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THE INTRIGUING SUPERCONDUCTIVITY OF STRONTIUM RUTHENATE

Structurally, this metal oxide resembles the high-T_c cuprates, but its superconductivity is more like the superfluidity of helium-3.

Yoshiteru Maeno, T. Maurice Rice, and Manfred Sigrist

The superconducting state of strontium ruthenate (Sr_2RuO_4) was discovered in 1994 by Yoshiteru Maeno and his collaborators after they had succeeded in making high-quality samples of the material.[1] At about 1.5 K, the value of T_c is unremarkable, but interest was immediately aroused by a possible relationship to the high-T_c cuprate superconductors. Both kinds of material are highly two-dimensional (2D), and, as figure 1 shows, the crystal structure of Sr_2RuO_4 is almost identical to that of the (La, Sr)$_2$CuO$_4$ superconductors. Furthermore, both materials are oxides with conduction occurring in partially filled d-bands (of the strontium or copper ions) that are strongly hybridized with the oxygen ions' p orbitals.

We now know that these two superconductors are quite different. The high-T_c cuprate superconductors continue to form a unique class of materials. Extensive searches have failed to turn up any analogous materials in the transition metal oxides or elsewhere. Sr_2RuO_4, on the other hand, seems much closer to another famous material: superfluid helium-3.

Although the superfluidity of ^{4}He was discovered in the 1930s, it was not until the 1970s that a superfluid transition was found in the fermionic isotope ^{3}He. Two features of superfluid ^{3}He surprised investigators at first: 1) the p-wave internal symmetry of the Cooper pairs of fermions that make up the condensate and 2) the relatively high transition temperature of about 1 mK. Theorists soon realized that the strong enhancement of the spin fluctuations in space and time plays an important role in both the choice of the p-wave state and in the enhanced value of T_c. Immediately, the question arose of whether an analogous state could be found in metals.

Conventional metallic superconductors are described well by the Bardeen-Cooper-Schrieffer (BCS) theory in which the electrons' Coulomb repulsion is overcome by the attraction induced by the exchange of phonons between electrons close to the Fermi surface. To maximize this attraction, the Cooper pairs in BCS theory appear in the simplest s-wave channel. However, a few years after BCS was formulated, Walter Kohn and Quin Luttinger examined the possibility of generating a weak residual attraction out of the Coulomb repulsion between electrons. They found that this attraction could occur in principle, but only in a higher angular momentum channel in which the electrons in the Cooper pairs are prevented from close encounters by the centrifugal barrier.

The value of T_c estimated by Kohn and Luttinger was extremely small. However, the discovery of superfluidity in ^{3}He led to the hope that reasonable values of T_c would be found in those metals whose enhanced paramagnetism leads to strong spin fluctuations. Unfortunately, nothing came from these searches.

The first breakthrough in the quest for unconventional metallic superconductors came around 1980 with the discovery of superconductivity in the special class of heavy fermion metals. These are intermetallic compounds with a rare earth or actinide constituent. Under certain circumstances, the inner shell electrons in 4f or 5f states can be induced to participate weakly in the Fermi fluid of the outer conduction electrons. The result is a Fermi fluid with a very low characteristic temperature and strong residual interactions. Some heavy fermion metals have been found to exhibit superconductivity with a value of T_c that, though low in absolute terms ($T_c \sim 1$ K), is high relative to the temperature that characterizes the Fermi distribution.

Much progress has been made in heavy fermion metals in recent years, but their big drawback from a theorist's point of view is the complexity inherent in describing the physics of rare earth and actinide ions (see PHYSICS TODAY, February 1995, page 32). Even today, unambiguous determination of their unconventional symmetry has not proved possible.

Strongly correlated 2D Fermi liquid

The unexpected discovery of high-T_c superconductivity in the cuprates led to extensive searches for superconductivity in other transition metal oxides. The only success came in Sr_2RuO_4, but it was soon apparent that the differences between Sr_2RuO_4 and the cuprates were much larger than the general similarities.[1] In Sr_2RuO_4, superconductivity appears only at low temperatures, in samples with very low residual resistivity, and out of a normal state that is a well-formed Landau–Fermi liquid. These conditions contrast strongly with the highly anomalous normal state of the cuprates and the robustness of cuprate superconduc-

