# PARAMAGNETISM OF SUPERCONDUCTING CERAMICS

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Interaction between spontaneous current loops (orbital magnetic moments) induced by weak links with negative coupling energies ($\pi$-junctions) can cause paramagnetism of granular high-temperature superconductors. We show that at certain concentration of $\pi$-junctions the system consists of infinite percolating superconducting cluster and normal regions with frozen-in magnetic field and ordered orbital magnetic moments.

In was found experimentally [1] (see also Ref. [2] for further references and review) that magnetization of certain high-temperature superconducting ceramic samples can crucially depend on whether these samples are cooled below the critical temperature $T_c$ in zero or nonzero external magnetic field $H_e$. Whereas zero-field cooled samples showed a usual diamagnetic Meissner response, field cooled samples were found to be *paramagnetic* for $H_e \lesssim 1$ Oe. Below we will call this effect Wohlleben effect (WE) [2]. The experimental data [1] for the magnetic susceptibility of the WE samples $\chi$ are well described by the expression

$$\chi = \chi_0 + M_0/(H_e + H_0), \qquad (1)$$

where $\chi_0 = -b_1/4\pi$ ($b_1 \simeq 0.1 \div 0.2$) is a diamagnetic part of the sample susceptibility, $H_0 \sim 0.1$ Oe and $M_0 = b_2/4\pi$ G ($b_2 \simeq 0.01 \div 0.1$) is a constant magnetic moment. It was shown in Ref. [1] that the paramagnetic behavior (1) cannot be ascribed to the effect of isolated magnetic impurities or small ferromagnetic clusters inside the sample. An interpretation of WE suggested in Refs. [1, 3, 2] is based on the model of a random network of Josephson junctions with positive (usual junctions) and negative (so called $\pi$-junctions [4]) Josephson coupling energies. There are various microscopic mechanisms which might cause the presence of $\pi$-junctions in our system (e.g. tunneling via magnetic impurities, unconventional pairing etc. – see Ref. [2] for further discussion). Irrespectively to a particular physical mechanism one can show [4] that in the presence of $\pi$-junctions spontaneous current loops can occur in the ground state of a superconducting system. In the external magnetic field orbital magnetic moments associated with such loops become ordered in the direction of this field and the sample acquires nonzero total magnetization. According to Refs. [1, 3, 2] this may result in a paramagnetic contribution to $\chi$ (1).

Sharing the basic idea of this scenario we believe that it is by no means sufficient to understand the nature of WE. Indeed for $H_e < H_{c1} \sim 10 \div 100$ Oe the system is in the Meissner state and therefore orbital magnetic moments inside a massive 3$d$ superconducting sample cannot be ordered by an external magnetic field. Furthermore, as the critical temperature $T_c$ for the whole granular array is always smaller than that for individual grains local spontaneous current loops may appear already above $T_c$ resulting in some paramagnetic effect for $T > T_c$. No indication for this effect has been detected in [1]. At last, a simple estimate for

the loop magnetic moment $\mu \sim I_c a^2$ (the typical loop size is of order of the grain size $a$ and $I_c = 2eE_J$ is the intergrain Josephson critical current) shows that for typical experimental parameters $a \sim 1 \div 5$ $\mu$m and $E_J \sim 10$ K at $T \sim 100$ K orbital magnetic moments can be ordered only by the magnetic field $H_e \gtrsim T/\mu \sim 1 \div 30$ Oe, whereas WE persists down to much lower fields $H_e \sim 0.03$ Oe [1].

In this Letter we propose an explanation for WE which does not face with the above problems. We first illustrate the main idea of our explanation with the aid of phenomenological Ginzburg-Landau (GL) functional for a superconductor with a fluctuating in space critical temperature. Then we derive this GL functional for a rigorous model of a network which contains both usual Josephson junctions and $\pi$-junctions.

