Reconstruction from Small-Angle Neutron Scattering Measurements of the Real Space Magnetic Field Distribution in the Mixed State of Sr$_2$RuO$_4$

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We have measured the diffracted neutron scattering intensities from the square magnetic flux lattice in the perovskite superconductor Sr$_2$RuO$_4$, which is thought to exhibit p-wave pairing with a two-component order parameter. The relative intensities of different flux lattice Bragg reflections over a wide range of field and temperature have been shown to be inconsistent with a single component Ginzburg-Landau theory but qualitatively agree with a two-component p-wave Ginzburg-Landau theory.

The discovery of superconductivity at temperatures near 1 K in strontium ruthenate [1] has excited great interest because of the suggestion that it is a p-wave superconductor [2]. It is a stoichiometric *undoped* compound, in which the electrons form a Fermi liquid with a well-established quasi-two-dimensional Fermi surface [3]. Clear evidence of non-s-wave pairing in this compound has been provided by the observation [4] that *nonmagnetic* impurities strongly suppress T_c, which extrapolates to ≈ 1.5 K in the clean limit. Strong support for triplet (p-wave) pairing is given by the results of Ishida *et al.* who have measured the Knight shift with a field parallel to the RuO$_2$ planes [5]; the spin susceptibility measured by the Knight shift is not suppressed below T_c, unlike a singlet superconductor. Also, muon spin rotation (μSR) measurements in the Meissner state in zero field [6] have revealed spontaneous fields, which can be generated by domain boundaries, surfaces, and impurities in a superconductor which breaks time-reversal symmetry [7]. Such states can arise most naturally with p-wave pairing, but also are possible with d-wave singlet pairing.

Agterberg [8–10] argued that if the pairing was time-reversal symmetry breaking p wave, then in tetragonal symmetry the **d** vector [11] has the symmetry $\hat{\mathbf{z}} \exp(\pm i\varphi)$ (φ is the azimuthal angle about the tetragonal c axis), and a two-component Ginzburg Landau (TCGL) theory would be expected to describe the superconductor. With a field applied in the c direction perpendicular to the planes, a small amount of anisotropy in the Fermi surface would lead to a square flux lattice instead of a triangular one, with the orientation of the square flux line lattice (FLL) relative to the crystal axes determined by the orientation of the fourfold anisotropy of the paired electrons. The FLL structure has been observed in this material [12] and is observed to be square over a wide range of field and

temperature. The nearest-neighbor directions in the square FLL are at 45° to the Ru-O-Ru directions in the crystal lattice [13].

These results are consistent with the pairing wave function described above. However, a square FLL is also seen in borocarbide superconductors, which are definitely non-p wave [14–16]. Also, one can measure spontaneous fields in a superconductor by μSR due to other causes or from other states than that proposed, and application of a strong field in the basal plane to observe the Knight shift might alter the pairing state. Hence, it is important to obtain further evidence as to what kind of superconductivity occurs in strontium ruthenate. Here we present a detailed study of the scattered neutron intensities from the FLL. We show that they are not consistent with a single component Ginzburg-Landau model. Also we demonstrate how the local $B(\mathbf{r})$ may be reconstructed from our data and show that the FLL structure is quite different from the Abrikosov one.

We shall present measurements of intensities of higher-order Bragg reflections from the FLL so we consider how they are related to the FLL structure. The formula [17] for the integrated intensity I_{hk} of a (h, k) diffracted peak of wave vector $\mathbf{q}_{hk}$ gives

$$I_{hk} \propto \frac{F_{hk}^2}{q_{hk}}, \tag{1}$$

where F_{hk} is a spatial Fourier component of the local field $B(\mathbf{r})$ in the mixed state,

$$B(\mathbf{r}) = \sum_{h,k} F_{hk} \exp(i\mathbf{q}_{hk} \cdot \mathbf{r}). \tag{2}$$