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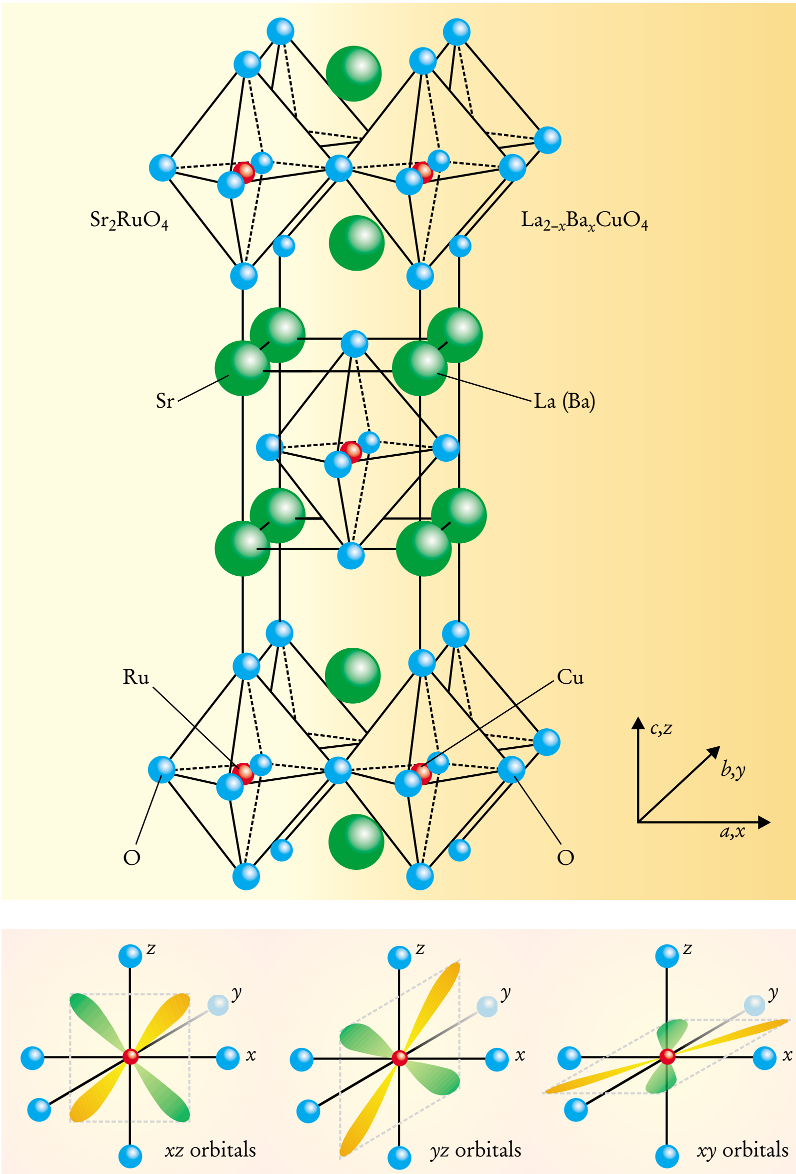


FIGURE 1. STRONTIUM RUTHENATE (Sr_2RuO_4) forms a layered perovskite structure. As shown in the upper panel, the crystal's RuO_2 layers are separated by Sr layers, and each Ru ion is enclosed in an octahedral cage of oxygen ions. The same structure is also found in La_2CuO_4, which is the parent compound of the high-T_c superconductor $La_{2-x}Ba_xCuO_4$. Despite their structural similarity, the ruthenate and the cuprate have very different electronic properties: Sr_2RuO_4 is strongly metallic and a superconductor at low temperature, whereas La_2CuO_4 is an antiferromagnetic insulator. The lower panel shows the configuration of the orbitals responsible for the superconductivity of Sr_2RuO_4, namely, the 4d t_{2g} orbitals.

tivity with respect to disorder.

A hallmark of a Landau–Fermi liquid is that the resistivity at low temperatures should rise as T^2, a power law that can be derived from the simplest perturbative treatment of electron–electron collisions. The observation of this power law in the resistivity of Sr_2RuO_4—both in the RuO_2 planes and perpendicular to these planes (but with very different coefficients)—clearly indicates that the perturbative Landau theory of electron–electron interactions is applicable. Likewise, liquid ^3He in the normal phase is described well by Landau theory, even though the interactions in ^3He are also very strong.[2]

In Sr_2RuO_4, the formal valence (or oxidation state) of the ruthenium ion is Ru^{4+}, which leaves four electrons remaining in the 4d shell. The Ru ion sits at the center of a RuO_6 octahedron, and the crystal field of the O^{2-} ions splits the five 4d states into threefold (t_{2g}) and twofold (e_g) subshells. The negative charge of the O^{2-} ions causes the t_{2g} subshell to lie lower in energy because these orbitals (xy, xz, yz) have lobes that point not toward, but between, the O^{2-} ions lying along the x-, y-, and z-axes, as shown in the lower panel of figure 1. Electrons in these orbitals form the Fermi surface.

