Magnetic impurity induced $id_{xy}$ component and spontaneous time reversal and parity breaking in a $d_{x^2−y^2}$-wave superconductor

A.V. Balatsky

Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(September 17, 2018)

It is shown that the patches of complex $d_{xy}$ component are generated around magnetic impurity in the presence of the coupling between orbital moment of the condensate and impurity spin $S_z$. Locally induced $d_{xy}$ gap leads to the fully gapped quasiparticle spectrum near impurity. The phase of the induced $±id_{xy}$ component is determined by impurity spin and averages to zero at high temperatures. It is suggested that at low temperature the well defined patches of $d_{xy}$ are formed and they can undergo a phase transition into phase locked state via Josephson effect. Violation of time-reversal symmetry and parity occurs spontaneously via the second order transition. In the ordered phase both impurity magnetization and $d_{xy}$ component of the order parameter develop and are proportional to each other.

PACS numbers: 74.25.Bt, 74.20De, 74.62.Dh

It is well known that magnetic impurities destroy the singlet superconducting state due to spin scattering which breaks pair singlets \cite{3}. In the case of the gapless (with the nodes of the gap) d-wave superconductor both magnetic and nonmagnetic impurities produce a finite density of states at zero energy. These effects are a simple and direct consequence of the lifetime effects produced by impurities. These are well known “incoherent” effects of impurities in unconventional superconductors. After recent experiments by Movshovich et.al. \cite{2} we are led to believe that another phenomenon is possible, namely the transition to the second superconducting phase as a result of condensate interactions with magnetic impurities. The time reversal violating state is formed at low energy and the order parameter of the new phase is $d_{x^2−y^2} + id_{xy}$ ($d + id$). In this phase the impurity spins acquire nonzero spin density along z-axis, i.e. out of plane.

The physical origin of the instability comes from the fact that the $d + id$ state has an orbital moment which couples to the magnetic impurity spins. The relevant interaction is the $L_zS_z$ coupling between impurity spin $S_z$ and the conduction electron orbital moment $L_z$:

$$ H_{int} = g \sum_i \int d^2r \frac{S_z(r_i)}{|r - r_i|} \psi_{\sigma r}^\dagger [r \times i \partial_{r_i}] z \psi_{\sigma r} \quad (1) $$

where $g$ is the coupling constant, $\psi_{\sigma r}$ – the electron annihilation operator and summation is over impurity sites $i$. In the pure phase one can think of d-wave state as an equal admixture of the orbital moment $L_z = ±2$ pairs:

$$ \Delta_0(\Theta) = \Delta_0 \cos 2\Theta = \frac{\Delta_0}{2} (\exp(2i\Theta) + \exp(-2i\Theta)) \quad (2) $$

Here $\Theta$ is the 2D planar angle of the momentum on the Fermi surface, $\Delta_0$ is the magnitude of the $d_{x^2−y^2}$ component. We consider 2D $d_{x^2−y^2}$ superconductor, motivated by the layered structure of the cuprates. In the presence of the (ferromagnetically) ordered impurity spins $S_z$ the coefficients of the $L_z = ±2$ components will shift linearly in $S_z$ with opposite signs:

$$ \Delta_0(\Theta) \rightarrow \frac{\Delta_0}{2} [(1 + gS_z) \exp(2i\Theta) + (1 - gS_z) \exp(-2i\Theta)] = \Delta_0(\Theta) + i S_z \Delta_1(\Theta) \quad (3) $$

where $\Delta_1(\Theta) \propto g/2 \sin 2\Theta$ is the $d_{xy}$ component. The relative phase $\pi/2$ of these two order parameters comes out naturally because $d + id$ state has a noncompensated orbital moment $L_z = +2$.

