Quantum Oscillations in the Layered Perovskite Superconductor Sr$_2$RuO$_4$

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We report a comprehensive study of magneto-oscillatory phenomena in the normal state of Sr$_2$RuO$_4$, the first layered perovskite superconductor ($T_c \cong 1$ K) not based on copper. The form of the quasiparticle spectrum observed may be interpreted in terms of an almost two-dimensional Fermi liquid model which is consistent with Luttinger's theorem and successfully predicts bulk thermodynamic and transport properties at low temperatures. A study of the spectra and transport along the c axis provides insights into the different normal state and superconducting behavior of Sr$_2$RuO$_4$ and the cuprates. [S0031-9007(96)00174-3]

A decade of intensive research on the cuprate superconductors and related systems has raised fundamental challenges to our understanding of the metallic state. A surprising development is the realization that not only the superconducting but also the normal phases can exhibit properties which are difficult to reconcile with the standard (Fermi liquid) description. A number of mechanisms for the breakdown of at least some of the predictions of the usual Fermi liquid model have been proposed, but their applicability to the cuprates remains controversial. Some of the proposals stress the unique chemistry of the planar Cu-O bond [1] while a common theme in many of the others is the importance of reduced dimensionality. The latter favors long range effective interactions between the quasiparticles which can lead to an instability of the standard Fermi liquid state or at least to temperature (T) dependences of physical properties at variance with those normally associated with this state. Perhaps the most novel of these proposals is that of Anderson [2] in which a singular quasiparticle pseudopotential arises quite generally in a two-dimensional system at not too low a density due to the reduced phase space available for recoil in collisions, an effect which in higher dimensions tends to stabilize the normal Fermi liquid.

Experimental constraints on these models come not only from studies of the cuprates, but also of other related layered perovskites which share with them a quasi-two-dimensional structure, but differ in other details. Of particular interest is the recently discovered superconductor Sr$_2$RuO$_4$ [3] which has a similar crystal structure to the parent compound, La$_2$CuO$_4$, of one of the best studied families of the cuprate superconductors, La$_{2-x}$Sr$_x$CuO$_4$, but has four valence electrons (for Ru^{4+}) instead of one hole per formula unit.

In stoichiometric La$_2$CuO$_4$ the holes in a starting half filled $d(x^2 - y^2)$-p_σ band undergo a transition to a Mott insulating state with spin $1/2$ per formula unit, and

finite conductivity is achieved only upon doping. For a corresponding description of Sr$_2$RuO$_4$, it is convenient to begin with the isostructural and isoelectronic relative Sr$_2$FeO$_4$ in which the four valence electrons that in a starting model occupy three $d(xy, xz, yz)$-p_π orbitals undergo a Mott transition to an insulator with a high spin. Finite conductivity might be achieved by the application of pressure which leads to the broadening of the d bands [4], or as in the present case via the replacement of Fe by Ru for which the d orbitals are more extended. Stoichiometric Sr$_2$RuO$_4$, which may thus be viewed a conductor not far removed from a Mott insulating state, shares with the cuprates a strong anisotropy in the resistivity ($\rho_c/\rho_{ab} > 500$ at low T) and hence provides us with an example in which the role of reduced dimensionality in a system of highly correlated electrons may be investigated without the complicating features of disorder found in randomly doped materials.

The high purity of the samples which have been produced and its low upper critical field make Sr$_2$RuO$_4$ well suited for a first comprehensive investigation of quasiparticle excitations in the normal state of a layered perovskite conductor by means of quantum oscillations of the resistivity (the Shubnikov–de Haas effect) or of the magnetization (the de Haas–van Alphen effect) as a function of magnetic field **B**. These oscillatory phenomena arise from the quantization of cyclotron motion of charge carriers in planes normal to **B** and can provide us with a detailed description of the Fermi surface together with the cyclotron masses m of carriers on the individual Fermi surface sheets. The oscillations are periodic in $1/B$ with a frequency F which yields the area A of an extremal Fermi surface cross section normal to **B** via the Onsager relation $A = 2\pi eF/\hbar$. For our discussion it will be useful to define an *average* Fermi wave vector as $k_F \equiv \sqrt{A/\pi}$. The amplitude is expected to be exponentially damped with increasing values of $X = 2\pi^2 k_B T/\hbar\omega_c$ and r_c/l, where

$\omega_c = eB/m$ is the cyclotron frequency, $r_c = \hbar k_F/eB$ is an average cyclotron radius, and l is the carrier mean free path on the Fermi surface sheet concerned. The prediction of Fermi liquid theory for the form of this attenuation factor, namely, $\exp(-\pi r_c/l)X/\sinh X$, has been found to be in accord with experiments in a wide range of correlated electron systems studied thus far in which the value of m can be enhanced by 1 to 2 orders of magnitude over that predicted by standard band theory.