The highly planar structure of Sr_2RuO_4 prevents substantial energy dispersion from developing along the z-axis due to the large interplanar separation of the RuO_6 octahedra. However, in the ab plane, neighboring RuO_6 octahedra share O ions, which, in turn, are π-bonded with the Ru ions. The xy orbital acquires a full 2D energy dispersion thanks to the O ions that lie along the x- and y-axes, whereas the xz and yz orbitals have only a restricted one-dimensional energy dispersion. The result, as shown on the cover, is a Fermi surface with three cylindrical sheets: one of xy character (the γ sheet) and two of slightly mixed xz and yz characters (the α and β sheets).

Mixing between xy and xz or yz orbitals is exceptionally weak because their different parity under the reflection $z \to -z$ forbids mixing within a single plane. Detailed calculations of the electronic band structure confirm these considerations and distribute the four electrons more or less equally among all three orbitals.[3]

The detailed shape of a metallic Fermi surface can be directly determined in experiments that exploit the de Haas–van Alphen effect, that is, the oscillation of magnetization in response to an external magnetic field.[4] In de Haas–van Alphen experiments, the modulations of the Fermi surface along a given direction can be related to the periods of the observed oscillations. Only metallic samples with long mean free paths are suitable for these experiments, again proving the importance of sample purity. The shape and volumes of the three Fermi surface sheets predicted by the band structure were nicely confirmed.

De Haas–van Alphen experiments can also measure the Fermi velocities perpendicular to the Fermi surface, which can be used to define an effective electron mass locally on the Fermi surface. Here, the discrepancy between band structure calculations and experiment is substantial. Typically, measurements reveal that the effective mass is enhanced by a factor of 3–5. This large enhancement agrees with values deduced from the T-linear specific heat coefficient.

The linearity is consistent with Landau theory, a cornerstone of which states that electron–electron interactions cannot alter the total volume enclosed by the Fermi surface but will renormalize the effective masses. The

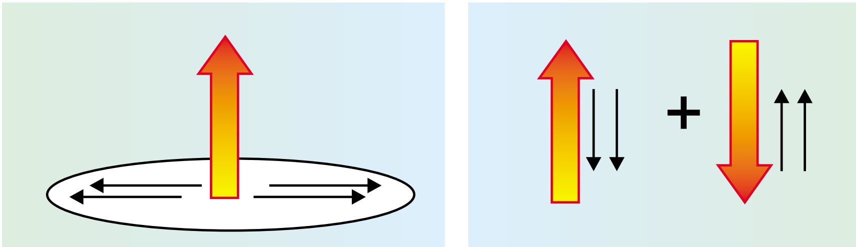


FIGURE 2. THE SUPERCONDUCTING STATES, corresponding to $\mathbf{d}(\mathbf{k}) = \hat{\mathbf{z}}\,(k_x + ik_y)$ (left) and $\mathbf{d}(\mathbf{k}) = \hat{\mathbf{x}}k_x + \hat{\mathbf{y}}k_y$ (right), have different spin orientations and total angular momentum. The $\hat{\mathbf{z}}\,(k_x + ik_y)$ state has an angular momentum along the *z*-axis (thick arrow) and spin perpendicular in the plane (thin arrows). Its total angular momentum therefore has a value of 1 and points along the *z*-axis. The $\hat{\mathbf{x}}k_x + \hat{\mathbf{y}}k_y$ state has vanishing total angular momentum because the orbital angular momentum is compensated by the spins of the Cooper pair. Both states represent equal-spin-pairing states, but have very different physical properties. Experiments identify the superconducting phase in Sr_2RuO_4 as being of the type in the left panel—that is, a state with finite angular momentum.

fact that closely related oxides such as $SrRuO_3$ are ferromagnetic.[5] By contrast, the cuprates, which are antiferromagnets rendered superconducting by doping, are now known to have spin-singlet pairing in a *d*-wave ($l = 2$) orbital channel.

