Localization and transport in pseudoternary ruthenates

G. Cao[a], V. Dobrosavljevic[a], S. McCall[a], J. E. Crow[a] and R. P. Guertin[b]

a. National High Magnetic Field Laboratory, 1800 East Paul Dirac Drive, Tallahassee, FL 32310. b. Physics Dept., Tufts University, Medford, MA 02155

ABSTRACT:

The temperature dependence of the electrical resistivity of two chemically substituted Ca-ruthenates is examined with the Efros-Shklovskii mechanism invoking Coulomb interactions between carriers. Additional mechanisms causing an energy dependence to the density of states at the Fermi surface may explain the unusually wide temperature and conductivity range obeyed by one system.

Corresponding Author: R. P. Guertin, Science and Technology Center 201, Tufts University, Medford, MA 02155. Fax: 617-627-3244. Email: Rguertin@Magnet.FSU.Edu.

Electronic transport in 4d- and 5d-based transition metal oxides is strongly mediated by hybridization between oxygen p-orbitals and the d-orbitals, which generally have larger spatial extent than their 3d counterparts [1]. For these systems it is reasonable to expect stong electron-phonon interactions, and as a result many 4d and 5d transition metal oxides border on the metallic/non-metallic interface. For those on the metallic side of the interface, small of substituted impurities on the d sites should cause concentrations a transition to a non-metallic phase, most likely due to localization of the charge carriers rather than opening of an activation gap at the Fermi surface. For those on the non-metallic side, substitutions may move the system closer to the metallic conductivity. Here we detail the temperature dependence of the electrical resistivity, r(T), of two representative ruthenates to illustrate transitions near the metal/non-metal interface.

The Ruddlesden-Popper Ca-base sequence, $Ca_{n+1}Ru_nO_{3n+1}$ for n=1, 2 and ∞ spans the range of conductivity from highly insulating to "bad" metallic [2]. The index n signifies the number of repeated Ru-O planes. The n=2 member, $Ca_3Ru_2O_7$, undergoes a Mott-like transition at T_M=48 K [3]. The transport and magnetic data for two isoelectronic systems, the n=1 member, Ca_2RuO_4, which has the distorted K_2NiF_4 structure of the high T_c materials, and the n= ∞ member, $CaRuO_3$, which has a distorted perovskite structure, show opposite behaviors: The latter does not magnetically order nor show a metal insulator transition above T=0 K [4], and the former is insulating at room temperature and undergoes an antiferromagnetic transition at T_N=105 K [5]. We will see that the two end points of this series, Ca_2RuO_4 and $CaRuO_3$ are highly sensitive to small changes in the chemical composition.

In Fig. 1 we show r(T) for all three systems, the data covering an impressive 14 orders of magnitude below 100 K. (For the n=1 case, the resistance becomes immeasurably large below about T=70 K.) For the n=2 system, the metal-to-non-metal transition at T_M=48 K is evident from the figure. However, the resistivity quickly saturates for $T<<T_M$, unlike the case for the canonical Mott insulator, V_2O_3, for example [1]. It was this feature, suggesting an alternative conduction mechanism in the system that led to measuring the

current voltage characteristics of $Ca_3Ru_2O_7$: highly non-linear I-V behavior was found with current controlled negative differential resistance [6]. Also indicated in Fig. 1 are the antiferromagnetic ordering, Neel, temperatures for two systems. There is a small anomaly at T_N for n=2, but none for n=1.

