2.8]$ , suggesting that  $Sr_2RuO_{4+\delta}$  may be close to the metal-insulator boundary. Recently, it was reported that  $Sr_{1-x}La_xTiO_3$ , where values as large as  $\gamma = 17.5$  mJ/mole K<sup>2</sup> were obtained, exhibits strongly correlated electron behavior as x is increased and the Mott-insulating state at x = 1 is approached.<sup>28</sup> Similarly, high pressure was recently shown to strongly influence  $\gamma$  in the Mott-Hubbard system  $V_{2-\nu}O_3$ , <sup>29</sup> where values as large as  $\gamma = 47$  mJ/mole K<sup>2</sup> were observed near the metal-insulator transition. Further studies are in progress to investigate if similar effects play a role in  $Sr_2RuO_{4+\delta}$ .

Interactions between conduction electrons and phonons also may be a source of the enhanced  $\gamma$ . Strong electron-phonon interactions, possibly resulting in the formation of polarons, are usually associated with ionic solids and are manifested by long-range Coulombic interactions between the charge carriers and both the anions and cations of the solid.<sup>30</sup> Materials containing oxygen are exceptionally susceptible to the formation of polarons, as are low-dimensional electronic systems.<sup>30</sup> A more careful look into the bond lengths and electronegativities of Ru and Cu reveals several interesting aspects concerning the Ru-O bond compared to the Cu-O bond. The electronegativities of  $Ru^{4+}$  and  $Cu^{2+}$  are comparable at 2.1 and 2.0, respectively.<sup>31</sup> The significant difference occurs in the bond lengths. The ionic radii for sixfold-coordinated  $Cu^{2+}$  and  $Ru^{4+}$  are 0.73 and 0.62 Å, respectively.<sup>32</sup> Although the ionic radius of  $Cu^{2+}$  is significantly larger than that of Ru<sup>4+</sup> and the electronegativies are similar, the Cu-O1 bond length is 2.2% shorter than the Ru-O1 bond length (see Table I). This indicates that the ruthenium-oxygen bond in  $Sr_2RuO_{4+\delta}$  is less covalent in nature, thereby suggesting the ruthenate to be a more ionic solid than the cuprate. Therefore, the ruthenate may be more susceptible to polaronic behavior. The linear heat-capacity term indicates that the charge carriers obey Fermi statistics while simultaneously acquiring a large value of  $m^*$ . This, coupled with the structural observations indicative of ionic bonding, may suggest that the charge carriers are large polarons which are mobile electrons in a conduction band with an enhanced effective mass due to strong electron-phonon coupling. In contrast, small polarons are self-trapped electrons which move by thermally activated hopping; at low temperatures they would contribute little to the specific heat. Similar effects occur in  $La_{2-x}Sr_xNiO_4$ , which is isostructural to  $Sr_2RuO_{4+\delta}$ , where polarons (presumably small polarons) were observed directly by electron diffraction.<sup>33</sup> Measurements of the optical and static dielectric constants may provide further information concerning the feasibility of large polarons as a realistic interpretation for the  $\gamma$  observed in  $Sr_2RuO_{4+\delta}$ .

The Ru-oxide compounds SrRuO<sub>3</sub> and Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub> each possess magnetic states quite different than  $Sr_2RuO_{4+\delta}$ .<sup>2,4-6</sup> Simple charge counting, under the assumption that the valences of Sr and O are +2 and -2, respectively, suggests a ruthenium valence of +4.50 $\pm$ 0.12. Considering Ru<sup>4+</sup> for simplicity, since ruthenium's outer shell has a  $4d^{7}5s$  state, four d electrons may contribute to the magnetic moment. According to Hund's rules, J=0 and  $\mu_{\text{eff}}=0$  are calculated. A similar calculation, assuming the orbital angular momentum is quenched, yields S=2 and  $\mu_{eff}=4.89\mu_B$ . Neither of these results agrees with the observed magnetic moment. Understanding the magnetic state of  $Sr_2RuO_{4+\delta}$  requires thought concerning the crystalline electric field at the Ru site. In Table I it is observed that the Ru site possesses nearly octahedral symmetry. An ion with a  $d^{4}$  state in such symmetry should have one of two magnetic states, either S = 1 or 2. The case of S = 1 is easy to understand. Of the five possible d orbitals, the four available d electrons choose the  $d_{xy}$ ,  $d_{xz}$ , or  $d_{yz}$  orbitals since these are furthest from the high electron density concentrated at the  $O^{2-}p$  orbitals (assuming  $d_{2}$  is oriented along the crystallographic c-axis). This means that two of the four electrons must pair, leaving two unpaired electrons and an S = 1 state. If the energy required to pair two electrons is greater than that required for an electron to go in either the  $d_{x^2-y^2}$  or  $d_{z^2}$  orbitals, the electron will choose the latter, resulting in the S=2 high-spin state; to our knowledge such a magnetic state has not been observed in Ru oxides.

