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Effect of electron doping the metamagnet $Sr_{3-y}La_yRu_2O_7$

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We study the effects of adding electrons to the conduction bands of the itinerant metamagnet $Sr_3Ru_2O_7$ using substitution of La^{3+} onto the Sr^{2+} site. Small changes to the chemical potential have a large effect: adding only 0.03 electrons per Ru reduces the electronic specific-heat coefficient by 30%, but makes no corresponding change to the temperature (~ 8 K) at which the electronic specific-heat coefficient shows its maximum. The observations are incompatible with a simple rigid-band shift, raising the possibility that a many-body resonance plays a key role in the physics of $Sr_3Ru_2O_7$.

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The low-temperature properties of the bilayer ruthenate metal $Sr_3Ru_2O_7$ are of considerable topical interest. Its itinerant electron metamagnetism[1,2] is associated with a first-order phase transition for magnetic fields applied parallel to the Ru-O planes. As the field is rotated toward crystallographic *c* axis, the finite temperature critical point that terminates the line of first-order transitions can be tuned toward zero temperature.[3,4] The resultant quantum critical point is unusual in the sense that it is not associated with any symmetry-breaking second-order phase transition, and has motivated extensive experimental and theoretical study.[5–11] When the crystal purity is sufficiently high, with a residual resistivity below 0.5 $\mu\Omega$ cm (corresponding to mean free paths of several thousand Å), further unusual properties are observed. In these samples, the approach to quantum criticality is cut off by the formation of a possible low-temperature phase,[12–14] which possesses a large resistive anisotropy with similar characteristics to that previously observed in high-purity two-dimensional electron gases in large applied magnetic fields.[15,16] This unusual behavior may be related to the formation of an "electronic liquid crystal" of the kind discussed a decade ago.[17] These intriguing states have been studied theoretically by a number of authors, and significant recent interest has been focused on constructing models specific to $Sr_3Ru_2O_7$.[18–23]

Any $Sr_3Ru_2O_7$-specific model must have as its foundation a postulate about the underlying mechanism of the metamagnetism. Since the early work of Wohlfarth and Rhodes on Pd,[24] a common hypothesis for explaining itinerant electron metamagnetic transitions has been that the Fermi level (E_F) sits at a minimum between two maxima in the density of states (DOS) or that an asymmetric DOS peak sits either just above or just below E_F. This fixed DOS structure at and near E_F means that applying a magnetic field allows at least one of the spin species to sample a higher density of states and, therefore, comes closer to satisfying the Stoner criterion for a magnetic phase transition. A key challenge is to establish whether such rigid DOS features exist in $Sr_3Ru_2O_7$.

As has been pointed out by a number of authors,[11,14,19–23] a candidate for producing a DOS peak near E_F in $Sr_3Ru_2O_7$ is the set of van Hove singularities (vHs) expected from the band structure. However, the metamagnetic field scale of <10 tesla implies an energy scale for the peak(s) that is so low (~ 1 meV) that establishing whether a vHs sits so close to E_F cannot be done reliably on the basis of first-principles electronic structure calculations, and it must, therefore, be determined experimentally.

To our knowledge, two surface-sensitive studies aimed at elucidating this issue have so far been reported. In the first, using the spectroscopic capabilities of a cryogenic scanning tunneling microscope, Iwaya *et al.*[25] reported two peaks in the tunneling conductance at $E_F \pm 4$ meV. In the most simple interpretation of their data, these would correspond to peaks in the bare density of states. To reconcile such symmetric peaks in the conductance with underlying band-structure features would require postulating a pair of vHs lying on either side of E_F. This cannot be ruled out *a priori* since the bands of $Sr_3Ru_2O_7$ can be expected to be affected by bilayer splitting, but it is an interpretation that relies on a special set of circumstances. A second experiment, employing high-resolution angle-resolved photoemission (ARPES), reports two DOS peaks at approximately 1 and 4 meV below E_F (Ref. 26) but has no sensitivity to empty states above E_F. A DOS peak at 1 meV is compatible with previous work on the heat capacity (C_{el}) which shows a pronounced maximum in C_{el}/T at approximately 8 K.[1–5]