Investigations in these layered perovskites have been hampered by strong attenuation of the amplitude due to scattering (i.e., small l) in the randomly doped systems, and in the intrinsically doped materials (e.g., $YBa_2Cu_3O_7$ or $YBa_2Cu_4O_8$) by the high critical magnetic fields which prevent accessing the normal (nonsuperconducting) state at low T except with impulsive field methods based on explosive flux concentration techniques, the development of which is currently the subject of active research [5].

Sr_2RuO_4 is the only layered perovskite system known to us which does not suffer from these technical limitations. Conducting samples may be produced without random doping and hence with low residual resistivities ($\rho_{ab} \cong 1\ \mu\Omega$ cm for our samples grown via the floating zone technique [3,6]) and the low upper critical field (below 0.05 T with **B** along the c axis) enables us to access the normal state at very low T with a low noise superconducting magnet system. We have measured ρ_{ab} and the field derivative $\partial^2 M/\partial B^2$ of the magnetization M as a function of temperature and magnetic field **B** between 20 mK and 1.2 K and up to 18 T. Shown in Fig. 1 are typical results for the weak oscillatory components of $\partial^2 M/\partial B^2$ in the range near 18 T at 20 mK. The Fourier transform of $\partial^2 M/\partial B^2$ as a function of $1/B$, presented in Fig. 2, reveals the existence of three fundamental peaks labeled α, β (a splitting of which is clearly resolved), and γ, together with a harmonic 2α. Measurements of the variation of the frequencies as a function of the angle θ between **B** and the c axis of the crystal find
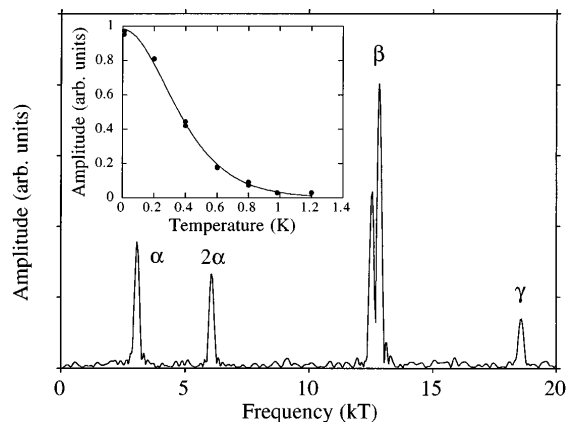
FIG. 2. Fourier transform of the data of Fig. 1 revealing three fundamental components α, β, and γ, plus a harmonic 2α. A splitting expected from slight modulations of the Fermi surface sheets along the c axis is clearly resolved for β and may be inferred for α via a beat pattern seen in long sweeps between 5 and 18 T; the data offer only an upper bound for γ which is detected only in the narrow field range 17–18 T. Inset: Temperature variation of the amplitude of the β component (symbols) and that predicted by Fermi liquid theory (solid line) in which the only free parameter is m (see text). Values of m obtained are shown in Table I.

largely a $1/\cos(\theta)$ dependence, confirming that the three branches correspond to three essentially cylindrical sheets of the Fermi surface. However, beats in the spectrum and the detailed orientation dependence of all three branches reveal tiny modulations in the cross sectional areas of the cylinders along the c axis that can provide us with insights into the out of plane properties.

It is interesting that the highest frequency detected (γ) is much larger than any observed thus far in other two-dimensional metals. Since the amplitude is damped exponentially with increasing frequency, components such as β and γ in Sr_2RuO_4 are normally very weak and extremely difficult to detect in metallurgically complex systems in which l tends to be small (i.e., typically below 10^3 Å). We also note that the three components α, β, and γ are observed not only in $\partial^2 M/\partial B^2$, but also, albeit with weaker signal to noise, in ρ_{ab} (β and γ, in particular, are the highest frequency components thus far detected via the *resistivity* in any metal).