Specifying the complete symmetry of the superconducting state requires more than just the angular momentum channel and the spin state. The pairs in a superconductor are in a spatially uniform state with respect to their center-of-mass coordinate, and their possible internal motion will be classified by those symmetry operations centered on a Ru ion that leave the crystal invariant—that is, the "point group" of the crystal. Sr_2RuO_4 has tetragonal symmetry and its highly planar character suggests attention be restricted to pairing states that maximize the intraplanar, rather than interplanar, pairing.

In a triplet superconductor, the pairing state is conveniently represented by a three-dimensional (3D) vector $\mathbf{d}(\mathbf{k})$, whose magnitude and direction vary over the Fermi surface in $\mathbf{k}$ space. The presence of the pairing condensate causes a finite difference in the energy needed to add (or remove) electrons singly, rather than in pairs. This "energy gap" in the single electron spectrum (or density of states) may depend also on the position, $\mathbf{k}$, on the Fermi surface and is given by the magnitude of $\mathbf{d}(\mathbf{k})$. How $\mathbf{d}(\mathbf{k})$ varies depends on which representation of the point group $\mathbf{d}(\mathbf{k})$ belongs to; in some cases, it will even have nodes (or zeroes). Additionally, the pairing state corresponds to the $\mathbf{d}(\mathbf{k})$ that maximizes the energy gained when the superconducting condensate forms (the condensation energy). Under weak coupling conditions, this choice will be a nodeless form. However, these criteria alone are insufficient to determine the form of the pairing amplitude uniquely. Several pairing states have the same condensation energy under weak coupling conditions.

This degeneracy is related to the spin rotation symmetry and is eventually lifted by spin–orbit coupling. A comparison with superfluid ^{3}He is illuminating here. At ambient pressure, the *p*-wave superfluid state of ^{3}He is the B-phase, whose energy gap is nonzero in all directions. However, under pressure, close to the liquid–solid phase boundary, enhanced spin fluctuations favor the A-phase, even though it has two point nodes.

large mass enhancement and the large measured value of the T^2 coefficient in the resistivity reveal that residual interactions in the Landau description are unusually strong—as they are in ^{3}He. These measurements, therefore, confirmed suspicions that the dominant interactions at low energies are of the strong electron–electron kind, rather than the weaker electron–phonon kind. They also boosted the prospects that the superconductivity would turn out to be unconventional.

In fact, as soon as unconventional superconductivity turned out to be increasingly likely in Sr_2RuO_4, the questions arose which total spin (spin singlet or triplet) and angular momentum channel (*s*-wave, *p*-wave, and so forth) characterize the fermions' internal motion in the Cooper pairs. Pairs of fermions must have antisymmetric wave functions under particle interchange. For a Cooper pair, this requirement implies a relationship between the orbital and spin character: Orbital wavefunctions with even values of the orbital quantum number ($l = 0, 2, \ldots$) are even under particle interchange and therefore require odd symmetry in the spin wavefunction (that is, they are spin singlets); odd ($l = 1, 3, \ldots$) require spin triplets.

Cooper pairing symmetry

Soon after the discovery of superconductivity in Sr_2RuO_4, Maurice Rice and Manfred Sigrist—and, independently, Ganapathy Baskaran—proposed *p*-wave ($l = 1$) and spin-triplet pairing on the basis of similarities to ^{3}He and on the

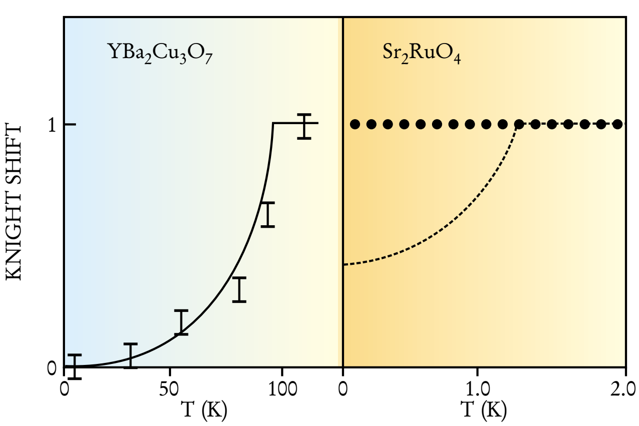


FIGURE 3. THE KNIGHT SHIFT for oxygen-17 in yttrium barium copper oxide (left) and strontium ruthenate (right). In materials whose superconductivity is mediated by spin-singlet Cooper pairing, Knight-shift data exhibit a drop in the spin susceptibility in the superconducting state. Such a drop occurs in $YBa_2Cu_3O_7$, but not in Sr_2RuO_4, whose superconductivity is most likely mediated by spin-triplet Cooper pairs (the dashed line is a prediction based on spin-singlet Cooper pairing). (Adapted from ref. 7.)

