Unusual paramagnetic phenomena in granular high-temperature superconductors—A consequence of d-wave pairing?

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This colloquium reviews some unusual paramagnetic phenomena in granular high-temperature superconductors. These are consistently explained by assuming that there is frustration in the coupling patterns between the neighboring grains. Such frustration effects occur in a natural way in a multiply connected superconductor with Josephson junctions if the order parameter has unconventional symmetry due to Cooper pairing in a higher angular momentum channel, e.g., d-wave pairing. A simple model is introduced to describe the magnetic properties of a frustrated granular superconductor. Large orbital magnetic moments are spontaneously created, leading to superparamagnetic behavior. These results suggest that the unusual paramagnetic phenomena are a consequence of unconventional symmetry of the pairing state in the high-temperature superconductors.

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I. INTRODUCTION

The discovery of the high-temperature superconductors (HTSC), a class of materials based on planar copper oxide structures, has raised many questions that are linked to long-standing theoretical challenges in solid-state physics. The HTSC state is achieved by doping insulating parent compounds with a relatively small number of carriers, usually holes (electron vacancies). The parent insulators, however, are not conventional band insulators where an even number of electrons per unit cell is an essential requirement to fill completely a set of Bloch bands. This requirement is not fulfilled here; rather, there are nine d electrons per Cu ion, and a single-electron band theory wrongly predicts a half-filled band showing metallic behavior. The solution to this puzzle is the very strong Coulomb repulsion between electrons which forces them to be localized on individual ionic sites. This type of insulator, known as a Mott insulator, is immediately distinguished from conventional insulators by the spin degrees of freedom which are active at low energy. In the present case the Cu^{2+} ions are missing one electron from the $3d$ shell, and the resulting $S = 1/2$ spin degrees of freedom are coupled by a nearest-neighbor Heisenberg interaction causing them to order antiferromagnetically. Anderson (1987) realized very early that the appropriate description for the superconductor must be an extension of the Heisenberg model to include the mobility of the spins which arises when they exchange position with the dopant holes that are introduced onto a fraction of the Cu ions. A relatively small concentration of holes is sufficient to destroy the magnetic order and to trigger a transition to a "metallic" phase exhibiting superconductivity with an unprecedentedly high transition temperature of the order 100 K.

The classical BCS theory describes superconductivity as a state in which electrons with opposite momenta, $\mathbf{k}$ and $-\mathbf{k}$, and opposite spin form bound pairs (so-called Cooper pairs) with a definite relative angular momentum. If we assume that superconductivity in HTSC is also due to Cooper pairing, then we encounter the possibility that the strong on-site repulsive interaction among the electrons, responsible for the Mott insulating behavior in the parent compounds, may prevent the formation of pairs with s-wave (angular momentum $\ell = 0$) symmetry. However, Cooper pairs can form in a higher angular momentum state that, due to the symmetry of the pair wave function in real space, does not have configurations with both electrons on the same site and so they reduce the effect of the Coulomb repulsion. Conventional metallic superconductors all have s-wave symmetry, and only in the special case of the heavy-fermion superconductors (another case with strong intra-atomic Coulomb repulsion) is there strong experimental evidence of unconventional pairing in a metal. In the case of the HTSC, the issue of whether the pairing symmetry is conventional or unconventional has been hotly debated for some time. The most discussed candidate for unconventional pairing is the so-called $d_{x^2-y^2}$ state, in which the angular momentum of the pair is quenched by the lattice potential, but the pairing channel is $\ell = 2$ or d wave. Such pairing states occur in various theories based on microscopic models for the CuO_2 planes (Bickers *et al.*, 1987; Gros

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et al., 1987; see also Dagotto, 1994). Additionally, this symmetry is supported by phenomenological theories in which the pairing is mediated by the exchange of spin fluctuations, which are especially strong since the HTSC are very close to antiferromagnetic order (Moriya *et al.*, 1990; Monthoux *et al.*, 1992; Ueda *et al.*, 1992; Monthoux and Pines, 1993; see also Rice, 1994).

