Competing magnetic fluctuations in Sr$_3$Ru$_2$O$_7$ probed by Ti doping

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We report the effect of nonmagnetic Ti$^{4+}$ impurities on the electronic and magnetic properties of Sr$_3$Ru$_2$O$_7$. Small amounts of Ti suppress the characteristic peak in magnetic susceptibility near 16 K and result in a sharp upturn in specific heat. The metamagnetic quantum phase transition and related anomalous features are quickly smeared out by small amounts of Ti. These results provide strong evidence for the existence of competing magnetic fluctuations in the ground state of Sr$_3$Ru$_2$O$_7$. Ti doping suppresses the low temperature antiferromagnetic interactions that arise from Fermi surface nesting, leaving the system in a state dominated by ferromagnetic fluctuations.

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The Ruddlesden-Popper-type perovskite strontium ruthenates Sr$_{n+1}$Ru$_n$O$_{3n+1}$ show a great diversity of electronic and magnetic ground states. Sr$_3$RuO$_4$ (n=1), the most widely studied member of the series, is an unconventional superconductor with a spin-triplet pairing $^1$ $^2$ $^3$. Sr$_3$RuO$_3$ (n=$\infty$) is an itinerant ferromagnet with a Curie temperature of 160 K $^4$. The n=2 bilayered member, Sr$_3$Ru$_2$O$_7$, has an intermediate dimensionality between these two; its magnetic ground state was originally identified as an exchange-enhanced paramagnet $^5$. Moderate applied fields induce a metamagnetic transition in this material, with the transition field ranging from 4.9 T (for $H \parallel ab$) to 7.9 T (for $H \parallel c$) $^6$ $^7$.

The metamagnetism in Sr$_3$Ru$_2$O$_7$ has generally been interpreted as a field-tuned Stoner transition into a highly polarized magnetic state; since there is no broken symmetry, this transition is expected to be first order $^8$ $^9$. In the phase diagram one will thus have a first-order phase boundary line which terminates in a critical end point $^{10}$; there is considerable experimental evidence that the characteristic temperature of this end point is close to zero, indicating the presence of quantum criticality $^5$. A variety of unusual features, including non-Fermi liquid behavior and a possible novel phase at the critical point, have been observed in this material $^8$ $^{11}$ $^{12}$. This finding has generated a great deal of interest and opened new routes to exploring the novel physics of quantum criticality.

Based on the metamagnetic features, we might expect that the relevant magnetic correlations in Sr$_3$Ru$_2$O$_7$ are predominantly ferromagnetic in nature $^{10}$. However, inelastic neutron scattering measurements have revealed that the system is dominated by 2D ferromagnetic (FM) fluctuations only at high temperatures, crossing over to 2D antiferromagnetic (AFM) fluctuations for temperatures below 20 K $^{13}$. Furthermore, recent $^{17}$ O-NMR measurements have suggested that these low-temperature AFM fluctuations continue to be dominant at high fields, including directly at the quantum critical point $^{14}$. This suggests a more complicated magnetic ground state for Sr$_3$Ru$_2$O$_7$, in which band FM correlations and AFM correlations due to nesting effects might be in competition. Thus, further experiments to elucidate the low-temperature magnetic ground state are highly desirable.

Ti doping has been used as an effective probe of magnetic correlations in the single-layered ruthenate Sr$_2$RuO$_4$. There, Ti was found to enhance the anisotropic, incommensurate AFM fluctuations, ultimately giving rise to a spin-density wave ordering with the same nesting wavevector seen in the undoped material $^{15}$ $^{16}$ $^{17}$ $^{18}$ $^{19}$. Thus, to further probe the magnetic correlations in Sr$_3$Ru$_2$O$_7$, we have investigated the effects of doping nonmagnetic Ti in Sr$_3$Ru$_2$O$_7$. In contrast to Sr$_2$RuO$_4$, small levels of Ti suppress the AFM correlations, leaving the system in a state with strong FM fluctuations. This provides strong evidence for the existence of competing magnetic fluctuations in the ground state of pure Sr$_3$Ru$_2$O$_7$.

