Heavy-Electron Behavior and Structural Change in Ca$_{1.7}$Sr$_{0.3}$RuO$_4$

R. Jin$^1$, J. R. Thompson$^{2,1}$, J. He$^{2,1}$, J. M. Farmer$^{3,1}$, N. Lowhorn$^4$, G. A. Lamberton, Jr.$^4$, T. M. Trimm$^4$, and D. Mandrul$^{1,2}$

$^1$Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
$^2$Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996
$^3$Department of Chemistry, Baylor University, Waco, Texas 76798 and
$^4$Department of Physics, Clemson University, Clemson, South Carolina 29634

(Dated: November 7, 2021)

Sr$_2$RuO$_4$ is an unconventional superconductor with a tetragonal structure, whereas Ca$_2$RuO$_4$ is a Mott insulator with orthorhombic symmetry. The substituted Ca$_{2-x}$Sr$_x$RuO$_4$ has yielded a rich phase diagram that is just beginning to be explored in detail. Experimental investigation of the resistivity $\rho$, susceptibility $\chi$, specific heat $C_p$, Hall coefficient $R_H$, and X-ray diffraction of Ca$_{1.7}$Sr$_{0.3}$RuO$_4$ reveals a structural phase transition near $T_0 = 190$ K and heavy-Fermion (HF) behavior below a coherence temperature $T^* \sim 10$ K, resembling that of the $f$-electron HF compound UPt$_3$. The observation of $T^2$-dependence of $\rho$ below $\sim 0.5$ K suggests a Fermi-liquid ground state. Based upon our data and theoretical calculations, we argue that the structural change at $T_0$ may be responsible for the formation of the HF state.

PACS numbers: 61.66.-f, 71.27.+a, 72.15.Eb, 72.80.Ga

The discovery of unconventional superconductivity in Sr$_2$RuO$_4$ has stimulated great interest in the electronic properties of ruthenates. Despite its high electrical conductivity, a rather large ratio of the Coulomb repulsion $U$ to the bandwidth $W$ indicates that Sr$_2$RuO$_4$ is close to a Mott transition. Both strong electron-electron correlations and Fermi-liquid (FL) ground state appear to play a crucial role in its physical properties. In particular, intriguing connections have been revealed between these correlations and unconventional superconductivity. The partial substitution of the smaller Ca$^{2+}$ for Sr$^{2+}$ changes both $U$ and $W$, leading to rich and unusual phenomena in Ca$_{2-x}$Sr$_x$RuO$_4$. With increasing Ca content (decreasing $x$), superconductivity is rapidly destroyed and the in-plane resistivity $\rho_{ab}$ increases, turning into insulating behavior ($d\rho_{ab}/dT < 0$) as $x < 0.2$. This is consistent with the expected increase in the density of states (DOS) associated with the band narrowing due to the Ca substitution. However, the magnetic properties are not in complete accord with this picture. It was found that the low-temperature paramagnetic susceptibility increases with Ca concentration, peaking at $x = x_c = 0.5$. Near this critical concentration, the effective magnetic moment tends to saturate with $S = 1/2$. Neutron diffraction results suggest that the crystallographic distortion in Ca$_{2-x}$Sr$_x$RuO$_4$ may lead to a variation in the shape and the effective filling of the triply degenerated Ru $t_{2g}$ bands through a Jahn-Teller (JT) type orbital rearrangement. Of particular interest is the intermediate regime with $0.2 < x < 0.5$, where an electronic state containing both localized and itinerant electrons is proposed.