For a long time experimental data seemed to rule out unconventional pairing, branding it as nothing but a peculiarity of certain theories. However, recent improvements in sample quality and new techniques have led to results that are very suggestive of d-wave pairing symmetry. [For a discussion, see the recent article by Levi (1993)]. The first class of experiments addresses the question indirectly through the properties of the quasiparticle excitations of the superconductor. One of the important results of BCS theory is the existence of a gap in the quasiparticle energy spectrum, $|\Delta(\mathbf{k})|$, proportional to the strength of the pairing amplitude. While in the simplest case of an s-wave superconductor this amplitude, and therefore the gap, is more or less direction independent on the Fermi surface, we expect that a higher angular momentum pairing has sign changes in the pairing amplitude as one varies the direction on the Fermi surface. This, in turn, leads to zeros or nodes in the gap along specific directions in momentum space as a consequence of symmetry. The thermodynamics of a superconductor at low temperatures is determined by excitations involving two quasiparticles. It follows that in an s-wave superconductor at low temperatures these have a finite minimum excitation energy Δ, which is reflected in an exponential temperature dependence $e^{-\Delta/k_BT}$ for properties such as the electronic specific heat. This behavior contrasts with that of a superconductor with nodes in the energy gap which lead to two-quasiparticle excitations at arbitrary small energies and to a power-law behavior [$\sim T^n$ (n: some integer)] in electronic properties at low temperatures.

The first clear signs of the existence of low-energy excitations in HTSC were found in NMR measurements (Martindale *et al.*, 1993), and simultaneously in data on the London penetration depth at low temperatures when Hardy *et al.* (1993) reported a deviation linear in T from the value at $T = 0$ K. The detailed interpretation of these experiments is complicated by a sensitivity of the measurement and the theory to sample imperfections. Angle-resolved photoemission, in principle, measures directly the single-quasiparticle energy-momentum relation. Shen *et al.* (1993) reported the vanishing of the energy gap for quasiparticles moving along the (1,1) axes in the CuO_2 planes, i.e., $k_x = \pm k_y$. This behavior is consistent with $d_{x^2-y^2}$ character for the pairing amplitude, which vanishes along $k_x = \pm k_y$ and has its maximal strength along the (1,0) and (0,1) directions. Recent studies of the angle-integrated density of states of quasiparticles using a scanning tunneling microscope (Barbiellini *et al.*, 1994) also gave support to d-wave symmetry, with evidence of a tail in the density of states stretching down to the chemical potential. All these experiments, although very sophisticated, are indirect and are sensitive only to changes in the magnitude of the pairing amplitude. They cannot distinguish a strong angular variation without an actual sign change, i.e., an anisotropic s-wave form, from the case of d-wave pairing where the amplitude changes sign upon a rotation through $\pi/2$ in $\mathbf{k}$ space.

This article is devoted to a discussion of phenomena that reflect in a direct way the symmetry of the superconducting state in HTSC. The first sign of such phenomena was observed in the unusual paramagnetic response of some granular HTSC, the understanding of which will be the main topic here. It is widely believed that intrinsic frustration in the granular system is the cause of this effect, as we shall discuss below in detail. Meanwhile, a number of beautiful test experiments that can probe the unconventional nature of a HTSC in controlled geometries evolved from the idea of frustration. We shall address them briefly at the end of this article, and they will be further discussed in a companion article by Van Harlingen.

II. EXPERIMENTS ON GRANULAR HIGH-TEMPERATURE SUPERCONDUCTORS

A granular superconductor consists of many superconducting islands, the grains. The contacts where the grains touch each other act as weak links interconnecting the grains to form a complex network. Such a system has the properties of a multiply connected superconductor. If it undergoes the superconducting transition in zero external magnetic field, it exhibits, usually, a complete Meissner effect at low temperatures, provided the probing field is small enough to affect only weakly the screening currents flowing through the links. On the other hand, if it is cooled in a finite field, a certain amount of magnetic flux is trapped in the voids of the multiply connected sample, so that the Meissner effect is only partial even at very low temperatures (Fig. 1).

