Complex state induced by impurities in multiband superconductors

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We study the role of impurities in a two-band superconductor, and elucidate the nature of the recently predicted transition from $s_{\pm}$ state to $s_{++}$ state induced by interband impurity scattering. Using a Ginzburg-Landau theory, derived from microscopic equations, we demonstrate that close to $T_c$ this transition is necessarily a direct one, but deeper in the superconducting state an intermediate complex state appears. This state has a distinct order parameter, which breaks the time-reversal symmetry, and is separated from the $s_{\pm}$ and $s_{++}$ states by continuous phase transitions. Based on our results, we suggest a phase diagram for systems with weak repulsive interband pairing, and discuss its relevance to iron-based superconductors.

It has been long recognized that nonmagnetic impurities strongly influence properties of multiband superconductors\textsuperscript{1,2}, especially in the case of an order parameter with sign change between different bands ($s_{\pm}$ state$^{2,7–9}$). Recently, it has been pointed out that impurities-induced interband scattering can continuously change the order parameter of a two-band superconductor from $s_{\pm}$ to $s_{++}$ state$^{10–12}$. This is particularly relevant for iron-based superconductors$^{13,14}$, most of which are believed to be in some form of the $s_{\pm}$ state, see recent reviews$^{15,16}$.

As we demonstrate in this Letter, the $s_{\pm}$-to-$s_{++}$ transformation may follow a nontrivial scenario, and occur via an intermediate complex state at which a finite phase shift develops between the gap parameters in the two bands. We derive the simplest possible two-band Ginzburg-Landau (GL) free energy of the system from microscopic equations, and show that the presence of interband impurity scattering has important consequences for the different possible order parameters the theory can support. In the case of repulsive interband pairing we indeed observe the $s_{\pm}$ to $s_{++}$ transition$^{17}$ with increasing the degree of disorder. We demonstrate that the transition is necessarily a direct one only close to the critical line; deeper in the superconducting state the $s_{\pm}$ state gives way to an intrinsically complex order parameter (which can be thought as an $s_{\pm} + is_{++}$ state), and only then to a pure $s_{++}$ state. This complex state breaks time-reversal symmetry and is separated from the other two superconducting states by continuous phase transitions.

We discuss the reason and conditions for the appearance of this state. Based on our results, we propose the phase diagram shown in Fig. 1 for two-band superconductors with weak repulsive interband coupling.

We consider a system of two parabolic bands, with partial and total densities of states (DOS) $N_1$, $N_2$, and $N = N_1 + N_2$ respectively. The pairing interactions are described by a $2 \times 2$ coupling matrix $\lambda$, with $\text{det}[\lambda] = w = \lambda_{11}\lambda_{22} - \lambda_{12}\lambda_{21}$. In the superconducting state there are two gap parameters $\Delta_1$ and $\Delta_2$, which are assumed to be complex constants for each band $\Delta_m = |\Delta_m|e^{i\varphi_m}$. The relative phase $\varphi = \phi_1 - \phi_2$ is a gauge-invariant quantity, and it is 0 or $\pi$ in the $s_{++}$ or $s_{\pm}$ states respectively. The presence of impurities introduces scattering rates parametrized by $\gamma_{mn}$, where $m, n = (1, 2)$ are the band indices. For the interband terms ($m \neq n$) we can write $\gamma_{mn} = N_n \Gamma$, with $\Gamma = n_{imp}\pi u^2$, where $n_{imp}$ and $u$ are the impurities’ concentration and potential respectively. On general grounds, point defects, such as atomic substitutions or vacancies, can scatter carriers with large momentum change and therefore are expected to give comparable intraband and interband scattering rates. In the case of the iron-based superconductors this was indeed confirmed by the first-principles calculations$^{18}$.