We have grown a series of Ti-doped crystals Sr$_3$(Ru$_{1-x}$Ti$_x$)$_2$O$_7$ using a floating-zone technique; growth conditions were similar to those previously reported for pure Sr$_3$Ru$_2$O$_7$ $^{20}$. Crystals selected for the measurements were characterized by x-ray diffraction and did not include any impurity phase of Sr$_2$RuO$_4$ or Sr$_3$Ru$_3$O$_{10}$. Magnetization measurements were taken in a SQUID magnetometer and specific heat was measured by a standard thermal relaxation method (Quantum Design, Model PPMS). Resistivity measurements were performed with a standard four-probe technique.
In Fig. 1 we present the temperature dependence of susceptibility $\chi(T) = M/H$ for Sr$_3$(Ru$_{1-x}$Ti$_x$)$_2$O$_7$ for (a) in-plane and (b) out-of-plane field orientations. For the undoped sample, we observe behavior similar to that previously reported by Ikeda et al. [2]; susceptibility shows a peak around 16 K for both field orientations. The origin of this peak is likely due to a crossover in the nature of magnetic correlations; inelastic neutron scattering also shows a peak near 16 K for the dynamic susceptibility $\chi''$ near a FM wavevector, while AFM correlations increase rapidly below this temperature [13]. Recent NMR results further suggest that below $\sim$16 K FM correlations are quenched and 2D incommensurate AFM fluctuations dominate [14].

We now consider the evolution of this feature in susceptibility under Ti doping. For $H \parallel ab$ (Fig. 1a), Ti impurities result in a supression of the peak near 16 K; specifically, the low-temperature susceptibility increases until, by 4.0% doping, only a small remnant of the peak remains. This trend is even more remarkable for fields $H \parallel c$, shown in Fig. 1b: by 4.0% doping the peak is completely suppressed and the susceptibility is reminiscent of a paramagnetic state. These features suggest a change in the magnetic ground state such that 2D AFM correlations are no longer dominant.

Above $\sim$180 K the susceptibility shows Curie-Weiss behavior. Table I shows the result of a fit to the usual expression $\chi(T) = \chi_0 + C/(T - \Theta_W)$ for the samples shown in Fig. 1 for an in-plane field, where $\chi_0$ is the temperature independent term and $C/(T - \Theta_W)$ is the Curie-Weiss term. The Weiss temperature $\Theta_W$ increases with Ti doping, consistent with the idea that the system is moving towards a FM ground state. However, the effective moment $\mu_{\text{eff}}$ derived from $C$ does not change remarkably with doping, which may suggest that Ti substitution is acting primarily to suppress the low temperature AFM correlations rather than directly enhancing the ferromagnetism (see below for further discussion).

The enhanced Stoner model of itinerant metamagnets by Yamada gives certain criterion for a first-order metamagnetic transition based on a Landau expansion of the free energy $\bar{F}$. Specifically, given the expansion $H = aM + bM^3 + cM^5$, where $H$ is the derivative of free energy with respect to the magnetization, the ratio $ac/b^2$ should be less than 0.45 for a first-order metamagnetic transition to occur. This ratio is related to the susceptibility by the expression $ac/b^2 = (5/28)[1 - \chi(0)/\chi(T_{\text{max}})]^{-1}$ where $T_{\text{max}}$ is the temperature where the peak in susceptibility occurs. For our samples, this ratio is 0.423 for pure Sr$_3$Ru$_2$O$_7$, 0.80 for 0.5% doping, and 6.13 for 3% doping. While the magnetic properties are likely more complex than a simple Stoner picture, this analysis suggests that Ti doping quickly moves the system away from conditions favorable for metamagnetism.

Measurements of the specific heat give strong evidence that Ti doping leaves the system in a ground state dominated by strong FM fluctuations. In Fig. 2 we present the specific heat divided by temperature for the identical samples used in magnetization measurements. All curves were taken at zero field. The undoped sample is consistent with previously reported results by Perry et al. [3]; $C/T$ shows an upturn close to 15 K, followed by a peak at lower temperatures. Ti doping suppresses this low temperature peak, such that by 4% doping we observe a rapid increase in $C/T$ as temperature decreases.

