Sensitivity to Disorder of the Metallic State in the Ruthenates

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We report the results of transport measurements on $SrRuO_3$, $Sr_3Ru_2O_7$, and $CaRuO_3$. In $SrRuO_3$ and $Sr_3Ru_2O_7$, our findings are consistent with the predictions of Fermi liquid theory, in contrast to previous reports based on samples with much shorter mean free paths. In $CaRuO_3$, however, a $T^{1.5}$ power law is seen in the resistivity in the high purity samples studied here. Our work gives concrete evidence that even the metallic state of the ruthenates is highly sensitive to disorder.

Ruthenate metals continue to be a subject of intense study, because the ruthenate family is acknowledged to be well suited to the study of correlated electrons in itinerant systems. The most closely investigated ruthenate, Sr_2RuO_4, is known to be a nearly two-dimensional Fermi liquid metal [1,2] whose quasiparticles condense to form an unconventional superconductor [3]. Strong evidence has emerged to support the idea of spin triplet Cooper pairing, a very unusual form of superconductivity which has focused considerable attention on the magnetic properties of Sr_2RuO_4 and other ruthenates [4,5]. A central feature of the progress that has been made in understanding Sr_2RuO_4 was the successful growth of extremely high purity single crystals. Residual resistivities (ρ_{res}) of less than 0.1 $\mu\Omega$ cm have been achieved by now, and thorough tests of both the validity of Fermi liquid theory and the precise nature of the superconducting order parameter have been performed on crystals with mean free paths in excess of 1 μm. In fact, the superconductivity that generated all the interest can be completely destroyed by impurity scattering [6].

In other ruthenates, there are as yet no further observations of superconductivity (possibly because sufficiently long mean free paths have not yet been achieved), but a range of other fascinating itinerant magnetic properties have been uncovered. Pseudocubic $SrRuO_3$ is an itinerant ferromagnet [7–9], while the bilayer material $Sr_3Ru_2O_7$ is an itinerant metamagnet [10]. $CaRuO_3$ is metallic, and has generally been thought to be paramagnetic [9], but signs of magnetic ordering have also been reported recently [11]. These unusual magnetic or nearly magnetic ruthenate metals have been used by a number of groups to probe possible deviations from the standard Fermi liquid picture of the metallic state in materials with strong electron interactions. Although Sr_2RuO_4 is a fully confirmed Fermi liquid at low temperatures, its properties at temperatures of approximately 30 K and above are more anomalous, raising the question of what should set such a low "crossover" scale in a material with a relatively high Fermi temperature of greater than 1000 K [12]. The behavior of $Sr_3Ru_2O_7$ was reported to be qualitatively similar [13], in the sense that an approximately T^2 resistivity at low temperatures crossed over to a much lower power at higher temperatures. Recently, however, this has been questioned, a power as low as $T^{1.4}$ at low temperatures having been suggested by one group [14]. Powers of less than 2 have also been reported in thin films of $CaRuO_3$ [15]. The situation in $SrRuO_3$ is more interesting still. High frequency measurements at relatively elevated temperatures suggested an anomalous $\sqrt{\omega}$ frequency dependence, leading to the proposal of a non-Fermi liquid metallic state [16]. Observation of a T^2 scattering rate and Shubnikhov−de Haas oscillations appeared to confirm a low temperature Fermi liquid [17], but new high frequency measurements have again led to the suggestion of deeply anomalous behavior. On the basis of a combination of infrared and terahertz measurements on thin films of $SrRuO_3$ to temperatures as low as 8 K, Dodge and coworkers have made a radical proposal about the existence of a metallic state whose conductivity is related to its scattering rate by an anomalous power law [18].

The nature of the metallic state in itinerant ruthenates is, therefore, the subject of considerable interest and some controversy. In an effort to settle some of the outstanding issues, we report here a study of the simple low temperature low frequency conductivity of $SrRuO_3$, $CaRuO_3$, and $Sr_3Ru_2O_7$, concentrating on the highest purity single

crystals and thin films available. The results give a concrete demonstration that disorder plays an even more important role in this class of system than had previously been assumed. The fragility of superconducting and magnetic ground states to disorder scattering is well established; here we show that even the correlated electron metallic state is remarkably sensitive to disorder.