Close to the critical temperature the free energy can be expanded in powers of $|\Delta_1|$ and $|\Delta_2|$. (Although

FIG. 1. Phase diagram of systems with weak repulsive interband pairing. The $x$-axis represents the interband impurity scattering rate. The orange dashed line denotes the direct $s_{\pm}$ to $s_{++}$ transition, and the orange region represents the complex $s_{\pm} + is_{++}$ state. The phase transition lines between the complex state and the other states are shown with red, and the dashed red indicate the conjectured extension of the complex state at low temperatures.
GL theory has been generalized to the case of multicomponent order parameters without impurities\textsuperscript{19,20}, the proper justification of this multiband extension is a matter of ongoing debate\textsuperscript{21–25}.) In the presence of impurities this can be done systematically, starting from the Usadel equation\textsuperscript{6,21}. The resulting GL free energy up to quartic in $\Delta$ terms can be written as

$$ F_{GL} = F_1 + F_2 + F_{12} + F_{EM}. $$

(1)

We present the derivation of $F_{GL}$ from the microscopic theory, and give exact expressions for its coefficients in the Supplemental Material\textsuperscript{28}. If the gap parameters are uniform in space and constant within each band, the intraband impurity scattering rate $\gamma_{nn}$ drops out of the theory completely, as a direct consequence of the Anderson theorem\textsuperscript{28}. In contrast, the interband terms play an important role. The first two terms look similar to the standard GL theory

$$ F_{mm}(\Delta) = a_{mm} |\Delta_m|^2 + b_{mm} |\Delta_m|^4, $$

(2)

but with $a_{mm}$ and $b_{mm}$ modified by the presence of impurities\textsuperscript{28}, $F_{EM}$ combines the electromagnetic field contribution, and the derivative terms that couple $\Delta_1$ and $\Delta_2$ to the electromagnetic vector-potential. For the rest of this paper we assume no field and uniform order parameter, so $F_{EM} = 0$. The third term in $F_{GL}$ couples $\Delta_1$ and $\Delta_2$, and without impurities it is

$$ 2a_{12} |\Delta_1| |\Delta_2| \cos \varphi. $$

In the presence of interband scattering processes, however, $F_{12}$ becomes more complicated:

$$ F_{12} = 2a_{12} |\Delta_1| |\Delta_2| \cos \varphi + b_{12} |\Delta_1|^2 |\Delta_2|^2 $$

$$ + 2(c_{11} |\Delta_1|^2 |\Delta_2| + c_{22} |\Delta_1| |\Delta_2|^2) \cos \varphi $$

$$ + c_{12} |\Delta_1|^2 |\Delta_2|^2 \cos 2\varphi. $$

(3)

We can see that the presence of impurities introduces several new quartic interband terms in the GL theory\textsuperscript{28}. In the limit $G \rightarrow 0$ $a_{12}$ becomes proportional to $\lambda_{12}$ and all other coefficients in Eq. (3) vanish. As a consequence, for a clean system the only possible solutions for $\varphi$ are 0 and $\pi$, and which one minimizes $F_{GL}$ is determined by the sign of $a_{12}$. When impurities are present, this is not necessarily true any more, and other solutions are possible, due to the $\cos 2\varphi$ term – it can destabilize the $s_{\pm}$ and $s_{++}$ states, provided $c_{12}$ is positive\textsuperscript{28}. Thus, the dirty two-band superconductor can have quite rich phase diagram.

The critical temperature at a given disorder strength is determined by the quadratic terms in Eq. (4). The equation for $T_c$ derived in the Supplemental Material\textsuperscript{28} takes the form $\det [M - I] = 0$, with $I$ being the $2 \times 2$ identity matrix, and

$$ M = \left[ \begin{array}{cc} \lambda_{11} I_2 + \lambda_{12} n_1 (I_1 - I_2) & \lambda_{12} I_2 + \lambda_{12} n_2 (I_1 - I_2) \\ \lambda_{21} I_2 + \lambda_{21} n_1 (I_1 - I_2) & \lambda_{22} I_2 + \lambda_{22} n_2 (I_1 - I_2) \end{array} \right]. $$

We have defined $n_m = N_m / N$, $\lambda_m = \lambda_{mm} + \lambda_{nn}$, and

$$ I_1 = 2\pi T \sum_{\omega_n > 0} \frac{1}{|\omega_n|}, \quad I_2 = 2\pi T \sum_{\omega_n > 0} \frac{1}{|\omega_n| + \gamma_{12} + \gamma_{21}}, $$

where $\omega_0$ is a high-energy cut-off (e.g., the Debye frequency). In the clean limit, $\Gamma = 0$, this equation gives transition temperature $T_{c0} \approx 1.13 \omega_0 \exp(-1/\lambda)$, where $\lambda$ is the largest eigenvalue of the $\lambda$-matrix. Note that the interband impurity scattering processes are always pair-breaking (unless $\Delta_1 = \Delta_2$), and suppress $T_c$, in contrast with the intraband scattering, which has disappeared.

