Rigid-Band Shift of the Fermi Level in a Strongly Correlated Metal: Sr$_{2-y}$La$_y$RuO$_4$

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We report a systematic study of electron doping of Sr$_2$RuO$_4$ by non-isovalent substitution of La$^{3+}$ for Sr$^{2+}$. Using a combination of de Haas-van Alphen oscillations, specific heat, and resistivity measurements, we show that electron doping leads to a rigid-band shift of the Fermi level corresponding to one doped electron per La ion, with constant many-body quasiparticle mass enhancement over the band mass. The susceptibility spectrum is substantially altered and enhanced by the doping but this has surprisingly little effect on the strength of the unconventional superconducting pairing.

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The layered perovskite transition-metal-oxide Sr$_2$RuO$_4$ has been the subject of intensive research over the past decade. In its stoichiometric form, it can be grown with very high purity, allowing the observation of what is now known to be an unconventional, probably spin-triplet, superconducting state at low temperatures 1, 2, 3. Extensive de Haas-van Alphen (dHvA) studies have revealed precise information about its Fermi-surface topology with three nearly cylindrical sheets based on bands with combined Ru $d$ and oxygen $p$ character: one hole sheet ($\alpha$) and two electron sheets ($\beta$ and $\gamma$) 1, 2, 3, 4, 5, 6, 7, 8, 9. The dynamical susceptibility has features both at the wave vector $q \sim (2\pi/3, 2\pi/3, 0)$ 10, and around $q \sim (0, 0, 0)$ 11, both of which can be accounted for in terms of the known Fermi surfaces 12, 13, 14.

In contrast to the unusually depth understanding of the normal metallic state, far less is known about the superconducting mechanism. While our experimental and phenomenological knowledge of the superconductivity of pure Sr$_2$RuO$_4$ is exhaustive 3, it still provides insufficient constraints for models for the microscopic pairing mechanism. Here, the most common assumption is that the dominant sheet is $\gamma$, since it has the largest mass-enhancement and low-$q$ susceptibility 14. One method for obtaining additional and complementary information on correlated electron systems is chemical doping, a technique that has been widely applied in recent years 15. This has motivated studies of Sr$_2$RuO$_4$ in which the Ru has been doped with Ti 16, 17, 18, 19 and Ir 20, and the Sr substituted by Ca 21, focusing on the magnetic properties in each system. Each of these has revealed rich new physics, but with the commonly-experienced complication of introducing strong potential scattering and structural distortion.

In this paper, we concentrate on non-isovalent counter-ion substitution of Sr$^{2+}$ with La$^{3+}$. In contrast to iso- valent Ca-doping, the primary effect of La doping is the introduction of extra electrons to the metallic bands at the Fermi energy. At the same time, the main electronic “building blocks”—the RuO$_2$ planes—remain structurally unaffected, unlike the previously studied case of Ti/Ir substitution. Also, since the ionic radii of Sr$^{2+}$ and La$^{3+}$ are very similar, structural distortions are minimized. La substitution therefore provides a gentle way to study electron doping and the effect of changing carrier concentration in the correlated metal and unconventional superconductor Sr$_2$RuO$_4$.

We present here the results of a combined dHvA, resistivity, specific heat, and magnetic susceptibility study on samples of Sr$_{2-y}$La$_y$RuO$_4$ extending up to $y = 0.10$. It is remarkable in itself that the dHvA effect is observable, and we are able to show in detail that the normal state undergoes a rigid shift of the Fermi level with unchanged correlation quasiparticle mass enhancement: an unexpected result for this multi-band, correlated metal 22, especially considering the vicinity of the van Hove singularity associated with the $\gamma$ band. Although the absolute quasiparticle masses and the spin susceptibility spectrum are strongly affected by carrier doping, the evolution of the superconducting transition temperature $T_c$ indicates no change in pairing strength, which introduces new and strong constraints on candidate pairing mechanisms.

Single crystals of Sr$_{2-y}$La$_y$RuO$_4$ with $y$ up to 0.10 were grown by a floating-zone method 23 with an infrared image furnace (NEC Machinery, model SC-E15HD) at Kyoto University. The La concentrations were determined by electron-probe microanalysis (EPMA). Tetragonal symmetry was confirmed for all crystals by x-ray powder diffraction measurements at room temperature. The lattice parameter along the in-plane direction increases by $\sim 0.2\%$ and that perpendicular to the plane decreases by $\sim 0.15\%$ continuously up to $y = 0.10$.

The dHvA experiments were performed at the University of St. Andrews by a field modulation technique 24 at temperatures down to 40 mK, with the magnetic field applied along the $c$ axis with an accuracy of better than $3^\circ$. The in-plane resistivity $\rho_{ab}$ was measured by a
low frequency ac method between 0.3 and 5 K. Magnetic susceptibility measurements were performed using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-XL). The specific heat was measured by a thermal relaxation method from 0.5 K to 30 K (Quantum Design, model PPMS).