In this Letter, we report the electronic, magnetic and thermodynamic properties of Ca$_{1.7}$Sr$_{0.3}$RuO$_4$ ($x \sim 0.3$) single crystals. Investigation of the specific heat $C_p$ and $c$-axis resistivity $\rho_c$ indicates a continuous phase transition at $T_0 \sim 190$ K. Consistent with previous results, a structural transition from tetragonal ($T > T_0$) to orthorhombic ($T < T_0$) symmetry is observed. This is remarkable, the Hall coefficient $R_H$, measured by applying $H$ perpendicular to $ab$-plane ($H \parallel c$), behaves similarly to $\chi_c(H \parallel c)$: $R_H(T)$ scales with $\chi_c(T)$ above $T^* \sim 10$ K, a characteristic temperature corresponding to a maximum $\chi_c$ and $R_H$. This behavior has been attributed to skew scattering due to magnetic moment effects in heavy-fermion (HF) systems such as UPt$_3$. Surprisingly, the resistivity $\rho_{ab,c}$ and specific heat $C_p$ also reveal features remarkably similar to those of UPt$_3$ below $T^*$. A large Sommerfeld coefficient $\gamma = 266$ mJ/mol-K$^2$ also provides evidence for HF behavior in Ca$_{1.7}$Sr$_{0.3}$RuO$_4$, unexpected in a 4$d$-electron system. To our knowledge, this is the first report of a 4$d$-electron material exhibiting HF behavior. In contrast to previous conclusions based upon resistivity measurements above 0.3 K, we find that the resistivities $\rho_{ab,c}$ follow $T^2$-dependence below $\sim 0.5$ K, showing a recovery of a Fermi-liquid ground state in the high Ca concentration regime. Again, this is similar to what is observed in UPt$_3$. We discuss this heavy-electron behavior in terms of recently developed theoretical models.

Single crystalline Ca$_{1.7}$Sr$_{0.3}$RuO$_4$ was grown using an NEC SC-M15HD image furnace. For feed-rod preparation, a mixture of CaCO$_3$, SrCO$_3$ and RuO$_2$, with molar ratio of 1.70:0.30:1.15, was pre-reacted in air at 1100 °C for 12 h. After regrounding, the powder was pressed into rods and heated in air at 1100 °C for another 12 h. Single crystals were grown using a feed rate of 30 mm/h and a

email address: jiar@ornl.gov
growth rate of 15 mm/h in an atmosphere of 10% oxygen and 90% argon. Shiny black crystals are produced with actual Ca:Sr ~ 1.7:0.3 as determined by energy dispersive X-ray analysis. The crystal structure was refined using an Enraf-Nonius four-circle autodiffractometer with Mo Kα radiation and a nitrogen-gas-stream cryocooler. Table I presents the lattice parameters at various temperatures between 100 and 200 K. Note that $a < b$ at T < 200 K, indicating that the system undergoes a structural change from tetragonal at high temperatures to orthorhombic symmetry at low temperatures, in good agreement with that obtained by neutron diffraction.[8, 9]

As given in Table I, there is no drastic change in cell volume between 160 and 200 K. Below 160 K, the refinement data show negative thermal expansion along the $b$-axis while both $a$ and $c$ continuously decrease with decreasing T. These results suggest that the structural phase transition is continuous. This is confirmed by specific heat data. Fig. 1 shows the temperature dependence of the specific heat $C_p$ of a Ca$_{1.7}$Sr$_{0.3}$RuO$_4$ single crystal between 0.38 and 300 K. Note a kink occurs at a characteristic temperature $T_0 \sim 190$ K, corresponding to the structural phase transition. No hysteresis was observed in specific heat, which is consistent with a continuous phase transition.

For a non-magnetic metallic solid, the low-temperature specific heat $C_p$ is usually analyzed by considering contributions from electrons ($C_p^e = \gamma T$) and lattice ($C_p^l = \beta T^3$), i.e., $C_p = \gamma T + \beta T^3$. Here, $\gamma$ and $\beta$ are T-independent constants. Thus, a plot of $C_p/T$ vs. $T^2$ should be linear. For Ca$_{1.7}$Sr$_{0.3}$RuO$_4$, the temperature dependence of $C_p/T$ between 0.38 and 20 K is shown in the inset of Fig. 1. The nonmonotonic $T^2$-dependence of $C_p/T$ with a dip at $T^* \sim 10$ K indicates a departure from normal metallic behavior in Ca$_{1.7}$Sr$_{0.3}$RuO$_4$. We recall that a similar temperature dependence of $C_p/T$ has been seen in HF materials,[8] which can be expressed as 

