THEORY OF DISORDERED UNCONVENTIONAL SUPERCONDUCTORS

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In contrast to conventional *s*-wave superconductivity, unconventional (e.g., *p*- or *d*-wave) superconductivity is strongly suppressed even by relatively weak disorder. Upon approaching the superconductor-metal transition, the order parameter amplitude becomes increasingly inhomogeneous, leading to effective granularity and a phase ordering transition described by the Mattis model of spin glasses. One consequence of this is that at sufficiently low temperatures, between the clean unconventional superconducting and the diffusive metallic phases, there is necessarily an intermediate superconducting phase that exhibits *s*-wave symmetry on macroscopic scales.

This article is dedicated to A. F. Andreev on the occasion of his 75th birthday

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1. INTRODUCTION

Generally, the superconducting order parameter depends on two coordinates and two spin indices, $\Delta_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$. A classification of possible superconducting phases in crystalline materials was given in Refs. [1, 2]. The majority of crystalline superconductors with low transition temperatures have a singlet order parameter with an *s*-wave orbital symmetry that does not change under rotation of the coordinates. In the simplest case,

$$\Delta_{\alpha\beta}(\mathbf{r},\mathbf{r}')\approx i(\hat{\sigma}_2)_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}')\Delta^{(s)}(\mathbf{r})$$

depends significantly only on a single coordinate, where $\hat{\sigma}_2$ is the second Pauli matrix in spin space, $\Delta^{(s)}(\mathbf{r})$ is a complex-valued function, and the superscript s indicates that it has s-wave symmetry. However, over the last decades, a number of superconductors have been discovered in which the order parameter transforms according to a nontrivial representation of the point group of the underlying crystal. Although such superconductors are quite common by now, following

the terminology in Ref. [3], we refer to them as "unconventional."

Important examples include the high-temperature cuprate superconductors that have a singlet d-wave symmetry [2, 4]: $\Delta_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = i(\hat{\sigma}_2)_{\alpha\beta}\Delta^{(d)}(\mathbf{r} - \mathbf{r}'),$ where $\Delta^{(d)}(\mathbf{r} - \mathbf{r}')$ changes sign under coordinate rotation by $\pi/2$. The best-known example of a *p*-wave superfluid is superfluid ³He. One of the leading candidates for *p*-wave pairing in electronic systems is Sr_2RuO_4 [5]. There are numerous pieces of experimental evidence that the superconducting state of Sr_2RuO_4 has odd parity, breaks time reversal symmetry, and is a spin triplet $[5-10]^{1}$. An order parameter consistent with these experiments is given by the chiral p-wave state [13], which has the form $\Delta_{\alpha\beta}(\mathbf{p}) \sim p_x \pm i p_y$, where $\Delta_{\alpha\beta}(\mathbf{p})$ is the Fourier transform of $\Delta_{\alpha\beta}(\mathbf{r}-\mathbf{r}')$. Anderson's theorem accounts for the fact that superconductivity in s-wave superconductors is destroyed only when the disorder is so strong that $p_F l \sim 1$, where p_F is the Fermi momentum and \boldsymbol{l} is the electronic elastic mean free path. However, in unconventional superconductors, $\Delta_{\alpha\beta}(\mathbf{p})$ depends on the direction of the rela-

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¹⁾ There are, however, some subset of experimental observations that are not easily reconciled with the existence of a chiral p-wave state in Sr₂RuO₄. See, e.g., Refs. [11] and [12] for a discussion.

tive momentum **p** of electrons in the Cooper pair, and therefore they are much more sensitive to disorder; even at the temperature T = 0, unconventional superconductivity is destroyed when l is comparable to the zero temperature coherence length ξ_0 in the pure superconductor, $l \sim \xi_0 \gg 1/p_F$. The fate of unconventional superconductivity subject to increasing disorder depends on the sign of the coupling constant in the *s*-wave channel. It is straightforward to see that if the interaction in the *s*-wave channel is attractive, but weaker than the attraction in an unconventional channel, then as a function of increasing disorder, there first occurs a transition from the unconventional to an *s*-wave phase when $l \sim \xi_0$, which is followed by a transition to a nonsuperconducting phase when $l \sim p_F^{-1}$.

