Metamagnetism and Critical Fluctuations in High Quality Single Crystals of the Bilayer Ruthenate Sr₃Ru₂O₇

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We report the results of low temperature transport, specific heat, and magnetization measurements on high quality single crystals of the bilayer perovskite $Sr_3Ru_2O_7$, which is a close relative of the unconventional superconductor Sr_2RuO_4 . Metamagnetism is observed, and transport and thermodynamic evidence for associated critical fluctuations is presented. These relatively unusual fluctuations might be pictured as variations in the Fermi surface topography itself.

DOI: 10.1103/PhysRevLett.86.2661

PACS numbers: 75.30.Kz, 71.27.+a

Research over the past decade has shown the potential of perovskite ruthenate metals to play a pivotal role in our understanding of the behavior of strongly correlated electrons. The position of the Fermi level in bands resulting from the hybridization of oxygen 2p and ruthenium 4d levels leads to ground state behavior covering a wider range than that seen in almost any other transition metal oxide series. Pseudocubic SrRuO₃ is a rare example of an itinerant ferromagnet based on 4d electrons, and has a good lattice match to the cuprates [1,2]. Sr₂RuO₄ has the layered perovskite structure with a single RuO₂ plane per formula unit. It is strongly two dimensional, and shows a Paulilike paramagnetic susceptibility [3]. It is best known for its unconventional superconductivity [3], which is thought to involve spin triplet pairing [4]. Structural distortions in Sr-based ruthenates are either small or absent, but substituting Ca for Sr introduces larger rotations of the Ru-O octahedra, causing bandwidth narrowing and changes to the crystal field splitting. Thus, although Ca and Sr are both divalent cations, the properties of the Ca-based materials are markedly different. CaRuO₃ is a paramagnetic metal with a large mass enhancement [5], while Ca₂RuO₄ is an antiferromagnetic insulator [6]. This diversity shows that the ruthenates are characterized by a series of competing, nearly degenerate instabilities, giving a clear motivation for the careful investigation of all the compounds in the series. An even more important feature of the ruthenates is that, in contrast to 3d oxides such as most manganites and many cuprates, no explicit chemical doping is required to produce metallic conduction. This gives a unique opportunity to probe a wide range of correlated electron

physics in the low disorder limit. The superconductivity of Sr_2RuO_4 , for example, is strongly disorder dependent [7], and further examples of unconventional superconductivity may be expected in other ruthenates if they can be grown with mean-free paths as long as those of Sr_2RuO_4 . Of particular interest is the subject of this paper, $Sr_3Ru_2O_7$, which has a Ru-O bilayer per formula unit, and hence an effective dimensionality that is intermediate between those of Sr_2RuO_4 and $SrRuO_3$.

The synthesis of $Sr_3Ru_2O_7$ in polycrystalline form has been reported by several groups over the past three decades [8–10], but investigations of its electrical and magnetic properties were not carried out until the past few years. There has been some variation in the reports and interpretation of its ground state. Cava and co-workers showed that the magnetic susceptibility (χ) of powders obeyed a Curie-Weiss law with a maximum in the susceptibility at approximately 20 K and a negative Weiss temperature, which they interpreted in a local moment picture as antiferromagnetism [11]. Early reports on single crystals grown from a SrCl₂ flux in Pt crucibles, however, gave evidence for weak itinerant ferromagnetism [12].

Recently, Ikeda and co-workers succeeded in growing much purer crystals (residual in-plane resistivity, ρ_{res} , of $3-4 \ \mu\Omega$ cm) in an image furnace [13]. The magnetic susceptibility of these crystals reproduces the basic features of the paramagnetic susceptibility reported in Ref. [11], with a pronounced maximum at approximately 16 K [14]. Below 5 K, χ becomes completely isotropic and temperature independent. If the maximum were associated with an antiferromagnetic phase transition, an easy axis would be expected. The data of Ref. [14] therefore support the conclusions of elastic neutron scattering measurements [15] that no long-range order exists at low fields. Combined with the observation of a T^2 dependence of ρ below 10 K, the data strongly suggest that at low applied magnetic fields, Sr₃Ru₂O₇ is an exchange-enhanced Fermi liquid.