$$C_p = \gamma T + \beta T^3 + \delta T^3 \ln(T/T_1), \tag{1}$$

where $\delta$ and $T_1$ are constants. The last term describes the contribution from interactions between quasiparticles due to spin fluctuations, where $T_1$ is a cut-off temperature with regard to the spin fluctuations.[3] Using Eq. 1 to fit our specific heat data between 0.38 and 13 K yields that $\gamma = 266$ mJ/mol-K$^2$, $\beta = 1.86$ mJ/mol-K$^4$ and $\delta = 0.28$ mJ/mol-K$^3$. As illustrated in the inset of Fig. 1 by the solid line, the above formula fits the experimental data (0.38 - 13 K) quite well.

The $\gamma$ value extracted from the above fitting procedure is large compared with the parent compound Sr$_2$RuO$_4$ ($\gamma = 37.5$ mJ/mol-K$^2$[10]) and is comparable to HF materials such as UPt$_3$ ($\gamma = 422$ mJ/mol-K$^2$[11]). Heavy-electron behavior was first recognized in $f$-electron systems. Recently, similar behavior has also been seen in the 3$d$ transition metal oxide LiV$_2$O$_4$.[3] In general, HF behavior is not anticipated in systems containing 4$d$/5$d$ electrons because of the extended nature of these orbitals.

In a Fermi-liquid system, information about the effective mass of the quasiparticles can be extracted from the low-temperature electrical resistivity when expressed as $\rho = \rho_0 + AT^2$ as $T \to 0$ K. Here, the residual resistivity $\rho_0$ and coefficient $A$ are constants. According to Kadowaki and Woods (KW), the ratio $A/\gamma^2$ is expected to approach the universal value $A/\gamma^2 = 1.0 \times 10^{-5}$ $\mu\Omega$ cm/(mJ/mol-K)$^2$, if the electronic conduction and specific heat are governed by the same quasiparticles.[3] Shown in Fig. 2 are the temperature dependences of the $ab$-plane and $c$-axis resistivities of Ca$_{1.7}$Sr$_{0.3}$RuO$_4$ between 0.05 and 300 K, measured using a standard four-probe technique. Note that $\rho_{ab}$ increases with temperature ($d\rho_{ab}/dT > 0$), reflecting the itinerant nature of electrons. The $c$-axis resistivity $\rho_c$, however, undergoes a crossover from metallic behavior ($d\rho_c/dT > 0$) at $T < T_0$ to non-metallic character ($d\rho_c/dT < 0$) at $T > T_0$. Although $\rho_{ab}$ and $\rho_c$ of Ca$_{1.7}$Sr$_{0.3}$RuO$_4$ superficially resemble those of undoped Sr$_2$RuO$_4$, it is clear that the metallic-nonmetallic transition in $\rho_c$ of Ca$_{1.7}$Sr$_{0.3}$RuO$_4$ is due to the structural change, which shortens the lattice parameter $c$ and subsequently enhances the interlayer coupling below $T_0$. Interestingly, $\rho_{ab}$ remains metallic without any noticeable anomaly, although lattice parameters $a$ and $b$ are also spontaneously changed.

**TABLE I: Lattice parameters and lattice volume in Ca$_{1.7}$Sr$_{0.3}$RuO$_4$ at T = 200, 160, 140, 120 and 100 K.**

| T (K) | 200 K | 160 K | 140 K | 120 K | 100 K |
|-------|-------|-------|-------|-------|-------|
| $a$ (Å) | 5.320(2) | 5.310(2) | 5.308(3) | 5.307(1) | 5.305(2) |
| $b$ (Å) | 5.320(2) | 5.316(1) | 5.319(1) | 5.321(1) | 5.322(1) |
| $c$ (Å) | 12.551(7) | 12.546(3) | 12.542(3) | 12.541(4) | 12.537(2) |
| vol. (Å$^3$) | 355.2(2) | 354.1(1) | 354.3(2) | 354.1(2) | 354.0(3) |