Here, we study controlled substitution of La^{3+} onto the Sr^{2+} site of the crystal. Many dopant atoms can be incorporated in ruthenates, and (Ti, Mn, Cr)/Ru and Ca/Sr substitutions have all been demonstrated in $Sr_3Ru_2O_7$.[25,27–29] However, the La^{3+}/Sr^{2+} cross substitution is unique because it is heterovalent, produces only mild scattering in the RuO_2 planes,[30] and, because of a good lattice match, results in much milder structural distortion than that produced by the Ca^{2+}/Sr^{2+} substitution. The main effect is that each La^{3+} ion donates an electron to the conduction bands, and so La substitution can be viewed as a bulk probe of the states lying above E_F in the undoped material. In $Sr_{2-y}La_yRuO_4$, the substitution has been shown to produce a "rigid-band" shift, namely a shift of the Fermi level through a fixed DOS produced by renormalized bands whose structure could be determined by ARPES and de Haas–van Alphen

measurements.[30–32] We have grown a series of crystals of $Sr_{3-y}La_yRu_2O_7$ with $0<y<0.06$ and measured their in-plane electrical resistivity (ρ), C_{el}, and metamagnetic transition field. In contrast to the situation in Sr_2RuO_4, our data suggest that the origin of the maximum in C_{el}/T is not a rigid-band feature of the underlying DOS, but has its origin in a many-body resonance that tracks E_F.

$Sr_{3-y}La_yRu_2O_7$ crystals were grown using methods derived from previous published work.[33] To compensate for Ru evaporation during growth, predried starting powders of $SrCO_3$, RuO_2, and La_2O_3 were mixed in the empirically determined ratio $3-y$:2.52:$y/2$, pelletized and prereacted at 1200 °C for 16 h. They were then reground, pressed into a growth rod, and resintered at 1420 °C for 2 h. Finally, growth was performed in an NEC Machinery SCI-MDH-11020 image furnace. Direct electron probe microanalysis measurements confirmed both bulk overall homogeneity and the y values of the crystals. A persistent challenge when growing any multilayer ruthenate from the Ruddlesden-Popper series $Sr_{n+1}Ru_nO_{3n+1}$ is the incorporation in the crystals of intergrowths with n values other than the desired one (in this case $n=2$). Care was, therefore, taken to identify such impurity phases by performing x-ray diffraction measurements on powder produced by grinding sections of each grown crystal. Using the growth parameters adopted in this work, the most numerous intergrowths were found to be $SrRuO_3$ and $Sr_4Ru_3O_{10}$. Both are ferromagnetic, with Curie temperatures of 160 K and 110 K, respectively, so field-cooled magnetization measurements (0.01 T, Quantum Design MPMS) coupled with literature values for the low-temperature magnetization of these ferromagnets[34,35] were employed to obtain a quantitative measure of the impurity volume fraction of each crystal. Only those containing a few molar percent impurity phases or less were selected for the work reported here. Magnetotransport measurements were carried out using standard four-terminal ac methods ($f<100$ Hz) in a ^{4}He continuous flow cryostat, an adiabatic demagnetization refrigerator (Cambridge Magnetic Refrigeration), and a dilution refrigerator (Oxford Instruments), while specific heat was measured in a commercial ^{3}He-cooled calorimeter (Quantum Design).

Before presenting and discussing our results, we estimate the energy scale ΔE over which we probe the electronic structure as a function of y. This can be done by summing the area change ΔA for each individual Fermi surface sheet subject to the constraints that ΔE is common for all sheets and that the sum of all the area changes preserves the electron count in the presence of the doping. Using known electronic structure parameters for $Sr_3Ru_2O_7$ gives $\Delta E \sim 0.2$ meV/y,[36] meaning that by $y=0.06$ we can increase the Fermi level by 1.2 meV and study a range of energies that are key to the physics of the material.