Existence of magneto-oscillatory phenomena, in itself, is not sufficient to provide unequivocal support for the validity of a Fermi liquid description. Quantum oscillations are also expected to survive in a non-Fermi-liquid state if, e.g., the field is high enough that charge carriers, though not necessarily in stationary states, have a finite probability of completing a cyclotron orbit without decay. A more searching test of the applicability of Fermi liquid theory results from examining the detailed dependence of the spectrum of the oscillations on T and B and by comparing parameters obtained from the spectrum and properties inferred by other techniques.

We begin with an examination of the temperature dependence of the amplitude which, as shown in the
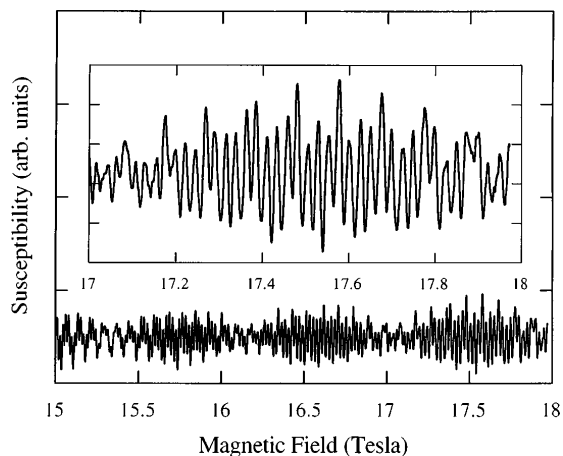

FIG. 1. de Haas–van Alphen oscillations in $\partial^2 M/\partial B^2$ detected with the field modulation technique in the dc field range 15–18 T at 20 mK.

inset of Fig. 2, does indeed follow closely the form given above for a Fermi liquid with well defined (i.e., T and B independent) cyclotron mass. Comparisons with predictions of standard band calculations (Fig. 3) show, however, that m is enhanced in all cases by a factor of 3–4, indicating that electron correlations are important [7]. The simplicity of the Fermi surface allows us to make further key tests of the internal consistency of the Fermi liquid description. From the measured cyclotron masses (Table I) we deduce, in a two-dimensional model for the Fermi surface, a linear coefficient of the heat capacity ($\pi N_A k_B^2 a^2 m / 3\hbar^2$, where a is the lattice parameter of 3.86 Å and N_A is Avogadro's number) of 5.0, 9.7, and 17.6 in units of mJ/K^2 mol for α, β, and γ, respectively, and hence a total 32, in broad agreement with the range of values (30–40) inferred from bulk heat capacity data on metallic samples [5,8]. Also, if, guided by band theory ([9] and Fig. 3), we associate α with *holes* and β and γ with *electrons*, having fractional volumes $k_F^2 a^2 / 4\pi$ in the Brillouin zone of 0.108, 0.457, and 0.667, respectively, the observed Fermi surface sheets correspond to four electrons in the Brillouin zone to an accuracy of 1% [10]. This is in keeping with the prediction of Luttinger's theorem that the Fermi volume is conserved even in the presence of strong electron interactions. The magnetic field dependence of the amplitude yields Dingle temperatures (T_D) or mean free paths similar to those deduced from transport measurements, although the presence of long-period beats in the spectrum complicates the analysis [11].

Other properties consistent with a conventional description include the T^2 dependence of both ρ_{ab} and ρ_c observed below approximately 25 K [6], and the BCS-Gorkov form of the temperature variation of the upper critical field H_{c2} [12]. We stress, however, that bulk properties may not identify a Fermi liquid state without
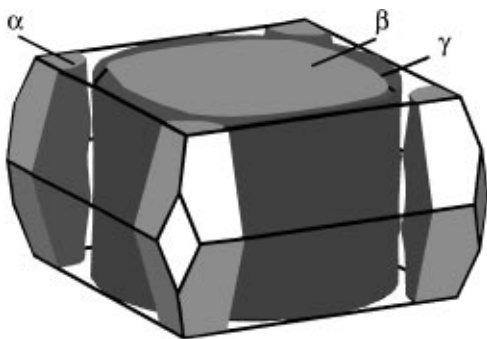

FIG. 3. Observed frequencies as a function of the orientation of **B** are consistent with a Fermi surface (FS) composed of two large electron cylinders (β and γ) centered on the ΓZ line and one narrow hole cylinder (α) running along the corners of the body centered tetragonal Brillouin zone, as expected from band theory. A number of calculations based on the local density approximation (LDA) for the lattice potential all lead to similar models of the FS [9]. This shows a typical result for the three FS sheets. Values of the calculated FS parameters are compared with experiment in Table I.