Here I argue that time reversal (T) and parity (P) symmetries can be broken spontaneously in the bulk of the d-wave state due to coupling to the impurity spins. Original $d_{x^2−y^2}$ is unstable towards the formation of the bulk $d_{x^2−y^2} + id_{xy}$ phase. In the new phase both the spontaneous magnetization of impurity spins and second component of the order parameter are developed simultaneously. To show how complex $d_{xy}$ component appears, I first consider the single magnetic impurity and find that the spin-orbit interaction between impurity spin and orbital moment of the conduction electron generate a finite complex $d_{xy}$ anomalous amplitude near impurity in $d_{x^2−y^2}$ state. This patch of $d_{xy}$ state is formed near impurity site, as long as $d_{x^2−y^2}$ amplitude is finite, and has a spatial extent of coherence length $\xi_0 = 20\AA$. It is therefore possible for these patches to form a long range phase coherent state at some lower temperature as a result of Josephson tunneling between different patches. I also present a macroscopic Ginzburg-Landau functional (GL) and find that there is a linear coupling between the original $d_{x^2−y^2}$ order parameter $\Delta_0(\Theta) = \Delta_0 \cos 2\Theta$ and the spontaneously induced $d_{xy}$ component: $\Delta_1(\Theta) = \Delta_1 \sin 2\Theta$. The GL functional contains the linear coupling term:
\[ F_{\text{int}} = -\frac{b}{2}(\Delta_0^2 \Delta_1 - h.c.)S_z \]  
\[ \text{where } b \propto n_{\text{imp}} g \] is the macroscopic coupling constant, \( n_{\text{imp}} \) is the impurity concentration per unit cell of linear size \( a \), \( \Delta_{0,1}, g/a \) have dimension of energy. The time reversal violation is natural in this case as it allows the order parameter \( \Delta_0 + i \Delta_1 \) to couple directly to the impurity spin. This coupling is possible only for \( d+i \) and not for \( d+i \) symmetry of the order parameter. From the GL description it follows that instability develops as a second order phase transition where both the out-of-plane magnetization \( S_z \) and \( d_{xy} \) component developed together and are proportional to each other \cite{3}.

Recent experimental observation of the surface-induced time-reversal violating state in YBCO suggests that the secondary component of the order parameter \( d+i \) can be induced \cite{4}. Theoretical explanation, based on surface-induced Andreev states has been suggested by Sauls and co-workers \cite{4}. The source of the secondary component is the bending of the original \( d_{xy} \) order parameter at the surface.

In a different approach Laughlin \cite{5} argued that the \( d_{xy} \) state is unstable towards \( d+i \) state in the bulk in the perpendicular magnetic field at low enough temperatures. The time reversal and parity are broken by external field in this case. The linear coupling of the secondary order parameter to the external field is central to his consideration and results in the first order phase transition into \( d+i \) state. This transition was suggested to be responsible for the kink-like feature in the thermal conductivity in experiments by Krishana et.al. \cite{6}.

Recent experiments reported the anomaly in the thermal conductivity in Bi2212 at low temperatures: the thermal conductivity of the Bi2212 with Ni impurities was observed to have a sharp reduction at \( T^*_c = 200 \text{mK} \) \cite{2}. These experimental data indicate the possible superconducting phase transition in the Bi2212 in the presence of the magnetic impurities in a certain concentration range. So far the transition has been seen only in the samples with magnetic impurities, e.g. Ni as opposed to the nonmagnetic impurities such as Zn \cite{2}. It was reported that the feature in the thermal conductivity is completely suppressed by applying the field of \( H \sim 200 \text{Gauss} \). The low field and the fact that feature disappears is consistent with the superconducting transition into second phase. Results presented here might be relevant for the experimentally observed transition at \( T^*_c \) in Bi2212 with Ni.