^3He is a 3D Fermi liquid with a spherical Fermi surface; the nodes can be placed at the north and south poles. By contrast, because of its highly planar nature, the Fermi surface of Sr_2RuO_4 consists of cylindrical sheets. With this topography, one can construct for Sr_2RuO_4 a 2D analog of the A-phase of ^3He that is nodeless and, therefore, stable over a wider range of parameters. For this reason, states of both type are strong competitors: the B-phase-like state $\mathbf{d}(\mathbf{k}) = (k_x, k_y, 0)$, and the A-phase-like state $\mathbf{d}(\mathbf{k}) = (0, 0, k_x \pm ik_y)$.

The different orientations of the spin and orbital angular momenta of the Cooper pairs are illustrated in figure 2. At present, it is difficult to decide the pairing symmetry theoretically from a simple microscopic approach. A theory of spin-fluctuation-driven superconductivity is even more difficult to construct for Sr_2RuO_4 than it is for the superfluidity of ^3He. For example, the influence of spin–orbit coupling strongly depends on details of the band structure and on the pairing mechanism.

Evidence for spin-triplet pairing

The next question, therefore, is how to determine the pairing symmetry experimentally. Unlike the more familiar cases of determining crystalline or magnetic order, this goal is far from easy. Consequently, one must proceed indirectly and ask what are the special properties of each type of symmetry and what experiments will directly test them.

First, consider how one discriminates between conventional (that is, *s*-wave) and unconventional (non-*s*-wave) forms in a weak-coupling superconductor. In the case of Sr_2RuO_4, weak coupling can be inferred from the low value of T_c (~ 1 K) relative to the effective Fermi temperature (~ 50 K) at which quantum coherence sets in.

Conventional superconductivity is largely immune to scattering from impurities, imperfections, and so on. As Philip Anderson showed, Cooper pairs can be formed from pairs of single fermion states related by time reversal symmetry. However, in an unconventional superconductor, the pairing amplitude is a nontrivial function of the wave vector $\mathbf{k}$ around the Fermi surface. The wave vector must therefore be well defined. Because it mixes different $\mathbf{k}$ values, impurity scattering is deleterious to unconventional superconductivity, hence, the need for high-quality samples to see unconventional superconductivity in the first place.

Andrew Mackenzie and his collaborators undertook detailed investigations of the sensitivity to impurity scattering in a series of aluminum-doped samples. They showed that Sr_2RuO_4 behaved as expected for an unconventional superconductor.[6]

Next, the question of whether the pairing is spin-singlet or spin-triplet must be settled. The most effective way to do this is by measuring the spin susceptibility through the superconducting transition. This can be conveniently done by measuring the Knight shift in nuclear magnetic resonance (NMR) experiments. The Knight shift describes the small change in the resonance line frequency caused by the weak spin polarization of the electrons in the applied magnetic field. In a singlet superconductor, the electrons in the Cooper pairs are bound in spin singlets; they are not polarized at all in the small fields applied in NMR experiments. As a result, the Knight shift vanishes at zero temperature. But for triplet superconductors with the parallel spins lying in the plane, the application of a magnetic field in the plane changes the relative numbers of pairs with spin parallel and antiparallel to the field, and the Knight shift is unchanged from its value in the normal state.

Box 1. Chiral Superconductivity

According to muon spin resonance experiments, the superconducting state of Sr_2RuO_4 has a pairing order that breaks time reversal symmetry.[8] The form of the gap function represented by $\mathbf{d}(\mathbf{k}) = \hat{\mathbf{z}}\ (k_x \pm ik_y)$ implies that the Cooper pairs have the internal angular momentum $L_z = \pm 1$. This means that the superconducting phase analogous to the A-phase of ^3He is, in principle, an orbital ferromagnet.[2] In general, superconductivity and magnetism are antagonistic phenomena, but in this case, the superconducting state generates its own magnetism. The Meissner–Ochsenfeld effect, however, prevents uniform magnetization inside the superconductor and magnetism is restricted to areas of inhomogeneities—that is, around impurities and domain walls or at interfaces and surfaces. In these regions, spontaneous supercurrents flow, generating local magnetic field distributions that can be detected by muon spins.