In the Abrikosov solution of the Ginzburg-Landau (GL) equations (as applied to a square lattice) [18], the F_{hk} are given by

TABLE I.   Calculated and experimental flux lattice Fourier components and intensities for $B = 20$ mT, $B_{c2} = 58$ mT.

h, k of diffraction peak:	$\{1, 1\}$	$\{2, 0\}$	$\{2, 1\}$
q_{hk}/q_{10}	1.414	2.0	2.236
F_{hk}/F_{10} (London $\lambda = 152$ nm):	0.53	0.27	0.22
F_{hk}/F_{10} (Abrikosov):	0.2079	$-0.008\,98$	0.001 87
F_{hk}/F_{10} (Agterberg $\nu = 0.0$):	0.5657	-0.1051	0.0353
F_{hk}/F_{10} (Agterberg $\nu = 0.2$):	0.7711	-0.0667	0.0503
F_{hk}/F_{10} (Heeb and Agterberg $\nu = 0.05, \kappa = 1.6$):	0.484	-0.019	0.046
I_{hk}/I_{10} (London):	0.199	0.0365	0.0216
I_{hk}/I_{10} (Abrikosov):	0.0306	0.000 04	0.000 002
I_{hk}/I_{10} [GL (Brandt)]:	0.0783	0.000 91	0.000 298
I_{hk}/I_{10} (Agterberg $\nu = 0.0$):	0.2263	0.005 52	0.000 56
I_{hk}/I_{10} (Heeb and Agterberg $\nu = 0.05, \kappa = 1.6$):	0.166	0.000 95	0.000 18
I_{hk}/I_{10} (Expt. at 20 mT, 100 mK):	0.197(2)	0.011(3)	0.007(1)

$$F_{hk} \propto -(-1)^{(h^2 + k^2 + hk)} \exp\left(-\frac{\pi}{2}(h^2 + k^2)\right); \quad (3)$$

this rapidly falls off with q (see Table I).

The Abrikosov solution is valid only near B_{c2}. In high-κ superconductors, with the field not close to B_{c2}, the London expression [19] is appropriate instead. This gives $F_{hk} \propto 1/(1 + q_{hk}^2 \lambda^2)$. Note that unlike the Abrikosov solution, all the F_{hk} are positive. Table I shows that the Fourier components fall off much less rapidly with q. However, strontium ruthenate has a value of the Ginzburg-Landau parameter $\kappa = \lambda/\xi \sim 2.0$ for the field along the c axis, which means that the London approach is not realistic except at *very* low inductions. Therefore, to see what conventional GL theory predicts for this material at lower fields, one must use the Brandt numerical solution of the GL equations [20]. Typical results are given in Table I.

Next, we consider the Agterberg TCGL solution [8–10], which is equivalent to the Abrikosov one, except that there are two complex order parameters instead of only one. In the mixed state with B parallel to c both components are automatically present because of mixed gradient terms in the free energy functional [8–10]. Typical values from this theory for F_{hk}, relative to F_{10}, and the resulting SANS intensities are given in Table I. It may be seen that the two-component theory gives intensities that fall off *much less rapidly* with q than those given by the one-component Abrikosov solution.

Under the conditions of our experiments, where the field is not close to B_{c2}, it may be argued that the Abrikosov approximation used by Agterberg is not appropriate. However, recently Heeb and Agterberg have solved numerically the GL equations at all fields for the TCGL case [21]. We also give in Table I a list of Fourier components from these calculations, using values of parameters that appear to describe our results quite well.

