Marginal stability of d-wave superconductor: spontaneous P and T violation in the presence of magnetic impurities

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We argue that the $d_{x^2-y^2}$-wave superconductor is marginally stable in the presence of external perturbations. Subjected to the external perturbations by magnetic impurities, it develops a secondary component of the gap, complex $d_{xy}$, to maximize the coupling to impurities and lower the total energy. The secondary $d_{xy}$ component exists at high temperatures and produces the full gap $\sim 20K$ in the single particle spectrum around each impurity, apart from impurity induced broadening. At low temperatures the phase ordering transition into global $d_{x^2-y^2} + id_{xy}$ state occurs.

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The point of this note is to emphasize the recently recognized new aspect of the high temperature superconductors: a marginal stability of the $d_{x^2-y^2}$-wave superconductor towards secondary ordering in the presence of the symmetry perturbing field. Namely, in the presence of the perturbing field the $d_{x^2-y^2}$-wave superconductor generates the secondary superconducting component of the order parameter, likely to be $id_{xy}$ in our case, to maximize the coupling to this field and hence to lower the total energy.

This instability can occur in many different ways. Recently the surface-scattering induced s-wave component in high-Tc materials has been observed \[1\] and the model explaining the effect was proposed \[2\]. The existence of the secondary gap in the external magnetic field was suggested to explain the anomalies in thermal transport in Bi2212 \[4\]. In both of these cases the superconductor was subjected to the perturbing fields: the surface scattering or the external magnetic field. The above examples can be thought of as a specific realizations of the general phenomena of marginal stability of $d_{x^2-y^2}$-wave superconductor.

Specifically we investigated the role of magnetic and nonmagnetic impurities on the $d_{x^2-y^2}$-wave superconductors. We find that in the vicinity of each magnetic impurity, in the presence of the spin-orbit coupling, there is a patch of local complex $id_{xy}$ gap generated from impurity scattering. This is the first example, to the best of our knowledge, when impurity scattering produces the coherent component, i.e. secondary $id_{xy}$ gap, as shown in Fig.1. We suggest that the secondary phase transition $d_{x^2-y^2} \rightarrow d_{x^2-y^2} + id_{xy}$ occurs spontaneously at lower temperatures with simultaneous impurity spin ordering. Below we present the summary of the results using mostly qualitative description. For more technical approach reader is advised to look at the original papers \[3\].

\[ a) \] Single magnetic impurity. The essence of the argument is to consider the single magnetic impurity with large spin $S$ in the $d_{x^2-y^2}$-wave superconductor. Locally the time reversal (T) and parity (P) symmetries are violated as the direction of the spin is fixed. Consequently, in the presence of the symmetry perturbing field it is favorable for superconducting state to generate the secondary component, i.e. the $id_{xy}$, so that the superconducting condensate couples to the impurity spin and lowers the total energy.

\[ + i S \]

\[ d_{x^2-y^2} \]

\[ d_{xy} \]

FIG. 1. The P and T violating condensate in the presence of magnetic impurity is shown. The phase of the induced $d_{xy}$ component is determined by the $S_z$, the impurity spin. At high temperatures the phase of induced component is disordered due to spin flips. At low temperatures the Josephson tunneling locks the phase between patches, leading to the global $d_{x^2-y^2} + id_{xy}$ state.

Consider scattering of a $d_{x^2-y^2}$ pair off the single impurity site. Interaction Hamiltonian is $H_{int} = g L_z S^z$, $L_z = i\hbar \hat{\theta}_y$ is the angular momentum operator, $\theta$ is the angle on the cylindrical 2D Fermi surface, $S_z$ is the out of plane component of the impurity spin and $g$ is the spin orbit coupling constant. There is a finite scattering amplitude $\langle x^2 - y^2 | H_{int} | xy \rangle$ in the vicinity of impurity:

\[ \langle x^2 - y^2 | H_{int} | xy \rangle \]
\[ \langle \Delta_0 \cos 2\theta | i g S^z h \partial_\theta | \Delta_1 \sin 2\theta \rangle \sim i S^z \Delta_0^* \Delta_1 \] (1)

where \( x^2 - y^2 \sim \cos 2\theta \) and \( xy \sim \sin 2\theta \) order parameter amplitudes are \( \Delta_0 \) and \( \Delta_1 \) respectively. This scattering amplitude \( \langle x^2 - y^2 \rangle H_{int}(xy) \) does imply the existence of the finite \( d_{x^2-y^2} + i d_{xy} \) gap near each Ni site. The local second phase grows out of these patches at lower temperatures.

The precursors of the ordered phase, i.e. a finite quasiparticle gap near each impurity site should be seen even at temperatures above the second transition into \( d_{x^2-y^2} + i d_{xy} \) state.