In this article, we consider the more interesting and realistic case where the interaction in the s-channel is repulsive. In this case, we show that there is necessarily a range of disorder strengths in which, although locally the pairing remains unconventional, the system has a global s-wave symmetry with respect to any macroscopic superconducting interference experiments. Therefore, there must be at least two phase transitions as a function of increasing disorder: a d-wave (or p-wave) to s-wave, followed by an s-wave to normal metal transition. Qualitatively, the phase diagram of disordered unconventional superconductors is shown in Fig. 2 (see below). (An incomplete derivation of these results, only in the d-wave case, was obtained in Refs. [14, 15].)

The existence of the intermediate s-wave superconducting phase between the unconventional superconductor and the normal metal (and of the associated s-wave to unconventional superconductor transition) can be understood at a mean-field level, which neglects both classical and quantum fluctuations of the order parameter. The electron mean free path is an average characteristic of disorder. We introduce a local value of the mean free path $\bar{l}(\mathbf{r})$ averaged over regions with a size of the order of ξ_0 . When the disorder is sufficiently strong such that, on average, $\bar{l} < \xi_0$, the superconducting order parameter can be large only in the rare regions where $l(\mathbf{r}) > \xi_0$. In this case, the system can be visualized as a matrix of superconducting islands that are coupled through Josephson links in a nonsuperconducting metal. (The superconductivity inside an island can also be enhanced if the pairing interaction is stronger than average, i.e., if the local value of ξ_0 is anomalously small.) At sufficiently large values of disorder, the distance between the islands is larger than both their size and the mean free path.

2. MATTIS MODEL DESCRIPTION OF DISORDERED UNCONVENTIONAL SUPERCONDUCTORS

Below, we show that in the vicinity of the superconductor-normal-metal transition, the superconducting phase can be described by the Mattis model.

2.1. An isolated superconducting island

We first consider the mean-field description of an isolated superconducting island. The order parameter in an individual island is written as $\hat{\Delta}_a(\mathbf{r}, \mathbf{r}')$, where the hat indicates the two-by-two matrix structure in spin space and we label individual islands with Latin indices a, b, \ldots Generally, as a consequence of the random disorder, neither the shape of the island nor the texture of pairing tendencies within it have any particular symmetry, and hence the resulting gap function $\hat{\Delta}_a(\mathbf{r}, \mathbf{r}')$ mixes the symmetries of different bulk phases. Since there is no translational symmetry, it is convenient to define $\hat{\Delta}_a(\tilde{\mathbf{r}}, \mathbf{p})$ as the Fourier transform of $\hat{\Delta}_a(\mathbf{r}, \mathbf{r}')$ with respect to the relative coordinate $\mathbf{r} - \mathbf{r}'$ and to use $\tilde{\mathbf{r}} = (\mathbf{r} + \mathbf{r}')/2$ as the center-of-mass coordinate. (Because all coordinates to appear in what follows are the center-of-mass coordinates, we henceforth drop the tilde.) In the absence of spin-orbit coupling, a sharp distinction exists between spin-0 (singlet) and spin-1 (triplet) pairing, although even that distinction is entirely lost in the presence of spin-orbit coupling. The most general form of the gap function (with a phase convention that we specify later) expressed as a secondrank spinor in terms of Pauli matrices is

$$\hat{\Delta}_a(\mathbf{r}, \mathbf{p}) = e^{i\phi_a} \ i\hat{\sigma}_2 \left(\Delta_a \hat{1} + \mathbf{\Delta}_a \cdot \hat{\boldsymbol{\sigma}} \right), \tag{1}$$

where the **r** and **p** dependence of the scalar Δ_a and vector Δ_a quantities that represent the singlet and triplet components of the order parameter is implicit.

The energy of a single grain is independent of the overall phase of the order parameter ϕ_a . In the absence of spin-orbit interaction, it is also independent of the direction Δ_a . An additional discrete degeneracy can be associated with time-reversal invariance of the problem. It implies that the state described by a time-reversed order parameter

$$\hat{\bar{\Delta}}_a(\mathbf{r}, \mathbf{p}) \equiv -i\hat{\sigma}_2 [\hat{\Delta}_a(\mathbf{r}, -\mathbf{p})]^* i\hat{\sigma}_2 \tag{2}$$

leads to the same energy of the grain. In the absence of spontaneous breaking of time reversal symmetry, the time reversal operation leads to the same physical state $\hat{\Delta}_a = \hat{\Delta}_a$; otherwise, the time-reversed state is physically different.