The in-plane electrical resistivity (ρ_{ab}) of four crystals with $y=0$, 0.015, 0.03, and 0.06 is shown in Fig. 1 between 100 mK and 10 K. The first clear effect of the substitution is the residual resistivity increasing from 1.1 $\mu\Omega$ cm for undoped material to 4.4 $\mu\Omega$ cm for $y=0.06$ (top inset). This relatively mild increase in scattering rate is qualitatively what would be expected from the insertion of scattering centers adjacent to the main conducting planes of the material,

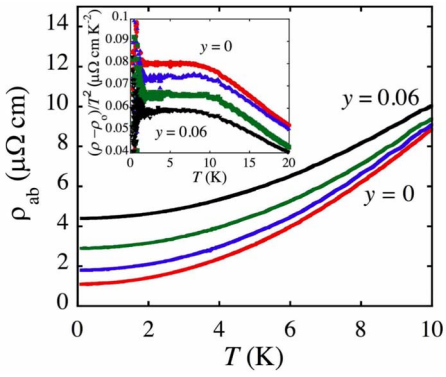

FIG. 1. (Color online) Low-temperature electrical resistivity of four crystals of $Sr_{3-y}La_yRu_2O_7$ with $y=0$, 0.015, 0.03, and 0.06. The residual resistivity rises at approximately 330 $\mu\Omega$ cm/y. Accompanying the increase in residual scattering is a marked decrease in the strength of the inelastic part of the resistivity, as demonstrated in the inset (for discussion see text). The increased noise at the lowest temperatures in the inset is due to the rapidly falling denominator.

and the rate of increase of 55 $\mu\Omega$ cm/y is similar to that of 40 $\mu\Omega$ cm/y seen in Sr_2RuO_4.[30] An accompanying change is also seen in the inelastic scattering rate, as highlighted in the inset, where the temperature dependent part of ρ_{ab} is divided by T^2 and plotted against T. In such a plot a horizontal line corresponds to a pure T^2 dependence, and its intercept measures the strength of that dependence. In agreement with previous work[37] the undoped material has a pure T^2 scattering rate below approximately 7 K. As y is increased no clear change is observed in the onset temperature of this pure T^2 scattering, but the strength clearly decreases.

In the simplest interpretation a decrease in T^2 scattering implies a decrease in effective mass. The observation was slightly surprising to us in light of knowledge of Sr_2RuO_4 in which the effective mass increases with y.[31] To check directly for the mass decrease we performed measurements of the heat capacity of our crystals as a function of y. The results are shown in Fig. 2. For $y=0$ the data agree closely with previous published work,[1–5] with a low-temperature electronic specific-heat coefficient (γ) of 110 mJ/mol Ru K^2. As y increases γ falls rapidly to 78 mJ/mol Ru K^2.

The heat-capacity measurements, therefore, confirm the inference drawn from the resistivity, namely that La^{3+} substitution for Sr^{2+}, shifting E_F by only ~ 1 meV, dramatically decreases the density of states at the Fermi level of $Sr_3Ru_2O_7$. However, this rapid change in γ is not accompanied by a similar rapid change in the characteristic temperature $T_{max} \sim 8$ K of the peak in C_{el}/T. By $y=0.06$ the peak is slightly broadened, but it sits at the same temperature within experimental error. As shown in Fig. 3, the corresponding effect on the metamagnetic transition is mild. In addition to a disorder-induced broadening, the signatures of metamagnetism move systematically to higher fields as y is increased, but rather slowly: less than a 10% increase by $y=0.06$.

These results offer surprising insights into the electronic structure and the physics of the metamagnetism of $Sr_3Ru_2O_7$. The key point is that to explain such a rapid drop of γ with