Let us consider a 3d superconducting system and make two assumptions. First, following [1, 3, 2] we assume that $\pi$-junctions induce spontaneous current loops (orbital magnetic moments) in the ground state of our system. Second, we assume that the presence of such orbital magnetic moments leads to a local suppression of a superconducting order parameter which can be described by the fluctuating in space critical temperature $\delta T_c(\mathbf{r})/T_c = t(\mathbf{r})$. Then close to a superconducting phase transition one can describe the system by the phenomenological GL functional [5, 6]

$$F[\psi]/T = \int \frac{d\mathbf{r}}{a^3} \left[ (\tau + t(\mathbf{r})) \, |\psi|^2 + \frac{ca^2}{2} \left| \left( \nabla_{\mathbf{r}} - \frac{2\pi i}{\phi_0} \mathbf{A} \right) \psi \right|^2 + \frac{\gamma}{2} |\psi|^4 \right], \qquad (2)$$

where we define $\tau = T/T_c - 1$ and $\langle t(\mathbf{r})t(\mathbf{r}')\rangle = g\delta(\mathbf{r} - \mathbf{r}')$. Here $T_c$ is the mean field critical temperature, $c \sim 0.1 \div 1$ depending on the lattice type, $\mathbf{A}$ is the vector potential and $\phi_0$ is the flux quantum. The parameters $\gamma$ and $g$ depend on the details of the model and will be fixed later.

Thermodynamic fluctuations of a superconducting order parameter $\psi$ around its mean field value $\langle \psi \rangle = \sqrt{|\tau|/\gamma}$ for $T < T_c$ can be treated in a standard way. With the aid of (2) we get $\langle(\delta\psi)^2\rangle = \kappa|\tau|^{1/2}/c^{3/2}$, where $\kappa \sim 1$. Thermodynamic fluctuations are small provided $|\tau| \gg \tau_G$, where the Ginzburg parameter $\tau_G \sim (\kappa\gamma)^2/c^3$. According to the results of Ref. [6] *statistical* fluctuations of $\psi$ due to disorder lead to a small renormalization of the critical temperature $T_c^{ren} = T_c(1 + \eta)$, $\eta \ll 1$ and to the dispersion

$$\langle(\delta\psi)^2\rangle/\langle\psi\rangle^2 = (\tau_D/ |\tau|)^{1/2}, \quad \tau_D = g^2/(8\pi^4 c^3). \qquad (3)$$

For $\tau_D \lesssim \tau_G$ such statistical fluctuations are not important and a usual second order superconducting phase transition takes place at $T = T_c^{ren}$ . In this case the system shows a usual diamagnetic Meissner response and no WE occurs.

For $\tau_D > b\tau_G$, $(b \simeq 2.5)$ the physical picture becomes more complicated. It was shown in Refs. [5, 6] that due to space fluctuations of $T_c$ already above $T_c^{ren}$ there appear superconducting domains with an average size $\xi \sim a(c/\tau)^{1/2}$ and concentration $\rho(\tau)$

$$\rho(\tau) \approx \xi^{-3} S \exp(-S), \qquad S(\tau) = A(\tau/\tau_D)^{1/2} \gg 1, \qquad A \simeq 37.8. \qquad (4)$$

If one lowers the temperature both concentration of domains and their size become larger and at $\rho\xi^3 = w_c \simeq 0.15$ (see e.g. [7]) they form an infinite percolating cluster. This condition is roughly equivalent to $S(\tau_p) \approx 3$ and yields

$\tau_p \approx (3/A)^2 \tau_D \sim 10^{-5} g^2/c^3$. Thus for $\tau_D > b\tau_G$ global superconductivity appears at $T = T_p = T_c^{ren}(1 + \tau_p)$ due to a percolation phase transition. At $T$ slightly below $T_p$ the superconducting state is essentially inhomogeneous: it consists of normal regions surrounded by infinite superconducting cluster. The volume of superconducting phase increases with decreasing temperature and eventually normal regions disappear.

