# Broken time-reversal symmetry probed by muon spin relaxation in the caged type superconductor $Lu_5Rh_6Sn_{18}$:SUPPLEMENTAL MATERIAL

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(Dated: November 25, 2014)

Here we expound in detail our group-theoretical arguments about the symmetry of the superconducting order parameter. We also present the associated nodal structure of the quasiparticle spectrum. The analysis presented here applies to any superconductor with $D_{4h}$ point group symmetry, broken time-reversal symmetry and strong spin-orbit coupling. Besides $Lu_5Rh_6Sn_{18}$, the ruthenate superconductor $Sr_2RuO_4$ has been recently argued to fall within this category [1]. We note, however, that our present analysis does allow for singlet-triplet mixing as put forward in reference [1].

Barring an independent magnetic transition whose critical temperature is fine-tuned to coincide with the superconducting critical temperature, the sudden increase in the muon spin relaxation at $T_c$ suggests that the superconducting state breaks time-reversal symmetry. Assuming that the superconductivity is static and does not break the translational symmetry of the lattice, it can be characterised by a momentum-dependent pairing potential $\Delta_{\alpha,\beta}(\mathbf{k})$. Here $\alpha, \beta = \uparrow$ or $\downarrow$ are the spin indices of the two electrons in a Cooper pair and $\hbar\mathbf{k}$ is the momentum of one of the electrons with respect to the centre of mass of the pair. Standard symmetry analysis [2, 3] yields $\Delta_{\alpha,\beta}(\mathbf{k}) = \sum_{n=1}^{D} \Delta_n \Gamma^n_{\alpha,\beta}(\mathbf{k})$ just below $T_c$, where the functions ${\Gamma^n}_{n=1,2,...,D}$ form a basis set of one of the irreducible representations of the point group of the crystal, of dimension $D$. The form of the coefficients $\Delta_n$ is obtained by minimizing generic free energies of the appropriate symmetry. The superconducting state breaks time-reversal symmetry if $D > 1$ and two or more coefficients have different complex phases [2]. The quasiparticle spectrum is then given by the diagonalisation of the Bogoliubov-de Gennes Hamiltonian

$$H_{\mathrm{BdG}} = \begin{pmatrix} \epsilon(\mathbf{k}) - \mu & 0 & \Delta_{\uparrow\uparrow}(\mathbf{k}) & \Delta_{\uparrow\downarrow}(\mathbf{k}) \\ 0 & \epsilon(\mathbf{k}) - \mu & \Delta_{\downarrow\uparrow}(\mathbf{k}) & \Delta_{\downarrow\downarrow}(\mathbf{k}) \\ \Delta^*_{\uparrow\uparrow}(\mathbf{k}) & \Delta^*_{\downarrow\uparrow}(\mathbf{k}) & -\epsilon(\mathbf{k}) + \mu & 0 \\ \Delta^*_{\uparrow\downarrow}(\mathbf{k}) & \Delta^*_{\downarrow\downarrow}(\mathbf{k}) & 0 & -\epsilon(\mathbf{k}) + \mu \end{pmatrix}, \tag{1}$$

where $\epsilon(\mathbf{k})$ is the single-electron dispersion relation, measured from the chemical potential. Note that in non-centrosymmetric systems (not considered here) the off-diagonal elements in the single-electron dispersion relation would be essential.

For the space group $I4_1$/acd the relevant point group is tetragonal $D_{4h}$ [4] which has been thoroughly examined in the context of cuprate superconductivity [2, 3]. Let us first consider the case of singlet pairing. Quite generally, $\hat{\Delta}(\mathbf{k}) = \Delta_0(\mathbf{k}) i\hat{\sigma}_y$ (where $\hat{\sigma}_y$, is the second Pauli matrices). Following Ref. [2], for the point group of interest, there are 7 possible instabilities, only one of which (corresponding to the ${}^1E_g(c)$ irrep) breaks time-reversal symmetry. The gap function in this case has the form [2]

$$\Delta_0(\mathbf{k}) = (X + iY)Z \tag{2}$$

where $X, Y, Z$ are three real functions of $\mathbf{k}$ that transform as $k_x$, $k_y$ and $k_z$, respectively, under the point group symmetry operations. Fig. 1 (a) depicts the size, at the Fermi surface, of the corresponding gap in the quasiparticle energy spectrum, $\propto \Delta_0(\mathbf{k})$, obtained by assuming an isotropic single-electron dispersion relation, $\epsilon(\mathbf{k}) = \hbar^2|\mathbf{k}|^2/2m^*$ (yielding a spherical Fermi surface) and taking the simplest forms for the functions $X, Y, Z$, namely $k_x$, $k_y$ and $k_z$, respectively. The gap is given as follows

$$\Delta(\mathbf{k}) \propto |k_z|\sqrt{k_x^2 + k_y^2} \tag{3}$$

and so the low energy excitations would be dominated by a line node at the equator ($k_z = 0$), leading to a specific heat proportional to $T^2$ at low temperatures $T \ll T_c$ (the only exception being if the Fermi surface does not traverse the $k_z = 0$ plane, which is unlikely). In addition,

