Impurities and orbital dependent superconductivity in Sr$_2$RuO$_4$

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There now exists a wealth of experimental evidence that Sr$_2$RuO$_4$ is an odd-parity superconductor. Experiments further indicate that among the bands stemming from the Ru $\{xy, xz, yz\}$ orbitals, the portion of the Fermi surface arising from the $xy$ orbitals exhibits a much larger gap than the portions of the Fermi surface arising from the $\{xz, yz\}$ orbitals. In this paper the role of impurities on such an orbital dependent superconducting state is examined within the Born approximation. In contrast to expected results for a nodeless $p$-wave superconductor the unique nature of the superconducting state in Sr$_2$RuO$_4$ implies that a low concentration of impurities strongly influences the low temperature behavior.

Since the discovery of superconductivity in the layered oxide Sr$_2$RuO$_4$ in 1994 [1] and the prediction of odd-parity superconductivity [2] it has been quickly established that the symmetry of the superconducting order parameter is indeed of odd parity. Early NQR [3], tunneling [4], and impurity studies [5] clearly indicated that Sr$_2$RuO$_4$ is not a conventional superconductor. More recently $\mu$Sr measurements reveal that the superconducting state breaks time reversal symmetry [6] and Knight shift measurements show no change in the spin susceptibility when passing through the superconducting transition [7]. These measurements indicate that the superconducting state is described by a spin-triplet pair amplitude with an orbital dependence $\eta_1 k_x + \eta_2 k_y$ where $(\eta_1, \eta_2) \propto (1, i)$ when no magnetic field is applied. Such a superconducting state is nodeless in a quasi-2D material. The effect of impurities within the Born approximation on a nodeless $p$-wave state has been well studied [8,9]. The results indicate that impurities do not drastically change the low temperature properties of the superconducting state unless a sufficiently large impurity concentration is present. For Sr$_2$RuO$_4$ the experiments of Nishizaki et al. indicate that impurities strongly alter the low temperature properties even in the small impurity concentration limit [10]. This has previously been interpreted as an indication that Sr$_2$RuO$_4$ is in the unitarity scattering limit [11]. Here it is shown that the Born approximation can explain the experimental results once the the unique microscopic (orbital dependent) nature of the superconducting state in Sr$_2$RuO$_4$ is considered.

The superconducting state described above is fully gapped so it is difficult to understand the experimental observation that only approximately half of the Fermi surface exhibited an energy gap [12]. It was suggested that this feature can be understood when the highly planar character and the electronic structure of the Ru ions are considered [2]. The formal valence is Ru$^{4+}$ which implies that the electronic properties are due to four electrons in bands described by Wannier functions with Ru $d_{xy}, d_{xz}$ and $d_{yz}$ orbital character. The quasi-2D nature of the electronic dispersion and the different parity under the reflection symmetry $\sigma_z$ ($z \rightarrow -z$) of the $xy$ and the $\{xz, yz\}$ Wannier functions implies that the bands are derived from either the $xy$ or the $\{xz, yz\}$ Wannier functions (strictly speaking this is correct only in the 2D limit). The parity difference under $\sigma_2$ further inhibits Cooper pair scattering between the $xy$ and the $\{xz, yz\}$ bands [12]. Consequently, the superconductivity in the $xy$ and the $\{xz, yz\}$ bands can be considered as nearly independent and to a first approximation the specific heat data can be understood as the appearance of superconductivity in either the $xy$ sheet or the $\{xz, yz\}$ sheets of the Fermi surface. This theory has experimental support beyond the specific heat measurements. In particular which band is responsible for the superconductivity has been addressed experimentally by Riseman et al. using small angle neutron scattering [13]. For the superconducting state with the two component order parameter described above it has been predicted that a square vortex lattice is expected to occur when the field is applied along the $c$-axis [14]. The orientation of the square vortex lattice depends upon which of the bands are involved in the superconductivity. Riseman et al. observed a square vortex lattice and its orientation implies that the $xy$ sheet of the Fermi surface is superconducting [13]. Furthermore, the measured size of the penetration depth is consistent with pairing on the $xy$ sheet of the Fermi surface but not consistent with pairing over the whole Fermi surface [13]. It is of interest to note as well that the measurements of Imai et al. indicate that only the spin susceptibility of the $xy$ orbitals exhibits a significant increase with decreasing temperature [15].