Surprisingly, the magnetic behavior of granular $Bi_2Sr_2CaCu_2O_8$ under field cooling (FC) conditions is quite different. For very small fields (H_{ex} ~0.01–1 Oe), a paramagnetic response appears below the superconducting transition temperature. A characteristic signature of this effect is the strong nonlinearity of the dc susceptibility defined as χ_{dc}, the ratio between the measured magnetization M and the applied field H_{ex} (Fig. 2). The smaller the H_{ex}, the larger is the paramagnetic response χ_{dc} (Svedlindh *et al.*, 1989; Braunisch *et al.*, 1992, 1993; Heinzel *et al.*, 1993; Niskanen, 1993; Niskanen *et al.*, 1993; Shrivastava, 1994). For fields $H_{ex} \gtrsim 1$ Oe, χ_{dc} changes sign to become weakly diamagnetic. This behavior suggests the existence of magnetic degrees of freedom associated with orbital currents spontaneously created in the superconducting state which interact weakly, so that even rather small fields are suf-

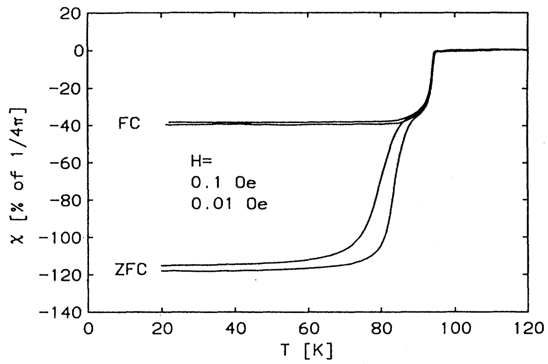

FIG. 1. Standard behavior of the dc susceptibility in granular superconductors ($Bi_2Sr_2CaCu_2O_8$) under ZFC and FC conditions. The FC susceptibility shows only a fractional Meissner effect, about 1/3 of the complete Meissner effect for ZFC. The measurements were done on a high-quality sintered sample (Braunisch *et al.*, 1992, 1993).

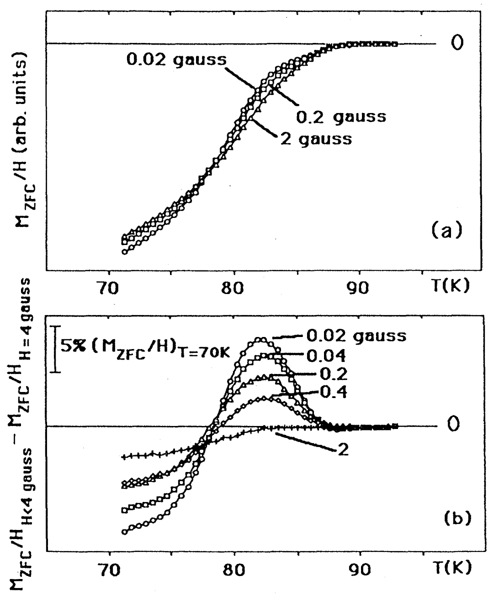

FIG. 3. ZFC dc susceptibility close to T_c: (a) bare dc susceptibility and (b) reduced dc susceptibility where the nonlinear signal is emphasized by subtraction of the linear diamagnetic signal, $\chi(H) - \chi(H^*)$ with $H^* = 4$ gauss (Svedlindh *et al.*, 1989).

ficient to enforce nearly complete polarization. Their (positive) paramagnetic contribution M_0 to the magnetization competes with the linear (negative) diamagnetic response of the system. The total magnetization takes the form $[M(H_{\rm ex}) = M_0(H_{\rm ex}) + \chi_{\rm dia}H_{\rm ex}]$ and leads to $\chi_{\rm dc} = M_0(H_{\rm ex})/H_{\rm ex} + \chi_{\rm dia}$. A rather good fit of the experimental data is obtained using the following field dependence of M_0 suggested by Kusmartsev (1992a, 1992b): $M_0(H_{\rm ex}) = M_0' H_{\rm ex}/(H_0 + H_{\rm ex})$ (Braunisch *et al.*, 1992, 1993; Niskanen, 1993; Niskanen *et al.*, 1994). The characteristic field H_0 can be interpreted as the field scale below which thermal and interaction effects act to suppress complete polarization. As $T \to 0$, H_0 is of the order 0.1 Oe.