It is important to note that generally (at the present mean-field level), time reversal symmetry is violated in droplets of unconventional superconductors of a random shape. This occurs even in the case where the bulk phase of the unconventional superconductor is timereversal invariant, such as *d*-wave superconductors or the p_x and p_y phases realized in strained Sr_2RuO_4 [16]. For example, *d*-wave superconducting droplets of a random shape embedded into a bulk metal can have, with a nonvanishing probability, a local geometry analogous to that of a corner SQUID experiment [4], in which two sides of a droplet with different signs of the order parameter are connected by a metallic Josephson link with an effective negative critical current. An equilibrium current then flows if the critical current of the "negative link" is sufficiently large.

We characterize the degeneracy with respect to time reversal by a pseudo-spin index $\xi_a = \pm 1$. In this case, it is convenient to introduce a pseudospin ξ_a in each grain to distinguish the two time-reversed states,

$$\hat{\Delta}_{a}^{\xi_{a}}(\mathbf{r},\mathbf{p}) = \begin{cases} \hat{\Delta}_{a}(\mathbf{r},\mathbf{p}), & \xi_{a} = +1, \\ \hat{\bar{\Delta}}_{a}(\mathbf{r},\mathbf{p}), & \xi_{a} = -1, \end{cases}$$
(3)

and write the general expression for the order parameter in each grain as

$$e^{i\phi_a}\hat{\Delta}_a^{\xi_a}(\mathbf{r},\mathbf{p}),$$
 (4)

where we explicitly separate the U(1) phase of the order parameter.

2.2. Josephson coupling between islands

Electrons propagating in nonsuperconducting metals experience Andreev reflection [17] from the superconducting islands. This induces Josephson coupling between the islands. So long as the separation between islands is large, the spatial dependence of the order parameter within each grain, $\hat{\Delta}_{a}^{\xi_{a}}(\mathbf{r}, \mathbf{p})$, is not affected. Therefore, the low-energy Hamiltonian of the system can be expressed in terms of the phases ϕ_{a} only. The energy of this coupling can be expressed in the form

$$E_{J} = -\frac{1}{2} \sum_{a \neq b} J_{ab}(\xi_{a}\xi_{b}) \cos[\phi_{a} - \phi_{b} + \theta_{ab}(\xi_{a},\xi_{b})], \quad (5)$$

where $J_{ab}(\pm 1) > 0$ is the Josephson coupling energy between the islands *a* and *b*, and $\theta_{ab}(\xi_a, \xi_b)$ is a phase determined by the spatial dependence of the complex order parameter in the grains, $\hat{\Delta}_a^{\xi_a}(\mathbf{r}, \mathbf{p})$ (which in turn still depends on which state, $\xi_a = \pm 1$, is involved). Our goal is to show that in the limit in which the distance between the islands is sufficiently large compared to their size, the link phases can be written as

$$\theta_{ab}(\xi_a,\xi_b) \approx \theta_a^{\xi_a} - \theta_b^{\xi_b}.$$
 (6)

Equations (5) and (6) represent the xy Mattis model, which is well known in the theory of spin glasses [18]. We can gauge away θ_a , reducing Eq. (5) to a conventional form familiar from the *s*-wave superconductor, or xy ferromagnet,

$$E_J = -\frac{1}{2} \sum_{a \neq b} E_{ab}^{\xi_a \xi_b} =$$
$$= -\frac{1}{2} \sum_{a \neq b} J_{ab}(\xi_a \xi_b) \cos\left[\tilde{\phi}_a - \tilde{\phi}_b\right], \quad (7)$$

where $\tilde{\phi}_a = \phi_a + \theta_a^{\xi_a}$. Therefore, the system is not a superconducting glass because its ground state has a hidden symmetry.