The crystals used in this study were grown in Tallahassee from a chloride flux in Pt crucibles ($SrRuO_3$ and $CaRuO_3$ [9]) and in Kyoto in an image furnace ($Sr_3Ru_2O_7$ [19]). In each case, there is significant crystal-crystal variation in purity, and in total over 60 crystals were characterized as part of this project. We also performed new resistivity measurements on the thin film samples of $SrRuO_3$ grown at Stanford whose properties were previously reported in Ref. [17]. The resistivity measurements were carried out by standard four-terminal low frequency ac methods ($\omega < 1000$ rad/sec) in several cryostats. Here we show data taken using ^{4}He based cooling, since it can be easily extended to the higher temperature range, but we have also checked that the T^2 dependences that we see below approximately 10 K in $SrRuO_3$ and $Sr_3Ru_2O_7$ are still observed for the region 50 mK $< T <$ 1 K that we can access using our dilution refrigerators. The crystals with the highest purity are often quite small (typical largest linear dimension less than 500 μm), so there is a temperature-independent geometrical uncertainty of 10%–15% in the absolute values of the resistivity that we report.

The resistivity from room temperature of four representative single crystal samples is shown in Fig. 1 and inset. In $SrRuO_3$, the Curie temperature is clearly seen by the kink in ρ at approximately 160 K, with strong curvature below approximately 30 K. The best crystal that we studied had ρ_{res} of approximately 8 $\mu\Omega$ cm, compared to approximately 3 $\mu\Omega$ cm for the best film (Ref. [17] and inset of Fig. 2). For $CaRuO_3$ we concentrate on two single crystal samples from either end of the purity range (ρ_{res} of 55 and 4 $\mu\Omega$ cm, respectively). The resistivity of $Sr_3Ru_2O_7$

is shown in the inset. In this material, the feature in ρ at approximately 20 K is clearly magnetic in origin, since it correlates with a pronounced hump in the magnetic susceptibility [13].

The main theme of this paper is the analysis of measurements of the low temperature resistivity of these high purity samples, so we will now report and discuss low temperature data from each material in turn. In Fig. 2, we show ρ plotted as a function of T^2 for our best single crystal (main figure) and thin film (inset) of $SrRuO_3$. In both cases, the closely spaced data points appear as a thick line, and the temperature dependence of ρ is very close to quadratic, especially below 15 K.

On the basis of their infrared/terahertz study on $SrRuO_3$, Dodge and collaborators [18] proposed a radical departure from the relationship between conductivity and scattering rate of a standard Fermi liquid. They fitted their data to a general form discussed recently in the context of the cuprates [20,21]:

$$\sigma(\omega) = \frac{A}{(1/\tau - i\omega)^\alpha} . \tag{1}$$

In a Fermi liquid, the power α is one, which corresponds to the physically intuitive result that the resistivity is proportional to the microscopic scattering rate. As stressed in Ref. [18], a departure of α from one would have the profound implication that metallic states exist for which the scattering rate cannot be simply inferred from measurements of low frequency electrical transport. This issue is so important that it warrants careful analysis. In their paper, Dodge et al. point out that their measurement
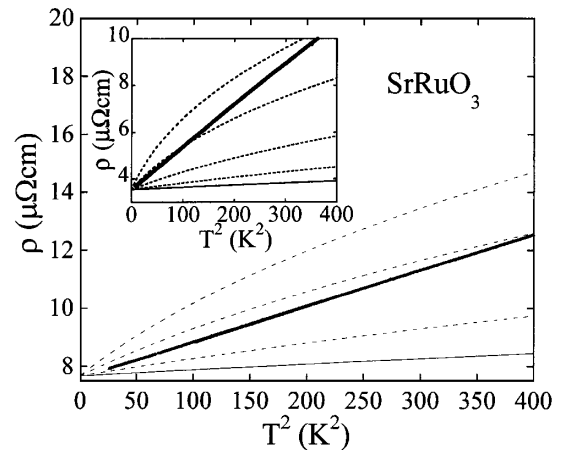

FIG. 1. The resistivity of single crystals of $SrRuO_3$, $CaRuO_3$, and (inset) $Sr_3Ru_2O_7$.

