A polarized-neutron scattering study of the Cooper-pair moment in Sr$_2$RuO$_4$

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We report a study of the magnetization density in the mixed state of the unconventional superconductor Sr$_2$RuO$_4$. On entering the superconducting state we find no change in the magnitude or distribution of the induced moment for a magnetic field of 1 Tesla applied within the RuO$_2$ planes. Our results are consistent with a spin-triplet Cooper pairing with spins lying in the basal plane. This is in contrast with similar experiments performed on conventional and high-$T_c$ superconductors.

$\text{Sr}_2\text{RuO}_4$ has attracted attention since it was discovered to be a superconductor. The superconductivity of this compound is interesting because it is isostructural with the high-$T_c$ material La$_{2-x}$Sr$_x$CuO$_4$ and because the superconducting state appears unconventional (i.e. not of the $s$-wave singlet type). The low-temperature normal-state of Sr$_2$RuO$_4$ is a quasi-2D Fermi liquid with enhanced quasiparticles. Soon after the discovery of superconductivity in Sr$_2$RuO$_4$, it was suggested that the superconducting state might be unconventional. This suggestion is now supported by a number of experiments including: the observation of a very strong dependence of $T_c$ on impurities, a temperature-independent $^{17}\text{O}$ Knight shift on entering the superconducting state, a muon-spin rotation study indicating broken time-reversal symmetry, Andreev reflection, and the observation of power law $T$-dependences in the superconducting state for the electronic heat capacity and NQR $T_1^{-1}$.

While there is general agreement that the superconducting state of Sr$_2$RuO$_4$ is unconventional, the nature of the wavefunction is still controversial. A knowledge of the spin susceptibility in the superconducting state provides constraints on the pairing wavefunction of a superconductor. Such information can be obtained indirectly by nuclear-resonance techniques through the measurement of the polarization of the $s$ electrons on a given site. Alternatively, neutron scattering can directly measure the magnetization density induced by an applied magnetic field. This technique was first used by Shull and Wedgewood to study V$_3$Si and more recently it has been applied to heavy-fermion and high-$T_c$ superconductors. In this letter we report a study of the induced magnetization of Sr$_2$RuO$_4$ through the superconducting transition. On entering the superconducting state we find no change in the magnitude or distribution of the induced moment. Our results are in contrast to similar observations on conventional and high-$T_c$ superconductors and are consistent with triplet spin-pairing in Sr$_2$RuO$_4$.

The single crystal of Sr$_2$RuO$_4$ used in this study (C117) was prepared by a floating-zone method in an infrared image furnace. A piece of approximate dimensions $1.5\,\text{mm}\times\,2\,\text{mm}\times\,5\,\text{mm}$ was cut using a diamond saw. A.c. susceptibility measurements indicated a sharp superconducting transition with $T_c=1.47$ K and $B_{c2}(T=100\,\text{mK})=1.43$ T for $\mathbf{B}\parallel[1\overline{1}0]$. To perform our neutron scattering experiments, the sample was glued to a copper stage using Stycast 2850FT. The copper support was connected to a dilution refrigerator via two $1\,\text{mm}^2$ diameter copper wires. In the present experiment we applied the magnetic field along the $[1\overline{1}0]$ direction. The large anisotropy in $B_{c2}$ means that the mutual alignment of the magnetic field and $[1\overline{1}0]$ is crucial. Accurate alignment was achieved by mounting the sample and copper stage on a micro-goniometer inside a 2.5 T magnet. In order to verify that the crystal was correctly aligned and at low temperature, we performed an in-situ a.c. susceptibility measurement by mounting two co-axially wound coils near the sample but out of the neutron beam.