Although our conclusions are quite general, for simplicity we consider the situation where the characteristic radius of the grain is of order of the zerotemperature superconducting coherence length and the value of the order parameter in the puddles is much smaller than in pure bulk superconductors, $\Delta \ll \Delta_0$. This situation applies, for example, near the point of a quantum superconductor-metal transition, where the typical distance between the superconducting grains is larger than their size, which is of the order of the zerotemperature coherence length [19]. In this case, at large separations between the grains, the Josephson coupling energy can be written in the form

$$E_{ab}^{\xi_a \xi_b} = 2 \operatorname{Re} \left[e^{i(\phi_a - \phi_b)} Z_{ab}^{\xi_a \xi_b} \right], \tag{8}$$

where

$$Z_{aa'}^{\xi\xi'} = \operatorname{tr} \int d\mathbf{r} \, d\mathbf{r}' d\mathbf{p} \, d\mathbf{p}' \hat{\Delta}_a^{\xi}(\mathbf{r}, \mathbf{p}) \times \\ \times \hat{C}(\mathbf{r} - \mathbf{r}'; \mathbf{p}, \mathbf{p}') \hat{\Delta}_{a'}^{\xi'\dagger}(\mathbf{r}', \mathbf{p}'). \tag{9}$$

Here, tr denotes the trace over all spin indices and $\hat{C}(\mathbf{r} - \mathbf{r}'; \mathbf{p}, \mathbf{p}')$ is the integral over energies of the Cooperon diagrams illustrated in Fig. 1. The exchange energies $J_{aa'}^{\xi\xi'}$ and the phase $\theta_{aa'}(\xi, \xi')$ are related to the modulus and phase of

$$2Z_{aa'}^{\xi\xi'} = J_{aa'}(\xi\xi') \exp[i\theta_{aa'}(\xi,\xi')].$$

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2.2.1. Singlet pairing

We begin by considering the case where the Cooper pairing occurs in the singlet channel $\hat{\Delta}_{a}^{\xi} = i\hat{\sigma}_{2}\Delta_{a}^{\xi}(\mathbf{r},\mathbf{p}),$



Fig. 1. Diagrammatic representation of the Cooperon ladder. Solid lines are electron Green's functions, whereas dashed lines are impurities. $\hat{C}(\mathbf{r} - \mathbf{r}'; \mathbf{p}, \mathbf{p})$ in Eq. (9) is obtained by integrating this ladder over energy

which includes s- and d-wave superconductors. In the presence of disorder, even in the case where the clean bulk phase is a pure d-wave superconductor, the order parameter in each grain contains an s-wave component

$$\Delta_a^{\xi}(\mathbf{r}, \mathbf{p}) = \Delta_a^{(s), \xi}(\mathbf{r}, \mathbf{p}) + \Delta_a^{(d), \xi}(\mathbf{r}, \mathbf{p}), \qquad (10)$$

where the superscript in the parenthesis stands for the orbital symmetry, whereas ξ indicates the Ising variable that specifies which of the two time-reversed versions of the gap function is being considered. Substituting Eq. (10) in Eq. (9) and evaluating the Cooperon, we obtain three terms corresponding to s-s, s-d, and d-d Josephson couplings:

$$Z_{aa'}^{\xi\xi'} = Z_{aa'}^{(ss),\xi\xi'} + Z_{aa'}^{(dd),\xi\xi'} + Z_{aa'}^{(sd),\xi\xi'}.$$
 (11)

At distances long compared to p_F^{-1} but small compared to the thermal dephasing length, the *s*-*s* component is given by

$$Z_{aa'}^{(ss),\xi\xi'} \propto \frac{\nu}{|\mathbf{r}_a - \mathbf{r}_{a'}|^D} \langle \Delta_a^{\xi} \rangle \langle \Delta_{a'}^{\xi'*} \rangle, \qquad (12)$$

where ν is the density of states at the Fermi level, D is dimensionality of the system, \mathbf{r}_a and $\mathbf{r}_{a'}$ are the locations of grains a and a', and $\langle \Delta_a^{\xi} \rangle$ denotes the order parameter integrated over a single grain,

$$\langle \Delta_a^{\xi} \rangle = \int d\mathbf{r} \, d\mathbf{p} \, \Delta_a^{\xi}(\mathbf{r}, \mathbf{p}). \tag{13}$$

Strictly speaking, the slow power-law decay of the Josephson coupling constant in Eq. (12) leads to a logarithmic divergence of the ground-state energy. However, multiple Andreev reflections [17] of diffusing electrons from the grains provide a cutoff of this divergence at large distances [19]. Since the cutoff length is greater than the typical distance between the grains, our results are not affected by the presence of this cutoff.