In this paper the role of impurities on orbital dependent superconductivity will be considered within the Born approximation. A standard approach using a nodeless $p$-wave state does not explain the rapid increase in the residual density of states with impurity concentration as seen by Nishizaki [10]. For this reason Maki and Puchkaryov proposed that the impurities in Sr$_2$RuO$_4$ are sufficiently strong scatterers that the unitarity limit of the impurity problem should be used [11]. The unitarity limit has also been argued to be relevant for heavy fermion systems [16,17] and for high
In the heavy fermion case this limit is plausible due to small Fermi temperature ($\approx 10$ K) that occurs in these materials while for high-$T_c$ materials the filled $d$-shell of Zn impurities may justify the unitarity limit. However neither of these two plausibility arguments apply to Sr$_2$RuO$_4$ so, while the unitarity limit cannot be ruled out, it is worthwhile considering the Born limit in more detail. Here it is shown that a more realistic treatment of the impurity scattering within the Born approximation and within the context of orbital dependent superconductivity can explain the experimental results. The key element is inter-band scattering in which a quasiparticle with even parity under $\sigma_2$ is scattered to a quasiparticle state with odd-parity under $\sigma_2$. Such a scattering implies that reflection under $\sigma_2$ is locally broken by the impurity. This can occur for example if the impurity does not lie in the RuO$_4$ plane, or if it induces a rotation of the RuO$_6$ octahedra about an in plane axis, or if there are layer stacking defects. After averaging over all impurity positions, this inter-band scattering does not mix the quasiparticle states of different parity, but does affect decrease the quasiparticle lifetimes. Here calculations of the specific heat as a function of temperature are performed to examine the consequences of this model and to compare to existing experimental data.

LDA band structure calculations of Sr$_2$RuO$_4$ reveal that the density of states near the Fermi surface is due mainly to the four Ru $4d$ electrons in the $t_{2g}$ orbitals. There is a strong hybridization of these orbitals with the O $2p$ orbitals giving rise to antibonding $\pi^*$ bands. The resulting bands have three quasi-2D Fermi surface sheets labeled $\alpha, \beta$, and $\gamma$ (see Ref. [23]). In the planar limit due to the different parity under reflection ($z \rightarrow -z$) the $\alpha$ and $\beta$ sheets consist solely of $\{xz, yz\}$ Wannier functions and the $\gamma$ sheet of $xy$ Wannier functions. I assume an impurity potential that obeys the symmetry relation $V(\mathbf{r}) = V(\sigma_2 \mathbf{r})$ where $\sigma_2$ is reflection through the Ru$_2$O$_4$ plane and $\sigma_2 = 0$ lies in the Ru$_2$O$_4$ plane. On average such an impurity potential will not mix single particle excitations corresponding to different parity under $\sigma_2$. However the single particle excitations on each sheet will have two contributions to the lifetime: one from eigenstates of the same parity (intra-band) and one from eigenstates of opposite parity (inter-band) under $\sigma_2$. In the model considered below it will be assumed that the $\alpha$ and $\beta$ sheets are equivalent with respect to the single particle and superconducting properties. This is correct if a nearest neighbor tight binding dispersion is used to describe these sheets and is a reasonable approximation for more realistic dispersion relations. This leads to an effective two band model for the superconducting state in which the eigenstates of each band have opposite parity under $\sigma_2$. For simplicity two cylindrical Fermi surface sheets will be used: one with density of states equal to that of the $\gamma$ sheet and one with density of states equal to that of the $\alpha$ and $\beta$ sheets (based on the measurements of Ref. [24]). I take $N_\gamma : (N_\alpha + N_\beta)$ to be 0.55 : 0.45. The interaction leading to superconductivity is taken to have the form

$$V_{l,\nu}(\mathbf{k}, \mathbf{k}') = V_{l,\nu} \frac{\mathbf{k} \cdot \mathbf{k}'}{k_{F_l} k_{F_{l'}}},$$