**FIG. 1: Temperature dependence of the specific heat of a Ca$_{1.7}$Sr$_{0.3}$RuO$_4$ single crystal between 0.38 and 300 K. Note a kink occurs at $T_0 \sim 190$ K. The inset is the specific heat data between 0.38 and 20 K plotted as $C_p/T$ vs. $T^2$. Note that $C_p/T$ reaches a minimum at $T^* \sim 10$ K. The solid curve is the fit of experimental data between 0.38 and 13 K to Eq. 1 (see the text).**
Nevertheless, it is obvious that a sharp decrease occurs in both $\rho_{ab}$ and $\rho_c$ below $\sim 10$ K, coincident with the characteristic temperature $T^*$ in $C_p/T$ (see the inset of Fig. 1). In light of previous results, we note that such behavior can only be seen if $0.2 < x < 0.5$. In this regime, the low-temperature resistivity has been analyzed using $\rho = \rho_0 + AT^*$, with $\alpha < 2$, leading to the conclusion of non-FL ground state. In contrast, we find that, for Ca$_{1.7}$Sr$_{0.3}$RuO$_4$, both $\rho_{ab}$ and $\rho_c$ are well described by $\rho = \rho_0 + AT^2$ below $\sim 0.5$ K as shown in the inset of Fig. 2, characteristic of a Fermi-liquid ground state. The fits from 50 to 500 mK give $A_{ab} = 1.88 \mu\Omega cm/K^2$ and $A_c = 88.8 \mu\Omega cm/K^2$. Similar to what was found in Sr$_2$RuO$_4$, $A_c \gg A_{ab}$, indicating that the quasiparticles essentially form a 2D Fermi liquid. We estimate that $\Lambda_{ab}/T^2 = 2.7 \times 10^{-5} \mu\Omega cm/(mJ/mol-K^2)$, comparable to the expected universal value.

Given the heavy-mass Fermi-liquid behavior of Ca$_{1.7}$Sr$_{0.3}$RuO$_4$, it is natural to expect a large spin susceptibility. Measurements of the magnetic susceptibility $\chi$ were performed using a SQUID magnetometer. Fig. 3a displays the temperature dependence of $\chi$ at 0.1 T between 2 K and 300 K. Measurements performed in both zero-field-cooling and field-cooling conditions yield identical results. It may be seen that $\chi_{ab,c}$ shows strong temperature dependence. This local moment behavior is strongly in contrast with the relatively T-independent Pauli paramagnetism and superconductivity observed in undoped Sr$_2$RuO$_4$. Below $\sim 50$ K, anisotropy becomes apparent. While $\chi_{ab}(H \parallel ab)$ tends to saturate below $\sim 3.5$ K, $\chi_{c}(H \parallel c)$ clearly reveals a peak at $T^* \sim 10$ K. Again, these features resemble those observed in UPt$_3$.

Interestingly, both $\chi_{ab}$ and $\chi_c$ vary smoothly with temperature without noticeable anomaly across $T_0$. It was reported that, except for near $x = 2$, $\chi$ of Ca$_{2-x}$Sr$_x$RuO$_4$ can be described by a Curie-Weiss (CW) law in a wide temperature regime. For Ca$_{1.7}$Sr$_{0.3}$RuO$_4$, we plot the susceptibility data as $\chi_{ab,c}^{-1}$ vs. $T$ as shown in Fig. 3b. Note that both $\chi_{ab}^{-1}$ and $\chi_c^{-1}$ vary approximately linearly with $T$ between 25 K and $T_0$. This indicates that $\chi_{ab,c}$ can be expressed as