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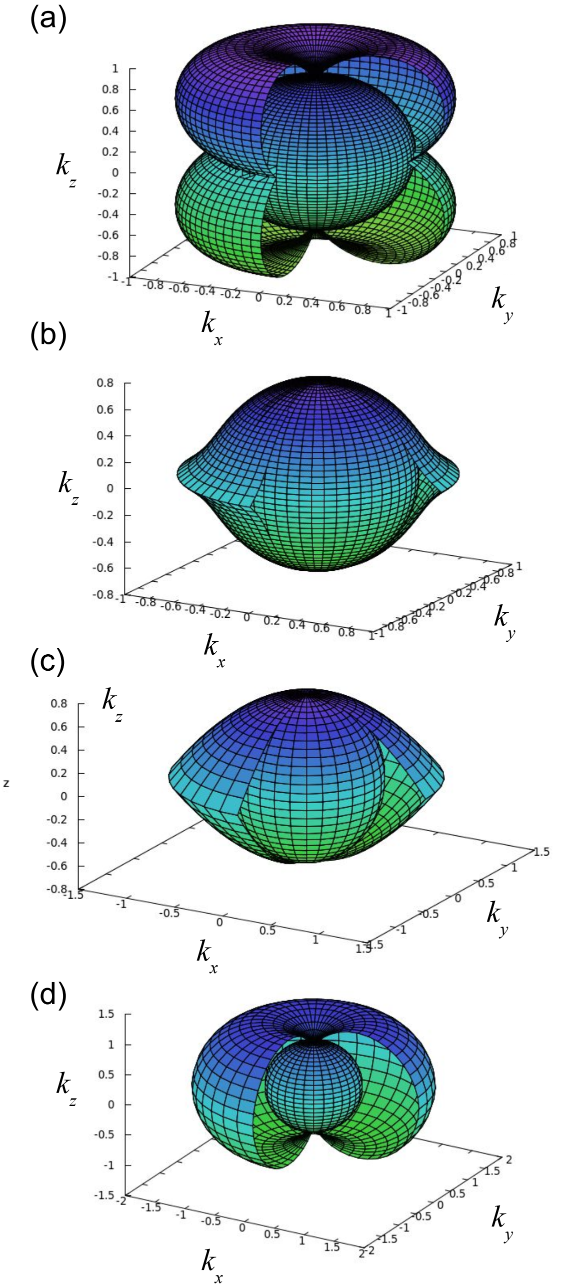


FIG. 1: Four possible forms of the gap in the quasi-particle energy spectrum, plotted on a spherical Fermi surface. (a) Singlet gap function [Eq. (2)] showing a line node on the equator and two linear point nodes at the "North" (N) and "South" (S) poles. (b-d) The same but for the triplet gap function [Eq. (4)] with $B \ll A$, $B \sim A$ and $B \gg A$, respectively. In all cases we assumed the functions $X, Y, Z$ in Eqs. (2,4) to take their simplest forms: $k_x$, $k_y$ and $k_z$, respectively.

there are point nodes at the "North" (N) and "South" (S) poles of the Fermi surface.

In the case of triplet pairing, i.e. $\hat{\Delta}(\mathbf{k}) = i\left[\mathbf{d}(\mathbf{k}).\hat{\boldsymbol{\sigma}}\right]\hat{\sigma}_y$, the double group combining the point group of the crystal with spin rotations has to be considered. Still following [2], for $D_{4h}$ we find once more that only one of 7 possible instabilities (corresponding to the $E_u(c)$ irrep of the double group) breaks time-reversal symmetry. The **d**-vector in this case is given by [2]

$$\mathbf{d}(\mathbf{k}) = (AZ, iAZ, B(X + iY)) \tag{4}$$

where the real coefficients $A$ and $B$ depend on details of the band structure and effective electron-electron interactions. This gap function corresponds to non-unitary triplet pairing as $\mathbf{d}^* \times \mathbf{d} \neq 0$.

The gap for this triplet case, with the same simplifying assumptions used above, is depicted in Fig. 1 (b-d). Its formula is

$$\Delta(\mathbf{k}) \propto \left| A|k_z| - \sqrt{A^2 k_z^2 + B^2\left(k_x^2 + k_y^2\right)} \right| \tag{5}$$

Interestingly, the spectrum also features two point nodes at $X = Y = 0$, but in this case the point nodes are "shallow" using the terminology of [5]. Indeed this instability is analogous to the $E_{2u}$ instability proposed for $UPt_3$ which also features a shallow node [6]. These nodes become ordinary linear nodes when $B \gg A$, while they expand to cover the whole Fermi surface in the opposite limit, $B \ll A$ (gapless superconductivity). Thus we expect the power-law exponent $n$ characterising the low-temperature behaviour of the specific heat, $C \sim T^n$, to be 1, 2, and 3 for the cases represented in panels (b), (c) and (d), respectively.

Non-unitary triplet pairing leads to the breaking of the two-fold degeneracy between the spin-up and spin-down parts of the quasi-particle spectrum. In this case we expect the superconducting instability to be accompanied by a bulk magnetisation that grows linearly with $T_c - T$ for $T \lesssim T_c$ and which acts as a sub-dominant order parameter [7, 8]. The linear increase of the muon spin relaxation rate $\lambda$ that we observe experimentally (see Fig. 4 of the main text) also increases linearly below $T_c$, which suggests that $\lambda$ is simply proportional to this (very small [8]) bulk magnetisation.

We emphasise that the power laws mentioned above are only expected to be realised in the limit of very low temperatures ($T \ll T_c$). Moreover, if the topology of the Fermi surface departs significantly from a sphere the spectrum may become fully-gapped i.e. $C \sim e^{-\Delta/T}$ for $T \ll T_c$. Specifically, the triplet pairing potential may lead to a fully-gapped spectrum if the Fermi surface is open at the top and the bottom, so that it never cuts the N and S poles (e.g. a warped cylinder). In contrast the singlet order parameter would lead to line nodes with $C \sim T^2$ at low temperatures always. Finally, we point out that a broader range of possibilities emerge if spin-orbit coupling happens to be weak enough to be neglected [2]. In that case two or more non TRS-breaking instabilities may merge to give new TRS-breaking ones [9].

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