In general, the dependence $T_c(\gamma_{nn})$ has to be found numerically but the extreme dirty limit can be analyzed analytically. Depending on $\lambda$, there are two qualitatively different regimes. If interband pairing is attractive, or negative but weak (i.e., when $\varphi$ is positive) no amount of disorder can completely suppress the superconductivity. In this case the critical temperature in the extreme dirty limit can be obtained\textsuperscript{28}:

$$ T_{c0} \approx 1.13 \omega_0 \exp \left( -\frac{n_1(\lambda_{22} - \lambda_{12}) + n_2(\lambda_{11} - \lambda_{21})}{\omega_0} \right). $$

(4)

However, if the interband pairing is repulsive and strong, such that $w$ is negative, there is a critical amount of disorder which brings $T_c$ down to zero, in analogy with the Abrikosov-Gor’kov theory\textsuperscript{28}. Numerical calculation of $T_c$ for the different regimes are shown in Fig. 2. We see that for some systems, after the initial drop in $T_c$ from its clean limit $T_{c0}$, the critical temperature saturates and stays finite in the limit $\Gamma \rightarrow \infty$. The reason is that the impurity scattering gradually averages the two gaps, and the closer they get to each other, the less effective the pair-breaking from the impurities is; thus the superconductivity can survive even in the extremely dirty regime (in that limit $\Delta_1 = \Delta_2$). The second regime is also easy to understand – if the sign change between the gaps is necessary for the existence of superconductivity (i.e., if the repulsive interband pairing interactions dominate) then the averaging produced by impurities completely suppresses the order parameter. Note that although our results are broadly consistent with the ones obtained in Ref. 11, our Eq. (4) somewhat disagrees with the dirty limit $T_c$ derived there, since in our expression the effective coupling constant is $(\lambda^{-1})^{-1}$ rather than $\lambda$.

For the rest of this Letter we concentrate on systems with positive $w$ and repulsive interband pairing – as we will see, these are the systems with the most interesting phase diagram. We turn to the coefficient $a_{12}$ of the Josephson-like term $|\Delta_1| |\Delta_2| \cos \varphi$, and its evolution with $\Gamma$. The role of $a_{12}$ is to couple the gaps, guaranteeing that they appear simultaneously, and close to $T_c$ its sign fixes the relative phase of $\Delta_1$ and $\Delta_2$. In the presence of impurity scattering it is

$$ a_{12} = -g - n_1 n_2 N(I_1 - I_2), $$

(5)

with $g = \lambda_{12} N_1 / w = \lambda_{21} N_2 / w$. In the clean limit $I_2 \rightarrow I_1$, $a_{12} \rightarrow -g$, and, as a result, $\varphi$ is temperature independent, and can only be 0 or $\pi$. For finite $\Gamma$, however, $a_{12}$ becomes function of both disorder strength and temperature, and can even change its sign. This has important consequences for the order parameter. Negative $g$ leads to the $s_{\pm}$ state in the clean limit. However, the
second term in Eq. (6) is negative, and for strong disorder it can overcome the $-g$ term. If $T_{c}$ is not completely suppressed (i.e., if the intraband pairing dominates), this sign change of $a_{12}$ means a transition from $s_{\pm}$ to $s_{++}$ state at the $T_{c}(\Gamma)$ line\(^{11}\). This happens at temperature $T_{\gamma} \approx 1.13\omega_{0}\exp\left[-(\lambda_{22} - \lambda_{12})/\omega_{0}\right]^{28}$. At this point the bands are effectively decoupled, and one of them stays normal. At smaller disorder strength the system condenses in the $s_{\pm}$ state, while at larger disorder strength it goes into the $s_{++}$ state.