The corresponding vortex structures in real space are shown in Figs. 1–4. Note that there is a minimum field point in the two-component theory (for the conditions of our experiment) which lies *between* the positions of the flux line cores, not in the center of the square. We give results of this theory for two values of the parameter ν ($-1 < \nu < 1$) [9] which describes the degree of fourfold
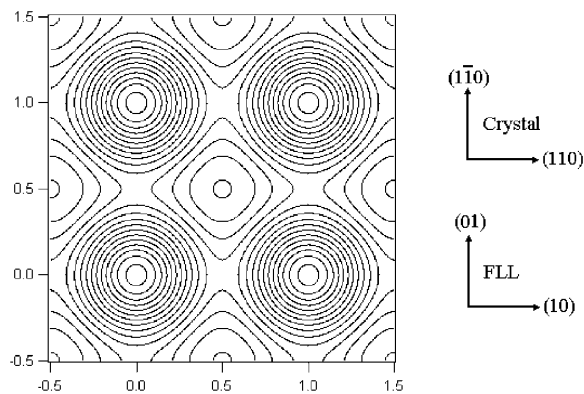

FIG. 1.   Contour plot of the magnetic field in a square flux line lattice as given by Brandt's numerical solution of the Ginzburg-Landau equations for the particular case of $\kappa = 2.0$, $B = 20$ mT, and $B_{c2} = 58$ mT. Contour lines are equally spaced. This result is very similar to that given by the Abrikosov solution valid near H_{c2} [18].
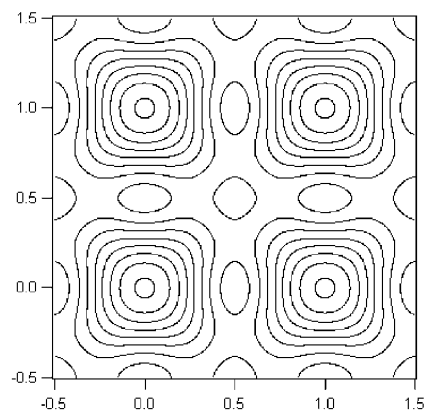

FIG. 2.   Contour plot of the magnetic field in a square flux line lattice as given by Agterberg's solution of his TCGL equations, valid near B_{c2}, in the case of a cylindrical Fermi surface ($\nu = 0.0$).
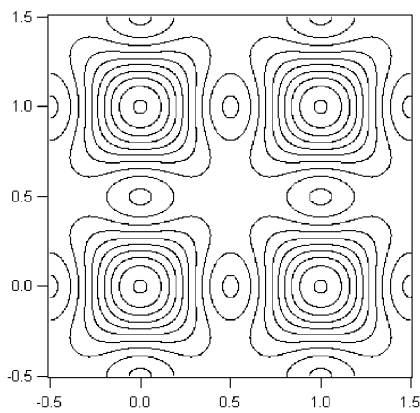
FIG. 3. As for Fig. 2 but with a fourfold distortion to the Fermi surface ($\nu = 0.2$).

anisotropy of superconducting electrons ($\nu = 0$ corresponds to a cylindrical Fermi surface). We note that the results do not change greatly with ν. Hence the qualitative difference between Figs. 1 and 3 is due to the difference between TCGL and GL theories rather than effects of fourfold crystal anisotropy. It may be that ν is quite small since $|\nu| > 0.0114$ is sufficient to stabilize a square FLL and align it to the crystal lattice with an orientation determined by the *sign* of ν [9].

We now turn to measurements of the FLL structure. Single crystal Sr_2RuO_4 was prepared by the floating zone technique with excess RuO_2 as a flux [22]. Six plates of total mass 556 mg were cleaved from the as-grown crystal and annealed for 72 hours in air at 1420 °C to remove defects and increase T_c, which was 1.39 K with a width (10%–90%) of $\approx$50 mK. With the field applied parallel to the c axis at 100 mK, the value of B_{c2} was 58 mT. For the small-angle neutron scattering (SANS) measurements, the samples were mounted with conducting silver paint as an aligned mosaic with their c axes perpendicular to a copper plate, which was mounted on the mixing chamber of a dilution refrigerator. A magnetic field was applied parallel to the c axes of the crystals (within 2°), and the FLL
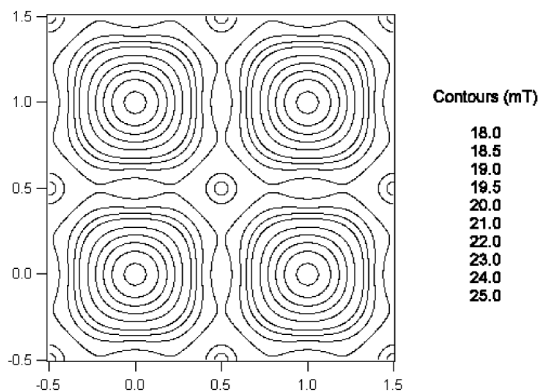