1. Single magnetic impurity and \( d_{xy} \) patch.

I begin by considering one impurity at site \( r_i = 0 \) and interacting with conduction electrons via \( H_{\text{int}} \) in Eq. (4). Similar to the approach of \cite{3}, one can find the anomalous propagator in the presence of the single impurity scattering potential: \( F^\omega_{\omega_n}(\mathbf{k}, \mathbf{k}') = F^\omega_{\omega_n}(\mathbf{k}) \delta(\mathbf{k} - \mathbf{k}') + F^\omega_{\omega_n}(\mathbf{k}, \mathbf{k}') \), where \( F^\omega = \frac{\Delta_0 \cos \Theta}{\frac{\Delta_0}{2} + \xi_k + \xi_k'} \) and \( G^\omega = -\frac{\Delta_0}{\xi_k + \xi_k'} \) are the pure system propagators, \( F^\omega_{\omega_n}(\mathbf{k}, \mathbf{k}') \) is the correction due to impurity scattering, \( \mathbf{k} = (k, \Theta) \) are the magnitude and angle of the momentum \( \mathbf{k} \) on the cylindrical Fermi surface, \( \omega_n \) is Matsubara frequency and \( \xi_k = \epsilon_k - \mu \) is the quasiparticle energy, counted form the Fermi surface. We take \( S \) to be a classical variable and ignore spin flip scattering. To linear order in small \( g \) one finds:

\[ F^\omega_{\omega_n}(\mathbf{k}, \mathbf{k}') = -i2\pi g S_z G^\omega_{\omega_n}(\mathbf{k}) \int d\mathbf{k} \delta(\mathbf{k} - \mathbf{k}') \left( \frac{1}{|\mathbf{k} - \mathbf{k}'|} F^\omega_{\omega_n}(\mathbf{k}) \right) \]

Where \( F^\omega_{\omega_n}(\mathbf{k}, \mathbf{k}') \) is the function of incoming and outgoing momenta because of broken translational symmetry. Upon integrating \( F^\omega \) over \( \mathbf{k} \) and going to integrated over \( \xi_k \) one finds:

\[ F^\omega_{\omega_n}(\Theta) = \int \frac{\Delta_0}{\xi_k + \xi_k'} \left( \frac{1}{\sqrt{\omega_n^2 + \Delta_0^2 \cos^2 \Theta}} \right) \]

Here \( \Delta_0 \simeq k_F \frac{\pi^2 n_{\text{imp}}}{2 \sqrt{3}} \) is the model dependent coupling, \( W \) is the energy cutoff, \( N_0 \) is the Density of States at the Fermi surface and \( \langle \rangle \) stands for Fermi surface averaging.

The angle dependence of \( F^\omega_{\omega_n}(\Theta) \sim ig S_z \sin 2\Theta \) is the one of \( d_{xy} \). Together with the fact that this amplitude is complex it indicates the existence of the \( id_{xy} \) component in the vicinity of magnetic impurity. This result also shows that incoming \( d_{xy} \)-wave state electron have a finite amplitude, linear in \( g S_z \), to be scattered into the \( d_{xy} \) outgoing state via the \( L_z S_z \) coupling. From the solution Eq. (3) it is easy to see that the typical size of the patch, ignoring nodal directions, is given by superconducting coherence length \( \xi_0 = 20 \text{\AA} \). For the relevant concentration of Ni \( n_{\text{imp}} \sim 1\% \) the Ni-Ni distance is about 35\AA. The patches are thus well overlapping in this limit making phase ordering due to tunneling form patch to patch possible. These patches work as a microscopic seed of \( d_{xy} \) component which grows into true long range state at low temperatures \( T \leq T^*_c \). Similar result for the \( d_{xy} \) patches in the mixed state of pure Bi2212 was shown in \cite{7}, where the role of impurities is assumed by vortices.

Important observable consequence of the local \( d_{xy} \) component near impurity is that the gap, as seen in STM tunneling near Ni impurity, will increase and the low energy part of Density of States will be suppressed because of finite gap everywhere on the Fermi surface, as opposed to nodes for pure \( d_{xy} \) state. The increase of the gap in the Ni-doped Bi2212, compared to the pure case, was observed in STM tunneling \cite{8}.