Below the critical line the quartic terms in the theory become important. Let us consider a system with $T_{c}$ slightly higher than $T_{\gamma}$ (meaning that immediately below $T_{c}$ it is in the $s_{\pm}$ state). If $a_{22}(T)$ is positive then $\Delta_{2}$ is non-zero solely because of its coupling to $\Delta_{1}$ through $a_{12}$. In the vicinity of $T_{c}$ we can keep only the linear in $\Delta_{2}$ terms in the equation $\partial F_{GL}/\partial \Delta_{2} = 0$ (while keeping the cubic in $\Delta_{1}$ terms), and at the $s_{\pm}$ side we get:

$$|\Delta_{2}| = \frac{a_{12} + c_{11}|\Delta_{1}|^{2}}{a_{22} + c_{12}|\Delta_{1}|^{2} + b_{12}|\Delta_{1}|^{2}}|\Delta_{1}|.$$ \hspace{1cm} (6)

It is clear that equation $a_{12} + c_{11}|\Delta_{1}|^{2} = 0$ defines a line in the $(\Gamma, T)$ space, originating from $T_{c}$, and separating the $s_{\pm}$ from the $s_{++}$ regions. On this line the bands are decoupled and $\Delta_{2}$ is zero. If, for a fixed $\Gamma$, given system has $T_{c}$ slightly higher than $T_{\gamma}$, with decreasing the temperature it will cross the line, and $\Delta_{2}$ will change its sign. We demonstrate this in Fig. 3. At this $s_{\pm}-s_{++}$ transition point the second band becomes normal again (remember that we are assuming that $a_{22}(T)$ is still positive). Note however, that neither of the gap parameters have any singularity at this point; in thermodynamic sense this is a crossover, rather than a real phase transition.

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**FIG. 2.** The $T_{c}$ lines for systems with different $\lambda$, as functions of $\gamma_{21}$. The coupling constants are shown inside the figure, in $(\lambda_{11}, \lambda_{22}, \lambda_{12}, \lambda_{21})$ format. In the cases of weak interband pairing (green, blue and purple lines) $T_{c}$ is initially suppressed, but eventually saturates. For repulsive and strong interband pairing (red line), superconductivity is completely suppressed by impurities. The dots indicate the position of the $T_{c}$ points for the blue and the purple curves.

**FIG. 3.** The behavior of $\Delta_{1}$ (blue) and $\Delta_{2}$ (red) with temperature, demonstrating the $s_{\pm}$-$s_{++}$ transition; $\Delta_{2}$ is negative close to $T_{c}$, but goes through zero and changes its sign. The coupling constants are $\lambda_{11} = 0.3$, $\lambda_{22} = 0.297$, $\lambda_{12} = -0.011$, $\lambda_{21} = -0.011$, and $\Gamma = 1.63$ (at the $T_{c}$, $\Gamma \approx 1.67$).

What happens if, with decreasing the temperature, the system gets close to the $a_{22}(T) = 0$ point before the $s_{\pm}$-$s_{++}$ transition occurs? It can be easily shown that on the $a_{12} + c_{11}|\Delta_{1}|^{2} = 0$ line the $|\Delta_{2}| = 0$ solution becomes unstable, and non-zero and purely imaginary $\Delta_{2}$ appears when $a_{22} - c_{12}|\Delta_{1}|^{2} + b_{12}|\Delta_{1}|^{2}$ turns negative. Since $\Delta_{2}$ is now a superconducting gap in its own right, we have to keep all cubic terms in the equations. More generally, apart from the always-present 0 and $\pi$ solutions, $\varphi$ can now take nontrivial values. From the condition $\partial F_{GL}/\partial \varphi = 0$ we obtain for $\varphi$ the equation:

$$\cos \varphi = \frac{-a_{12} + c_{11}|\Delta_{1}|^{2} + c_{22}|\Delta_{2}|^{2}}{2c_{12}|\Delta_{1}||\Delta_{2}|}.$$ \hspace{1cm} (7)

This solution represents a distinct, intrinsically complex superconducting state. The physical picture behind it is simple; instead of changing the relative sign of the gaps by taking one of them through zero, there is alternative, more elegant way – continuous evolution of $\varphi$ from $\pi$ to 0. This intermediate superconducting state can be understood as a linear combination (with complex coefficients) of the two “real” order parameters $s_{\pm}$ and $s_{++}$. More physically, this means that the fluctuations in the densities of the two condensates (which are induced by fixing the phases) are not in-phase, as in $s_{++}$, and not in antiphase, as in the $s_{\pm}$, but have some nontrivial time shift. One of the modes is lagging the other, and as a consequence the time-reversal symmetry is spontaneously broken (as it should in such intrinsically complex state). It is also easy to understand why such state appears at finite temperature below $T_{c}$, close to the critical line only the $s_{\pm}$ state exists. For the $s_{++}$ state to condense within the $s_{\pm}$ state $a_{22}(T)$ has to turn negative, and only then the complex admixture of $s_{+}$ and $s_{++}$ becomes possible. This strongly suggests the necessary condition for the existence of such complex state – the presence of two
attractive superconducting channels at the same temperature (which means that \( w \) has to be positive).