Now that the standard magnetic states are understood, the dilemma arises that none of these correspond to the effective moment of  $1\mu_B$  observed for  $Sr_2RuO_{4+\delta}$ . The contribution of  $Sr_3Ru_2O_7$  impurities to  $\mu_{eff}$  are ruled out due to the weak temperature dependence of the magnetic susceptibility observed in Fig. 3 for the range 150 K < T < 350 K. Assuming that orbital angular momentum has been quenched, the effective magnetic moment corresponds to a value of S = 0.21. This indicates that any one of a few possibilities is responsible for the value  $\mu_{\rm eff} = 1\mu_B$ . The neutron data show that a distortion of 6.5% from perfect octahedral symmetry exists at room temperature. This will influence the magnetic state by reducing the energy necessary to bring an electron into the  $d_{z^2}$  orbital while also reducing the energy of the  $d_{xz}$  and  $d_{yz}$  states relative to the  $d_{xy}$  state. This could result in a situation where the energy required for an electron to go into the  $d_{z^2}$ ,  $d_{xy}$ , or  $d_{x^2-y^2}$  states is higher than that required for the electrons to pair in the  $d_{xz}$  and  $d_{yz}$  states, thereby resulting in a value of S = 0. Assuming the  $d_{xz}$  $d_{yz}$  and  $d_{xy}$  states are closest in energy, if the pairing energy is in fact close to the energy difference between the  $d_{xz} d_{yz}$  states and the  $d_{xy}$  state, it is possible that the electron may jump from one low-spin S = 0 state to a highspin S = 1 state resulting in the observed value of S < 1. Altering the above arguments to consider the Ru valence of  $+4.50\pm0.12$ , this can be viewed as the existence of a mixture of Ru<sup>4+</sup> and Ru<sup>5+</sup>. The three *d* electrons of Ru<sup>5+</sup> could result in  $S = \frac{3}{2}$  or, with crystal-field effects,  $S = \frac{1}{2}$ . This will increase *S* but cannot account for the observed value of S = 0.21 unless some of the Ru<sup>4+</sup> is in a state of S > 0.

An obvious difference between  $Sr_2RuO_{4+\delta}$  and  $La_2CuO_4$  is simply their outer electronic-shell configurations. The Cu<sup>2+</sup> ion has a nearly filled  $3d^9$ outer shell, while the  $Ru^{4+}$  ion has a  $4d^4$  outer shell. Nonetheless, the ruthenate still develops a magnetic state with nearly one spin per Ru site, comparable to La<sub>2</sub>CuO<sub>4</sub>,<sup>25</sup> since, apparently, there exists a mixture of two unpaired spins and two sets of paired spins. Another important difference is that the cuprate exhibits a very pronounced Jahn-Teller distortion resulting in a more planar structure than the ruthenate. Therefore, the ruthenate probably would not possess the same nearly two-dimensional electronic structure as the cuprate. Finally, La<sub>2</sub>CuO<sub>4</sub> and its doped relatives, to our knowledge, possess values of  $\gamma < 5$  mJ/mole K<sup>2</sup>.<sup>25</sup> This is in strong contrast to  $\gamma$  observed in the ruthenate, vanadate, and titanate systems, suggesting a fundamental difference from the cuprate. Measurements of the heat capacity of La<sub>2</sub>NiO<sub>4</sub> would be valuable to classify it among these transition-metal oxides.

# **V. CONCLUSIONS**

Experimental studies of the ruthenate  $Sr_2RuO_{4+\delta}$  have provided samples with the lowest level of SrRuO<sub>3</sub> impurity studied thus far. The magnetic-susceptibility measurements reveal the magnetic state as being rather unusual among the ruthenium oxides, and may suggest that the charge carriers and Ru spins form a strongly correlated spin system. In addition,  $Sr_2RuO_{4+\delta}$  appears to exhibit weak antiferromagnetic order below T = 45 K, although this has yet to be confirmed by neutron diffraction. A neutron structural study of this compound has been presented which has yielded information useful in unraveling the crystalline electric-field effects responsible for the observed magnetic moment  $\mu_{\text{eff}} \approx 1\mu_B$ . The heatcapacity data indicate a very large linear term  $\gamma = 45.6$  $mJ/mole K^2$  suggestive of significant charge-carrier effective-mass enhancement. A number of possibilities which may explain this observation were proposed. Comparisons between this compound and La<sub>2</sub>CuO<sub>4</sub> indicate  $Sr_2RuO_{4+\delta}$  to be more ionic, and may suggest that the electrical properties are moderated by strong electron-phonon coupling. Perhaps the stronger covalent-type bonding in the cuprate is an important factor related to the superconductivity of the doped compound. Finally, comparisons to the Mott-Hubbard systems  $Sr_{1-x}La_x TiO_3$  and  $V_{2-y}O_3$  suggest that strong electron correlations may also be a viable approach to understanding the density of states enhancement in  $Sr_2RuO_{4+\delta}$ . Further studies are in progress to investigate these proposals.

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