While low temperature behavior consistent with a Schottky anomaly has been previously reported in pure Sr$_3$Ru$_2$O$_7$, it occurs only below 0.2 K and is likely not the source of the upturn observed here [21]. Under an applied magnetic field, $C/T$ in in pure Sr$_3$Ru$_2$O$_7$ also shows a sharp rise at low temperatures, consistent with a logarithmic divergence due to proximity to a quantum critical point (QCP) [2, 21]. In our case we have observed no other features which might suggest the presence of a doping-induced QCP; rather, we believe the upturn in specific heat arises from strong FM fluctuations. Further discussion of the origin of this feature is given below.

We next consider how the features of the metamagnetic transition change with doping. In Fig. 3 we present the magnetization and normalized resistance of Ti-doped Sr$_3$Ru$_2$O$_7$ for $H \parallel ab$. Consistent with previous reports, for the undoped sample we observe a superlinear rise in magnetization and a broad peak in resistance around the critical field. However, Ti impurities act to rapidly suppress both of these features; even 0.5% doping has nearly smeared out the metamagnetic features in magnetization and resistance. By doping levels of 3.0% and 4.0%, magnetization is nearly linear in field and only a very small feature is seen in resistance near 5 T. This observation is in agreement with Yamada’s criterion for metamagnetism to occur (see above).

One of the most prominent features of the metamagnetic transition in Sr$_3$Ru$_2$O$_7$ is the non-Fermi liquid behavior close to the critical field, manifested as a linear temperature dependence of resistivity [6]. In Fig. 4 we examine the electronic ground state of Ti-doped Sr$_3$Ru$_2$O$_7$ by means of bulk resistivity measurements. Figure 4a shows the temperature dependence of resistivity (normalized to its value at 10 K) for several doping levels; the system remains metallic until approximately 5% doping, where it transitions into a localized state. The metallic ground state remains a Fermi liquid, with

| TABLE I: Parameters from Curie-Weiss fits, $H \parallel ab$ |
|---|---|---|---|
| $x$ | $\chi_0$ | $\Theta_W$ | $\mu_{\text{eff}}$ |
| 0.0 | 0.78622 | -21.580 | 2.5075 |
| 0.5 | 0.66488 | -12.287 | 2.3059 |
| 3.0 | 0.58739 | 4.3060 | 2.1673 |
| 4.0 | 0.66827 | 9.4349 | 2.3117 |
resistivity proportional to $T^2$ at low temperatures (see Fig. 4). At a 3% doping level there is still a small peak in the in-plane susceptibility (see Fig. 4), but the metamagnetic transition is almost completely suppressed and there is only a small downturn in resistivity at 5 T. Figure 4 displays the resistivity of this 3% sample plotted against $T^2$ at various applied fields for the configuration $H \parallel ab$. We can see that the $T^2$ behavior of $\rho$ is unchanged by an applied field, even close to where the metamagnetic transition occurs in the pure sample; this indicates that quantum criticality is fully suppressed.

We now wish to discuss the origin of these features in Sr$_3$(Ru$_{1-x}$Ti$_x$)$_2$O$_7$. We begin by noting similarities between our results and previous studies on other itinerant metamagnets; for example, the intermetallic compound Y(Co$_{1-x}$Al$_x$)$_2$ has a transition from an itinerant metamagnetic state to a weakly FM one at a doping level of $x = 0.13$. For doping levels approaching 0.13, there is a suppression of the characteristic peak in susceptibility, a strong upturn in $C/T$, and a significant broadening of the metamagnetic transition. These features have been successfully interpreted quantitatively within the self consistent renormalized (SCR) theory of spin fluctuations as evidence for proximity to a weakly FM state. For Sr$_3$(Ru$_{1-x}$Ti$_x$)$_2$O$_7$, as described above, Ti doping results in similar changes as those seen in Y(Co$_{1-x}$Al$_x$)$_2$, clearly suggesting that FM fluctuations become dominant.