![Figure 4](image)

**FIG. 4.** The behavior of \(|\Delta_1|\) (blue), \(|\Delta_2|\) (red) and \(\varphi\) (green, dashed), for the same \(\lambda\) as in Fig. 3 but for \(\Gamma = 1.57\). Close to \(T_c\) the relative phase is \(\pi\) (the system is in the \(s_z\)-state), but around 0.95\(T_c\) it starts decreasing continuously. Both gaps stay finite.

By minimizing the GL free energy, we demonstrate that this solution is indeed realized, as illustrated in Fig. 4. The order parameter starts as \(s_{\pm}\) (\(\varphi = \pi\)) at the critical temperature. However, at some finite temperature below \(T_c\), \(\varphi\) deviates from the \(\pi\) solution, and superconducting state is no longer pure \(s_{\pm}\), but an intrinsically complex state. According to our model, the time-reversal symmetry breaking state is separated from the critical temperature. However, at some finite temperature (which means that \(\lambda\) is implied. Notice that we are treating the impurities in a two-band superconductor. We derived a Ginzburg-Landau theory to describe the system, and we showed that the interband impurity scattering has a significant impact on the theory. Due to the impurities-induced \(\cos 2\varphi\) term in the theory a complex order parameter may appear between the \(s_z\) and \(s_{++}\) states.

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**Appendix A: Supplemental Material**

We start our derivation of the GL free energy from the Usadel equations for the quasiclassical Greens functions \(f_\mathbf{k} (\mathbf{r}, \omega)\) and \(g_\mathbf{k} (\mathbf{r}, \omega)\). We only study uniform states so these functions reduce to \(f(\omega)\) and \(g(\omega)\). In the two-band case the equations have the form:

\[
\omega f_m = \Delta_m g_m + \gamma_{mn} (g_m f_n - g_n f_m), \tag{A1}
\]

where \(m, n = (1,2)\) are the band indices and \(m \neq n\) is implied. Notice that we are treating the impurities in the Born approximation. We do not expect going beyond that approximation to qualitatively change our result.

These equations have to to supplemented by the self-consistency equations for the gap parameters \(\Delta_1\) and \(\Delta_2\):

\[
\Delta_m = 2\pi T \sum_n \sum_{\omega > 0} \lambda_{mn} f_n, \tag{A2}
\]

and normalization condition

\[
|f_m|^2 + g_m^2 = 1. \tag{A3}
\]
To derive the GL equations we solve Eqs. (A1) for $f_1$ and $f_2$, and expand the solutions in powers of $\Delta_1$ and $\Delta_2$. To do this we also have to expand $g_m$:

$$g_m = \sqrt{1 - |f_m|^2} \approx 1 - \frac{|f_m^{(0)}|^2}{2}$$

where $f_m^{(0)}$ is the zero-th order approximation:

$$f_m^{(0)} = \frac{(\omega + \gamma_{nm})\Delta_m + \gamma_{mn}\Delta_n}{\omega(\omega + \gamma_{mn} + \gamma_{nm})}. \quad (A4)$$

The sums for all coefficients can be carried out, and closed-form analytic results can be obtained. Unfortunately, these results are complicated combinations of polygamma functions (digamma function and its derivatives), and since they do not provide any further insight into the problem, we will not show them.