FIG. 4. Heeb and Agterberg's numerical solution to the TCGL equations [21], with the parameters $\kappa = 1.6$, $\nu = 0.05$ chosen to give a good fit to our data, with an applied field of $B = 20$ mT and $B_{c2}(100 \text{ mK}) = 58$ mT.
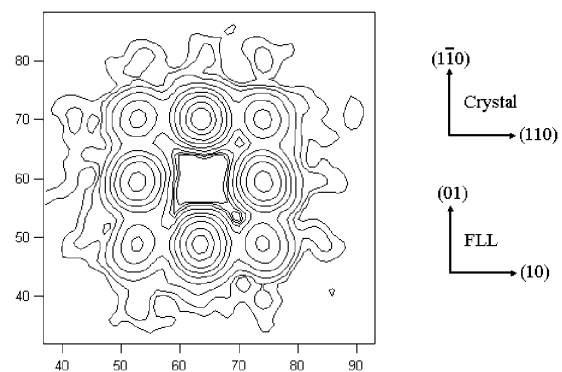

FIG. 5. Contour plot of FLL diffraction pattern. A field of 20 mT was applied parallel to c above T_c; the weak diffracted beams due to the flux lattice were extracted from background scattering by subtracting data taken above T_c. The axes are pixel numbers and the central region of the detector has been masked. The data shown is a sum of five patterns obtained by rocking the FLL up $\pm0.3°$ about the [110] axis.

was observed using long-wavelength neutrons on instrument D22 at the Institut Laue Langevin. Typical wavelengths employed were 14.6 Å, with a wavelength spread (FWHM) of 12%; the neutron beam was incident nearly parallel to the applied field, and the transmitted neutrons were registered at a 128×128 pixel multidetector (pixel size 7.5×7.5 mm^2) placed 17.71 m beyond the sample. Typical results are shown in Fig. 5. In addition to the strongest {10} reflections, the {11} reflections are strong, and higher orders are present. The intensity of the strongest diffraction spot is $<10^{-3}$ of the incident beam intensity, so these higher-order reflections are not due to multiple scattering. Their intensities are recorded in Table I: it will be noted that they are much larger than those given by the Abrikosov structure.

To reconstruct the $B(\mathbf{r})$ of the FLL corresponding to these results, we require the sign of F_{hk} relative to F_{10} (the FLL is centrosymmetric, so all the F_{hk} are real). The most important component after F_{10} is F_{11}. If it has the same sign as F_{10}, then the {11} components add in phase at the flux line cores to give a field peak that is sharper than the field minimum. Measurements of the field distribution in strontium ruthenate by μSR [23,24] show that this is the case. This sign for F_{11} is not surprising, since all models in Table I give it as positive. For the small contributions

TABLE II. Experimental FLL Fourier components at 100 mK. Errors represent statistical errors; FLL disorder or static Debye Waller factors may reduce F_{hk} for high $\mathbf{q}$.