$$\chi = C/(T - \theta), \quad 25K < T < T_0,$$

where $\theta$ is the CW temperature and $C$ is the Curie constant. For Ca$_{2-x}$Sr$_x$RuO$_4$, it is well justified to assume that $C = N_A\mu_B^2g^2(S(S+1))/3k_B$, as the orbital angular momentum for transition metal ions is quenched. Here, $N_A$ is the Avogadro’s number, $g = 2$, $k_B$ is the Boltzmann’s constant and $\mu_B$ is the Bohr magneton. Our fits for the range 25 K $< T < T_0$ (solid lines in Fig. 3b) yield $S = 0.55$ and $\theta_{ab} = -2.4$ K from $\chi_{ab}(T)$, and $S = 0.66$ and $\theta_c = -9.5$ K from $\chi_c(T)$. However, both $\chi_{ab}$ and $\chi_c$ appear to slowly deviate from the CW behavior above $T_0$, and tend to follow a simple Curie law ($\chi \propto T^{-1}$) as demonstrated in the inset of Fig. 3b. This implies that the interactions between local moments become important due to the structural change. The negative $\theta_{ab}$ and $\theta_c$ suggest antiferromagnetic (AF) spin interactions within the $ab$-plane and along the $c$-direction below $T_0$. While evidence for long-range magnetic order has not been found, the peak in $\chi_c$ indicates that short-range AF correlation develops along $c$-direction below $T^*$, consistent with the downturn of the resistivity (see Fig. 2) and the upturn of $C_p/T$ (see Fig. 1).

The above analysis indicates that the magnetic susceptibility of Ca$_{1.7}$Sr$_{0.3}$RuO$_4$ is dominated by the spin susceptibility. Thus, the Wilson ratio, $R_W =$
\( \pi^2 k_B^2 \chi_{\text{spin}} / 3 \mu_H^2 \gamma \), may be estimated using \( \chi_{\text{spin}} = \chi \). Given the saturated value \( \chi_{ab} = 0.0333 \text{ cm}^3/\text{mol} \) below 3.5 K, we obtain \( R_H = 1.7 \), exceeding the value of unity expected for free electrons. For comparison, we estimate \( R_W = 1.7 - 3.2 \) for UPt3 using the data given by Ref. \[1\]. It may be seen that the values of \( R_W \) are similar in the two systems.

Considering Hund’s coupling in the \( t_{2g} \) bands and the large crystal field splitting in a 4d system, the S = 1 configuration is naturally expected for Ca\(_{2-Sr_2RuO_4}\). However, our susceptibility data yield \( S = 0.55 - 0.66 \), in agreement with previous work.\[2\] A theoretical investigation\[3\] suggests that this unusual behavior is driven by the crystal structural distortion (tilting and rotation of RuO\(_6\) octahedra), which narrows the \((xz, yz)\)-subbands and changes the crystal field splitting. In the regime of \( 0.2 < x < 0.5 \), it was proposed that 3 electrons in the \((xz, yz)\)-subbands are localized and produce a net local moment of \( S = 1/2 \). The remaining electron is in the itinerant \( xy \)-band and is responsible for the metallic character. Within this picture, the conduction band is essentially half-filled.

To test the above proposal, Hall measurements were performed by applying current \( I \) along the \( ab \)-plane (\( I \parallel ab \)) and magnetic field \( H \) along the \( c \)-direction (\( H \parallel c \)). Fig. 4 presents the temperature dependence of the Hall coefficient \( R_H \) (hollow circles) at 8 Tesla between 2 and 300 K. Note that \( R_H \) is positive and shows strong temperature dependence over the entire temperature range. Similar to \( \chi_c \), upon cooling, \( R_H \) initially increases and then decreases, revealing a peak around 14 K. For comparison, we replot \( \chi_c \) into Fig. 4 (solid circles). Remarkably, the two sets of data scale very well between 14 and 300 K without any adjustable parameters. A similar scaling relationship has been seen in UPt\(_3\).\[7\] In the latter material, the temperature-dependent \( R_H \) above \( T^* \) is interpreted as the sum of an ordinary Hall coefficient \( R_0 \), arising from the Lorentz force, and an extraordinary term representing the incoherent skew scattering from local moments, i.e., \( R_H \) can be described by

\[
R_H = R_0 + 4\pi \chi R_s, \tag{3}
\]

where \( R_s \) is a T-independent constant. Using Eq. 3 and \( \chi = \chi_c \), we fit our \( R_H \) data between 15 and 300 K, yielding \( R_0 = 7.22 \times 10^{-11} \text{ m}^3/\text{C} \) and \( R_s = 2.65 \times 10^{-3} \text{ mol/C} \). The rather small \( R_0 \) suggests the conduction band is close to half-filling, consistent with the theoretical prediction cited above.