Next order corrections are unwieldy, but straightforward to obtain. For $f_m^{(1)}$ we get:

$$f_m^{(1)} = \frac{\gamma_{mn}(\omega + \gamma_{nm})(\Delta_m - \Delta_n)|f_m^{(0)}|^2 - (\omega + \gamma_{mn})(\omega + 2\gamma_{nm})\Delta_m + \gamma_{mn}(\omega + \gamma_{mn})\Delta_n}{\omega(\omega + \gamma_{mn} + \gamma_{nm})} |f_m^{(0)}|^2. \quad (A5)$$

Introducing $f_m^{(0)}$, we get an expression for $f_m^{(1)}$ which is of order $\Delta^3$. If we define

$$R_m = 2\pi T \sum_{\omega > 0} (f_m^{(0)} + f_m^{(1)}),$$

the self-consistency equations give:

$$R_m = \frac{1}{\omega}(\lambda_{nm}\Delta_m - \lambda_{mn}\Delta_n),$$

with $\det[\hat{\lambda}] \equiv \omega = \lambda_{11}\lambda_{22} - \lambda_{12}\lambda_{21}$. Expressing $R_m$ via $\Delta_m$ and $\Delta_n$, we get two equation for the two gap parameters up to $\Delta^3$. They are identical to the equations $\delta F_{GL}/\delta \Delta_m = 0$ obtained by varying the GL free energy with respect to $\Delta_m$. Collecting all the terms, multiplying by the density of states $N_m$, and using the notation introduced in the main text, we get:

$$a_{mm}\Delta_m + a_{mn}\Delta_n + b_{mn}\Delta_m|\Delta_m|^2 + b_{mn}\Delta_n|\Delta_n|^2 + c_{mn}(\Delta_m^2\Delta_n^* + 2|\Delta_m|^2\Delta_n) + c_{mn}|\Delta_n|^2\Delta_m + c_{mn}\Delta_m^2\Delta_n^2 = 0. \quad (A6)$$

The coefficients are defined as follows:

$$a_{mm} = N_m \left( \frac{\lambda_{mn}}{\omega} - 2\pi T \sum_{\omega > 0} \frac{\omega + \gamma_{mm}}{\omega(\omega + \gamma_{mn} + \gamma_{nm})} \right),$$

$$a_{mn} = -N_m \left( \frac{\lambda_{mn}}{\omega} + 2\pi T \sum_{\omega > 0} \frac{\gamma_{mn}}{\omega(\omega + \gamma_{mn} + \gamma_{mm})} \right),$$

$$b_{mm} = N_m \pi T \sum_{\omega > 0} \frac{(\omega + \gamma_{nm})^4}{\omega^3(\omega + \gamma_{mm} + \gamma_{mn})^4} + N_m \pi T \sum_{\omega > 0} \frac{(\omega + \gamma_{nm})\gamma_{mn}(\omega^2 + 3\omega^2\gamma_{nm} + \gamma_{mm})}{\omega^3(\omega + \gamma_{mn} + \gamma_{mm})^4},$$

$$b_{mn} = -N_m \pi T \sum_{\omega > 0} \frac{\gamma_{mn}\omega^3}{\omega^3(\omega + \gamma_{mm} + \gamma_{mn})^4} + N_m \pi T \sum_{\omega > 0} \frac{\gamma_{mn}(\gamma_{mn} + \gamma_{mm})(\gamma_{mm}(\omega + 2\gamma_{mm}) + \omega_{mm})}{\omega^3(\omega + \gamma_{mm} + \gamma_{mm})^4},$$

$$c_{mm} = N_m \pi T \sum_{\omega > 0} \frac{\gamma_{mn}(\omega + \gamma_{mn})(\omega + \gamma_{nm})(\gamma_{mm} + \gamma_{mn})}{\omega^3(\omega + \gamma_{mm} + \gamma_{mn})^4},$$

$$c_{mn} = N_m \pi T \sum_{\omega > 0} \frac{\gamma_{mn}(\omega + \gamma_{mn})(\omega + \gamma_{nm})(\gamma_{mm} + \gamma_{mn})}{\omega^3(\omega + \gamma_{mm} + \gamma_{mn})^4}.$$
ing transition, and the sign change of $a_{12}$ drives the $s_{-} \to s_{++}$ crossover. Close to $T_c$ the quartic coefficients are only weakly temperature dependent, and, with the exception of $b_{12}$, are all positive. In addition, $c_{12}$ tends to be the smallest.

As emphasized in the main text, in the limit $\Gamma \to 0$ all quartic coefficients that couple $\Delta_1$ and $\Delta_2$ vanish, and we recover the clean two-band GL theory. For non-zero $\Gamma$, however, we have to use the full free energy $F_{GL}$.

