Molecular Pairing and Fully Gapped Superconductivity in Yb-doped CeCoIn$_5$

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Introduction: CeCoIn$_5$ is an archetypal heavy fermion superconductor with $T_c = 2.3K$ [1]. The Curie-Weiss susceptibility signaling unquenched local moments, persists down to the superconducting transition [1]. Local moments, usually harmful to superconductivity actually sits down to the superconducting transition [1]. Local susceptibility signaling unquenched local moments, persists down to the superconducting transition [1]. Local susceptibility signaling unquenched local moments, persists down to the superconducting transition [1].

The behavior of this material upon Yb doping is quite unusual: the depression of superconductivity with doping is extremely mild with an unusual linear dependence of the transition temperature $T_c(x) = T_c(0) \times (1-x)$, where $x$ is the Yb doping [2]. Moreover, recent measurements [3] of the temperature dependent London penetration depth $\Delta \lambda(T)$ suggest that the nodal d-wave superconductivity (where $\Delta \lambda(T) \sim T - T^2$) becomes fully gapped ($\Delta \lambda(T) \sim T^n, n \gtrsim 3$) beyond a critical Yb doping $x_c \approx 0.2$. Normally the disappearance of nodes would suggest that they are accidental, as in $s^\pm$ superconductors. However directional probes of the gap, including scanning tunneling spectroscopy (STM) [4] [5], thermal conductivity measurements in a rotating magnetic field [6] and torque magnetometry [7] strongly suggest that pure CeCoIn$_5$ is a d-wave superconductor with symmetry-protected nodes. How then, can a nodal d-wave superconductor become fully-gapped upon doping?

Here we provide a possible resolution of this paradox, presenting a mechanism by which nodal superconductors can become fully gapped systems without change of symmetry, through the formation of composite pairs. A composite d-wave superconductor contains two components: a d-wave BCS condensate and a molecular superfluid of d-wave composite pairs [8]. Here we show when the scattering phase shift off the magnetic ions is tuned via doping, a Lifshitz transition occurs which removes the nodal heavy Fermi surface, without losing the superfluid stiffness, revealing an underlying molecular superfluid of d-wave composite pairs (see Fig. 1).

In the absence of an underlying Fermi surface, a composite paired superconductor can be regarded as Bose-Einstein condensate of weakly interacting, charge 2e d-wave bosons in which the Bogoliubov quasiparticle spectrum is fully gapped [9], with a residual linear sound mode with dispersion $E_p \sim v_s q$, cut off by the plasma frequency $\omega_p \sim v_s / \lambda_L$ at wavevectors below the inverse penetration depth $q \ll 1 / \lambda_L$. At temperatures above the plasma frequency, the superfluid stiffness is governed by Landau’s two-fluid theory of superfluids, in which the excitation of the normal superfluid is predicted to give rise to a power law dependence of the penetration depth $\Delta \lambda(T) \sim T^4$ in three dimensions, consistent with experiments [3].

A quantum critical point recently observed for $x \sim x_c$ in transverse magnetoresistance measurements [10] appears to coincide with the disappearance of the superconducting nodes. At larger Yb doping, we expect a second quantum critical point into a reentrant gapless phase...
as shown in Fig. 1 with the redevelopment of a d-wave paired heavy electron pocket around the $\Gamma$ point in the Yb rich Kondo lattice.

We now expand on the idea of composite pairing and discuss its detailed application to Yb doped CeCoIn$_5$ and the consequences and the predictions of our theory.