Next, I consider simple example of magnetically ordered state: the ferromagnetically ordered impurity spins. This does not have to be the case experimentally but makes the point clearer. Calculation, similar to the one above, yields:

\[ F_{\omega_n}^1(\mathbf{k}) = -in_{\text{imp}} g S_z G_{\omega_n}^0(\mathbf{k}) \langle \delta_k \times \mathbf{k} \rangle z F_{\omega_n}^\omega(\mathbf{k}) \]
The existence of the homogeneous $d_{xy}$ component $F^{1}_{\omega_{n}}(k) \sim -i n_{imp} \frac{2\pi}{a} g S_x \Delta_0 \sin 2\Theta$ is evident from this equation. The relative phase of $d_{xy}$ component with respect to $d_{x^2-y^2}$ is determined by the sign of $S_z$. The gap $\Delta_1$ has to be determined selfconsistently provided there is interaction in $xy$ channel. This interaction does not have to be attractive, since $d_{x^2-y^2}$ plays the role of the source and $\Delta_1$ will be generated for any sign of interaction. I will assume there is such interaction and results below will be expressed in terms of the induced gap $\Delta_1$. With the help of this equation I find for the free energy change due to $\Delta_1$: $\delta F = 1/2T \sum_{\omega_n, k} F^{1}_{\omega_n}(k) \Delta^*_1(k) + h.c.$

$$\delta F = -i/2(N_0\Delta^*_1)(N_0\Delta_0) \frac{2\pi}{a} (g S_z) n_{imp} + h.c. \quad (8)$$

Eq.(8) together with single impurity result Eq.(6) are the main results of this section. From this equation I find the linear term Eq.(3) with

$$b = N^2_0 g \frac{2\pi}{a} n_{imp} \quad (9)$$

The relative phase of second component is determined by the sign of $S_z$. At high temperatures $T \gg T_c$, when spins are strongly fluctuating, the relative phase of the $d_{xy}$ component is fluctuating strongly as well. This phenomenon is an interesting new realization of the superconducting phase ($d_{xy}$) coupled to the heat bath (fluctuating spins).

If and when the impurity spins are slowing down or even are freezing out then the phase scattering time becomes large and the phase ordering of the patches is possible, see Fig.1. Measurements indicate that spin flips of Ni spins are slowing down at low temperatures $T \leq 2K$. Specific heat measurements on Ni-doped Bi2212 indicate additional entropy, compared to undoped Bi2212, on the order of $n_{imp} R \log 3$, accumulated near $1K$ [13]. This additional specific heat has a broad maximum around 1K and linear slope at lower temperatures. The general shape of the specific heat, associated with the impurity spins is strikingly similar to the specific heat, observed in spin glasses [13]. Broad peak in the specific heat might indicate the glassy behavior of spins at lower temperatures.

2. Mean field formulation.

Below I will ignore the fluctuations in the magnetic subsystem and consider simple mean field theory of the coupled magnetic impurities and superconducting condensate. From the specific heat measurements we know that some type of order (spin-glass or other) might occur at $T_m \sim 1K$. I will assume that impurities develop a ferromagnetic order at some temperature $T_m$. This is a drastic oversimplification because of the possible spin-glass ordering discussed above. Nevertheless the model presented below is useful to understand how the coupling between impurity spins and condensate leads to the $d+id$ instability of the original state.

I will consider the GL theory of the secondary superconducting transition: $\Delta_0 \rightarrow \Delta_0 + \Delta_1$ at $T_c^*$, where both $\Delta_{0,1}$ are homogeneous variables corresponding to the macroscopic ordering. The relative phase of $\Delta_1$ with respect to the phase of $\Delta_0$ is not fixed and will be determined by the free energy minimization. Assume that the second transition, if at all, occurs at $T_m \ll T_c$, where $T_c \sim 90K$ is the first transition temperature. Hence the order parameter $\Delta_0$, which can be assumed to be real, is robust and its free energy $F(\Delta_0)$ can not be expanded in $\Delta_0$.

The relevant fields to enter the GL functional are: $\Delta_0$, $\Delta_1$, and $S_z$.