The sensitivity of the present magnetic-moment measurement can be dramatically increased by the use of polarized neutrons. Our measurements were performed on the IN20 spectrometer at the Institut Laue-Langevin, Grenoble. A beam of neutrons with a polarization greater than 93% and with energy $E_i=34.8\,\text{meV}$ was produced using the (111) Bragg reflection of a Heusler monochromator. We searched for possible depolarization of the beam caused by the presence of the vortex lattice by measuring the polarization of neutrons scattered by the (002) Bragg reflection using a Heusler analyzer. However, the presence of the vortex lattice produced no detectable depolarization for fields $B\geq1\,\text{T}$ under the experimental conditions used.

In the present experiment we measure the magnetization density $\mathbf{M}(\mathbf{r})$ in the presence of an applied magnetic field $\mathbf{B}$. Because of the periodicity of the crystal, an applied magnetic field induces a magnetization density with spatial Fourier components $\mathbf{M}(\mathbf{G})$ corresponding to
reciprocal lattice vectors $G$, where

$$\mathbf{M}(\mathbf{r}) = \frac{1}{V_0} \sum_G \mathbf{M}(G) \exp(-iG \cdot \mathbf{r}) \quad (1)$$

and $V_0$ is the unit-cell volume. The Fourier components of the magnetization density are given by

$$\mathbf{M}(G) = \int_{\text{cell}} \mathbf{M}(\mathbf{r}) \exp(iG \cdot \mathbf{r}) d\mathbf{r}. \quad (2)$$

A diffraction experiment allows these spatially varying components of the magnetization to be measured, even in the superconducting state.

Neutrons interact with condensed matter both through the strong nuclear interaction and through the electromagnetic interaction. If the neutron momentum transfer $\mathbf{k} = \mathbf{k_i} - \mathbf{k_f}$ equals a reciprocal lattice vector $G$, i.e. we satisfy the Bragg condition, then scattering occurs both because of the periodicity of the nuclear density and because of the microscopic periodicity of the magnetization density. The two scattered waves interfere. For neutrons with initial and final spin polarizations $\sigma_i$ and $\sigma_f$, the total cross section is $\left[13,21\right]$

$$\frac{d\sigma}{d\Omega_{\sigma_i} \rightarrow \sigma_f} \propto \left| \frac{\gamma r_0}{2\mu_B} \sigma \cdot \hat{k} \times \{\mathbf{M}(\mathbf{k}) \times \hat{k}\} + \mathbf{F}_N(\mathbf{k})|\sigma_f \right|^2 \quad (3)$$

where $\gamma r_0 = 5.36 \times 10^{-15}$ m, $F_N(\mathbf{k})$ is the nuclear structure factor (in units of m f.u.$^{-1}$) and $\mathbf{M}(\mathbf{k})$ has units of $\mu_B$ f.u.$^{-1}$. The sign of the magnetic term in Eq. 3 is controlled by the polarization of the neutrons. By reversing the polarization of the incident neutrons we are able to isolate the term due to the interference between magnetic and nuclear contributions, yielding the magnetization density. Experimentally we measure the flipping ratio $R$, defined as the ratio of cross sections for initial neutron-spin states which are parallel or antiparallel to the applied magnetic field and with arbitrary final spin state. In the present experiment, the applied field, and hence neutron polarization, is perpendicular to the scattering vector $\mathbf{k}$. Under these circumstances the flipping ratio $R$ evaluated from Eq. 3 is only sensitive to the component of magnetization parallel to the applied field, $M_\parallel(\mathbf{k})$. Because the induced moment is small, the experiment is carried out in the limit $(\gamma r_0/2\mu_B)|\mathbf{M}(\mathbf{k})|/|F_N(\mathbf{k})| \approx 0.001 \ll 1$. In this limit, the flipping ratio derived from Eq. 3 is

$$R = \frac{|F_N(\mathbf{k}) - (\gamma r_0/2\mu_B)M_\parallel(\mathbf{k})|^2}{|F_N(\mathbf{k}) + (\gamma r_0/2\mu_B)M_\parallel(\mathbf{k})|^2} \approx 1 - \frac{2\gamma r_0 M_\parallel(\mathbf{k})}{\mu_B F_N(\mathbf{k})}. \quad (4)$$