In order to learn more about the conduction mechanism for the n=1 system several fitting schemes were attempted. Activation fits, i.e., $r(T)=Aexp(-D/k_BT)$ were not successful over the entire temperature range, but force fitting yielded $D\approx0.02$ eV ($\approx200K$) around room temperature. A much more satisfactory fit to the data utilized the Efros-Shklovskii (ES) Coulomb interaction mechanism, $r(T)=Aexp(-T_o/T)^{-1/2}$, and this is illustrated in Fig. 2 along with data for samples, slightly doped with the divalent cation, Sr [7]. (Note Sr_2RuO_4, which is isomorphic to Ca_2RuO_4, is the well-known ruthenate superconductor [8].) ES theory predicts that a small Coulomb gap, d, opens up at the Fermi surface as a result of Coulomb interactions between the quasiparticle carriers, with $d\approx e^3N(E_F)^{1/2}/k^{3/2}$, e being the electronic charge, k the effective dielectric constant, and $N(E_F)$ the density of states at the Fermi surface. Using $N(E_F)$ from our own low temperature heat capacity measurements (4 mJ/mole-K^2) and our own measurements of k (≈100 at 1 MHz at 170K), we make a very rough estimate of d $\approx$1-3 meV ($\approx$10-30 K). The large value of T_o for both the x=0 and x=0.02 ($Ca_{1-x}Sr_x)_2RuO_4$ samples is consistent with the temperature range of validity must be much less than T_o. The lower value of T_o ($\approx10^3$ K) for the x=0.04 sample implies the doped system is close to a transition to a metallic phase. The $T^{-1/2}$ dependence depends on a parabolic curvature to N(E) within the gap near E_F, i.e. $N(E+\_) \propto (E-E_F)^2$ for $E/E_F<<1$.

The remarkable feature of the data of Fig. 2 is that the temperature range over which the ES mechanism works is so large, i.e., it seems to work for $k_BT>>d$. For $k_BT>>d$, the system should obey Mott variable range hopping, $r(T)=A'exp(T_o'/T)^{-1/4}$. However, if there are mechanisms giving an <u>energy</u> dependence to the density of states at E_F even at high temperatures, the observed $T^{-1/2}$ behavior of r(T) would be anticipated. One such a mechanism is dynamic in nature, based on a thermal activation of tipping of the RuO_6 octahedra in

Ca_2RuO_4 and its associated M-O-M bond angle: Because the Ru d-electron bandwidth, D, is associated with the M-O-M bond angle (D increasing with decreasing bond angle) one may expect a thermally generated variation in the density of states. Another mechanism is based on a static argument: The Ca_2RuO_4 structure is considerably distorted from the ideal K_2NiF_4 structure, evidence from neutron scattering data being that the M-O-M bond angle at room temperature is 152°, rather far from the ideal 180° [9]. Quenching of the sample from high temperature during fabrication could freeze in a distribution of bond angles, again widening the d-bandgap and giving rise to a temperature independent variation in the density of states near the Fermi surface. Details of these calculations with justification using simultaneous minimization of the elastic and electronic free energies will be presented elsewhere.

Turning to the other end member of the sequence in Fig. 1, we show in Fig. 3, r(T) for several polycrystalline $Ca(Ru_{1-x}Rh_x)O_3$ samples [4]. Rh was chosen to increase Ru sublattice disorder because there is essentially no change in the lattice constant and because Rh is isoelectronic with Ru. $CaRuO_3$ is a very narrow band gap metal, with weakly temperature dependent resistivity, most likely a "bad" metal [2], as the room temperature single particle mean free path is unrealistically small, ≈ 0.03 A. Thus small perturbations of the chemical composition, either through cation substitution for Ca^{2+} (e.g., monovalent Na, see Ref. 10), or for Ru^{4+} are likely to cause large changes in the conduction process, as is evident in the data of Fig. 3. The data show a smooth transition from metallic to insulating for 0<x<0.15. For the most insulating of the series, $CaRu_{0.85}Rh_{0.15}O_3$, we attempted fits to activated conductivity, Mott variable range hopping and the ES mechanism. None were successful over the entire range of temperature.

Whether the transition from "bad" a metallic conductivity mechanism to a localization mechanism is characteristic of all heavy transition metal oxides requires additional data from more doped systems similar to those discussed here.

FIGURE CAPTIONS

Fig. 1: Semilog plot of the electrical resistivity of three Ca-based ruthenate Ruddelsden-Popper sequence systems.

Fig. 2: Electrical resistivity of $(Ca_{1-x}Sr_x)_2RuO_4$ showing wide range of applicability of the Efros-Shklovskii conduction mechanism.

Fig. 3: Transition from "bad" metal to non-metal in polycrystalline Rh doped $CaRuO_3$.