Assuming expansion in powers of small $S_z, \Delta_1$ near second transition, the GL functional $F = F_{sc} + F_{magn} + F_{int}$ is:

$$F_{sc} = F(\Delta_0) + \alpha_1/2|\Delta_1|^2 + \alpha_2/4|\Delta_1|^4 + \beta|\nabla|\Delta_1|^2, \alpha_{1,2} \geq 0$$

$$F_{magn} = \frac{a_1(T_c)}{2} |S_z|^2 + \frac{a_2}{4} |S_z|^4 + \frac{a_3}{2} |\nabla S_z|^2$$

$$F_{int} = -\frac{b}{2\pi} (\Delta^*_0 \Delta_1 - h.c.) S_z \quad (10)$$

$\Delta_0$ should enter in $F_{int}$ for it to be invariant under the global $U(1)$ symmetry $\Delta_{0,1} \rightarrow \Delta_{0,1} \exp(i\theta)$ [13]. Homogeneous solution will have lowest energy and therefore gradient terms are take to be zero hereafter.

All but $F_{int}$ terms in the free energy Eq.(10) are positive and can not produce the instability of the original $d_{x^2-y^2}$ state. $F_{int}$ can be negative since it is linear in $\Delta_1$ and $S_z$ and this term is crucial in producing second transition.
Magnetic energy $F_{magn}$ has a temperature dependent coefficient
\[ a_1(T) = a_1 n_{imp}(T - T_m) \]  
(11)
and vanishes at $T_m$. $a_1$ is dimensionless. With this choice I will assume that Ni impurities would order ferromagnetically at $T_m \simeq 1K$ in the absence of the interaction with condensate.

Consider $F_{sc}$. The second and third terms in $F_{sc}$ describe be the energy cost of opening the fully gapped state with $\Delta_1$ when interaction prefers to keep node, i.e. pure $d_{xy}$ state. The change in free energy due to secondary order parameter is given by the difference in energy of quasiparticles before and after $\Delta_1$ component is generated. One can calculate the change in the energy of the superconductor subjected to the homogeneous external $d_{xy}$ source field: $H_{xy} = \kappa \sum_k \Delta_1(k) \psi_k^\dagger \psi_{-k,-\sigma}^\dagger$, where $0 < \kappa < 1$ is the integration constant. Using standard result $\partial_\kappa F_{sc} = 1/\kappa(H_{xy})$ one finds increase of energy at $\Delta_1 << T << \Delta_0$:
\[ \delta F_{sc} = \frac{\alpha_1}{2} |\Delta_1|^2 + \frac{\alpha_2}{4} |\Delta_1|^4 \]  
(12)

Here $\alpha_1 \simeq N_0$, and $\Delta_1$ is taken to be constant on the Fermi surface, see Eq.\[6\] $\[7\] $\[8\] .

Fix $\Delta_0$ to be real positive and the relative phase of $\Delta_1 = |\Delta_1| \exp(\nu)$ without loss of generality. Minimizing the functional Eq.\[9\] I find that the $\pi/2$ relative phase of $\Delta_1$ comes out naturally: phase will be determined by minimization of energy:
\[ \nu = \pi/2 \text{ sgn}(bS_z) \]  
(13)
This choice takes the maximum advantage of the $L_z S_z$ coupling and minimization requires a complex order parameter $\Delta_0 + i\Delta_1$ in the low temperature phase. $T$ and $P$ are violated spontaneously even with $T_m = 0$. The minimization yields:
\[ S_z = \frac{b}{a_1 n_{imp}(T - T_m)} \sin \nu \Delta_0 |\Delta_1| \]
\[ |\Delta_1|^2 = \frac{1}{\alpha_2} \left( a_1 n_{imp}(T - T_m) \Delta_0^2 - a_1 \right) = \chi(T^*_c - T) \]
\[ \delta F = -\frac{\alpha_2}{4} |\Delta_1|^4 \sim |T - T_c^*|^2 \]
\[ T_c^* \simeq T_m + 4\pi^2 (N_0 \Delta_0)^2 n_{imp} \frac{\chi}{a_1 n_{imp}} \]  
(14)
where I used the Eq.\[10\] in the last line. This is the main result of this paper. Solution Eq.\[11\] indicates that the transition is of the second order with the jump in the specific heat. I assumed that $|\Delta_0(T)|^2/a_1(T - T_m)$ has a linear temperature slope near $T_c^*$. It follows from the solution Eq.\[11\] that:

1) Even if $T_m = 0$ the ordering will occur at $T_c^* = 4\pi^2 n_{imp} (N_0 \Delta_0)^2 \frac{\chi}{a_1 n_{imp}}$. However the softness of the spin system near $T_m$ enhances the effect and makes $T_c^* \geq T_m$ within this mean field approach. Taking the typical values for Bi2212 of $\Delta_0 = 450K$, $E_F = 1/N_0 = 3000K$, assuming $a_1 = 1$ and taking the characteristic value of spin-rotation coupling of Ni $g/a \sim 320K$, I find $T_c^* \simeq 0.3K$. In the real system, if the spin-glass freezing occurs, the freezing will occur at first for the spins that are well separated. This will preclude the Josephson tunneling between the patches, as discussed above. Only at lower temperatures, when majority of spins are frozen, the tunneling would be able to lock in the superconducting phase. Hence the real phase ordering will occur at temperatures, substantially lower then the mean field estimated $T_c^* \leq T_m$.

2) As the function of impurity concentration two effects occur simultaneously. First, condensate density $|\Delta_0|^2$ decreases. Second, the suppression of $\Delta_1$ due to increased impurity scattering will also lower $T_c^*$. These effects will lead eventually to the disappearance of the transition. Quick suppression of the transition temperature $T_c^*$ with impurity concentration should be expected.

3) Strong magnetic field parallel to the layers, $H \gg H_{c1,ab} \sim 1 Gauss$ in plane, will suppress the second phase. In the field Ni spins will be aligned in the layers, linear coupling term on $H_{int}$ will be zero and $d_{xy}$ component will vanish. This effect might explain the suppression of the second transition by magnetic field $H_{c1,ab} \ll H \leq H_{c1,c} \sim 300 Gauss$, seen in experiment\[2\].

Weak localization of the quasiparticles\[13\], in principle, can cause the rapid decrease in the thermal conductivity. Experimental facts argue against localization in the layers for the following reasons: the field parallel to the layers suppresses the observed feature, it disappears at higher Ni concentration and the specific heat is increased near transition temperature. Specific heat and thermal conductivity in the field parallel to the layers will help to determine how relevant localization of quasiparticles is to the experimentally observed transition.

In the superconducting state with nonzero orbital current $L_z$ the dominant fraction of the orbital moment is “stored” at the edge of the sample, similar to $^3He - A$. The edge currents in $d + id$ state and their topological characteristics was addressed recently in $\[14\] , $\[15\] .

To test the proposed state following experiments can be done. The driving mechanism for the second phase clearly distinguishes between magnetic and nonmagnetic impurities, hence more experiments on Bi2212 with nonmagnetic impurities will be helpful\[3\]. Theory predicts the ordering of Ni moments below $T_c^*$, and one should be able to detect magnetization in $\mu SR$ experiments or in ac susceptibility. The increased superfluid density due to second component translates into the change in the penetration depth below $T_c^*$ which can be detected. These and other experiments will help to resolve if the proposed mechanism is correct.

In conclusion, I presented the mechanism for a second order phase transition of original d-wave state into
$d + id$ state with spontaneously broken $T$ and $P$. In the ordered phase both impurity spins $S_z$ and $d_{xy}$ component of the order parameter develop and are proportional to each other. The low temperature phase develops magnetic moment both due to magnetic impurities spin and because of the finite angular momentum of $d + id$ state.

I am grateful to R.B. Laughlin, D.H. Lee, A. Leggett, R. Movshovich, M. Salkola and G. Volovik for the useful discussions. This work was supported by US DOE.

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