When the experiment is done under zero-field cooling (ZFC) conditions, at first sight there is nothing more than the Meissner effect that appears in ordinary granular superconductors. However, Svedlindh and coworkers found, upon careful analysis, a rather small nonlinear contribution superposed on the dominant linear diamagnetic response. By subtracting the diamagnetic part (e.g., $\chi_{\rm dc}$ measured in a comparatively large external field H^*), one discovers a clear peak structure in $\delta\chi_{\rm dc} = \chi_{\rm dc}(H) - \chi_{\rm dc}(H^*)$ for $H < H^*$ in the vicinity of the superconducting transition. The magnitude of this structure is field dependent: the smaller the applied field, the more pronounced is the signal (Fig. 3; Svedlindh *et al.*, 1989; Niskanen, 1993).

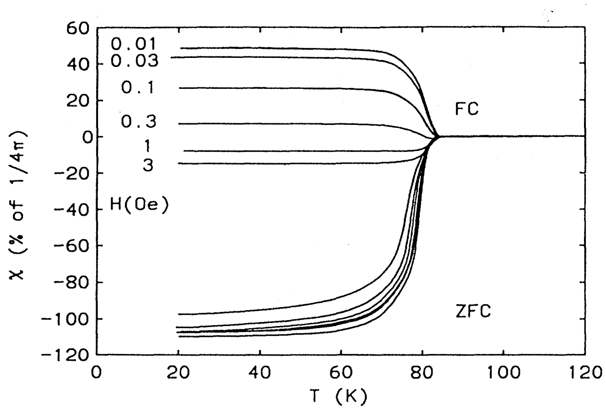

FIG. 2. Unusual behavior of the dc susceptibility in a granular superconductor ($Bi_2Sr_2CaCu_2O_8$) under ZFC and FC conditions. A strong paramagnetic signal is observed for FC in small fields (< 1 Oe): Wohlleben effect. The measurements were done on a melt-processed sample (Braunisch *et al.*, 1992, 1993).

This peculiar nonlinear paramagnetism has received various names in literature, such as the "anti-Meissner effect" or the "paramagnetic Meissner effect." It has become clear, however, that this effect has nothing to do with the screening behavior of a superconductor named after Meissner and Ochsenfeld, but represents a new phenomenon. As an alternative name, we proposed earlier to call it the Wohlleben effect.[1] We shall adopt this name here, too.

Actually, a number of other anomalous features are found in ceramic samples that show the Wohlleben effect—a nonmonotonic behavior of microwave absorption with a varying external magnetic field (Braunisch *et al.*, 1992, 1993; Kataev *et al.*, 1993) and an unusual

[1]This name was chosen after Dieter Wohlleben, who with his group explored the properties of this effect in detail and emphasized its importance in the context of high-temperature superconductivity. Dieter Wohlleben died tragically in summer 1992.

anomaly in the second harmonic of the ac susceptibility in a static field (Heinzel *et al.*, 1993). These features can also be explained within the framework outlined below, but it would take us into too much detail to discuss these effects here.

Standard granular superconductors are often modeled as networks of Josephson junctions (weak links) connecting the grains, i.e., a so-called Josephson network. Good Josephson junctions between two grains guarantee a phase-coherent tunneling of the Cooper pairs between different grains and allow the percolation of superconductivity throughout the whole granular sample. The simplified version of such a network is a model with the phases ϕ_i of the order parameter on each grain as the only degree of freedom, so that the Hamiltonian is given by the sum of all junction energies: $H = -\sum_{i,j} E_{ij}\cos(\triangle\phi_{ij})$ with $E_{ij} > 0$ as the random Josephson coupling between the grains i and j and $\triangle\phi_{ij} = \phi_i - \phi_j$. This system is unfrustrated, and the lowest energy state is given by $\phi_i =$ constant for all i, minimizing the energy of all junctions simultaneously. This changes as soon as a magnetic field is applied, since the phase ϕ_i is subject to gauge effects: $\triangle\phi_{ij} \to \triangle\phi_{ij} - (2\pi/\Phi_0)\int_i^j d\mathbf{s}\cdot\mathbf{A}$ where $\mathbf{A}$ is the vector potential. For finite $\mathbf{A}$, the system is frustrated and the energy cannot be minimized for each junction independently. This system is also called a *gauge glass*, because it exhibits various glass properties. It has been studied extensively for more than a decade (for a review, see Blatter *et al.*, 1994). However, to the best of our knowledge, such a system does not show any of the observed behavior discussed above.