FIG. 2. The low temperature resistivity of $SrRuO_3$ varies quadratically with temperature (thick line). The data cannot be matched using the expressions given in Ref. [16] and reproduced here as Eqs. (1) and (2). The thin solid line is the prediction using the parameters derived for $SrRuO_3$ in Ref. [18]; the dotted lines are the result of varying them to attempt a better fit to the data. The inset shows the same procedure applied to data from the higher purity thin film in which Shubnikov–de Haas oscillations were reported in Ref. [17].

of $\alpha = 0.4$ is not necessarily inconsistent with the observation of a quadratic temperature dependent resistivity, if τ has the form

$$\frac{\hbar}{\tau} = \frac{\hbar}{\tau_0} + \frac{k_B T^2}{T_0}. \tag{2}$$

On the basis of their analysis on the sample used in their experiment, they extracted values of 198 fs and 40 K for τ_0 and T_0, respectively. However, this can occur only if the combination of impurity scattering and temperature is such that $k_B \tau_0 T^2 / \hbar T_0 \ll 1$, so that only the leading order term in an expansion of the full conductivity expression is significant. In fact, our data are in rather severe disagreement with a low frequency extrapolation of their proposal. If we attempt to model them using their full expression including their value for the ratio of τ_0 to T_0, we obtain the thin solid lines in Fig. 2 and its inset. Allowing τ_0/T_0 to vary to attempt to account for the far higher strength of the T^2 term in our data does not improve the situation, since Eq. (1) cannot then support a quadratic resistivity over anything like the range that we observe.

On the basis of our observations and analysis of SrRuO$_3$, we are therefore forced to conclude that the conductivity form of Eq. (1) with $\alpha \neq 1$ does not apply in the low frequency limit to SrRuO$_3$ with $\rho_{\rm res} \leq 8 \ \mu\Omega$ cm. There is, therefore, little hope that a new framework for understanding conductivity in correlated systems as a whole has been uncovered. That does not, of course, mean that the results reported in Ref. [18] are without significance, but disorder may play an important role. For the very difficult transmission measurements of Dodge *et al.* to be possible, the thin films had to be grown on NdGaO$_3$ substrates that are transparent in the terahertz region. These films have a far higher residual scattering rate than those grown on vicinal SrTiO$_3$, which is terahertz opaque. It is, therefore, tempting to attribute the differences between the conclusions of Ref. [18] and those of Ref. [17] and the present work to the different levels of disorder in the samples studied, although other possibilities should also be considered [22].

We now turn our attention to Sr$_3$Ru$_2$O$_7$, in which a T^2 dependence of ρ has been reported [13] but subsequently questioned [14]. Resistivity data are shown in Fig. 3 as a function of T^2. Here, there is a rather sharp crossover to a pure quadratic T dependence of ρ below approximately 7 K. Viewed on the quadratic temperature axis, this is a fairly subtle effect, but if the residual term is removed and the data are divided by T^2 and plotted on a linear temperature axis, both the sharpness of the crossover and the purity of the low temperature power law can clearly be seen. These data are therefore in direct contradiction to those recently reported in Ref. [14], where $T^{1.4}$ was observed. Our data are plotted against $T^{1.5}$ in the main part of Fig. 4, and are clearly seen to be a very poor fit, which is even worse if 1.4 is used. The difference between the findings of the two groups is again likely to be related to disorder,
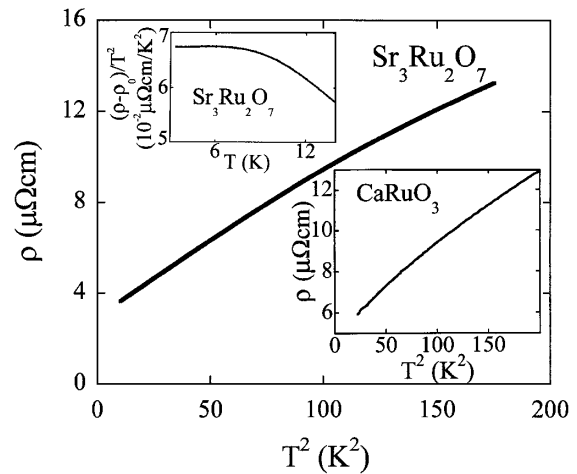

FIG. 3. The low temperature resistivity of Sr$_3$Ru$_2$O$_7$ crosses over to a quadratic temperature dependence below approximately 7 K (main figure and top inset; see text), but that of CaRuO$_3$ shows clear deviations from this temperature dependence (bottom inset).

a possibility also raised by the authors of Ref. [14]. The crystals used in their study had $\rho_{\rm res} = 20 \ \mu\Omega$ cm, significantly higher than our current value of 2–3 $\mu\Omega$ cm. Further evidence of the pronounced effect of disorder in Sr$_3$Ru$_2$O$_7$ comes from an examination of low temperature magnetoresistance (MR) in the samples of Ref. [14] and our crystals, for which we reported MR data in Ref. [10]. Sr$_3$Ru$_2$O$_7$ has a metamagnetic transition, the signature of which is seen in low temperature transport. Comparison of Fig. 2 of Ref. [10] and Figs. 3 and 4 of Ref. [14] shows that in less pure samples there is a dramatic broadening of the features concerned, conclusively demonstrating a high sensitivity to disorder in this material.