If one applies a small magnetic field $H_e$ above $T_p$ and then cools the system this field becomes *trapped* in N-regions below $T_p$ due to the Meissner effect in superconducting surroundings. For small enough $H_e < T_p/\mu$ magnetic moments inside N-regions are disordered due to thermal fluctuations. Therefore at $T$ just slightly below $T_p$ no paramagnetism occurs and the superconducting sample shows a diamagnetic response. However as the temperature is lowered the volume of N-regions shrinks and due to the magnetic flux conservation the frozen-in field $H(T)$ grows until the value $\mu H(T^*) \sim T^*$ is reached at a certain temperature $T^* < T_p$. Below $T^*$ magnetic moments are ordered, the magnetization $M$ of the sample is saturated ($M = M_0$) and its response becomes paramagnetic for not very large $H_e$ (1). A rough estimate for $M_0 \sim \mu/a^3$ yields $M_0 \sim 0.01/4\pi$ G. Further shrinking of the N-regions volume with decreasing $T$ is energetically forbidden (the magnetic energy $\mu H(T)$ exceeds the superconducting condensation energy) and the susceptibility $\chi$ (1) remains temperature independent at $T \lesssim T^*$. Exactly the same behavior (diamagnetic response very close to $T_c$ turning to paramagnetic at lower $T$) has been detected in Ref. [1]. Large magnetic fields $H_e > H_c$ destroy superconducting domains already at $T > T_p$ and WE does not take place. A rigorous analysis based on the method developed in Ref. [5] yields a physically transparent estimate $H_c(\tau) \sim \phi_0/\xi^2$. At $\tau \approx \tau_p$ for the parameters of Ref.[1] we estimate $\xi(\tau_p)$ to be of order several $\mu$m and get $H_c \sim 10$ Oe in a good agreement with experimental results [1].

Now let us derive the GL functional (2) for a granular superconductor described by the Hamiltonian

$$\widehat{H} = - \sum_{(\mathbf{r},\mathbf{r}')} E_J(\mathbf{r},\mathbf{r}') \cos(\varphi(\mathbf{r}) - \varphi(\mathbf{r}')), \qquad (5)$$

where the sum is taken over Josephson junctions between all neighboring superconducting grains with coordinates $\mathbf{r}$ and $\mathbf{r}'$ and superconducting phases $\varphi(\mathbf{r})$ and $\varphi(\mathbf{r}')$. We shall consider the Josephson coupling energies $E_J(\mathbf{r},\mathbf{r}')$ as independent stochastic variables equal to $E_J = E_0 > 0$ with the probability $1 - p$ and to $E_J = -E_\pi < 0$ with the probability $p$. For $E_\pi = 0$ this model has been considered in details in Ref.[10] with the aid of the replica method, the generalization for the case $E_\pi > 0$ is straightforward. Near the critical temperature $T_c$ it is sufficient to introduce only two order parameters $\psi_\alpha = \langle \exp(i\varphi^\alpha) \rangle$ and $Q_{\alpha\beta} = \langle \exp i(\varphi^\alpha - \varphi^\beta) \rangle$, $\alpha, \beta = 1, \cdots, m$ are replica indices. The $\psi$-field represents a standard superconducting order parameter for a granular superconductor (see e.g. [8]) and the Edwards-Anderson order parameter $Q_{\alpha\beta}$ [9] describes the ground state of a granular array with frozen-in spontaneous currents. Proceeding in much the same way as in Ref.[10] the configurationally averaged free energy of the system $F$ can be represented in terms of the path integral over replica fields $\psi_\alpha$ and $Q_{\alpha\beta}$

$$F = -T dF_m/dm \,|_{m=0}, \qquad \exp(-F_m/T) = \int D\psi(\mathbf{r}) DQ(\mathbf{r}) \exp\left[-(H_0 + H_{int})/T\right], \quad (6)$$

where

$$H_0\{\psi\} = \int \frac{d\mathbf{r}}{a^3} \sum_{\alpha=1}^{m} \left\{ \psi_\alpha \left[ \tau - \frac{ca^2}{2} \left( \nabla_\mathbf{r} - \frac{2\pi i}{\phi_0} \mathbf{A} \right)^2 \right] \psi_\alpha^* + \frac{1}{4} |\psi_\alpha|^4 \right\}, \qquad (7)$$

$$H_{int}\{\psi, Q\} = \int \frac{d\mathbf{r}}{a^3} \left[ -\frac{1}{3} \sum_{\alpha,\beta} Q_{\alpha\beta} \psi_\alpha^* \psi_\beta + \frac{\tau_q}{2} Sp Q^2 + \frac{ca^2}{2} Sp(\nabla_\mathbf{r} Q)^2 \right]. \qquad (8)$$