In the presence of the single impurity scattering potential: \( F_{\omega_n}(k, k') = F_{\omega_n}^0(k) \delta(k-k') + F_{\omega_n}^1(k, k') \), where

\[ F_0 = \frac{\Delta_0 \cos 2\theta}{\omega_n^2 + \xi_k + \Delta_0 \cos 2\theta} \]

\[ G_0 = -\frac{i \omega_n + \xi_k}{\omega_n^2 + \xi_k + \Delta_0 \cos 2\theta} \]

are the pure system propagators, \( F_{\omega_n}^1(k, k') \) is the correction due to impurity scattering, \( k = (k, \theta) \) are the magnitude and angle of the momentum \( k \) on the cylindrical Fermi surface, \( \omega_n \) is Matsubara frequency and \( \xi_k = \xi_k - \mu \) is the quasiparticle energy, counted form the Fermi surface. To linear order in small \( gN_0 \) \( (N_0 \) is the density of states at the Fermi surface), one finds \( [3] \):

\[ F_{\omega_n}^1(k, k') = -i 2\pi g S^z C_{\omega_n}^0(k) F_{\omega_n}^0(k') \left( \frac{|k \times k'|_z}{|k-k'|} \right) \] (2)

Where \( F_{\omega_n}^1(k, k') \) is the function of incoming and outgoing momentum because of broken translational symmetry. The first nontrivial correction to the homogeneous solution, after integration over \( k' \) and \( \xi_k \), is the \( xy \) component:

\[ F_{\omega_n}^1(\theta) = \int N_0 d\xi_k F_{\omega_n}^1(k) \propto i (N_0 g S^z) (N_0 \Delta_0) \sin 2\theta \] (3)

The finite induced \( xy \) component of the order parameter also leads to the \( xy \) gap:

\[ \Delta_1(k, k'') = T \sum_{n, k'} V_{xy}(k, k') F_{\omega_n}(k', k'') \]

\[ \Delta_1 \sim 2\pi g (N_0 \Delta_0) (N_0 V_{xy}) \sim 20K \] (4)

Where \( V_{xy}(k, k') N_0 \) is the arbitrary sign interaction in the \( xy \) channel, assumed to be of \( V_{xy} N_0 \sim 0.1 \) strength.

The finite minimal gap on the Fermi surface near impurity site is determined by: \( \text{Gap} = \sqrt{|\Delta_0(\theta)|^2 + |\Delta_1(\theta)|^2} \sim 20K \). Experimental prediction following from this picture is that the pseudogapped particle spectrum with minimal gap on the order of 20 K should be seen in scanning tunneling microscope experiments near each impurity site.

The usual impurity induced broadening of the states will be present as well. At low concentrations the broadening, being function of impurity concentration will be small compared to the induced \( d_{xy} \) gap. See also Fig.3.

b) Finite impurity concentration.

Recently Movshovich et.al. \( [3] \) measured thermal transport in high temperature superconductor with magnetic impurity (Bi2212 with Ni). The surprising outcome of these experiments is the observed sharp reduction in thermal conductivity at 0.2K in the samples with 1 – 2% Ni impurity concentration (see Fig. 2). The observed feature in thermal conductivity is consistent with the second superconducting transition into a \( d_{x^2-y^2} + i d_{xy} \) state as described. The secondary phase in many respects resembles the superfluid \( ^3He \): this is a chiral state that violates P and T. The superconducting condensate has a nonzero orbital moment \( L \).

![Image](image_url)

**FIG. 2.** The thermal conductivity of the Ni-doped Bi2212 is shown. The sharp reduction of thermal conductivity occurs at \( T_c^* = 0.2K \). The inset shows the effect of the applied magnetic field that suppresses the feature. The data are consistent with the secondary superconducting phase, such as \( d_{x^2-y^2} + i d_{xy} \), developing at \( T_c^* \) and with the full gap opening up. No effect has been observed in the nonmagnetic impurity (Zn) doped samples available to us.

The free energy admits the linear coupling between the \( d_{x^2-y^2} \) and \( d_{xy} \) channels, see Eq.\( [3] \):

\[ F_{int} = i \Delta_0 \Delta_0^* S_z + h.c. \] (5)

which can be thought of as a spin-assisted Josephson coupling between orthogonal \( x^2 - y^2 \) and \( xy \) channels. Since all other relevant terms are quadratic and higher powers in \( \Delta_1 \) and \( S_z \), this linear coupling is driving the transition into \( d_{x^2-y^2} + i d_{xy} \) state.

Impurities, in addition to the \( d_{xy} \) component produce the finite lifetime for quasiparticles. Standard arguments of Abrikosov-Gorkov theory imply that the transition temperature into \( d_{x^2-y^2} \) is suppressed. Moreover, the same impurity scattering will suppress the secondary transition into \( d_{x^2-y^2} + i d_{xy} \) state. We expect there is a finite impurity concentration window where induced phase can exist, see Fig.3.
FIG. 3. The suggested phase diagram for the normal, $d_{x^2-y^2}$ and $d_{x^2-y^2} + id_{xy}$ phases as a function of impurity concentration is shown. At low impurity concentration the patches of $d_{x^2-y^2} + id_{xy}$ presumably can order, although at very low temperatures. The low impurity concentration cut off will be determined by quasiparticle scattering. The termination point at $n^*_c$, when the impurity scattering will suppress $T^*_c$ to zero, is expected. For $n \leq n^*_c$ the sequence of the transitions upon temperature lowering is shown by the dotted line. Note that the temperatures $T_c$ and $T^*_c$ are drawn out of scale.

The idea of marginal stability of high temperature superconductors and of the secondary superconducting phase might have a broader application for other unconventional superconductors such as heavy fermion compounds. It implies that the superconducting phase diagram in many of these compounds might be richer than we previously thought.

Observation of such a state would represent a significant new development in the field of high temperature superconductivity.

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