Several groups suggested that the anomalous effects could arise from a frustration due to intrinsic properties of the Josephson junctions rather than an extrinsic frustration due to an applied magnetic field. Some years ago Bulaevskii and co-workers (1977) showed that the presence of independent magnetic impurities in the junction opened up a new tunneling channel involving a spin-flip intermediate state which actually gave a negative contribution to the Josephson critical current, I_J, between singlet superconductors. If conditions could be realized in which this spin-flip channel dominates over the regular tunneling channel, then a negative total critical current ($I_J < 0$) would appear in the Josephson relation, $I = I_J\sin(\Delta\phi)$, which we discuss below. Alternatively, we could express the relationship as $I = I_c\sin(\Delta\phi + \pi)$ with $I_c(= |I_J|)$ as the magnitude of the Josephson critical current. Such a junction with a phase shift π is called a π *junction*. It is, however, debatable whether the conditions necessary to make $I_J < 0$ can be realized in practice, since an increase in the concentration of magnetic impurities in the junctions will lead to coupling between the impurity spins, which in turn will lead to inelastic tunneling processes. To the best of our knowledge, no controlled example of such a π junction has been realized. Nonetheless, the idea that such junctions might exist led Bulaevskii *et al.* (1977) to predict some interesting consequences, as we shall discuss below, and also inspired others to look into related possibilities (Glazman and Matveev, 1989; Spivak and Kivelson, 1991).

An alternative mechanism for generating an intrinsic π-phase shift in a Josephson junction is based on the idea of an unconventional order parameter. Non-s-wave pair wave functions possess a phase that depends on the angular direction in k space. It has been pointed out by Geshkenbeĭn and co-workers that, in the context of heavy-fermion superconductivity, Josephson junctions are sensitive to this phase, and special arrangements may lead to frustration effects (Geshkenbeĭn and Larkin, 1986; Geshkenbeĭn *et al.*, 1987). Later, Sigrist and Rice analyzed the situation for high-temperature superconductors, assuming $d_{x^2-y^2}$ symmetry for the superconducting order parameter (Sigrist and Rice, 1992). As the emphasis of this paper lies on the consequences of d-wave superconductivity, we shall go into more detail here on this mechanism.

III. JOSEPHSON EFFECT IN d-WAVE SUPERCONDUCTORS

The Josephson effect is certainly one of the most intriguing phenomena in superconductivity. It is a consequence of coherent tunneling between two superconducting condensates, each of which is represented by a complex macroscopic wave function, which is the order parameter of superconductivity. On a microscopic level we can describe this effect as the tunneling of Cooper pairs from the pairing state on one side of the junction to that of the other side. In a tunneling process, electrons moving perpendicularly to the interface make the largest contribution. So it follows that the strength of Josephson tunneling will depend on a weighted average over the pairing wave function, weighted in favor of electronic momenta in this perpendicular direction. Therefore the Josephson effect is a direction-sensitive phenomenon connected with the orientation of the junction and with the crystal axis of the superconductor on each side. This fact is of minor importance for conventional s-wave superconductors with an essentially isotropic pair wave function. However, in the case of non-s-wave superconductivity, where pair wave functions have an internal angular structure, this property can lead to intriguing new effects.

We discuss here as a concrete example the properties of a Josephson junction for the above-mentioned $d_{x^2-y^2}$-wave superconductors. For simplicity, we assume that the basic crystal symmetry of the superconductor is tetragonal (z axis is the fourfold rotation axis), described by the point group D_{4h}, neglecting for the moment the orthorhombic distortion actually present in most of the HTSC. In this symmetry the typical form of the pair wave function in k space is

$$\psi(\mathbf{k}) = \langle a_{\mathbf{k}\uparrow}a_{-\mathbf{k}\downarrow}\rangle = \cos k_x - \cos k_y, \qquad (1)$$

where $a_{\mathbf{k}s}$ is the annihilation operator for an electron with momentum $\mathbf{k}$ and spin s, and $\langle ... \rangle$ denotes the thermal average. The anisotropic function $\cos k_x - \cos k_y$ has the same symmetry properties in D_{4h} as $k_x^2 - k_y^2$, a homogeneous polynomial of second order in $\mathbf{k}$. For this reason, this state is referred to as the "d-wave state"—i.e., the relative angular momentum is $\ell = 2$—although the classification with respect to the angular momentum has no real meaning under discrete crystal-field symmetry. The electrons are paired in a spin singlet, and the parity of the orbital wave function is even.