The presence of orbital angular momentum introduces a form of chirality to the superconducting state. Among the chirality's various implications, the most striking is perhaps the set of quasiparticle states that are localized at the surface and possess a chiral spectrum. These chiral states carry spontaneous dissipation-free currents along the surface. They are gapless, in contrast to bulk quasiparticles of the superconductor, and can be detected by spectroscopic measurements.[14]

Chirality in a quasi-2D system suggests a connection with the quantum Hall effect. Indeed, it was proposed that chiral superconductors could show quantum Hall-like effects even in the absence of an external magnetic field.[14] This spontaneous Hall effect would appear as a transverse potential difference in response to a supercurrent. Unfortunately, the effect is rather small and difficult to detect. Nevertheless, Sr_2RuO_4 could become the ideal test ground for this phenomenon.

The first NMR test came from Kenji Ishida and his coworkers, who found that the ^{17}O Knight shift was totally unaffected by the transition into the superconducting state[7] (see figure 3). Note, however, that the spin–orbit interaction blurs the distinction between spin-singlet and spin-triplet pairing. If, contrary to expectations, spin–orbit coupling is very strong, it could negate the simple interpretation of the Knight shift experiments.

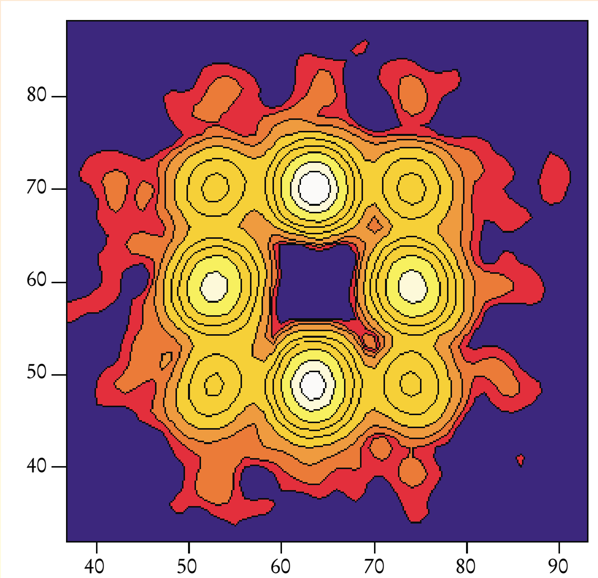
Another way to identify the nature of the pairing stems from the fact that one of the proposed forms for $\mathbf{d}(\mathbf{k})$, $(0, 0, k_x \pm ik_y)$, breaks time reversal symmetry. This special property forces a local charge disturbance to be accompanied by a local supercurrent distribution, which in turn creates a small magnetic moment distribution. A good way to test for this phenomenon is to inject spin-polarized μ^+ leptons into the sample and observe the time evolution of their spin polarization by monitoring their decay products. The muons create a local charge disturbance and their spin makes it possible to directly test for an accompanying magnetic moment distribution. Graeme Luke and his collaborators performed a series of μSR (muon spin relaxation) experiments on Sr_2RuO_4 and found an enhancement of the zero field relaxation rate in the superconducting state that agreed with expectations for a broken time-reversal symmetry state.[8] (For more on time reversal symmetry, see box 1 above.)

Thus, assuming that nature has not confused matters by having a magnetic phase of a different origin appearing coincidentally at the same T_c, one can conclude that the three main features of the superconducting state in Sr_2RuO_4—namely, the non-*s*-wave form, the spin-triplet pairing, and the broken time reversal symmetry—have been confirmed by these three independent tests (see also

Box 2. Vortex Physics

For magnetic fields along its *c*-axis, Sr_2RuO_4 is a weakly type-II superconductor and can support a mixed phase, where vortices (magnetic flux lines) enter the superconductor. Here, the pairing symmetry is crucial for the interaction among vortices and the way they arrange in a lattice. In contrast to conventional and high-T_c superconductors, where the superconducting phase is represented by a single complex order parameter, the A-phase-like state in Sr_2RuO_4 involves two complex components. Daniel Agterberg showed that this implies that the vortices would form a square lattice.[15] Subsequent small-angle neutron scattering experiments have confirmed this prediction nicely.[16]