(1)

where $k_{F_l}$ is the magnitude of the Fermi wavevector on sheet $l$. The gap matrix on each sheet is then of the form

$$\hat{\Delta}(l, \mathbf{k}) = \begin{pmatrix} 0 & c_l(k_x + ik_y)/k_{F_l} \\ c_l(k_x + ik_y)/k_{F_l} & 0 \end{pmatrix}. $$

(2)

Only the $s$-wave scattering potential is included and the $s$-wave scattering between band $l$ and $l'$ is characterized by $u_{l,\nu}$. The resulting gap and self-energy equations are

$$c_l = T \pi \sum_{l',\nu} \frac{V_{l,\nu} c_{l'}}{\sqrt{\bar{w}_{n,\nu}^2 + c_{l'}^2}} $$

(3)

and

$$\bar{w}_{n,l} = w_n + \sum_{l'} \frac{\Gamma_{l,l'} \bar{w}_{n,l'}}{\sqrt{\bar{w}_{n,l'}^2 + c_{l'}^2}} $$

(4)

where $\bar{V}_{l,\nu} = N_l V_{l,\nu}$, $\Gamma_{l,l'} = \pi n_i N_l |u_{l,\nu}|^2$, $N_l$ is the normal density of states on sheet $l$, and $n_i$ is the concentration of impurities. Note that due to the odd-parity symmetry of the order parameter there is no re-normalization of the gap, consequently strong inter-band scattering does not lead to a state with an equal gap over the whole Fermi surface as is the case in $s$-wave superconductors. This is partially a consequence of keeping only the $s$-wave Born scattering amplitude. If anisotropic contributions to the inter-band scattering amplitude are also included then in principle these terms will induce a gap on the $\{\alpha, \beta\}$ sheets of the Fermi surface (if none exists in the clean limit). However this induced gap is subject to pair breaking due to the $s$-wave scattering amplitudes. This indicates that provided the anisotropic scattering amplitude is not too large keeping only the $s$-wave scattering amplitudes will capture the
underlying physics of Sr$_2$RuO$_4$ (see References 27,28 for a discussion of physical consequences of anisotropic impurity potentials).

The equation for $T_c$ deviates slightly from the standard Abrikosov-Gor’kov form and is given by

$$\ln(T_c/T_c^0) = f_+ - \sqrt{(V_{11}-V_{22})^2 + 4V_{12}V_{21}}$$

$$= \frac{2(V_{11}V_{22} - V_{12}V_{21})}{2(V_{11}V_{22} - V_{12}V_{21})}$$

where $f_+ = [\Psi(\frac{1}{2} + \rho_1) + \Psi(\frac{1}{2} + \rho_2)]/2 - \Psi(\frac{1}{2})$, $f_- = [\Psi(\frac{1}{2} + \rho_1) - \Psi(\frac{1}{2} + \rho_2)]/2$, $\Psi(x)$ is the digamma function, $\rho_1 = (\Gamma_{11} + \Gamma_{22})/(2\pi T_c)$, and $T_c^0$ is the transition temperature in the presence of no impurities.