It is easy to formulate a Ginzburg-Landau theory of this d-wave superconducting state based on its symmetry properties. We introduce a complex order parameter η, which behaves the same way as the pair wave function in Eq. (1) under symmetry transformations and depends on temperature and position in space, $\eta = \eta(\mathbf{r}, T)$. The Ginzburg-Landau free-energy functional is an expansion in η near the superconducting transition temperature T_c where η is small. It has to be a scalar under the operations of the complete symmetry group of the system, which consists of the crystal symmetry, D_{4h}, time reversal $\mathcal{K}$, and the U(1) gauge symmetry. Hence its general form is given by

$$F = \int d^3r[A(T)|\eta|^2 + \beta|\eta|^4 + K_1(|D_x\eta|^2 + |D_y\eta|^2) + K_2|D_z\eta|^2 + \frac{1}{8\pi}\mathbf{B}\cdot(\mathbf{B} - 2\mathbf{H})] \tag{2}$$

(for reviews, see Gor'kov, 1987; Annett, 1990; and Sigrist and Ueda, 1991). The real coefficients β and K_i are phenomenological parameters, and $A(T)$ $[= a(T - T_c)]$ changes sign at the superconducting transition temperature T_c. The symbols $D_{x,y,z}$ denote the components of the gauge-invariant gradient $\mathbf{D} = (\nabla - 2\pi i\mathbf{A}/\Phi_0)$, where $\mathbf{A}$ is the vector potential (with $\mathbf{B} = \nabla \times \mathbf{A}$) and Φ_0 is the flux quantum $hc/2e$. This free energy for the d-wave order parameter is identical to that of an s-wave superconductor in a tetragonal system. Therefore on this level there is no obvious difference between them.

For the discussion of the Josephson effect, we introduce the coupling between the order parameters of two linked superconductors. Within the Ginzburg-Landau theory this is straightforwardly formulated in terms of boundary conditions (see de Gennes, 1966 and Landau and Lifshitz, 1980). We consider two superconductors, (1) and (2), connected by tunneling through a planar interface. This can be included in the Ginzburg-Landau theory by adding an interface term to the free energy which represents the coupling between the two order parameters, $\eta_{(1)}$ and $\eta_{(2)}$, to lowest order and generates the correct boundary conditions (Geshkenbeĭn and Larkin, 1986; Annett, 1990; Yip *et al.*, 1990; Sigrist and Ueda, 1991),

$$F_{1,2} = \int dS \quad t_0\chi_{(1)}(\mathbf{n}_{(1)})\chi_{(2)}(\mathbf{n}_{(2)}) \times[\eta^*_{(1)}\eta_{(2)} + \eta_{(1)}\eta^*_{(2)}], \tag{3}$$

where the integral runs over the whole interface and t_0 is a real parameter denoting the coupling strength. The functions $\chi_{(j)}(\mathbf{n}_{(j)})$ are symmetry functions of the interface normal vector $\mathbf{n}_{(j)}$ given in the crystal basis of the side (j). This interface term is invariant under independent D_{4h} transformations on each side, if we choose $\chi_{(j)}(\mathbf{n}_{(j)})$ to have the same symmetry properties as the order parameter $\eta_{(j)}$ or the pair wave function. Thus $\chi_{(j)}(\mathbf{n}_{(j)})$ should be a constant if the superconductor (j) is an isotropic s-wave superconductor. However, $\chi_{(j)}(\mathbf{n})$ has essentially the same form as $\psi(\mathbf{k} = \mathbf{n})$ in Eq. (1) for a $d_{x^2-y^2}$-wave superconductor $[\chi(\mathbf{n}) = \cos n_x - \cos n_y$ or $n_x^2 - n_y^2]$.