Here we report the results of low temperature transport, magnetic, and thermodynamic measurements in applied fields up to 14 T on the crystals studied in Ref. [14] and some even cleaner ones ($\rho_{res} = 2 \ \mu\Omega \ cm$). We conclude that the low temperature properties of Sr₃Ru₂O₇ are strongly influenced by critical fluctuations associated with itinerant electron metamagnetism.

Several growth runs of single crystals of Sr₃Ru₂O₇ were performed crucible-free in an image furnace in Kyoto. The resistivity of over 50 pieces taken from three growth rods was studied down to 4 K using standard low frequency ac methods in a small continuous flow cryostat. Residual resistivities ranging between 2–15 $\mu\Omega$ cm were observed, with most samples from the latter batches toward the high purity end of the range. Six of these ($\rho_{res} < 4 \ \mu\Omega$ cm) were used for further study. Magnetization measurements were performed down to 2.8 K in a commercial vibrating sample magnetometer. Magnetotransport was studied at ambient pressure in both ⁴He systems and a dilution refrigerator in Birmingham, and in a ⁴He system in Karlsruhe. Specific heat measurements were performed in Kyoto using commercial magnetothermal apparatus.

Our magnetization results for $Sr_3Ru_2O_7$ are summarized in Fig. 1. For magnetic fields applied in the *ab* plane, a rapid superlinear rise in the magnetization is seen with a characteristic field of approximately 5.5 T. Such behavior can be described as metamagnetism (for further discussion see below). As the temperature is raised, the metamagnetism broadens until it is impossible to define. We have checked extensively for anisotropy with respect to the direction of the in-plane field, but none is observed within our resolution. There is some anisotropy if the field is applied along c, as shown in the inset. For each orientation, data were taken at a total of 18 temperatures below 30 K, but the traces lie sufficiently close to confuse the plot, so, for clarity, only a few are shown.

In order to obtain information on the metamagnetism to lower temperatures, we have studied its effects on the magnetoresistance (MR). Field sweeps to 14 T were performed between 50 mK and 20 K for three standard configurations of the in-plane MR ρ : $B \parallel c$, $I \parallel ab$; $B \parallel I \parallel ab$; and $(B \perp I) \parallel ab$. The results are summarized in Fig. 2, in which a small subset of representative data is presented. For $B \parallel c$, $I \parallel ab$, the weak-field MR is quadratic in B. At higher fields, the metamagnetism is clearly seen in the MR. For $T \ge 5$ K, the width of the feature is similar to that seen in the magnetization, but at low temperatures it sharpens considerably, although there is evidence for extra structure at 11 T. For $B \parallel ab$ there is clear evidence of a split transition for both $B \parallel I$ and $B \perp I$. The transport measurements show that the metamagnetic transition field is essentially temperature independent for any direction of the applied field.

The term metamagnetism can be applied to qualitatively different physical phenomena. In insulators, it describes changes from ordered antiferromagnetic states at low field to ferromagnetically polarized states at high field via "spin-flip" or "spin-flop" processes [16]. In metallic systems such as $Sr_3Ru_2O_7$, the change in magnetization is due to a rapid change from a paramagnetic state at low fields to a more highly polarized state at high fields via either a crossover or a phase transition. Although the distinction



FIG. 1. The magnetization of single crystal $Sr_3Ru_2O_7$ for magnetic fields applied in the *ab* plane. The high field data drop monotonically with the measurement temperatures of 2.8, 5, 7, 9, 12, 16, and 20 K. Metamagnetism is seen for all temperatures below 10 K, centered on a field of approximately 5.5 T. Inset: data for magnetic fields along the *c* axis. For this field orientation, the metamagnetic field is approximately 7.7 T (see Fig. 2).