ambiguity. A T^2 variation of the resistivity, in particular, may arise even when the quasiparticle relaxation rate has a highly anomalous energy and temperature dependence over most or all parts of the Fermi surface [2,13]. Taken together, however, the thermodynamic, transport, and Fermi surface properties would seem to suggest that a Fermi liquid description of some sort provides a consistent account of Sr_2RuO_4 in the temperature and field ranges of the experiments described thus far. Quantum oscillatory studies of the highly anisotropic organic BEDT and ET salts have also been interpreted in terms of a Fermi liquid model [14], but an important difference between Sr_2RuO_4 and the organics is that the carrier concentrations in the organics are much smaller.

This apparent simplicity is remarkable for highly correlated electrons not far removed from a Mott insulating state and confined primarily in two dimensions. It is possible that an anomalous conducting state may be induced in Sr_2RuO_4 by "tuning" closer to the cross over between the conducting and insulating states (provided the transition is not too strongly first order) or by generating more strictly two-dimensional conduction. In fact, an examination of transport in the third direction reveals an intriguing difference between Sr_2RuO_4 and the cuprates.

A plausible self-consistent criterion for a three-dimensional band description leading to an anisotropic Fermi liquid is that the conventional mean free path along the c axis, $l_c = v_c \tau_c$, where v_c is the rms group velocity along the c direction on the Fermi surface and τ_c is the relaxation time, is greater than the interlayer spacing. To estimate l_c we consider an energy dispersion for each band near the Fermi level of the elementary form $\delta \varepsilon_k = \hbar^2 k_F \delta k_F / m - 2t \cos(k_c jc/2)$, where t, k_c, and c represent, respectively, a hopping matrix element, the wave vector, and the body centered tetragonal lattice parameter (12.7 Å) along the c axis, and j is an integer which may be set to 2 for a minimal description of La_2CuO_4. In general, $j = 1$ and 2 terms can be important for electron surfaces such as β and γ in Sr_2RuO_4, but in the following we retain the $j = 2$ approximation for simplicity. Then t is defined by the splittings in the branches via $t = \hbar^2 k_F \Delta k_F / 4m$, and hence all of the parameters entering $\delta \varepsilon_k$ (i.e., k_F, m, and t) may be inferred from our Fermi surface data (Table I) [15]. An elementary analysis now yields $v_c = \sqrt{2} tc/\hbar$, and conductivities $\sigma_{ab} = e^2 v \langle k_F^2 \tau / m \rangle / \pi c$ and $\sigma_c = 4e^2 c v \langle t^2 m \tau_c \rangle / \pi \hbar^4$, where $\langle \rangle$ denotes an average over v bands.

In the following we set $\tau_c = \tau$, which is physically reasonable since $v_F = \hbar k_F / m \gg v_c$. Taking $v = 1$, we then find $l_c = l \sqrt{\rho_{ab} / 2\rho_c}$, and $l = \hbar k_F \tau / m = \hbar \sqrt{\pi c/n} / e^2 \rho_{ab}$, where n is the carrier density. From known values of ρ_{ab}, ρ_c, and n for the cuprates (among which examples may be found where ρ_c vs T has either positive or negative slopes at low T) l_c is in all cases less than the interlayer spacing ($c/2$), and hence *the above consistency condition is violated.*

TABLE I. Measured and calculated Fermi surface parameters for Sr_2RuO_4. The uncertainties in the measured frequencies and cyclotron masses are 1% and 5%, respectively.

	α	β	γ
Frequency F (kT)	3.05	12.7	18.5
Average k_F (Å^{-1})	0.302	0.621	0.750
$\Delta k_F/k_F$ (%)	0.21	1.3	<0.9
Cyclotron mass (m_e)	3.4	6.6	12.0
Band calc. F (kT)	3.4	13.4	17.6
Band calc. $\Delta k_F/k_F$ (%)	1.3	1.1	0.34
Band mass (m_e)	1.1	2.0	2.9

For Sr_2RuO_4, in which $\nu = 3$, a check on this consistency condition may be made for each band individually with the aid of our Fermi surface data. From the above analysis, we may rewrite $l_c = lc\Delta k_F/2\sqrt{2}$. At low T, in the impurity scattering limit, it is a good approximation to take l to be independent of band and, for our sample with $\rho_{ab} \sim 1 \mu\Omega$ cm, it is approximately equal to 10^3 Å. Using values of Δk_F from Table I we find l_c to be of order 3 Å, 36 Å, and $\leq$30 Å for α, β, and γ, respectively. In this same model we obtain a high value of $\geq$600 for ρ_c/ρ_{ab} (given by $4\langle k_F\rangle/c^2\langle k_F\Delta k_F^2\rangle$), which is consistent with low temperature resistivity data [3,6].