As before the parameter $\tau$ is equal to $\tau = T/T_c - 1$, where for our particular model the mean field superconducting critical temperature is $T_c = z[(1-p)E_0 - pE_\pi]$ [11]. Due to the presence of $\pi$-junctions it turns out to be smaller than the standard mean field result $T_c = zE_0$ [8]. The parameter $\tau_q$ is defined by the expressions

$$\tau_q = (T/T_q)^2 - 1, \qquad T_q = \sqrt{zp(1-p)/2}(E_0 + E_\pi). \qquad (9)$$

In this paper we restrict our attention to the replica-symmetric case $Q_{\alpha\beta} = Q$ described by the unique ground state for each disorder configuration. Calculating the Gaussian integral over $Q$ in (6)-(8) we get

$$H_{int}\{\psi\} = \frac{g}{2} \int \frac{d\mathbf{r}}{a^3} \left[ \sum_{\alpha=1}^{m} |\psi_\alpha|^4 - \left( \sum_{\alpha=1}^{m} |\psi_\alpha|^2 \right)^2 \right], \qquad g = \frac{1}{9\tau_q}. \qquad (10)$$

It is easy to see that after an identification $\psi = \psi_\alpha$ and averaging over the stochastic variable $t(\mathbf{r})$ the GL functional (2) coincides with $H_0\{\psi\} + H_{int}\{\psi\}$ (7), (10). Comparing the expressions obtained by these two methods we find $\gamma = g + 1/2$. Note that the replica-symmetric solution of our problem is valid only for $T_c > T_q$ or, equivalently, for $p < p_c \simeq (E_0 - \sqrt{E_0 E_\pi/2z})/(E_0 + E_\pi)$. For larger values of $p > p_c$ at $T < T_q$ the symmetry between replicas is broken and the phase diagram of the system is more complicated. In this case it consists of normal and superconducting spin-glass-like phases with nonzero average value of the order parameter $Q_{\alpha\beta}$. The physical properties of these phases will be studied in details elsewhere [11].

Let us summarize the results of our analysis. For $\tau_D < b\tau_G$ or, equivalently, for $p < p_c - \varepsilon$, $\varepsilon \sim 10^{-2}/c$ and a sufficiently high temperature $T > T_c^{ren}$ there is no global phase coherence in our system and the array is in the normal state. Spontaneous current loops [4] can occur already in this state provided individual grains are superconducting. Due to the lack of global superconductivity these loops - if present - are confined to the scale of order $a$ and are completely uncorrelated in different parts of the sample. For $p < p_c - \varepsilon$ effect of disorder is not important and at $T = T_c^{ren}$ the system suffers a usual second order phase transition into a global superconducting state with $\psi \neq 0$, correlated spontaneous current loops of the typical scale $\sim \lambda_L \gg a$ and standard Meissner properties in relatively small magnetic fields. No WE occurs in this state.

For larger values of $p > p_c - \varepsilon$ effect of disorder is strong and interaction between current loops becomes crucially important. In this case superconducting domains with an average size $\xi$ and concentration $\rho$ (4) appear already above $T_c^{ren}$. At $T = T_p$ these domains form an infinite percolating cluster and the system becomes globally superconducting. For $T < T_p$ the system consists of an infinite superconducting cluster and normal regions with frozen-in magnetic field

and ordered orbital magnetic moments. This physical picture allows to explain all main features of WE in superconducting ceramics [1]. We believe that similar arguments based on the GL free energy (1) also describe WE in single crystal samples [12].

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