FIG. 2. The magnetoresistance of single crystal $Sr_3Ru_2O_7$ at a series of temperatures below 10 K. For $B \parallel c$, the very broad peak at 5 K [comparable to the total width of the feature seen in M(B)] sharpens considerably at low temperatures. For in-plane fields, the low temperature MR gives evidence for some peak splitting, as shown by data at 1 K for this orientation.

between a crossover and a phase transition can be an important one, in this case it is less relevant, because some of the basic physics is common to both. First, the observation of itinerant metamagnetism demonstrates the existence of strong ferromagnetic coupling in the system. Second, low temperature critical points are likely in either scenario. A crossover might be linked to close proximity in phase space to a quantum critical point that can be reached only by the application of some other control parameter. If the metamagnetism is due to a T = 0 phase transition along the magnetic field axis, the transition would be expected to be first order (since it is like a density transition of spins in the presence of a symmetry-breaking field). However, the first order transition line might terminate in a critical point at very low temperatures. A natural question, then, is whether there is evidence for critical fluctuations associated with the metamagnetism in Sr₃Ru₂O₇. To address this issue, we have performed measurements of the temperature-dependent resistivity and specific heat.

In Fig. 3 we show a color plot of the power-law behavior of the resistivity of $Sr_3Ru_2O_7$ as a function of temperature and field, for $I \parallel ab \parallel B$. At low and high fields, the quadratic temperature dependence expected of a Fermi liquid is seen at a sufficiently low temperature, but, near the metamagnetic field, the Fermi liquid region is suppressed to below our lowest temperature of measurement (2.5 K for these precise temperature sweeps). These data are strongly suggestive of the existence of a critical point at a temperature low on the scale of the measurement temperature, at a field close to the metamagnetic field. They do not constrain it to lie exactly on the field axis, but the applied field is clearly pushing the system very close to it, and its associated critical fluctuations are playing a central role in determining the properties of the metallic state.

Measurement of the specific heat gives further experimental support for the existence of critical fluctuations. Data for the electronic specific heat (C_{el}) divided by temperature are shown in Fig. 4. In zero field, $C_{\rm el}/T$ (a measure of the quasiparticle mass) rises as the temperature falls below 20 K, but it then crosses over at lower temperatures on a scale similar (but not identical) to the crossover to the quadratic dependence of the resistivity seen in Fig. 3. The application of fields parallel to the c axis suppresses this crossover, so that $C_{\rm el}/T$ rises steeply at low temperatures. At 7.7 T, the slope increases as the temperature falls, consistent with a low temperature $\log(T)$ divergence. By our maximum field of 9 T, however, the slope decreases below 2.3 K, which would be consistent with the onset of a crossover cutting off the divergence. As well as giving thermodynamic support for the critical fluctuations suggested by the transport measurements, the specific heat data emphasize the closeness of the link between the metamagnetism and these fluctuations. If the critical point dominating the fluctuations seen in Fig. 3 was primarily controlled by some parameter other than the field, then changing the field orientation would be expected to make very little difference. Here, however, we have tuned into the divergence of $C_{\rm el}/T$ by cooling at the metamagnetic field for $B \parallel c$ (identified as 7.7 T by the peak in Fig. 2) rather than the value of approximately 5.5 T that would be deduced from Figs. 2 and 3 for $B \parallel ab$.



FIG. 3 (color). The evolution of the temperature dependence of the resistivity of Sr₃Ru₂O₇ as a function of temperature with $B \parallel I \parallel ab$. The plot was constructed by interpolating the results of temperature sweeps at fourteen values of applied field (0 to 12 T in 1 T steps, with an additional sweep at 5.5 T). The colors show the change in the parameter α for a temperaturedependent resistivity of the form T^{α} . The T^2 behavior expected of a Fermi liquid is observed at low temperatures only for fields well away from the metamagnetic field of approximately 5.5 T identified from Fig. 2.