Figure 1 shows the temperature dependence of $\rho_{ab}$ in Sr$_{2-y}$La$_{y}$RuO$_4$ with $y$ up to 0.10. Inset: The $T_c$ as a function of the in-plane residual resistivity $\rho_{ab0}$ for Sr$_{2-y}$La$_{y}$RuO$_4$. Previous results for different sources of disorder are also shown. The broken line shows the Abrikosov-Gor’kov pair-breaking function.

The rate at which the La dopants between the RuO$_2$ planes introduce scattering is, as expected for an out-of-plane dopant, much smaller than that for in-plane substituted impurities such as Ti and Ir for Ru [18, 20]. The residual resistivity, $\rho_{ab0}$, increases systematically with $y$ at the rate of $d\rho_{ab0}/dy \sim 40 \mu\Omega\text{cm}/y$, that is, with a phase shift for impurity scattering $\delta_0 \sim \pi/12$. In contrast, Ti and Ir act as unitary scatterers with $\delta_0 \sim \pi/2$ [20]. However, we reiterate that although the rate at which the La ions affect the resistivity is lower than for Ti or Ir, the effect of that change of resistivity on the superconductivity is independent of the dopant species.

Figure 2 shows the Fourier transform of the dHvA oscillations for Sr$_{2-y}$La$_{y}$RuO$_4$ up to $y = 0.06$, in a narrow frequency region around the $\alpha$ branch. Sample oscillations are shown in the left inset of Fig. 2 for $y = 0$ and 0.06. For pure Sr$_2$RuO$_4$ with $T_c = 1.44$ K, not only the whole frequency spectrum with three Fermi-surface sheets but also additional harmonics $\alpha$ and linear combinations such as $\alpha + \beta$ are detected. The oscillatory amplitude is exponentially suppressed by La substitution, reflecting the introduction of weak disorder, as seen in the right inset in Fig. 2. The effect is strongest on the large $\gamma$ sheet so that even at $y = 0.02$ ($\rho_{ab0} \sim 0.7 \mu\Omega\text{cm}$) its signal is unobservable. For $y = 0.06$, only the $\alpha$ frequency remains detectable (left inset of Fig. 2), and no oscillations at all are found for $y = 0.10$ in our current study.

The exponential decay of the signal with doping gives the opportunity for a reliable Dingle analysis. The suppression factor is $\exp(-\pi r_c/\ell)$, where $r_c$ is the cyclotron radius and $\ell$ is the carrier mean free path. The values obtained for the $\alpha$ sheet range from 990 ± 100 nm for $y = 0$ to 76 ± 9 nm for $y = 0.06$. These agree, within the stated error, with the values obtained by an analysis of the resistivity under the “isotropic mean-free-path approximation” [12, 13]. This is interesting because it implies that the resistivity, which is biased towards large angle scattering, still gives a good estimate of the scattering (including small angle events) that damps the quantum oscillations, even though the out-of-plane La ions act as relatively diffuse scattering centers.

A more significant feature of the data is that we ob-
FIG. 3: (a) La concentration dependence of the carrier number of the α and the β sheets. The γ sheet dependence is not shown since we have data only at y = 0, but it corresponds to an increase of approximately 0.03 electrons by y = 0.06. Inset: A sketch of the Fermi surface of Sr$_2$RuO$_4$. (b) Temperature dependence of $C_P/T$ in Sr$_{2-x}$La$_x$RuO$_4$ up to y = 0.10. (c) Doping dependence of $\gamma_N$ (for definition see text). Closed (open) circles represent data from specific heat (dHvA) measurements. The dotted lines show the prediction of the calculation described in the text. The error bars on the dHvA-derived sheet-specific contributions reflect the combined uncertainties of the data and the parameters used in the calculation.

serve progressive changes in the dHvA oscillation frequencies $F_{ext}$, as shown in Fig. 2. Since these frequencies directly relate to the cross-sectional areas of the Fermisurface sheets via $A_{ext} = \frac{2\pi e F_{ext}}{\hbar}$, this reflects a change in the carrier concentration associated with each sheet. As seen in Fig. 3(a), the hole-like α sheet shrinks while the electron-like β sheet grows in size, which is completely consistent with the La acting as an electron donor.