In the same long-distance limit, the s-d and d-d contributions are given by

$$Z_{aa'}^{(sd),\xi\xi'} \propto \nu \langle \Delta_a^{\xi*} \rangle Q_{a',ij}^{\xi'} \partial_i \partial_j \frac{1}{|\mathbf{r}_a - \mathbf{r}_{a'}|^D}$$
(14)

and

$$Z_{aa'}^{(dd),\xi\xi'} \propto \nu \, Q_{a,ij}^{\xi} Q_{a',kl}^{\xi'\dagger} \partial_i \partial_j \partial_k \partial_l \frac{1}{|\mathbf{r}_a - \mathbf{r}_{a'}|^D}.$$
(15)

In the above formulas, the *d*-wave component of the order parameter in grain *a* is described by the second-rank tensor $Q_{a,ij}^{\xi}$. For example, for a spherical Fermi surface in which $\Delta_a^{(d),\xi}(\mathbf{r},\mathbf{p}) = Q_{a,ij}^{\xi}(\mathbf{r})p_ip_j$ (with $Q_{a,ii}^{\xi}(\mathbf{r}) = 0$), we have

$$Q_{a,ij}^{\xi} = \int d\mathbf{r} \, Q_{a,ij}^{\xi}(\mathbf{r}). \tag{16}$$

It is important to note that $Z_{ab}^{(sd)}$ and $Z_{ab}^{(dd)}$ fall off faster with the distance between the grains than $Z_{ab}^{(ss)}$ does. Therefore, they can be neglected at large inter-grain separations. The leading term $Z_{ab}^{(ss)}$ given by Eq. (12) has a phase factor that can be written as a sum of phase factors of individual grains, which are independent of the direction of the link $\mathbf{r}_a - \mathbf{r}_b$. Therefore, we arrive at the Mattis model, Eqs. (5) and (6), where θ_a^{ξ} is the phase of $\langle \Delta_a^{\xi} \rangle$ in Eq. (13). Indeed, in this limit, $J_{ab}(1) = J_{ab}(-1) \equiv J_{ab}$ is independent of ξ_a and ξ_b .

2.2.2. Triplet pairing

We now turn to triplet superconductivity and begin with the case where spin-orbit coupling is negligible. Even in the case where $p_x + ip_y$ superconductivity occurs in the absence of disorder, the order parameter in a particular grain acquires an admixture of other *p*-wave components. However, the triplet and singlet components of the order parameter do not mix. In this case, we obtain the following form of the Josephson coupling from Eq. (9):

$$Z_{aa'}^{(pp),\xi\xi'} \propto \nu A_{a,i}^{\xi,\alpha} A_{a',j}^{\xi',\alpha*} \partial_i \partial_j \frac{1}{|\mathbf{r}_a - \mathbf{r}_{a'}|^D}, \qquad (17)$$

where the matrix $A_{a,i}^{\xi,\alpha}$ describes the *p*-wave order parameter in grain *a*. For example, for a spherical Fermi surface with $\hat{\Delta}_a(\mathbf{r}, \mathbf{p}) = \hat{\sigma}_{\alpha} A_{a,i}^{\xi,\alpha}(\mathbf{r}) p_i$, it is given by

$$A_{a,i}^{\xi,\alpha} = \int d\mathbf{r} \, A_{a,i}^{\xi,\alpha}(\mathbf{r}). \tag{18}$$

The phase of the Josephson coupling in Eq. (17) depends on the relative orientation between the spatial structure of the order parameter $A_{a,i}^{\xi,\alpha}$ (where the index *i* indicates a preferred axis) and the direction of the bond between the grains. As a result, the phase of $Z_{aa'}^{(pp),\xi\xi'}$ in Eq. (17) cannot be represented in the form

of Eq. (6) in which the phases θ_a and $\theta_{a'}$ depend only on the grain properties but not on the direction of the link connecting them, $\mathbf{r}_a - \mathbf{r}_{a'}$. This means that we obtain a Josephson junction array with frustration.