Nevertheless, the realization of a vortex square lattice is not an unambiguous proof for a two-component order parameter. Fortunately, the detailed form of the magnetic field distribution associated with the vortices gives a further tool to identify the order parameter symmetry for weakly type-II superconductors. The accompanying figure (courtesy of Paul Kealey and Ted Forgan) shows the diffraction pattern from the flux-line lattice in Sr_2RuO_4 obtained from small-angle neutron scattering.[16] (The numbers on the axes indicate the pattern's actual size in centimeters of the position-sensitive neutron detector.) Kealey and Forgan's neutron scattering experiments established recently that the magnetic field distribution in Sr_2RuO_4 in the mixed phase could be fitted best with a two-component order parameter, whereas a single-component order parameter state always showed substantial deviations.[16]



The mixed phase for fields parallel to the RuO_2 planes is no less interesting. In particular, the low-temperature high-field regime exhibits a variety of unusual properties that imply a more complex phase diagram involving different superconducting phases.[17] Experiments concerning this aspect of Sr_2RuO_4 are in progress. Because they require magnetic fields in this quasi-2D system to be aligned inplane with very high precision, these experiments are extremely demanding.

box 2 above). They are consistent with a single state of the basic form $\mathbf{d}(\mathbf{k}) = (0, 0, k_x \pm ik_y)$, which is the analogue of the ^{3}He A-phase.

Multi-orbital effects

As is often the case in condensed matter physics, things are not as simple and straightforward as they seem initially. The first experiments to uncover essential complications were the specific heat measurements of Shuji Nishizaki and his coworkers. Their results revealed a reduced jump in the specific heat at the superconducting transition and the emergence of a substantial term proportional to T as T tends to zero. The results also implied a residual density of states in the superconducting state of about half the value in the normal state.

These findings are clearly at odds with the prediction of a complete energy gap in the proposed superconducting state. Such a state would have a specific heat that vanishes exponentially as T tends to zero. A little later, NMR experiments on the relaxation rate as a function of T also showed evidence of a residual density of states of about the same size.

Offering an explanation for this seeming contradiction, Daniel Agterberg, Rice, and Sigrist pointed out that the Fermi surface separates into two distinct parity regions—namely, the α,β sheets and the γ sheet (see cover). The α,β sheets are derived from orbitals with the symmetry (xz, yz), which are odd under the reflection $z \to -z$ about the center of a RuO_2 plane. The γ sheet is derived from the xy orbital, which has even parity.[9] Agterberg, Rice, and Sigrist showed that, in this highly planar material, pair scattering between the two parity regions would be greatly inhibited. They also proposed an orbital-dependent form of superconductivity that would be essentially confined to one of the regions. Typically, such confinement does not occur because, according to the usual conservation laws of energy and momentum, a Cooper pair may be scattered to all parts of the Fermi surface. If the confinement thesis is valid, the next question is which parity region is responsible for the superconductivity.

Using an ingenious ^{17}O NMR analysis, Takashi Imai and his coworkers separated the contributions of the α,β and γ sheets to the susceptibility and found that the spin susceptibility was more strongly enhanced on the γ sheets.[10] Imai's result implies that, when the temperature drops below T_c, superconductivity initially appears in this sheet.

The first experiments, which showed a residual density of states of about half the normal state value, were all carried out on rather impure samples. The value of T_c is a sensitive indicator of sample quality. The initial samples had values of $T_c \sim 1$ K. More recently, improvements in sample growing techniques (see figure 4) have raised the value of T_c to 1.48 K, which is very close to the predicted maximum value.

When the specific heat and NMR relaxation rate experiments were repeated on the newer high-quality samples, the results changed substantially. Instead of a clear linear term in the NMR relaxation rate at low temperature, a continuous crossover to a higher power ($\sim T^3$) was observed. This behavior can only be explained if all parts of the Fermi surface participate in the superconducting state.

Theoretically, there are two possible ways that the superconductivity can spread from the γ sheet to the α,β sheets. Either a pairing amplitude of the same symmetry on the α,β sheet is directly induced or a pairing amplitude of a different symmetry could spontaneously appear. In