As the nuclear structure factors $F_N(\mathbf{k})$ are known from the crystal structure, Eq. 4 directly gives the magnetization $\mathbf{M}(\mathbf{G})$. Fig. 4 shows the susceptibility $\chi(\mathbf{k},0) = M(\mathbf{k})/B$ for a number of wavevectors $\mathbf{k}$ determined from the measured flipping ratios $R$ and converted into magnetic moment using Eq. 4. The measured flipping ratios were corrected for imperfect beam polarization and finite flipper efficiency. Other possible corrections including extinction, absorption, incoherent scattering, the neutron spin-orbit interaction [14], half-wavelength contamination in the incident beam were estimated to be small. In order to allow us to enter the mixed state, measurements were generally made with an applied field of 1 Tesla. However, Fig. 1 shows that measurements in the normal state at $k = (002)$ and $B = 2$ Tesla yielded consistent results.

Neutron scattering measures the total moment, thus Fig. 1 includes contributions from diamagnetic, orbital and spin components of the susceptibility. The fall off of the susceptibility $\chi(\mathbf{k},0)$ with increasing $|\mathbf{k}|$ is due to the finite extent of the induced moment in space. Fig. 1 shows the Ru form factor (solid line) [21] scaled to the measured bulk susceptibility [21] of Sr$_2$RuO$_4$, $\chi_{ab} = 0.9 \times 10^{-3}$ e.m.u. mole$^{-1}$. The poor agreement of the $\kappa = (110)$ component with the Ru form factor may suggest the presence of a significant induced moment on the oxygen atoms.

Before discussing our results in the superconducting state of Sr$_2$RuO$_4$, we will briefly discuss the same measurement of the spin susceptibility in the conventional superconductor V$_3$Si. In a conventional superconductor with spin-singlet pairing, the spin susceptibility is suppressed on entering the superconducting state because electrons with anti-parallel spins pair up. For $B \ll B_{c2}$ the temperature dependence is described by the Yosida function [23]. Wedgewood and Shull [15] performed a polarized-neutron measurement of the susceptibility on the conventional superconductor, V$_3$Si, and observed a reduction of the susceptibility, due to the formation of...
spin singlets \((S = 0)\) [see Fig. 2(a)]. We have reproduced the Wedgewood-Shull result using the same experimental set-up as for our \(\text{Sr}_2\text{RuO}_4\) measurements. Our results are consistent with Wedgewood and Shull and are shown as open circles in Fig. 2(a).

Having observed the induced moment in the normal state of \(\text{Sr}_2\text{RuO}_4\), we proceeded to investigate the effect of the superconductivity. Because of the low \(T_c\) and strongly anisotropic \(B_{c2}\) it was important to verify that the sample was in good thermal contact with the dilution refrigerator and well aligned with the applied magnetic field. Fig. 2(c) shows an in-situ measurement of the a.c. susceptibility, made using the balance output of an inductance bridge, plotted against applied field \(B\) for \(T=100\) mK. The kink corresponds to \(B_{c2}=1.43\) Tesla, which is indistinguishable from the published value \([23]\), demonstrating that the sample was well-aligned. In order to ensure penetration of the magnetic field throughout the sample the sample was always “field-cooled”.

Fig. 2(b) shows the temperature dependence of the induced moment corresponding to the (002) Bragg position for \(B=1\) Tesla. This component was chosen for detailed study because its amplitude is proportional to the sum of the moments induced on the in-plane ruthenium and oxygen atoms \((m_{Ru} + 2m_{O})\). For a 1 Tesla field applied parallel to [110], \(T_c = 1\) K (See Fig. 2(d)). On entering the superconducting state, we find that there is no change in this component of the induced moment within the experimental error. In contrast to the \(V_3\text{Si}\) measurement, we investigated \(\text{Sr}_2\text{RuO}_4\) at relatively high fields, \(B/B_{c2} = 0.68\), thus the presence of normal vortices leads to a significant density of quasiparticles and finite spin susceptibility in the mixed state. Using the measured linear heat capacity in the superconducting state \([1]\) we estimate \([24]\) the zero-temperature spin susceptibility \(\chi(T \to 0, B = 1T) = 0.45\chi_{\text{normal}}\). The dashed line in Fig. 2(b) is a Yosida function modified to include the finite susceptibility in a field: this prediction is still at variance with the data. Thus, the absence of a change in spin susceptibility is not compatible with spin-singlet or even-parity pairing.