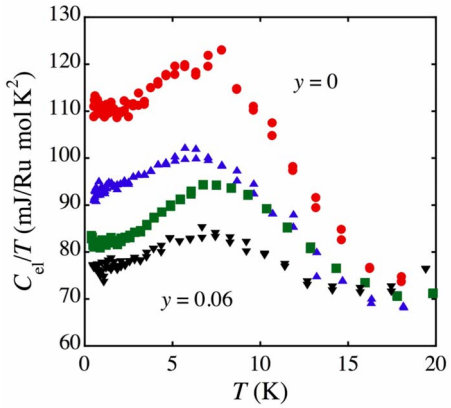

FIG. 2. (Color online) The electronic specific heat of crystals of $Sr_{3-y}La_yRu_2O_7$ with $y=0$, 0.015, 0.03, and 0.06, divided by temperature, after subtraction of phononic T^3 terms determined by fitting to data between 15 and 30 K. The pronounced maximum in the $y=0$ data is smoothed out as y increases, but the most striking change is to the overall scale. In particular, the zero temperature intercept, γ, falls by approximately 30% when y reaches 0.06.

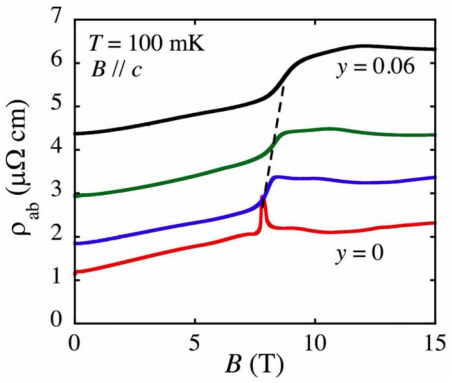

FIG. 3. (Color online) The in-plane magnetoresistance of $Sr_{3-y}La_yRu_2O_7$ with $y=0$, 0.015, 0.03, and 0.06 at 100 mK for $B\|c$. The pronounced peak in the $y=0$ data is associated with purity-dependent phase formation (Refs. 12, 13, and 38) and is known to be washed out at the levels of residual scattering present in the samples with $y>0$, but magnetoresistance is still a good way to identify the metamagnetic transition (Ref. 2). The dotted line is a guide to the eye, emphasizing the increase in critical field scale induced by the La doping.

y, any model postulating a simple shift of $E_F(y)$ through a rigid DOS would require that DOS to be dropping by ~30% over the first meV above $E_F(0)$. To simultaneously account for the peak in C_{el}/T at $T_{max}\sim 8$ K for $y=0$ would require placing $E_F(0)$ on the falling edge of a sharp DOS peak whose maximum sat at approximately −1 meV. However, to be self-consistent, the model would also predict a shift in the measured T_{max} from ~8 to ~20 K, in sharp contrast with the results shown in Fig. 2.[39] Instead, the data are more compatible with the existence of a many-body resonance of some kind which moves with the Fermi level. The fact that the metamagnetic transition field makes only a small change in response to a large change in the absolute magnitude of the DOS near E_F is also significant. Taken at face value, it suggests that the physics of the resonance rather than the DOS magnitude determines the metamagnetism.

Finally, we speculate on a possible source of a resonance that would track E_F. While it is known that the Kondo resonance for a spin-1/2 impurity in a conduction electron sea peaks at the Fermi level, the "frustration" caused by embedding higher spins in the Fermi sea leads to a broadening and then a split resonance.[40] Studies of Ru^{4+} ions in Sr_2IrO_4 show a spin-1 moment,[41] and a Curie-Weiss fit to the high-temperature susceptibility of $Sr_3Ru_2O_7$ is compatible with free spin-1 moments as well.[1] Could it be that a coherence crossover absorbing a lattice of these moments into the Fermi liquid produces a split Kondo-type resonance? It is not clear how to treat this in a system where both the moments and the quasiparticles are based on the same d electrons of ruthenium, but we believe that there is a strong motivation for theoretical and experimental work investigating this possibility.

In conclusion, we have used La^{3+} substitution onto the Sr^{2+} site to investigate the effects of adding electrons to the conduction bands of the itinerant metamagnet $Sr_3Ru_2O_7$. The addition of only 0.03 electrons per Ru-O plane results in a 30% drop of the density of states at the Fermi level, and a corresponding rise in the scale of the metamagnetic field. The findings are inconsistent with the doping, producing a simple rigid shift through the underlying bands, and suggest that more exotic physics might control the metamagnetism in this material.

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