Paramagnetism of superconducting ceramics

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The interaction between spontaneous current loops (orbital magnetic moments) induced by weak links with negative coupling energies (the junctions) can cause paramagnetism in granular high-temperature superconductors. It is shown that at a certain concentration of π junctions the system consists of infinite, percolating, superconducting clusters and normal regions with a frozen-in magnetic field and ordered orbital magnetic moments.

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

$$\chi=\chi_0+M_0/(H_e+H_0), \tag{1}$$

where $\chi_O=-b_1/4\pi$ $(b_1\simeq 0.1-0.2)$ is the diamagnetic component of the susceptibility of the sample, $H_0 \sim 0.1$ Oe, and $M_0=b_2/4\pi$ G $(b_2\simeq 0.01-0.1)$ is a constant magnetic moment. It was shown in Ref. 1 that the paramagnetic behavior (1) cannot be attributed to the effect of isolated magnetic impurities or small ferromagnetic clusters inside the sample. The interpretation of the WE suggested in Refs. 1–3 is based on the model of a random network of Josephson junctions with positive Josephson coupling energies (ordinary junctions) and negative Josephson coupling energies (so-called π junctions[4]). There are various microscopic mechanisms which might cause the presence of π junctions in our system (e.g., tunneling via magnetic impurities, unconventional pairing, etc; see Ref. 2 for a further discussion). Irrespective of the particular physical mechanism, one can show[4] that in the presence of π junctions the spontaneous current loops can occur in the ground state of a superconducting system. In an external magnetic field the 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, this may result in a paramagnetic contribution to χ [Eq. (1)].

Sharing the basic idea of this scenario, we believe that it is by no means sufficient to understand the nature of the WE. Indeed, for $H_e<H_{c1}\sim 10-100$ Oe the system is in the Meissner state, and therefore the orbital magnetic moments inside a massive 3D superconducting sample cannot be ordered by an external magnetic field. Furthermore, since the critical temperature T_c for the whole granular array is always smaller than that for

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individual grains, the local spontaneous current loops may appear above T_c, which gives rise to a paramagnetic effect at $T>T_c$. No indication of this effect has been detected in Ref. 1. Finally, a simple estimate of the loop magnetic moment $\mu \sim I_c a^2$ (the typical loop size is on the order of the grain size a, and $I_c=2eE_J$ is the intergrain Josephson critical current) shows that for typical experimental parameters $a\sim 1-5$ μm and $E_J\sim 10$ K at $T\sim 100$ K the orbital magnetic moments can be ordered only by the magnetic field $H_e \gtrsim T/\mu \sim 1-30$ Oe, while the WE persists down to much lower fields,[1] $H_e \sim 0.03$ Oe.

In this letter we propose an explanation of the WE which does not involve the problems discussed above. We will first illustrate the main idea of our explanation with the help of the phenomenological Ginzburg–Landau (GL) functional for a superconductor with a spatially fluctuating critical temperature. We will then derive this GL functional for a rigorous model of a network which contains the usual Josephson junctions and the π junctions.

Let us consider a 3D superconducting system and make two assumptions. First, following[1-3], we assume that the π 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 the superconducting order parameter, which can be described by the spatially fluctuating critical temperature, $\delta T_c(\mathbf{r})/T_c = t(\mathbf{r})$. Near the superconducting phase transition we can describe the system by the phenomenological GL functional[5,6]

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

where $\tau=T/T_c-1$ and $\langle t(\mathbf{r})t(\mathbf{r}')\rangle = g\delta(\mathbf{r}-\mathbf{r}')$. Here T_c is the mean-field critical temperature, $c\sim 0.1-1$ (depending on the lattice type), $\mathbf{A}$ is the vector potential, and ϕ_0 is the flux quantum. The parameters γ and g depend on the features of the model and will be specified below.

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

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

For $\tau_D \lesssim \tau_G$ such statistical fluctuations are not important and a usual second-order superconducting phase transition takes place at $T = T_c^{\rm ren}$. In this case the system shows the usual diamagnetic Meissner response and the WE does not occur.