We believe that the above data give good evidence for a close association between metamagnetism and critical



FIG. 4. The electronic specific heat divided by temperature for $Sr_3Ru_2O_7$ at low temperatures, for magnetic fields applied parallel to *c*. Subtracting the T^3 lattice contribution gave a Debye temperature of 360 K, in good agreement with previous work on polycrystalline samples [17]. Apparently divergent behavior is seen when the field is tuned to the metamagnetic field for this field orientation, identified from Fig. 2 to be 7.7 T.

fluctuations in Sr₃Ru₂O₇. These fluctuations have an interesting physical interpretation. In an itinerant ferromagnet, the moment is generated by a spontaneous polarization of the spin-up and spin-down Fermi surfaces at the Curie temperature. In an itinerant metamagnet, the extra moment appears at the metamagnetic field due to the same basic mechanism, so the fluctuations that we observe can be thought of as fluctuations of the Fermi surface itself. Although this is a $\mathbf{q} = 0$ picture, the polarized and unpolarized Fermi surfaces are likely to have different nesting properties in a nearly two-dimensional material, so a coupling with fluctuations at higher **q** is to be expected. Itinerant electron metamagnetism has previously been observed in several systems (notable recent examples are MnSi [18] and CeRu₂Si₂ [19]), but this is, to our knowledge, the first time that such clear evidence has been seen for a magnetic field driving a system closer to criticality. Sr₃Ru₂O₇ will therefore give an excellent opportunity to study a novel class of low temperature fluctuations.

The magnetic properties of Sr₃Ru₂O₇ are fascinating in their own right, but their significance is increased further by the close structural similarity between Sr₃Ru₂O₇ and Sr₂RuO₄. There is good and growing evidence for triplet superconductivity in Sr₂RuO₄, but, so far, little experimental evidence for the strong low-q fluctuations that might naively be expected to give the underlying binding mechanism. No metamagnetism has been observed in fields of up to 33 T [20]. In Sr₃Ru₂O₇, our results, in combination with those of Ref. [14], clearly demonstrate the existence of a low-q enhancement, but no superconductivity has been observed down to our best residual resistivity of 2 $\mu\Omega$ cm. It will be very interesting to see if there is a significant enhancement at high \mathbf{q} as well, and to investigate the underlying reasons for the pronounced differences in the magnetic properties between the two materials. In this respect, the orthorhombicity recently reported in Sr₃Ru₂O₇ [21] may prove to be significant, because it could mean that the Fermi surface differs from that of Sr₂RuO₄ by much more than a simple bilayer split [22,23]. The relationship between structural distortion and magnetism in Sr₂RuO₄ has been discussed in the context of a recent study in which it was proposed that a surface lattice reconstruction gives rise to ferromagnetism [24]. Continued work on Sr₃Ru₂O₇ is therefore likely to play an important role in efforts to understand the physics of magnetism and unconventional superconductivity in the ruthenates as a whole. A search for quantum oscillations, an investigation of the effect of pressure on the metamagnetism, and inelastic neutron scattering measurements are all desirable, in combination with further improvements in sample purity.

In conclusion, we have presented evidence that the low temperature properties of $Sr_3Ru_2O_7$ are strongly influ-

enced by critical fluctuations associated with the presence of metamagnetism. These fluctuations have an interesting interpretation as changes in the Fermi surface topography. Our observations also highlight important and somewhat unexpected differences with the metallic state that exists in its well-studied structural relative, the unconventional superconductor Sr_2RuO_4 .

We are grateful to C. Bergemann, N. R. Cooper, V. J. Emery, E. M. Forgan, H. v. Löhneysen, G. G. Lonzarich, A. J. Millis, A. Rosch, and D. J. Singh for fruitful discussions. This work was supported by the EPSRC (UK), the Royal Society, the Leverhulme Trust, NSERC (Canada), CREST-NST (Japan), and ESF (FERLIN Collaboration).

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