**Composite pairing:** The composite pairing concept was first introduced in the context of odd-frequency pairing [11], and later associated with the composite binding of a Cooper pairs with local moments [8 12 14]. Various other forms of composite pairing have been recently suggested in the context of cuprate superconductors [13]. Composite pairing naturally emerges within a two-channel Kondo lattice model where constructive interference between two spin-screening channels drives to local pairing. Composite pairing can be alternatively regarded as an intra-atomic version of the resonating valence bond pairing mechanism [16 17]. The composite pair amplitude is given by

$$\Lambda_C(j) = \langle \psi_{1j}^\dagger \sigma(i\sigma_2) \psi_{2j}^\dagger \cdot \vec{S}_f(j) \rangle$$

where $\psi_{1j}^\dagger$ creates conduction electrons in the Wannier state of channel $\Gamma \in (1, 2)$ and $\vec{S}_f(j)$ describes the spin operator of the local f-moment at site $j$. So, here two conduction electrons in orthogonal channels are screening the same local moment, giving rise to a singlet composite pair, which exists within a single-unit cell and thus can be regarded as a molecular unit. The $\psi$’s can be decomposed into plane waves using the relation $\psi_{1j}\sigma = \sum_k \Phi_{\Gamma \sigma}(k) e^{i k \cdot \vec{R}_j}$, where the form factor $\Phi_{\Gamma \sigma}(k)$ captures the different symmetries of the two types of hybridization. While in a simple model, one can take $\Phi_{1k}$ and $\Phi_{2k}$ to be s-wave and d-wave, in real materials the momentum dependence will be more complicated, and the $\Phi_{1k}$’s become matrices that are only diagonal in the absence of spin-orbit coupling. The Kondo coupling in the two $\Gamma$ channels $J_{\Gamma}$ are a consequence of virtual charge fluctuations from the singly occupied ground state into the excited empty and doubly occupied states.

The symmetry of the composite pair condensate is determined by the product of the two form factors $\Phi_{1k}\Phi_{2k}$. In the simple model, where $\Phi_{1k}$ and $\Phi_{2k}$ have s- and d-wave symmetries respectively, the composite pairs will have a d-wave symmetry. A more detailed analysis involving the underlying crystal field symmetries finds that the two channels have $\Gamma_6$ and $\Gamma_7$ symmetries, again leading to $d_{x^2-y^2}$-wave like composite pairs [14]. The superfluid stiffness

$$Q = Q^{BCS} + Q^M$$

has two components [3]: a BCS component

$$Q^{BCS} = \frac{n_s e^2}{m^*}$$

derived from the paired heavy electron fluid, where $n_s$ is the superfluid density, and a composite component

$$Q^M \approx \sum_k \frac{\Lambda^2_C(\Phi_{1k}\nabla\Phi_{2k} - \Phi_{2k}\nabla\Phi_{1k})^2}{\Sigma^2_N \sqrt{\epsilon_k^2 + 2\Sigma^2_N}} \sim \frac{e^2}{h^2 a} (k_B T_c)$$

here given at zero temperature, resulting from the mobility of the molecular pairs and derived ultimately from the non-local character (momentum dependence) of the hybridization form factors. Here, $a$ is the lattice constant, $\Sigma_N$ is proportional to the normal (hybridization) part of the conduction electron self-energy and $\epsilon_k$ is the conduction electron dispersion. $Q_M$ is directly proportional to the condensation energy, a consequence of “local pair” condensation and it does not depend on the presence of a Fermi surface. In three dimensions, $Q^{BCS} \sim (e^2/\alpha)(e/\hbar)^2$ is proportional to the Fermi energy: in conventional superconductors the superfluid stiffness is much greater than $T_c$ and the BCS component will dominate, but as the Fermi surface shrinks, $Q^{BCS}$ vanishes. Normally, this would drive a superconductor-insulator transition, but now the superconductivity is sustained by the additional stiffness $Q_M$ of the composite pair condensate.

Note that, within this picture, the BCS and composite components have the same origin and do not compete with one another.

For example, consider a single channel Kondo lattice model at half filling, for which the ground state is a Kondo insulator with a gap to quasiparticle excitations. The inclusion of a second Kondo channel leads to composite pairing beyond a critical ratio of the coupling constants. (There is no Cooper instability in this case since there is no Fermi surface.) As a result the Bogoliubov quasiparticle spectrum is fully-gapped even though the composite order parameter has d-wave symmetry. This state is an example of a Bose-Einstein condensate of d-wave molecules.