Close to $T_c$ only the linear terms matter. From Eqs. (A2) and (A3) we obtain the self-consistency equations

$$\Gamma, \quad \text{however, we have to use the full free energy} \quad \frac{\partial}{\partial\Gamma}$$

with $\gamma = 1(2)$ for $n = 2(1)$. These equations can be represented in the form of the matrix equation used in the main text,

$$\Delta_m = \sum_n \sum_{\omega > 0} \lambda_{mn} \frac{\omega + \gamma_m \Delta_n + \gamma_m \bar{n} \Delta_n}{\omega(\omega + \gamma_m + \gamma_m \bar{n})} \Delta_n$$

(A7)

where the matrix $M_{mn}$ is given by

$$M_{mn} = \lambda_{mn} I_2 + \lambda_{mn} n I_1.$$

Here we have used the relation $n_m = \gamma_{nm}/(\gamma_{mn} + \gamma_{nm})$, and defined $I_- = I_1 - I_2$, with

$$I_1 = 2\pi T \sum_0^{\omega_n} \frac{1}{\omega_n}, \quad I_2 = 2\pi T \sum_0^{\omega_n} \frac{1}{\omega_n + \gamma_1 \bar{I} + \gamma_2}.$$

The quantity $I_-$ can be expresses via the digamma function $\psi(x)$ as $I_- = \psi(1/2 + N \Gamma) - \psi(1/2)$ with $N \Gamma = \gamma_1 + \gamma_2$. Eq. (A7) can also be used to derive an analytic formula for $T_c$ in the extreme dirty limit. We rewrite this equation in somewhat different form, more convenient for analytical analysis. The sum $I_1$ can be represented as $I_1 = \ln(T_c/0) + 1/\lambda$, where $\lambda = \lambda_{11} + \lambda_{22} + \sqrt{(\lambda_{11} + \lambda_{22})^2 - 4 \lambda_{12} \lambda_{21}}$ is the largest eigenvalue of $\lambda$, which determines the clean-limit transition temperature, $T_{c0}$. This allows us to represent the matrix $M$ as

$$M_{mn} = \lambda_{mn} \left( \ln \frac{T_c}{c0} + \frac{1}{\lambda} \right) - \lambda_{mn} n I_- + \lambda_{mn} n I_1 I_-.$$

Multiplying both sides of the matrix equation (A7) with $\lambda^{-1}$ and using $\lambda_{mn}^{-1} n = 1$, we obtain

$$\sum_n \lambda_{mn}^{-1} \Delta_n = \left( \ln \frac{T_c}{c0} + \frac{1}{\lambda} - I_- \right) \Delta_m + I_- \sum_n n \Delta_n.$$

Introducing notation $w_{mn} = \lambda_{mn}^{-1} - \lambda^{-1} \delta_{mn}$, where $\delta_{mn}$ is the Kronecker delta, we can cast this in an equivalent form:

$$\sum_n \left( w_{mn} - \ln \frac{T_c}{c0} \delta_{mn} \right) \Delta_n = -I_- \sum_n n \left( \Delta_m - \Delta_n \right).$$

(A8)

General equation for $T_c$ is determined by vanishing of the determinant for this linear system which gives

$$\ln \frac{T_c}{c0} \left( w_{11} + w_{22} + I_- \ln \frac{T_c}{c0} \right) = I_- \left[ n_1 (w_{11} + w_{12}) + n_2 (w_{22} + w_{21}) \right].$$

(A9)

In the dirty limit, $N \Gamma \gg T_c$, we can use the asymptotics of $I_-$, $I_- \approx \ln \frac{N \Gamma}{T_c}$ with $A = \pi \exp(-\gamma E)/2$. In this case we obtain from Eq. (A9)

$$\ln \frac{T_c}{c0} = \frac{n_1 (w_{11} + w_{12}) + n_2 (w_{22} + w_{21})}{2} \ln \frac{N \Gamma}{T_c}.$$