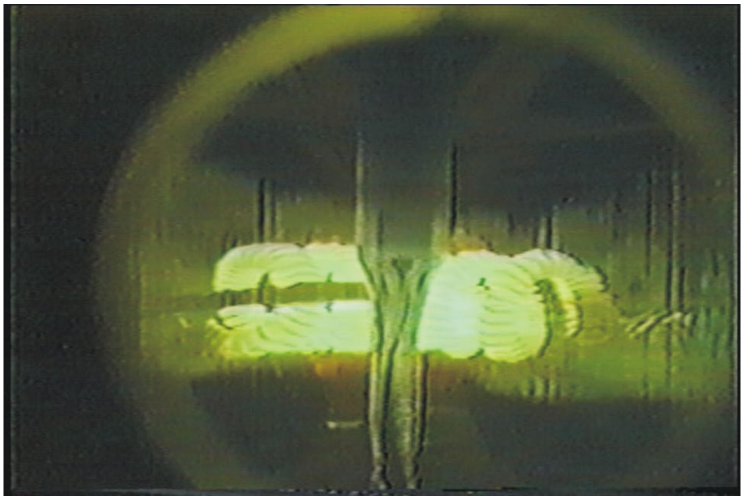


FIGURE 4. GROWING A SINGLE CRYSTAL of strontium ruthenate by the floating zone method. A polycrystalline rod fed from the top is melted at about 2100 °C in the central zone, where elliptical mirrors focus the infrared power emitted from two halogen lamps. The crystal is extracted from below. Because the material is not in contact with any container, which is often the main source of contamination, the crystal can be made extremely pure.

the latter case, a second phase transition in the superconducting state would arise as the overall symmetry was modified. The experiments to date appear to rule out this possibility. In the former case, the pairing on a γ sheet can be thought of as acting as a form of weak external field on the α,β sheets, whose response will be very sensitive to impurity scattering. Agterberg has analyzed the problem along this line, but at present the issue of how the 3D nature of the crystal causes pairing to spread to all parts of the Fermi surface remains unresolved. Indeed, the possibility of a major revision of the strongly orbital dependent hypothesis cannot be ruled out.

Phase-sensitive probes

For unconventional superconductors, the most direct way to determine the nature of the pairing is through phase-sensitive experiments. Such experiments proved decisive in the case of the high-T_c cuprate superconductors when they settled a long debate between proponents of conventional s-wave and unconventional d-wave pairing in favor of the latter.

Phase-sensitive experiments directly probe the sign of the pairing amplitude around the Fermi surface by making use of a suitable circuit of Josephson junctions. Sign changes in the pairing amplitude make it possible to create a frustration in the phase of $\mathbf{d}(\mathbf{k})$ that is relieved by a current flowing in the circuit. A measurement of magnetic flux then ascertains the presence or absence of the frustrating sign change in $\mathbf{d}(\mathbf{k})$.

The first proposal along these lines was made by Vadim Geshkenbein and his coworkers some years ago to test for p-wave pairing in heavy fermion superconductors.[11] To date, no such experiments have been reported for Sr_2RuO_4; until they are done, one cannot say that the identification of the symmetry is totally unambiguous. Josephson tunneling of pairs between Sr_2RuO_4 and conventional superconductors has been reported[12]—a hopeful sign that phase-sensitive experiments of this kind on Sr_2RuO_4 will prove possible.

Another class of phase-sensitive experiments is connected with the presence of surface quasiparticle states that lie within the gap in the density of states. These quasiparticle states, which can only exist when the phase of the pairing amplitude depends on direction, can be probed through the voltage dependence of the tunneling current from a normal metal to the superconductor. Recently, Frank Laube and his collaborators used a platinum point contact to observe an anomaly at zero bias in the current–voltage characteristics. Their experiments not only provide evidence for the surface quasiparticle states within the energy gap, but also strongly support the case for an odd-parity pairing state in Sr_2RuO_4.[13]

The discoveries made in Sr_2RuO_4 show that unconventional superconductivity driven by spin fluctuations or related mechanisms can appear in a well-formed Landau–Fermi liquid in metals as it does in ^{3}He. Many other metals show Landau–Fermi liquid behavior, but have never been observed to be superconducting. Metals such as the 3D cuprate $LaCuO_3$, V_2O_3 at high pressure, $Sr_3Ru_2O_7$, and $CaRuO_3$ fall into this category.

Already, the small number of unconventional superconductors has proven to be an immensely fruitful territory for finding novel phenomena in superconductivity. If the sample quality can be improved for other oxides, the field of unconventional superconductivity in metals may just be beginning.

We have benefited from many collaborations in this field and we would thank especially D. F. Agterberg, C. Bergmann, A. Furusaki, A. P. Mackenzie, Z. Q. Mao, M. Matsumoto, K. K. Ng, S. Nishizaki, and M. Zhitomirsky.

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