**Connection with Yb doped CeCoIn$_5$:** Due to the tetragonal crystal field, the low lying physics of CeCoIn$_5$ is governed by a low lying $\Gamma_7$ Kramers doublet [13]. The
Kondo effect in Ce and Yb heavy fermion compounds results from high frequency valence fluctuations. In Ce compounds the dominant valence fluctuations occur between the $4f^1$ and $4f^0$ configuration $4f^1 \approx 4f^0 + e^-$, giving rise to an average f-occupation below unity ($n_f^{\text{Ce}} \sim 0.9$) [19, 20]. Using the Friedel sum rule, this gives rise to a scattering phase shift $\delta < \frac{\pi}{2}$ and in the lattice, to hole-like heavy Fermi surfaces. By contrast, Yb heavy fermion materials involve valence fluctuations between the $4f^{13}$ and $4f^{14}$ configurations $e^- + 4f^{13} \approx 4f^{14}$, so the average f-occupation of the active Kramers doublet exceeds one ($n_f^{\text{Yb}} \sim 1.7$) [19, 21, 22], the corresponding scattering phase shift $\delta > \frac{\pi}{2}$ and an electron-like Fermi surface in the Kondo lattice (Fig. 2). As the Yb doping proceeds, the typical character of the resonant scattering changes from Cerium-like to Ytterbium-like and the occupancy of the low-lying magnetic doublet $n_f$ will increase as a function of Yb doping

$$n_f(x) \approx (1-x)n_f^{\text{Ce}} + xn_f^{\text{Yb}}$$ (5)
$$0.9 + 0.8x$$ (6)

Yb doping effectively increases the f-electron count $n_f$, causing the average scattering phase shift $\delta$ to rise. As a function of doping, the nodes of the gap move to the zone corner as shown in Fig. 1 (a), and annihilate once $\delta > \pi/2$, forming a Kondo insulator immersed within a composite d-wave superfluid.

STM quasiparticle interference experiments show that there are two hole-like bands and an electron-like band [5], where the superconducting gap has been identified on the hole-like bands. We predict that the annihilation of these nodes as a function of doping will be seen on these bands in particular in the Ce band as defined in ref. [4]. Indeed the disappearance an electron-like band is seen both in ARPES [20] and dHvA [21] experiments. However, the behavior of the electron-like band is unclear. At higher doping, the nodes should reappear (see Fig. 1). Indications of strong Fermi surface reconstructions seen in transport data around $x = 0.55$ [21] may be tentatively identified with this second quantum critical point. It would be interesting to see if the nodal quasiparticles reappear beyond this point.

Penetration depth: In nodal superconductors, the temperature dependence of the change of the penetration depth $\Delta \lambda(T) \sim T^n$ is either $n = 1$ in the clean limit or $n = 2$ in the dirty limit. A higher power is inconsistent with a nodal gap. Experiments [9] show that $n \sim 3-4$ for $x \sim 0.2$. By contrast, the temperature dependent penetration depth of a fully-gapped molecular condensate is governed by the superfluid sound mode whose scale is set by the superfluid stiffness $Q_C$. In a Landau two fluid model, the temperature dependence of the superfluid density is

$$\rho_s(T) = \rho_0 - \frac{(2\pi)^2}{d} \int \frac{d^3q}{(2\pi)^3} \left( -\frac{\partial n(\omega_q)}{\partial \epsilon_q} \right) \left( \frac{q}{m^*} \right)^2$$ (7)

where $d$ is the dimension and $m^*$ is the effective mass of the composite pairs. Since $[q] = T$, by power counting $\rho_s \propto T^{d+1}$, leading to a temperature dependence of the penetration depth given by $\lambda(T) = \lambda_0 + \beta T^n$ where $n = d + 1$. Since the condensate is charged, the linear sound spectrum will be gapped by the plasma frequency $\omega_p$. We estimate $\omega_p$ to be about 10-100 mK [30] and assuming the composite superfluid is three dimensional, the temperature dependence of the penetration depth will have a power law $n = 4$ for $T > \omega_p$ as shown in Fig 3 which is consistent with experiments. We should note that this power law is not uniquely identified with composite pairing, as the Gorter-Casimir two-fluid behavior of s-wave superconductors also gives a $T^4$ dependence at low temperatures. However, composite pairing provides an explanation for the transition from nodal d-wave to nodeless superconductivity within a single pairing mechanism.