In Sr$_3$Ru$_2$O$_7$ and SrRuO$_3$, our results suggest a strong sensitivity of the metallic state to disorder. The highest purity samples reveal a less exotic picture of the low temperature state (at least in zero applied magnetic field) than
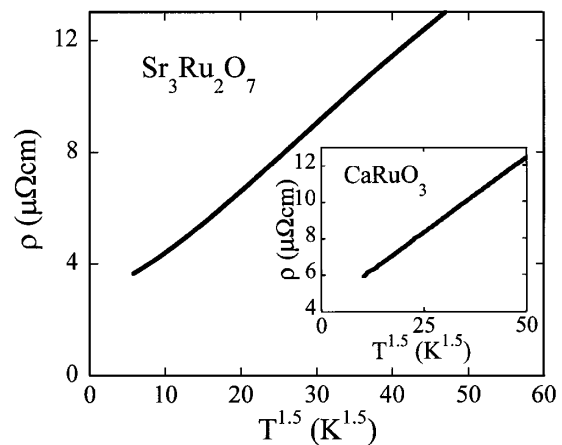

FIG. 4. The low temperature inelastic resistivity of Sr$_3$Ru$_2$O$_7$ is clearly incompatible with a $T^{1.5}$ dependence, but that of high purity CaRuO$_3$ is fully consistent with $T^{1.5}$ (inset).

would be inferred from results on lower purity samples. The final results that we report here concern single crystals of $CaRuO_3$. Again, we observe a marked impurity effect on the metallic state, but in this case, apparently non-Fermi liquid powers are seen in all the samples studied. Our findings are shown in Fig. 1 and insets to Figs. 3 and 4. In the impure sample, a power close to one is observed below 15 K (Fig. 1). In the best crystal which, with $\rho_{res} = 4 \ \mu\Omega$ cm is the purest sample of $CaRuO_3$ studied to date, a $T^{1.5}$ dependence is seen to high accuracy (inset to Fig. 4), consistent with previous work on thin films of $CaRuO_3$ by Klein et al. [15]. On the basis of the current data, a claim that $CaRuO_3$ is non-Fermi liquid would be premature, since a crossover to T^2 at lower temperature or still higher purity cannot be ruled out [23]. It certainly seems to be the most anomalous ruthenate metal studied so far, however, and its metallic state is worthy of further investigation, with measurements to dilution refrigerator temperatures a priority.

The work presented here has given three concrete examples of ruthenate metals in which disorder plays a nontrivial role in determining the nature of the metallic state. A key advantage of the ruthenates is that disorder can be controlled. The main sources of scattering centers in these materials are either chemical impurities (in crystals grown from fluxes in hot crucibles) or structural defects (in thin films or crystals grown using crucible-free methods). Oxygen vacancies do not appear to play an important role, since ruthenates are remarkably insensitive to different annealing/quenching treatments in varying atmospheres [24]. The fact that we observe a marked sensitivity to disorder has significance in the much wider field of correlated electrons in oxides and alloys, because the control of disorder that is possible in the ruthenates is far from universal. In many systems of interest, disorder is "intrinsic," as nonstoichiometric chemical doping is used either to induce the metallicity itself, or to tune the system through a region of quantum criticality. It is important that the role of disorder in these circumstances be acknowledged and, eventually, that an appropriate theoretical framework be found for treating its effects.

In conclusion, we have shown that anomalous metallic state behavior recently reported in the itinerant ferromagnet $SrRuO_3$ and the metamagnet $Sr_3Ru_2O_7$ does not appear to extend to the region of parameter space where Fermi liquid theory makes its most robust predictions: low temperatures and high purity samples. The Fermi liquid state in these materials appears, however, to be remarkably sensitive to both thermal and impurity scattering, behavior for which there is as yet no fully satisfactory understanding. In $CaRuO_3$, which has not so far been as widely studied as the other two materials, anomalous power laws are seen in the resistivity in even the best samples currently available, giving strong motivation for further experiments.

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