Polarized-Neutron Scattering Study of the Cooper-Pair Moment in Sr_2RuO_4

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We report a study of the magnetization density in the mixed state of the unconventional superconductor Sr_2RuO_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 T 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.

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Sr_2RuO_4 has attracted attention since it was discovered [1] to be a superconductor. The superconductivity of this compound is interesting because it is isostructural with the high-T_c material $La_{2-x}Sr_xCuO_4$ and because the superconducting state appears unconventional (i.e., not of the *s*-wave singlet type). The low-temperature normal state of Sr_2RuO_4 is a quasi-2D Fermi liquid with enhanced-mass quasiparticles [2]. The corresponding planes are perpendicular to the *c* axis. It has been suggested [3,4] 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 [5], a temperature-independent ^{17}O Knight shift on entering the superconducting state [6], a muon-spin rotation study indicating broken time-reversal symmetry [7], Andreev reflection [8], and the observation of power law T dependences in the superconducting state for the electronic heat capacity [9] and NQR T_1^{-1} [10].

While there is agreement that the superconducting state of Sr_2RuO_4 is unconventional, the nature of the wave function is still controversial [3,4,11–14]. A knowledge of the spin susceptibility in the superconducting state provides constraints on the pairing wave function 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 a magnetic field. This technique was first used by Shull and Wedgwood [15] to study V_3Si and, more recently, it has been applied to heavy-fermion [16] and high-T_c [17] superconductors. In this Letter, we report a study of the induced magnetization of Sr_2RuO_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_2RuO_4.

The single crystal of Sr_2RuO_4 used in this study (C117) was prepared by a floating-zone method [18] in an infrared image furnace. A piece of approximate dimensions 1.5 mm × 2 mm × 5 mm was cut using a diamond saw. Measurements of the ac susceptibility indicated a sharp superconducting transition with $T_c = 1.47$ K and $B_{c2}(T = 100\text{ mK}) = 1.43$ T for $\mathbf{B} \parallel [1\bar{1}0]$. 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 mm^2 diameter copper wires. In the present experiment we applied the magnetic field along the $[1\bar{1}0]$ direction, perpendicular to the scattering plane. The large anisotropy in B_{c2} means that the mutual alignment of the magnetic field and $[1\bar{1}0]$ is crucial. Accurate alignment was achieved by mounting the sample and copper stage on a microgoniometer inside a 2.5 T magnet. In order to verify that the crystal was both correctly aligned and at low temperature, we performed an *in situ* ac susceptibility measurement by mounting two coaxially wound coils near the sample but out of the neutron beam.

The sensitivity of magnetic-moment measurements 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 $E_i = 34.8$ 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 $\geq$ 1 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

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Fourier components $\mathbf{M}(\mathbf{G})$ corresponding to reciprocal lattice vectors $\mathbf{G}$, where

$$\mathbf{M}(\mathbf{r}) = \frac{1}{\nu_0} \sum_{\mathbf{G}} \mathbf{M}(\mathbf{G}) \exp(-i\mathbf{G} \cdot \mathbf{r}), \tag{1}$$

and ν_0 is the unit-cell volume. The Fourier components of the magnetization density are given by

$$\mathbf{M}(\mathbf{G}) = \int_{\text{cell}} \mathbf{M}(\mathbf{r}) \exp(i\mathbf{G} \cdot \mathbf{r})\, d\mathbf{r}. \tag{2}$$

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 strong nuclear interaction and through electromagnetic interaction. If the neutron momentum transfer $\boldsymbol{\kappa} = \mathbf{k}_i - \mathbf{k}_f$ equals a reciprocal lattice vector $\mathbf{G}$, 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 $\boldsymbol{\sigma}_i$ and $\boldsymbol{\sigma}_f$, the total cross section is [19,20],

$$\left(\frac{d\sigma}{d\Omega}\right)_{\sigma_i \to \sigma_f} \propto \left| \langle \sigma_i | \frac{\gamma r_0}{2\mu_B} \boldsymbol{\sigma} \cdot \hat{\boldsymbol{\kappa}} \times \{\mathbf{M}(\boldsymbol{\kappa}) \times \hat{\boldsymbol{\kappa}}\} + F_N(\boldsymbol{\kappa}) | \sigma_f \rangle \right|^2, \tag{3}$$

where $\gamma r_0 = 5.36 \times 10^{-15}$ m, $F_N(\boldsymbol{\kappa})$ is the nuclear structure factor (in units of m f.u.$^{-1}$) and $\mathbf{M}(\boldsymbol{\kappa})$ has units of μ_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 (the analyzer was removed). In the present experiment, the applied field, and hence neutron polarization, is perpendicular to the scattering vector $\boldsymbol{\kappa}$. Under these circumstances the flipping ratio R evaluated from Eq. (3) is sensitive only to the component of magnetization parallel to the applied field, $M_\parallel(\boldsymbol{\kappa})$. Because the induced moment is small, the experiment is carried out in the limit $(\gamma r_0/2\mu_B)\,|\mathbf{M}(\boldsymbol{\kappa})|/|F_N(\boldsymbol{\kappa})| \approx 0.001 \ll 1$. In this limit, the flipping ratio derived from Eq. (3) is