In the extreme dirty case corresponding to condition $\ln \frac{N \Gamma}{T_c} \gg n_2 (w_{11} - w_{21}) + n_1 (w_{22} - w_{12})$, we obtain for the limiting value of transition temperature, $T_{c\infty}$,

$$\ln \frac{T_c}{c0} = n_1 (w_{11} + w_{12}) + n_2 (w_{22} + w_{21}).$$

This result actually can be obtained directly from Eq. (A8) if we take $\Delta_1 = \Delta_2$ in the left-hand side. Using the definition of $T_{c0}$, the above result for $T_{c\infty}$ can be rewritten in somewhat more transparent form

$$\ln \frac{\omega_0}{A T_{c\infty}} = \frac{n_1 (\lambda_{22} - \lambda_{12}) + n_2 (\lambda_{11} - \lambda_{21})}{w}.$$

The quantity in the right-hand side represents the band-average of the inverse coupling constant $\lambda^{-1}$. Now let us derive the formula for $T_c$ given in the main text. Remember that $T_\gamma$ is defined as the $T_c$ point at which $a_{12}$ coefficient vanishes. This happens at:

$$w_{12} = -\frac{\lambda_{12}}{w} = n_2 I_-.$$

Using this condition in the general $T_c$ formula given above we get:

$$\ln \frac{T_c}{c0} = w_{11} + w_{12},$$

and combining this with the clean limit expression $\ln(\omega_0/A T_{c0}) = \lambda_{11}$ gives the formula in the main text

$$T_\gamma \approx 1.13 \omega_0 \exp \left[ \frac{-\lambda_{22} - \lambda_{12}}{w} \right].$$

(A10)
superconducting instabilities for two bands may occur at very close temperatures. In this case, which we consider in this Letter, the singe-order-parameter description shrinks to the very narrow range near $T_c$ and one has to use the full two-band GL equations.

See the Supplemental Material.

P.W. Anderson, J. Phys. Chem. Solids 11, 26 (1959).

The existence of such terms have been implicit in T.-K. Ng, Phys. Rev. Lett. 103, 236402 (2009).

Note that similar cos2$\phi$ terms have been introduced in Y. Tanaka, P. Shirage, and A. Iyo, Physica C 470, 2023 (2010), but on purely phenomenological level.

A.A. Abrikosov and L.P. Gor’kov, Zh. Eksp. Teor. Fiz. 39, 1781 (1960) [Sov. Phys. JETP 12, 1243 (1961)].

Y. Ren, J.-H. Xu, and C. S. Ting, Phys. Rev. B 53, 2249 (1996).

K. A. Musaelian, J. Betouras, A. V. Chubukov, and R. Joynt, Phys. Rev. B 53, 3598 (1996).

W.-C. Lee, S.-C. Zhang, and C. Wu, Phys. Rev. Lett. 102, 217002 (2009).

C. Platt, R. Thomale, C. Honerkamp, S.-C. Zhang, and W. Hanke, Phys. Rev. B 85, 180502 (2012).

D. F. Agterberg, V. Barzykin, and L. P. Gor’kov, Phys. Rev. B 60, 14868 (1999).

V. Stanev and Z. Tešanović, Phys. Rev. B 81, 134522 (2010).

Y. Tanaka and T. Yanagisawa, Sol. State. Commun. 150, 1980 (2010).

X. Hu and Z. Wang, Phys. Rev. B 85, 064516 (2012).

R. Dias and A. Marques, Supercond. Sci. Technol. 24, 085009 (2011).

N. V. Orlova, A. A. Shanenko, M. V. Milosevic, F. M. Peeters, A. Vagov, and V. M. Axt, Phys. Rev. B 87, 134510 (2013).

S. Maiti and A. V. Chubukov, Phys. Rev. B 87, 144511 (2013).

T. Bojesen, E. Babaev, and A. Sudbo, Phys. Rev. B 88, 220511(R) (2013).

A. M. Bobkov and I. V. Bobkova, Phys. Rev. B 84, 134527 (2011).

K. Kirshenbaum, S. R. Saha, S. Ziemak, T. Drye, and J. Paglione, Phys. Rev. B 86, 140505(R) (2012).

J. Li, Y. F. Guo, S. B. Zhang, J. Yuan, Y. Tsujimoto, X. Wang, C. I. Sathish, Y. Sun, S. Yu, W. Yi, K. Yamaura, E. Takayama-Muromachi, Y. Shirako, M. Akaogi, and H. Kontani, Phys. Rev. B 85, 214509 (2012).

T. Inabe, T. Kawamata, T. Noji, T. Adachi, and Y. Koike, J. Phys. Soc. Jpn. 82, 044712 (2013).