The density of states (DOS) is given by

$$N(w) = -\frac{1}{2\pi} \sum_{\alpha, \beta} \int \frac{d^2k}{(2\pi)^2} \Im [G_{\alpha\beta}(k, z)|_{z \to w+i0}]$$

$$= \sum_{\alpha, \beta} N_{\alpha\beta} \Im [\Gamma^{-1}]_{\alpha\beta}$$

It is of interest to determine $N(w = 0)$ in the limit of zero temperature as this quantity is measurable as the residual DOS in specific heat measurements. To date there has been no experimental evidence for a gap appearing on the $\alpha$ and $\beta$ sheets of the Fermi surface in Sr$_2$RuO$_4$. In view of this I consider initially the limit $c_2 = 0$. In Fig. 1 the residual DOS is plotted as a function of the transition temperature for the strong inter-band and intra-band scattering limits. Also shown in this Figure is the extrapolation from $T = 0.3$ K of the same quantity from the data of Nishizaki et al. 10 (in Fig. 1, $T_c^0$ has been assumed to be 1.5 K). While a detailed comparison to the experimental data will require measurements at lower temperature it is clear that the intra-band scattering limit cannot account for the data. This indicates that inter-band scattering cannot be neglected. Note that in the limit $\Gamma_{ii} = 0$ and $c_2 = 0$ the density of states can be found analytically:

$$N_1(w) = \frac{w^2 \sqrt{(c_1^2 + \Gamma_{12}^2 - w^2)^2 + 4\Gamma_{12}^2 w^2} + w^2 - c_1^2 - \Gamma_{12}^2 + \Gamma_{12} \sqrt{(c_1^2 + \Gamma_{12}^2 - w^2)^2 + 4\Gamma_{12}^2 w^2} + c_1^2 + \Gamma_{12}^2 - w^2}}{2 \sqrt{(c_1^2 + \Gamma_{12}^2 - w^2)^2 + 4\Gamma_{12}^2 w^2}}$$

In the zero frequency limit $N(0) = N_2 + \frac{\Gamma_{12}^2}{c_1^2 + \Gamma_{12}^2}$ showing that inter-band scattering increases $N(0)$ from $N_2$ for infinitesimal $\Gamma_{12}$ which gives rise to the residual DOS seen in Fig. 1. Also shown in Fig. 1 is the residual density of states when $c_2 = c_1/10$ in the strong inter-band scattering limit.

![Graph](https://example.com/graph.png)

**FIG. 1.** Residual density of states for different impurity concentrations. The curve labeled 1 (2) is in the strong intra-band (inter-band) scattering limit and the experimental estimates are shown as squares. The dotted curve is in the strong inter-band scattering limit when the gap on the $\{\alpha, \beta\}$ sheets is one tenth that of the $\gamma$ sheet.

The specific heat is calculated by numerically evaluating the temperature derivative of the entropy. The entropy is given by

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\[ S = \int_0^{\epsilon_c} d\epsilon N(\epsilon) \{ [1 - f(\epsilon)] \ln[1 - f(\epsilon)] + f(\epsilon) \ln f(\epsilon) \}. \] (10)

where \( \epsilon_c \) is the cut-off energy for the BCS interaction and \( f(\epsilon) \) is the Fermi distribution function. In Fig. 2, the results for \( C/T \) are shown for the intra-band scattering limit \( (u_{11} = u_{22} = 10u_{12}) \) and the inter-band scattering limit \( (u_{11} = u_{22} = u_{12}/10) \) in the limit \( V_{11} = 10V_{12} \) and \( V_{22} = 0 \).

Fig. 2 shows that inter-band scattering raises the apparent residual DOS \((i.e.\) that found by using entropy balance to extrapolate from measurements taken down to \( T = T_c^0/5 \)) and decreases the specific heat jump relative to intra-band scattering. Also any gap on the \( \{\alpha, \beta\} \) bands will be less rapidly destroyed by inter-band scattering than by intra-band scattering.

A theory of impurities within the context of orbital dependent superconductivity has been developed for Sr\(_2\)RuO\(_4\). In contrast to known results for nodeless \( p \)-wave superconductors, a strong dependence of the low temperature behavior of the specific heat on impurity concentration is shown to be a consequence of this theory in the Born approximation. This behavior is due to the impurity scattering between bands of opposite parity symmetry under reflection through the RuO\(_4\) plane. This theory accounts for the recent measurements of the specific heat for different impurity concentrations provided this inter-band scattering is not neglected.

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