In Y(Co$_{1-x}$Al$_x$)$_2$, the FM enhancement is believed to be associated with doping-induced structural changes which increase the density of states at the Fermi level. However, in the case of Sr$_3$(Ru$_{1-x}$Ti$_x$)$_2$O$_7$, the most likely mechanism is that both AFM and FM fluctuations coexist in the ground state of the undoped sample and that Ti doping primarily suppresses the AFM correlations. We believe that the FM fluctuations are only slightly affected by the presence of Ti, for the following reasons. First, at high temperatures, where FM interactions are dominant, the susceptibility and the effective moment do not change remarkably with increasing Ti (see Fig. 4 and Table 4). Second, since Ti$^{4+}$ has a very similar ionic radius as Ru$^{4+}$, substituting a small amount of Ti for Ru should have only a very small effect on the structure; this is the case for Ti-doped Sr$_2$RuO$_4$. All of these provide strong support for the previous suggestion about the presence of competing magnetic interactions in Sr$_3$Ru$_2$O$_7$.

The existence of competing magnetic correlations in Sr$_3$Ru$_2$O$_7$ is also consistent with the results of band structure calculations. The bands derived from the Ru $4d_{xy}$ orbitals are close to a van Hove singularity and thus close to a FM Stoner instability, while bands derived from the $4d_{xz,yz}$ orbitals have nesting features which would favor AFM fluctuations. The Ti doping reported here appears to be be band-selective, primarily affecting the character of the bands derived from $4d_{xz,yz}$ orbitals. This is similar to Ti doping in the related compound Sr$_2$RuO$_4$, in which small amounts of Ti have only minimal effects on the rotation of the octahedra and the main $\gamma$ band, but do remarkably affect the character of the 1D $\alpha$ and $\beta$ bands in such a way to enhance the nesting features of the Fermi surface and thus enhance the AFM correlations. In the case of Sr$_3$Ru$_2$O$_7$ it appears that Ti impurities result in a reduction of the nesting features, which is reasonable since the characteristics of the bands involved in nesting are different between the two materials.

The disappearance of the metamagnetic features with Ti doping also appears to suggest a possible relation between the short-range AFM correlations and the metamagnetic transition. However, this relationship may be complex; Ti doping levels of 5% and above result in a localized state as shown in Fig. 4, and this trend towards localization would drive the system away from the Stoner instability, thereby reducing the metamagnetic features. Thus, it is difficult from our data to draw direct conclusions about the role of AFM correlations in the metamagnetic transition.

In conclusion, we have investigated the properties of Ti-doped Sr$_3$Ru$_2$O$_7$. We observe evidence that the short range AFM correlations are quickly suppressed by small amounts of Ti, leaving the system in a state dominated by 2D FM correlations. The most likely mechanism for this is that Ti doping significantly alters the bands derived from the Ru $4d_{xz,yz}$ orbitals, which results in a suppression of AFM fluctuations due to nesting; however, it has less effect on the FM correlations arising from the bands derived from the Ru $4d_{xy}$ orbitals. Ti doping thus confirms previous suggestions about the presence of competing magnetic interactions in pure Sr$_3$Ru$_2$O$_7$. This result offers additional insight into the multiband nature of magnetic correlations in this material.

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FIG. 1: Temperature dependence of the uniform susceptibility $\chi = M/H$ of Ti doped Sr$_3$(Ru$_{1-x}$Ti$_x$)$_2$O$_7$ for (a) in-plane and (b) out-of-plane fields, taken using an excitation field of $\mu_0 H = 0.3$ T.
FIG. 2: The specific heat divided by temperature for Ti doped Sr$_3$(Ru$_{1-x}$Ti$_x$)$_2$O$_7$ at low temperatures.
FIG. 3: (a) Magnetization versus field and (b) resistance (normalized to its 0 T value) versus field for the Sr$_3$(Ru$_{1-x}$Ti$_x$)$_2$O$_7$ system. Magnetization is taken at 2 K and resistance is measured at 0.3 K.
FIG. 4: (a) The temperature dependence of resistivity for several Ti doping levels, normalized to the resistivity at 10 K. (b) Resistivity (normalized to its 0.3 K value) plotted versus $T^2$ for metallic doped samples. The data of the $x = 0.5\%$ sample is not shown here, since it nearly overlaps with that of the pure sample. This is likely due to Ti inhomogeneity. (c) Resistivity of the 3.0% doped sample versus $T^2$, under a range of applied fields.