Finally, it should be mentioned that \( R_H \) of Ca\(_{1.7}Sr_{0.3}RuO\(_4\) resembles that of UPt\(_3\) not only at high temperatures but also in the coherent state. As shown in the inset of Fig. 4, \( R_H \) exhibits a \( T^2 \) dependence below \( T^* \), as has also been observed in UPt\(_3\).\[7\] This implies that the anomalous Hall effect in both systems results from the same scattering mechanism.

In summary, our \( C_p(T), \rho(T), \chi(T), R_H(T) \) and X-ray diffraction measurements on Ca\(_{1.7}Sr_{0.3}RuO\(_4\) indicate a continuous structural transition at \( T_0 \sim 190 \text{ K} \), below which AF interactions between local moments develop. Remarkably, physical properties such as the upturn in \( C_p/T \), the downturn in \( \rho(T) \), \( \chi(T) \) and \( R_H(T) \), and the \( T^2 \)-dependence of \( \rho \) and \( R_H \) below \( T^* \sim 10 \text{ K} \) resemble those of the 5f HF compound UPt\(_3\), making Ca\(_{1.7}Sr_{0.3}RuO\(_4\) the only known 4d-HF material. This strongly suggests a similar underlying mechanism for the heavy-electron behavior in these two systems, characterized by the large \( \gamma, \chi \) and \( A \) values.

Acknowledgments

R.J. would like to thank Dr. L. Balicas for technical assistance and B.C. Sales for helpful discussions. This work is in part supported by NSF DMR-0072998 (UT) and by DOE DE-FG02-00ER45850 (CU). Oak Ridge National laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.

\[1\] Y. Maeno, Physica C 282-287, 206 (1997).
\[2\] S. Nakatsuji and Y. Maeno, Phys. Rev. B 62, 6458 (2000)
\[3\] V. I. Anisimov and I. A. Nekrasov and D. E. Kondakov and T. M. Rice and M. Sigrist, cond-mat/0107095 (2001).
\[4\] Z. Fang and K. Terakura, Phys. Rev. B 64, R20509 (2001)
\[5\] S. Nakatsuji and Y. Maeno, Phys. Rev. Lett. 84, 2666 (2000).
\[6\] O. Friedt, M. Braden, G. Andre, P. Adelmann, S. Nakatsuji and Y. Maeno, Phys. Rev. Lett. 84, 2666 (2000).
suji, and Y. Maeno, Phys. Rev. B 63, 174432 (2000).

[7] J. Schoenes and J.J.M. Franse, Phys. Rev. B 33, 5138 (1986).

[8] For a review, see H.R. Ott and Z. Fisk in, Handbook on the Physics and Chemistry of the Actinides (edited by A.J. Freeman and G.H. Lander, Elsevier Science, 1987).

[9] S. Doniach and S. Engelsberg, Phys. Rev. Lett. 17, 750 (1966).

[10] Y. Maeno, K. Yoshida, H. Hashimoto, S. Nishizaki, S. Ikeada, M. Nohara, T. Fujita, N. E. H. A. P. Mackenzie, J. G. Bednorz, and F. Lichtenberg, J. Phys. Soc. Jpn. 66, 1405 (1997).

[11] J.J.M. Franse and P.H. Frings and A. de Visser and A. Menovsky and T.T.M. Palstra and P.H. Kes and J.A. Mydosh, Physica B 126, 116 (1984).

[12] S. Kondo, D. Johnston, C. Swenson, F. Borsa, A. Mahajan, L. Miller, T. Gu, A. Goldman, M. Maple, D. Gajewski, et al., Phys. Rev. Lett. 78, 3729 (1997).

[13] K. Kadowaki and S.B. Woods, Solid State Commun. 58, 507 (1986).

[14] N. Ashcroft and N. Mermin, Solid State Physics (Holt, Rinehart and Winston, 1976).