The boundary conditions of the Ginzburg-Landau theory are obtained by variation of the complete free-energy functional with respect to $\eta_{(1)}$ (and $\eta_{(2)}$),

$$[K_1(n_{(1)x}D_x + n_{(1)y}D_y) + K_2 n_{(1)z}D_z]\eta_{(1)} = -t_0\chi_{(1)}(\mathbf{n}_{(1)})\chi_{(2)}(\mathbf{n}_{(2)})\eta_{(2)} \tag{4}$$

on the interface. A second analogous boundary condition is given by interchanging the side indices (1) and (2). These equations can be related to the supercurrent passing through the interface. The supercurrent density on side (j) along $\mathbf{n}$ has the form

$$\mathbf{n}\cdot\mathbf{J}_j = c\mathbf{n}\cdot\frac{\partial F}{\partial\mathbf{A}} = \frac{4\pi c}{\Phi_0}\mathrm{Im}\{\eta^*_{(j)}[K_1(n_xD_x + n_yD_y) + K_2n_zD_z]\eta_{(j)}\}. \tag{5}$$

Combining Eqs. (4) and (5), we obtain for the current density perpendicular to the interface

$$J = \frac{4\pi ct_0}{\Phi_0}\chi_{(1)}(\mathbf{n}_{(1)})\chi_{(2)}(\mathbf{n}_{(2)}) \times|\eta_{(1)}||\eta_{(2)}|\sin(\varphi_2 - \varphi_1), \tag{6}$$

where we introduced $\eta_{(j)} = |\eta_{(j)}|\exp(i\varphi_j)$ on each side of the interface. Equation (6) allows us to define the Josephson critical current, $I_J = (4\pi ct_0/\Phi_0)\chi_{(1)}(\mathbf{n}_{(1)})\,\chi_{(2)}(\mathbf{n}_{(2)})$, which depends on the normal vectors (Fig. 4). Obviously, I_J is determined by the matching of the pair wave functions of both sides at the junction, in particular, by their mutual misorientation. It can have either sign for specific choices of $\mathbf{n}_{(j)}$, if at least one of the two superconductors has d-wave pairing symmetry. A negative critical current is equivalent to an intrinsic phase shift of π in the junction. Because $\chi(\mathbf{n})$ has essentially the same structure as $\psi(\mathbf{k})$, the current through this interface exhibits a direct coupling to the phase of Cooper pair wave functions, which can be different for different directions in momentum space in the case of unconventional pairing. The Josephson effect is direction sensitive and therefore allows one to probe the phase of the pair wave function. The existence of π junctions is a natural consequence of this property in d-wave superconductors. It is important to notice that diffuse tunneling does not change the characteristics of the junction as long as the symmetry with respect to the interface normal vectors is preserved. One effect of diffuse scattering is the suppression of the tunneling due to destructive interference effects.

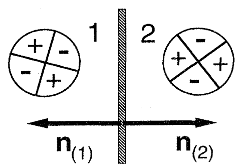

FIG. 4. Josephson junction between two d-wave superconductors. The circles show the orientation of the crystal lattice and the pair wave function $\psi(\mathbf{k}) \propto \cos k_x - \cos k_y$ on both sides of the junction. This example corresponds to a π junction.

IV. FRUSTRATION AND SPONTANEOUS CURRENTS IN MULTIPLY CONNECTED GEOMETRIES

The connection of two superconductors by a π junction does not, by itself, lead to any special observable effects. The phases of the order parameters on both sides simply arrange to minimize the Josephson-junction energy, $\propto -\cos(\phi_2 - \phi_1 + \pi)$, by setting the phase difference, $\phi_2 - \phi_1$, equal to π. There is no way to measure this phase shift directly. It merely corresponds to a phase change in one of the two superconductors, e.g., $\eta_{(1)} \to -\eta_{(1)}$ or $\phi_1 \to \phi_1 + \pi$. This transformation is equivalent to the exchange of the x and y coordinates in superconductor (1), an allowed redefinition in a tetragonal system. Hence whether a junction is a π or a 0 junction or not is, in this sense, only a matter of convention.

On the other hand, physical consequences arising from π junctions can be expected in multiply connected superconducting systems. Let us illustrate this by the example of three superconducting segments forming a loop with three junctions (Fig. 5). The arrangement is chosen so that all junctions are π junctions by our definition. We can now apply the above transformation ($x \leftrightarrow y$) to one of the segments to convert its adjacent junctions into 0 junctions, leaving one π junction only. There is no further transformation that could "remove" the remaining π junction without changing one of the two 0 junctions again into a π junction. This example leads us to the general statement that a loop with an *odd* number of π junctions in a multiply connected system, under all redefinitions of the crystal axis (or the order-parameter phases), has at least one π junction. Hence there is no way to minimize the energy of all junctions and, at the same time, to keep the order-parameter phase constant in each segment. This means *frustration* for this loop.