A much more quantitative analysis is also possible in this system. The years of work on pure Sr$_2$RuO$_4$ have led to the construction of an empirically determined tight-binding model for the electronic structure, derived from fits to the experimentally determined Fermi surface. The dotted lines in Fig. 3 are not fits or guides to the eye, but topography calculations based on this model, without free parameters, under the assumption that each La dopes one free electron and induces a rigid shift of the Fermi level. As can be seen, the agreement is excellent. This is remarkable, because although Luttinger’s theorem usually puts strong enough constraints on the Fermi-surface geometry for such rigid-band shift calculations to work at least approximately in single-band systems, the constraints are much less powerful for a multi-band system such as Sr$_2$RuO$_4$. In Ca-substituted Sr$_2$RuO$_4$, for example, doping lowers the $d_{yz}$ band with respect to the $d_{xy}$ band [21]; similarly, correlations among electrons can influence the evolution of the Fermi-surface geometry, especially in metals with both electron and hole pockets [22] —but in strongly correlated Sr$_{2-y}$La$_y$RuO$_4$, both effects are either absent or compensate each other.

We can also use the tight-binding model and its density of states to predict each sheet’s contribution to the specific heat $C_P/T$ as a function of y. The experimental $C_P/T$ is strongly enhanced over the bare density of states by electron-phonon and electron-electron interactions; we empirically set this enhancement to be independent of y and use the well-known values for pure Sr$_2$RuO$_4$ [23]. In Fig. 3(b), we show the $C_P/T$ as a function of temperature for various values of y. The phonon term has not been extracted, so the electronic contribution, defined as $\gamma_N$, is given by the extrapolation to zero temperature (well approximated by the lowest temperature value in each case). These values are plotted against y in Fig. 3(c) (filled circles); that plot also contains the individual sheets’ contributions (open circles) as inferred from analysis of dHvA temperature damping. The dashed lines are the calculations from the tight-binding model, in which the quasiparticle mass-enhancement over the band mass is taken to be constant enhancement over the band mass is taken to be constant.

The rapidly increasing experimental value for the electronic $C_P/T$, and the underlying tight-binding model, imply a large change (>15%) to the $C_P/T$ dependence as the $d_{xy}$ band towards the van Hove singularity [6, 11] from the $d_{yz}$ system [21]. We have observed an even more substantial (30%) change to the low temperature static susceptibility $\chi(q = 0)$ (data not shown): the increase in the density of states is augmented here by the feedback mechanism arising from the Stoner factor.

Along with the bulk $\chi(q = 0)$, the whole spin-susceptibility spectrum $\chi(q)$ has to change significantly on electron doping. In pure Sr$_2$RuO$_4$, $\chi(q)$ reflects the nesting properties of the Fermi surface [6, 12, 13] with features both at wave vector $q \sim (2\pi/3, 2\pi/3, 0)$ from $\alpha/\beta$ nesting, and at low $q$ [6, 11] from the $\gamma$ sheet [27]. Electron doping will shift the $\alpha/\beta$ nesting to smaller wave vectors, and enhance the low-$q$ susceptibility as the $\gamma$
sheet moves closer to the van Hove singularity.

Many theories attribute the superconducting pairing in Sr$_2$RuO$_4$ to spin fluctuations in either the $\gamma$ or $\alpha/\beta$ channel, where the more common assumption is that the dominant sheet is $\gamma$, since it has the largest mass-enhancement and low-$q$ susceptibility. The relation between the spin-fluctuation spectrum $\chi(q)$ and $T_c$ and $\xi$ is a subtle one and certainly beyond the scope of this paper. There are indications that in Sr$_2$RuO$_4$ the low value of $T_c$, especially when compared with the cuprate high-$T_c$ superconductors, is due to competition and near-cancellation between two different pairing symmetries $[28]$. It is to be expected, then, that changes in $\chi(q)$ would have drastic effects on $T_c$ and coherence length $\xi$ which should be visible as deviations from the universal Abrikosov-Gor’kov curve in the inset of Fig. 1. Within experimental errors, and for the doping range in which we were able to establish the superconducting properties, we see no such deviations. We therefore believe that our observations place significant constraints on the search for the mechanism of the superconductivity of Sr$_2$RuO$_4$. In this context, it would also be interesting to directly measure the dynamical susceptibility of these samples, to gauge the extent to which the spin-fluctuation spectrum is changing as a function of $q$.

In summary, we have studied the microscopic effects of doping La$^{3+}$ for Sr$^{2+}$ in the correlated electron metal Sr$_2$RuO$_4$. An empirical, rigid-band shift, tight-binding parameterization of the electronic structure that incorporates constant many-body renormalizations allows a quantitative prediction of the evolution of both the Fermi surface geometry and the thermal properties of the doped material. Although this is not the first time that dHvA has been observed in the presence of doping in a correlated electron metal (a notable previous example is Ce$_{1-x}$La$_x$B$_6$ [28]), it is to our knowledge the first time that the rigid-band model has been put to such a sensitive test, especially for multi-band system. The superconducting properties remain remarkably unchanged in the face of a rapidly evolving, enhanced susceptibility spectrum, which raises intriguing questions about the mechanism of the unconventional superconductivity.

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