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

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

Lowering the temperature causes the concentration of the domains and their size to increase and at $\rho\xi^3 = w_c \simeq 0.15$ (see, e.g., Ref. 7) they form an infinite percolating cluster. This condition is roughly equivalent to $S(\tau_p) \approx 3$ and it yields $\tau_p \approx (3/A)^2 \tau_D \sim 10^{-5} g^2/c^3$. Thus, at $\tau_D > b\tau_G$ global superconductivity appears when $T = T_p = T_c^{\text{ren}}\ (1 + \tau_p)$, because of the percolation phase transition. At T slightly below T_p the superconducting state is essentially inhomogeneous: it consists of normal regions surrounded by an infinite superconducting cluster. The volume of the superconducting phase increases with decreasing temperature and eventually the 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 the N regions below T_p due to the presence of the Meissner effect in the superconducting environment. For a small enough H_e, $H_e < T_p/\mu$, the magnetic moments inside the N regions become disordered due to the thermal fluctuations. Therefore, at T just slightly below T_p, there is no paramagnetism and the superconducting sample shows a diamagnetic response. As the temperature is lowered, however, the volume of the N regions shrinks and due to the magnetic flux conservation the frozen-in field $H(T)$ increases until the value $\mu H(T^*) \sim T^*$ is reached at a certain temperature $T^* < T_p$. Below T^* the magnetic moments are ordered, the magnetization M of the sample is saturated ($M = M_0$), and its response is paramagnetic at an intermediate value of H_e [Eq. (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 region with decreasing T is energetically forbidden [the magnetic energy $\mu H(T)$ exceeds the superconducting condensation energy] and the susceptibility χ [Eq. (1)] remains temperature independent at $T \lesssim T^*$. Exactly the same behavior (the diamagnetic response near T_c becomes a paramagnetic response at lower T) was detected in Ref. 1. Large magnetic fields, $H_e > H_c$, destroy the superconducting domains even at $T > T_p$ and the 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 on the order of several μm, and we obtain $H_c \sim 10$ Oe, in a good agreement with the experimental results. [1]

Let us now derive the GL functional (2) for a granular superconductor described by the Hamiltonian.

$$\hat{H} = -\sum_{\langle \mathbf{r},\mathbf{r}' \rangle} E_J(\mathbf{r},\mathbf{r}')\cos[\varphi(\mathbf{r}) - \varphi(\mathbf{r}')], \tag{5}$$

where the sum is taken over the Josephson junctions between all the neighboring superconducting grains with the coordinates $\mathbf{r}$, $\mathbf{r}'$ and superconducting phases $\varphi(\mathbf{r})$ and $\varphi(\mathbf{r}')$. We assume that the Josephson coupling energies $E_J(\mathbf{r},\mathbf{r}')$ are independent stochastic variables equal to $E_J = E_0 > 0$, with the probability $1-p$, and equal to $E_J = -E_\pi < 0$ with the probability p. For $E_\pi = 0$ this model was considered in detail in Ref. 10 with the help 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* $Q_{\alpha\beta} = \langle \exp i(\varphi^\alpha - \varphi^\beta) \rangle$, $\alpha,\beta = 1,\ldots,m$ are the replica indices. The ψ-field represents a standard superconducting order parameter for a granular superconductor (see, e.g., Ref. 8 and the Edwards–Anderson order parameter[9] $Q_{\alpha\beta}$ describes the ground state of a granular array with frozen-in spontaneous currents. Proceeding in much the same way as in Ref. 10, we can represent the configurationally averaged free energy of the system F in terms of the path integral over the replica fields ψ_α and $Q_{\alpha\beta}$:

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

where

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

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

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

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

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

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

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 $H_0\{\psi\}+H_{\mathrm{int}}\{\psi\}$ in (7) and (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 $p<p_c\simeq(E_0-\sqrt{E_0E_\pi/2z})/(E_0+E_\pi)$. 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 analyzed in detail elsewhere.[11]

Let us summarize the results of our analysis. For $\tau_D<b\tau_G$ or, equivalently, for $p<p_c-\varepsilon$, $\varepsilon\sim10^{-2}/c$ and a sufficiently high temperature $T>T_c^{\mathrm{ren}}$ there is no global phase coherence in our system and the array is in the normal state. Spontaneous current loops[4] can occur in this state provided that individual grains are superconducting. Because of the lack of global superconductivity, these loops—if present—are confined to the scale of order a and are completely uncorrelated in the different parts of the sample. For $p<p_c-\varepsilon$ the effect of disorder is not important and at $T=T_c^{\mathrm{ren}}$ the system undergoes the usual second-order phase transition to a global superconducting state with $\psi\neq0$.

It has correlated spontaneous current loops of the typical scale, $\sim\lambda_L \gg a$, and standard Meissner properties in relatively small magnetic fields. The WE does not occur in this state.

For larger values of p, $p > p_c - \varepsilon$, the effect of disorder is strong and the interaction between the current loops becomes crucially important. In this case the superconducting domains with an average size ξ and a concentration ρ [Eq. (4)] appear even above $T_c^{\rm ren}$. At $T = T_p$, these domains form an infinite percolating cluster and the system becomes globally superconducting. At $T < T_p$, the system consists of an infinite superconducting cluster and normal regions with a frozen-in magnetic field and ordered orbital magnetic moments. This physical picture allows us to explain all the main features of the WE in superconducting ceramics.[1] We believe that such arguments based on the GL free energy [Eq. (1)] also describe the WE in single-crystal samples.[12]

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