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

As the nuclear structure factors $F_N(\boldsymbol{\kappa})$ are known from the crystal structure, Eq. (4) directly gives $\mathbf{M}(\mathbf{G})$. Figure 1 shows the susceptibility $\chi(\boldsymbol{\kappa}, \omega = 0) = \mathbf{M}(\boldsymbol{\kappa})/B$ for a number of wave vectors $\boldsymbol{\kappa}$ determined from the measured flipping ratios R. The measured flipping ratios were corrected for imperfect beam polarization and finite flipper efficiency. Other corrections including extinction, absorption, incoherent scattering, the neutron spin-orbit interaction [19] and 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 T. However, Fig. 1 shows that measurements in the normal state at $\boldsymbol{\kappa} = (002)$ and $B = 2$ T yielded consistent results.

Neutron scattering measures the total moment, thus Fig. 1 includes contributions from diamagnetic, orbital, and spin components of the susceptibility. The induced magnetization density reflects the underlying atomic orbitals and lattice periodicity. Thus, we expect to observe an essentially atomic form factor in the normal and superconducting states. The solid line represents the Ru form factor [20] scaled to the measured bulk susceptibility [21] of Sr_2RuO_4, $\chi_{ab} = 0.9 \times 10^{-3}$ e.m.u. mole^{-1}. The poor agreement of the $\boldsymbol{\kappa} = (110)$ 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_2RuO_4, we will briefly discuss the same measurement of the spin susceptibility in the conventional superconductor V_3Si. In a conventional superconductor with spin-singlet pairing, the spin susceptibility is suppressed on entering the superconducting state because electrons with antiparallel spins pair up. For $B \ll B_{c2}$ the T dependence is described by the Yosida function [22]. Wedgwood and Shull [15] performed a polarized-neutron measurement of the susceptibility on the conventional superconductor, V_3Si, and observed a reduction of the susceptibility, due to the formation of spin singlets ($S = 0$) [see Fig. 2(a)]. We have reproduced the Wedgwood-Shull

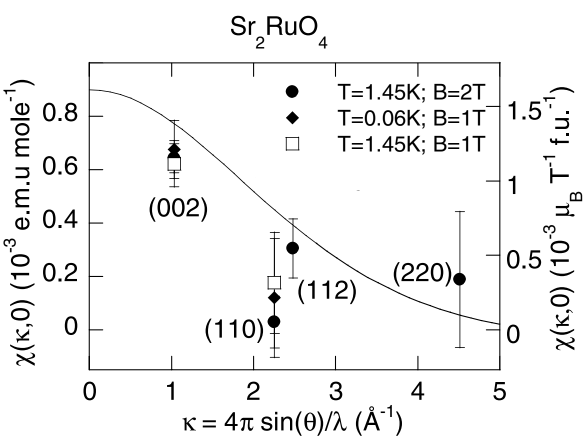

FIG. 1. The wave-vector-dependent susceptibility $\chi(\boldsymbol{\kappa}, 0)$ determined from the induced moment for magnetic fields of 1 and 2 T applied along the $[1\bar{1}0]$ direction. Solid line is a scaled Ru form factor [20].

result using the same experimental setup as for our Sr_2RuO_4 measurements. Our results are consistent with Wedgwood and Shull and are shown as open circles in Fig. 2(a).

Having observed the induced moment in the normal state of Sr_2RuO_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. Figure 2(c) shows an *in situ* measurement of the ac susceptibility, made using the balance output of an inductance bridge, plotted against applied field B for $T = 100$ mK. The kink corresponds to $B_{c2} = 1.43$ T, 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."

Figure 2(b) shows the T dependence of the induced moment corresponding to the (002) Bragg position for $B = 1$ T. 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 T field applied parallel to $[1\bar{1}0]$, $T_c = 1$ 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_3Si measurement, we investigated Sr_2RuO_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 [9] we estimate [24] the zero-temperature spin susceptibility $\chi(T \rightarrow 0, B = 1\ \mathrm{T}) = 0.45\chi_{\mathrm{normal}}$. 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}He by Anderson and Morel [25]. Within an ESP scenario the superconducting state is a superposition of the two possible ($S = 1$) parallel paired states. In an applied magnetic field, the Cooper pairs are simultaneously responsible for the superconductivity and the induced magnetization through the differing occupation of the $S_z = \pm 1$ states, leading to the same susceptibility as in the normal state [26]. An ESP-type pairing implies an odd-parity or spin-triplet state, thus the present experiment supports the notion that the superconducting wave function in Sr_2RuO_4 has an odd-parity representation. There are five unitary odd-parity representations (Γ^-_{1-5}) of the order parameter for the crystal point group C_{4h} [3,27]. Of the allowed representations only the degenerate Γ^-_5 (E_u) or $\mathbf{d}(\hat{\mathbf{k}}) = \hat{\mathbf{z}}(\hat{k}_x \pm i\hat{k}_y)$ 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 wave function. The Γ^-_5 state is special in that the orbital part of the wave function suggests that the paired electrons have relative angular motion with orbital angular