REFERENCES:

1. P. A. Cox, "Transition Metal Oxides", (Clarendon Press, Oxford, 1995).
2. V. J. Emery and S. A. Kivelson, Phys. Rev. Lett. 74 (1995) 3253.
3. G. Cao, S. McCall, J. E. Crow and R. P. Guertin, Phys. Rev. Lett. 78 (1997) 93.
4. G. Cao, F. Freibert and J. E. Crow, J. Appl. Phys. 81 (1997) 3884.
5. G. Cao, S. McCall, M. Shepard, J. E. Crow and R. P. Guertin, Phys. Rev. B56 (1997) R2916.
6. R. P. Guertin, J. Bolivar, G. Cao, S. McCall and J. E. Crow, to be published in Solid State Commun.
7. A. L. Efros and B. L. Shklovskii, J. Phys. C8 (1975) L49.
8. Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujito, J. G. Bednorz and F. Lichtenberg, Nature ¨372¨, 532 (1994).
9. Y. Maeno, private communication.
10. M. Shepard, G Cao, S. McCall, F. Freibert and J. E. Crow J. Appl. Phys. 79 (1996) 4821.
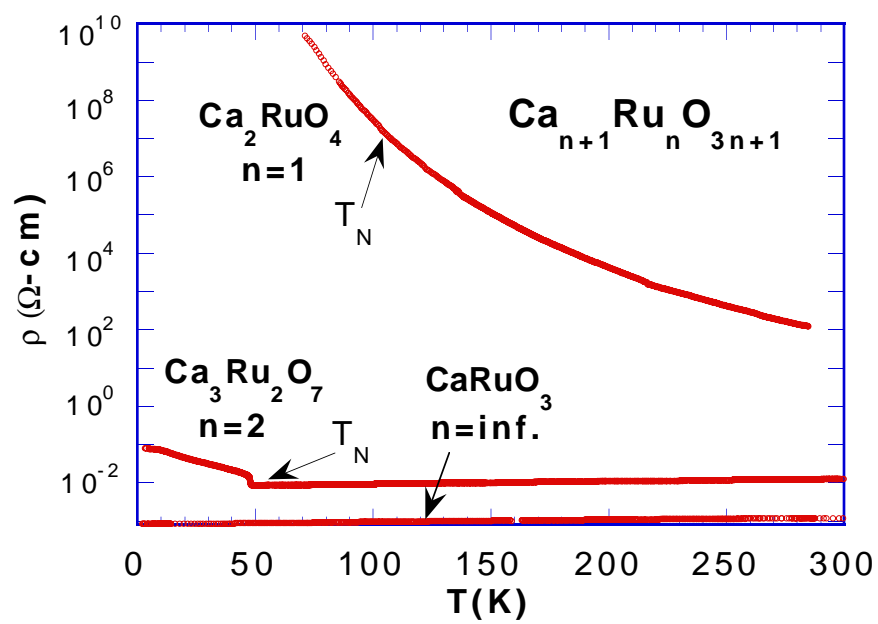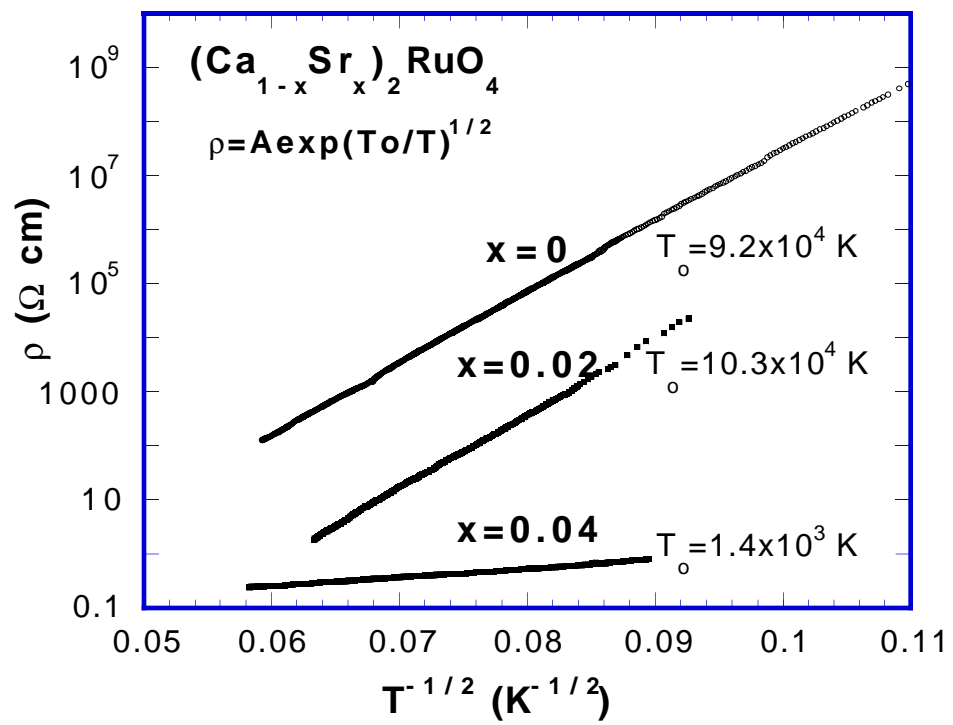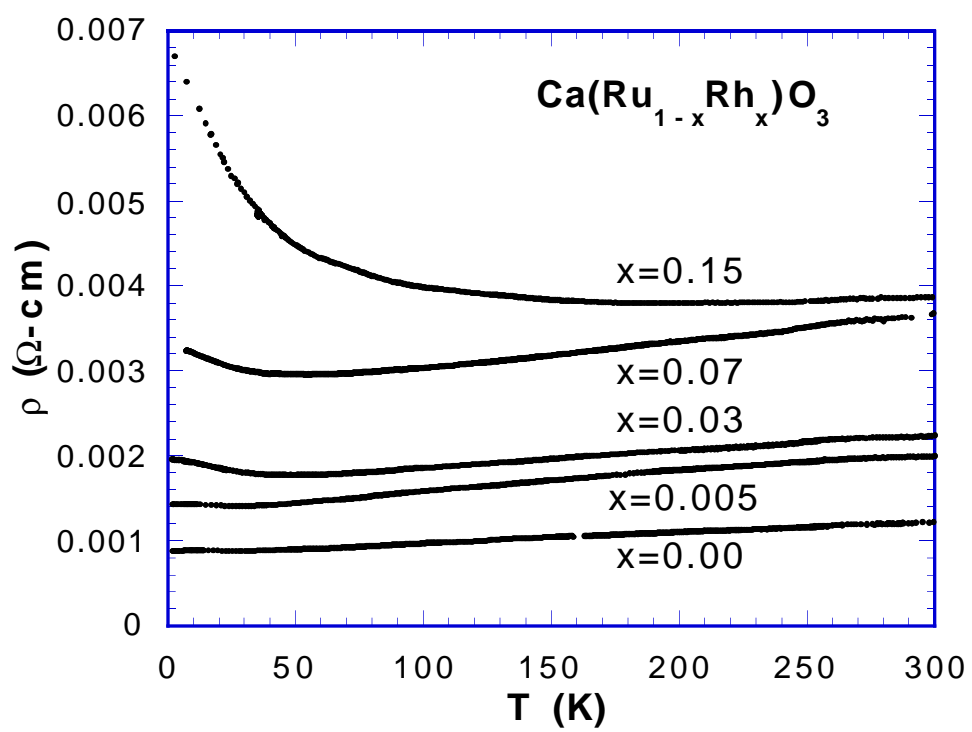
Figure 1

$(Ca_{1-x}Sr_x)_2RuO_4$

$\rho = A\exp(To/T)^{1/2}$

x = 0 $T_o = 9.2 \times 10^4$ K

x = 0.02 $T_o = 10.3 \times 10^4$ K

x = 0.04 $T_o = 1.4 \times 10^3$ K

ρ (Ω cm)

$T^{-1/2}$ ($K^{-1/2}$)

Figure 2

7

Figure 3