However, in the presence of spin-orbit interactions in nonuniform superconductors, the singlet, Δ , and triplet, Δ , components of the order parameter mix. In this case, at large separations between grains, the Josephson coupling is again dominated by the *s*-wave component of the order parameter and is described by Eq. (12), which again leads us to the Mattis model, Eqs. (5) and (6).

3. CORRECTIONS TO THE MATTIS MODEL AND THE GLOBAL PHASE DIAGRAM

We have shown that at sufficiently strong disorder, the properties of disordered unconventional superconductors at long spatial scales can be described by the effective Hamiltonian in Eq. (5). To the leading order in inverse powers of the typical integrain distance R, Eq. (5) reduces to the Mattis model in Eq. (7). In this limit, the random phases of the Josephson couplings between islands can be gauged away; as can be seen from the construction that leads to Eq. (7), the ordered state corresponds to uniform-phase (ferromagnetic) ordering of the s-wave components from grain to grain, even when the largest component of the order parameter on each grain is unconventional. Thus, at long distances, the system behaves as an s-wave superconductor with respect to all superconducting interference experiments. For example, corner SQUID experiments [4] would not exhibit trapped fluxes. In the case where, in the absence of disorder, there is a $p_x \pm i p_y$ state, where the disorder is nearly strong enough to quench the superconductivity, there are no edge currents, and in the presence of an external magnetic field, the long distance (topological) vortex structure becomes that of a conventional s-wave superconductor.

Corrections to the Mattis model come from the coupling between the non-s-wave components of the order parameter, and are therefore smaller than the leading contributions to J in proportion to a positive power of 1/R. However, even when R is large, these corrections can be qualitatively significant: since the s-s contribution to $J_{aa'}(\xi\xi')$ from Eq. (12) is independent of the pseudo-spin variables ξ and ξ' , the energy of the system is 2^N -fold degenerate to the leading order in 1/R, where N is the number of grains.

The leading correction to the Josephson coupling energies has the form of either Eq. (14) or (17). In



Fig. 2. Schematic picture of the phase diagram of an unconventional superconductor as a function of temperature and disorder

the presence of these corrections, the energy depends on the configuration of the pseudo-spins, and there is a level of frustration that cannot be removed (as in the Mattis model) by a gauge transformation. Specifically, although in the expression for the Josephson energy,

$$\sum_{ab} \tilde{J}_{ab}(\xi_a \xi_b) \cos(\tilde{\phi}_a - \tilde{\phi}_b + \tilde{\theta}_{ab}^{\xi_a \xi_b}),$$

the $\tilde{\theta}_{ab}$ are small,

$$\tilde{\theta}_{ab}^{\xi_a\xi_a} = \operatorname{Im} \ln \frac{Z_{ab}^{(pp),\xi_a\xi_b}}{Z_{ab}^{(ss),\xi_a\xi_b}} \ll 1,$$

they reflect intrinsic frustration in the couplings because the sum of the phases around a typical closed loop, $\sum_{O} \tilde{\theta}$, is generally nonzero. Moreover, both \tilde{J}_{ab} and $\tilde{\theta}_{ab}$ depend on ξ_a and ξ_b .

Therefore, one generic consequence of the corrections to the Mattis model is that they lift the energy degeneracy of the system with respect to the pseudo-spin variables ξ . Consequently, we expect the subsystem of pseudo-spins to form a glassy state. Another consequence of the corrections is that they result in the existence of equilibrium currents. In the three-dimensional case, the existence of corrections to the Mattis model does not destroy the long-range superconducting order characterized by the phase ϕ . Therefore, results from the Mattis model concerning the long-range s-wave-like nature of the superconducting state are robust to these corrections. In two spatial dimensions, the correction terms necessarily eliminate long-range phase coherence, since the correlation function of the phases in the ground state diverges logarithmically at large distances. However, as long as $\tilde{\theta}_{ab}^{\xi_a \xi_b} \ll 1$, the length at which the phase changes by a number of the order of unity is exponentially large in comparison to the intergrain distance.

At the intermediate strength of disorder, when R becomes comparable to the size of the superconducting islands, the effective energy of the system, Eq. (5), cannot even approximately be reduced to the Mattis model, Eq. (7). The phases $\tilde{\theta}_{ab}$ that cause frustration are then of the order of unity. In this case, the system is a superconducting glass [14, 15]. The global phase diagram of the system is schematically shown in Fig. 2.

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