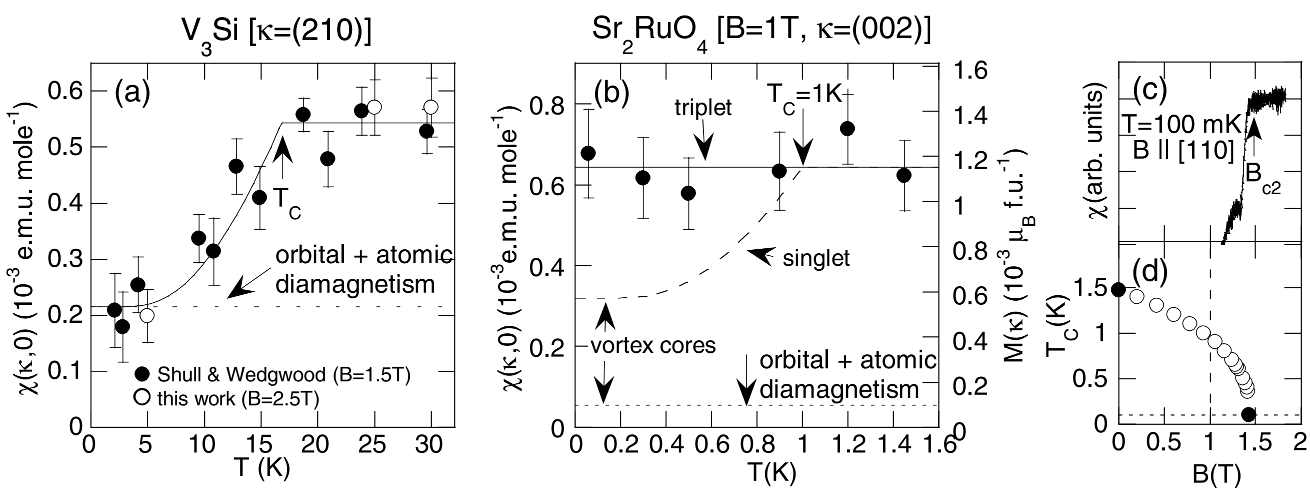

FIG. 2. (a) The susceptibility of the conventional s-wave singlet superconductor V_3Si measured by Shull and Wedgwood [15] using the present neutron scattering method. At low temperatures a residual orbital contribution to the susceptibility remains. (b) The T dependence of the susceptibility and induced moment of Sr_2RuO_4 measured using polarized neutron scattering. The dashed line is the Yosida [22] behavior expected for a singlet-paired superconductor. Counting times were 8 h per spin polarization. (c) *In situ* ac susceptibility measurement to demonstrate accurate alignment of the sample. (d) The $B_{c2}(T)$ for Sr_2RuO_4 for $\mathbf{B} \parallel [1\bar{1}0]$. Closed circles are the present measurements; open circles are from Ref. [23]. The horizontal dashed line denotes the trajectory of the *in situ* susceptibility measurement in panel (c) and the vertical line is the trajectory of the T-dependent susceptibility measurement in (b).

momentum $L_z = \pm 1$. μSR measurements [7] 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 ($\mathbf{S} + \mathbf{L}$) 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 Γ_5^- assignment above. First, because the moment is expected to be parallel to the c axis and, second, because the bulk orbital moment is expected to be small [28].

At first sight our results appear to contradict recent heat capacity [9] and other experiments [10] 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 Γ_5^- representation. For example, the anisotopic f states which have recently been proposed [14] still have the Γ_5^- representation and are consistent with our interpretation.

Our results complement and contrast with recent NMR measurements [6] of the ^{17}O Knight shift in the mixed state of Sr_2RuO_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-T_c superconductor $YBaCu_3O_{6+x}$ [17] 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} [16,29] 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_2RuO_4. We find that for a 1 T field applied parallel to the $[1\bar{1}0]$ 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_2RuO_4 as the Γ_5^- or $\mathbf{d}(\hat{\mathbf{k}}) = \hat{\mathbf{z}}(\hat{k}_x \pm i\hat{k}_y)$ state.

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