Resistivity above $T_c$: An over-simplistic application of Tinkham’s fluctuation conductivity theory [22] to our case, gives a resistivity of the form $\rho(T) = \rho(T_c) + AT(4-d)/2$ giving a $T^{1/2}$ power-law in three dimensions which reflects the phase space for superconducting fluctuations. Remarkably, experiments [10] display a robust $T^{1/2}$ resistivity at dopings $x > 0.2$, surviving over a decade in temperature up to 20K. However, this temperature range is far too great to be attribute to fluctuations about a weak-coupling BCS superconductor. One possibility is that the vicinity to unitary pairing enhances the range of the superconducting fluctuations. Alternatively, critical two-channel Kondo impurity physics may play a role in reinforcing the robust $T^{1/2}$ resistivity, in accordance with composite pairing.

Thermal conductivity: The thermal conductivity, $\kappa$, of a d-wave superconductor is dominated by the nodal quasiparticle excitations which leads to a linear temperature dependence [23] with a coefficient that oscillates in a perpendicular magnetic field as a function of in-

![FIG. 3: Temperature dependence of the London penetration depth. For $T < \omega_p$, the $\Delta \lambda(T)$ is exponentially suppressed, whereas it crosses over to $T^4$ for $T > \omega_p$.](image-url)
plane orientation\cite{6}. In the fully-gapped phase, the linear temperature dependence of $\kappa$ will be exponentially suppressed $\kappa/T \sim (\Delta/T)^2 e^{-\Delta/T}$, leading to a jump in $\kappa_0/T$ at the Lifshitz transition and $\kappa \sim T^3$ phonon behavior. The oscillations of $\kappa$ in magnetic field will also be suppressed due to the absence of nodal quasiparticles, and it should show activated behavior.

**Conclusion:** Composite pairing provides a natural explanation for the development of a fully-gapped state in Yb doped CeCoIn$_5$. As a function of Yb doping the chemical potential increases and the nodes move to the corner of the Brillouin zone. When the phase shift reaches $\pi/2$, the nodes annihilate, completely depleting the Fermi surface. The resulting fully-gapped state has a superfluid stiffness derived from the composite pairs, a form of “molecular” condensate. The predicted sound mode as the low energy excitation of the molecular condensate may be observable in ultrasound experiments. Moreover, the unusual linear doping dependence of the transition temperature $T_c$ can now simply understood as the BEC temperature of the composite pairs.

We also note that the mechanism presented here may apply to a much broader class of strongly interacting electron fluids: the recent observation of fully gapped superconductivity developing in CeCu$_2$Si$_2$ in a field\cite{27} and Ce doped PrPt$_4$Ge$_{12}$\cite{28} are interesting additional candidate examples of this phenomenon that deserve future examination.

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[29] Note that there is a rapid change in the valence for $x < 0.2$ which we ignore for simplicity.
[30] The plasma frequency is set by ratio of the speed of light to the penetration depth $\omega_p = c/e\lambda$. The mobility of the composite pairs results from the momentum dependence of the form factors and the scale is set by the hybridization $c^* \sim \sqrt{TKW/a}$ where $TK/a$ are the Kondo temperature, conduction electron bandwidth and the lattice constant respectively. We used $TK/a \sim 5 K, W/a \sim 10^3 K, a \sim 0.2 nm and \lambda \sim 300 nm$, which leads to $\omega_p \sim 100 mK.$