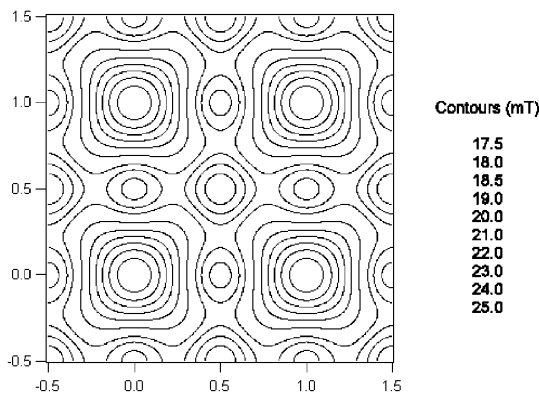| Magnetic field (mT)	F_{10} (mT)	F_{11} (mT)
10	1.14(3)	0.66(3)
15	1.02(9)	0.54(1)
20	0.88(1)	0.47(1)
25	0.71(1)	0.36(1)
30	0.58(1)	0.29(1)
35	0.45(1)	0.24(1)
40	0.30(2)	0.14(1)

FIG. 6. Temperature and field dependence of the ratio F_{11}/F_{10}. The {1, 1} intensity used is the direct average of all four spots, and the {1, 0} intensity is a weighted average of the top and side spots which allows for the different rocking-curve widths [12]. The increase in the dispersion of the points and error bars at high temperatures is due to the extreme weakness of the signals we detect (e.g., at 20 mT, 800 mK, the {1, 1} intensity is $\approx 1\%$ of background scattering from the sample and cryostat).

of F_{20} and F_{21}, we may assume the same signs as given by the Agterberg and Abrikosov solutions: taking the London sign makes a large difference to $B(\mathbf{r})$, and also can be ruled out by μSR results. The reconstruction of $B(\mathbf{r})$ is shown in Fig. 6. Note that it is completely different from the Abrikosov or Brandt solutions to the GL equations, and in good qualitative agreement with the TCGL predictions.

The results we have given so far correspond to low temperature and a particular magnetic field value; however, reconstruction of $B(r)$ at 10 and 30 mT show identical features [25]. In Table II we present the values of the strongest two form factors F_{10} and F_{11} for a range of fields at 100 mK. Also, in Fig. 7 we plot versus temperature the ratio of the Fourier components F_{11}/F_{10} at 10, 20, and 30 mT. Remarkably, this ratio varies little with field and
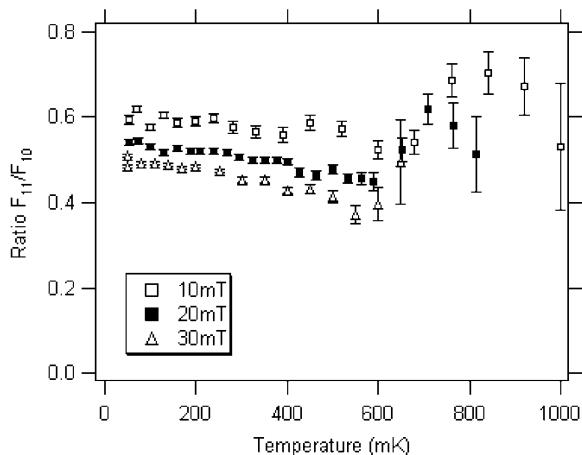

FIG. 7. Contour plot of the magnetic field in the mixed state of SRO as reconstructed from the data represented in Fig. 5, using the signs of the Fourier components as discussed in the text.

temperature and does not tend to the Abrikosov value as $T \rightarrow T_c$. Nonlocal effects [16] and deviations from GL theory in ultrapure superconductors [26] should both die away at high temperatures. Therefore, these effects are not expected to be the cause of the flux line shapes we report, although they may affect the details of $B(r)$ at low temperatures.

In conclusion, the strength of the higher-order reflections from the FLL in strontium ruthenate and their temperature dependence certainly show that a standard one-component Ginzburg-Landau model is insufficient to explain the observed diffraction pattern. However, our results are in good qualitative but not perfect agreement with a two-component Ginzburg-Landau theory. Unconventional flux line shapes in this material are strong evidence for unconventional superconductivity in Sr_2RuO_4.

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