These results show that in contrast to the cuprates, c-axis transport in Sr_2RuO_4 is dominated at low T by sheets (β and γ) for which $l_c \gg c/2$ ($\cong$6.3 Å). This condition is not satisfied for the α sheet which, although it plays little role in transport, may nevertheless deserve closer study. Interestingly, l_c becomes of order $c/2$ when ρ_{ab} and ρ_c begin to deviate significantly from a T^2 form above $\sim$25 K [6]. At still higher T ($>$100 K) ρ_{ab} is approximately linear and ρ_c *falls with increasing* T, a behavior analogous to that observed in the cuprates. In most cuprates, detailed low T normal state measurements have not been performed due to the very high upper critical fields. An exception (and in many ways the cuprate that is most similar to Sr_2RuO_4) is $Tl_2Ba_2CuO_{6+\delta}$, which has $H_{c2}(0) < 20$ T. The criterion $l_c > c/2$ is never satisfied, however, and in sharp contrast to the observations on Sr_2RuO_4 $\rho_{ab}(T)$ has a strong linear component which survives to low T ($<$1 K), and a very unusual non-BCS form of $H_{c2}(T)$ [16].

It is striking that both in $Tl_2Ba_2CuO_{6+\delta}$ and in Sr_2RuO_4 at elevated temperatures a number of anomalous properties appear to be correlated with an l_c smaller than the interlayer spacing. In Sr_2RuO_4, it is possible that the crossover from "coherent" to "incoherent" c-axis transport can be tuned to higher T by uniaxial stress or to lower T via a suitable form of doping.

In conclusion, we have reported the observation of quantum oscillatory phenomena in the layered perovskite oxide Sr_2RuO_4. All sheets of the Fermi surface, including the large ones, have been observed, allowing us to correlate a number of physical properties in a consistent manner. Our observations are compatible with a Fermi liquid description, the applicability of which may be linked with coherent interplane transport at low temperatures.

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[5] Discussions may be found in J.L. Smith et al., J. Superconductivity **7**, 271 (1994); for other references see A.I. Bykov et al., JETP Lett. **61**, 107 (1995).

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[7] The Lifshitz-Kosevich formula which we use to produce the fit shown in the inset of Fig. 2 is not expected to be valid in the very high field limit, where the Landau level separation becomes large compared with the overall broadening of the levels. Estimates based on our data suggest that we are well below this limit.

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[9] T. Oguchi, Phys. Rev. B **51**, 1385 (1995); D.J. Singh, Phys. Rev. B **52**, 1358 (1995); G.J. McMullan and M.P. Ray have performed calculations based on linear muffin tin and full potentials with and without consideration of spin-orbit effects (unpublished).

[10] Also important is that given their volumes, the conclusion β and γ are electron pockets is the only one that is consistent with the observation of a negative low temperature Hall coefficient by N. Shirakawa et al. J. Phys. Soc. Jpn. **64**, 1072 (1995); A.P. Mackenzie et al., (unpublished).

[11] Our best estimates of mT_D/m_e are approximately 2, 5, and 8 K for α, β, and γ, respectively. [See A.J. Diver, Ph.D. thesis, University of Cambridge (unpublished). The values of m/m_e are given in Table I.]

[12] K. Yoshida et al. (unpublished).

[13] R. Hlubina and T. M. Rice, Phys. Rev. B **51**, 9253 (1995).

[14] For example, J. Wosnitza, Int. J. Mod. Phys. B **7**, 2707 (1993); K. Oshima et al., Phys. Rev. B **38**, 938 (1988); J. Caulfield et al., Synth. Met. **61**, 63 (1993); N. Toyota, in Proceedings of Physical Phenomena at High Magnetic Fields II (to be published); J. S. Brooks et al., Synth. Met. **56**, 1791 (1993), and references contained in all these articles.

[15] An improved model with $j = 1$ and 2 leads to a splitting of the frequency branches into triplets. In our data doublet splitting dominates, and the orientation dependence of the amplitudes (not shown) favors $j = 2$ as a good approximation.

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