The absence of a change in the spin susceptibility can be explained if Cooper pairs form from electrons with parallel spins. Such “equal-spin pairing” (ESP) was first proposed in the context of \(^3\text{He}\) by Anderson and Morel \([23]\). Within an ESP scenario the superconducting state is a superposition of the two possible \((S = 1)\) parallel paired states. In an applied magnetic field, one state is favored yielding a net spin moment and the same susceptibility as in the normal state \([26]\). An EPS-type pairing implies an odd-parity or spin-triplet state, thus the present experiment supports the notion that the superconducting wavefunction in \(\text{Sr}_2\text{RuO}_4\) has an odd-parity representation. There are five unitary odd-parity representations \((\Gamma_{5}^{-})\) of the order parameter for the crystal point group \(C_{4h} \) \([27]\). Of the allowed representations only the degenerate \(\Gamma_5^+ (E_u)\) or \(d(k) = \hat{z}(\hat{k}_x \pm i\hat{k}_y)\) state is expected to show no change in its spin susceptibility for magnetic fields applied in the basal plane.

So far we have discussed the spin part of the Cooper-pair wavefunction. The \(\Gamma_5^+\) state is special in that the orbital part of the wavefunction suggests that the paired
electrons have relative angular motion with orbital angular momentum $L_z = \pm 1$. $\mu$SR measurements reveal a spontaneous internal magnetic field in the superconducting state which is thought to be associated with the internal orbital moment. The present experiment is sensitive to the total electronic moment $(S + L)$ in the superconducting state. Under the present experimental conditions, we measure magnetic moments parallel to the applied field. The absence of a change in the orbital moment measured by the present experiment is entirely consistent with the $\Gamma_5^-$ assignment above. Firstly, because the moment is expected to be parallel to the $c$-axis and, secondly, because the bulk orbital moment is expected to be small.

At first sight our results appear to contradict recent heat capacity measurements and other experiments which suggest that the superconducting gap is strongly anisotropic, possibly having nodes for certain directions. However, a strongly anisotropic gap function is still allowed within the $\Gamma_5^-$ representation. For example, the anisotropic $f$-states which have recently been proposed still have the $\Gamma_5^-$ representation and are consistent with our interpretation.

Our results complement and contrast with recent NMR measurements of the $^{17}$O Knight shift in the mixed state of Sr$_2$RuO$_4$. These do not detect a reduction in the spin susceptibility. The Knight shift measures the polarization of the $s$-electrons at a given site: electrons in other orbitals and on other sites are probed because of the overlap of orbitals. In contrast, the present neutron-scattering measurement directly measures the spatially-averaged total moment.

Measurements of the induced moment in the mixed state have also been performed on other unconventional superconductors. In the high-temperature superconductor YBa$_2$Cu$_3$O$_{6+x}$ a suppression of the spin susceptibility is observed which is consistent with an even-parity or singlet pairing. In contrast, the heavy-fermion superconductors UPt$_3$ and UBe$_{13}$ show no reduction in the spin susceptibility on entering the superconducting state suggesting that they have odd-parity pairing.

In summary, we have used a spin-polarized neutron-scattering technique to measure the magnetization in the mixed state of the unconventional superconductor Sr$_2$RuO$_4$. We find that for a 1 Tesla field applied parallel to the $[\overline{1}00]$ basal-plane direction, there is no detectable change in the component of the moment parallel to the applied field. Our results strongly support the identification of the paired state of Sr$_2$RuO$_4$ as the $\Gamma_5^-$ or $d(k) = \pm ik_y$ state.

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