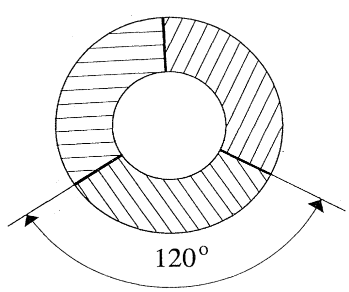

FIG. 5. Superconducting loop with three junctions. The lines of the shading represent the direction of the x axis in each segment, while the z axis is pointing out of the plane. In this arrangement every junction is a π junction by definition.

A rather simple arrangement for studying the properties of such a frustrated system is a single superconducting loop with just one junction (Fig. 6). This situation can, for example, be realized in a loop with many strong and just one rather weak junction, which, as the weakest link, determines the properties of the whole system. Assuming that the current I, which flows in the loop, is small compared to the critical current of the grains, we find the energy given by the simple form

$$F(I, \Delta\phi) = \frac{1}{2c^2} L I^2 - \frac{\Phi_0 I_c}{2\pi c} \cos(\Delta\phi + \alpha), \tag{7}$$

where L denotes the self-inductance of the loop and $I_c = \mid I_J \mid$ as discussed earlier. The phase shift α is 0 for an unfrustrated and π for a frustrated loop. In this reduced form the free energy consists only of the current-magnetic field energy (first term) and the junction energy (second term). A simple relation between $\Delta\phi$ and the current can be found from the integral

$$\int_C d\mathbf{s} \cdot \left(\nabla\phi - \frac{2\pi}{\Phi_0} \mathbf{A} \right) = \int_C d\mathbf{s} \cdot \frac{m \mathbf{v}_s}{\hbar} \tag{8}$$

along a path C within the loop starting at one side of the junction and ending on the other side. The path C is deep enough inside the superconductor so that the superfluid velocity $\mathbf{v}_s$ vanishes due to the Meissner screening effect. Under the simplifying assumption that the junction has no spatial extension, so that all the current flows through one point, this leads to

$$\Delta\phi = 2\pi n - \frac{2\pi}{\Phi_0} \Phi = 2\pi n - \frac{2\pi}{\Phi_0} \left(\Phi_{\rm ex} + \frac{1}{c} L I \right), \tag{9}$$

where Φ, the total flux threading the loop, consists of the contributions of the external field and the current I (and n is an integer phase winding number). Substituting $\Delta\phi$ in Eq. (7), we obtain

$$F(I, \Phi_{\rm ex}) = \frac{1}{2c^2} L I^2 - \frac{\Phi_0 I_c}{2\pi c} \cos\left[\frac{2\pi}{\Phi_0} \left(\Phi_{\rm ex} + \frac{1}{c} L I \right) + \alpha \right]. \tag{10}$$

This model of a superconducting loop has been discussed by Silver and Zimmermann (1967) for unfrustrated loops

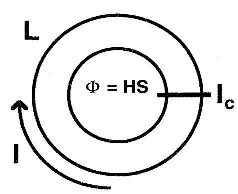

FIG. 6. Single loop with a single junction.

and by Bulaevskii *et al.* (1977) for frustrated loops. By minimizing F with respect to I for a given $\Phi_{\rm ex}$, we obtain the relation between I and $\Phi_{\rm ex}$ (Fig. 7). The properties of the solutions are determined by the dimensionless parameter $\gamma = 2\pi L I_c/\Phi_0 c$. For $\gamma < 1$, I is a single-valued periodic function of $\Phi_{\rm ex}$. However, if $\gamma > 1$, then $I(\Phi_{\rm ex})$ is multivalued near $\Phi_{\rm ex} = (2m+1)\Phi_0/2$ for $\alpha = 0$ and $\Phi_{\rm ex} = m\Phi_0$ for $\alpha = \pi$. In both cases the inner branch is always unstable, while the outer two branches are either stable or at least metastable (m: integer). The transition from the metastable to the stable state corresponds to a *phase slip* connected with the change of the phase winding number of the order parameter in the loop. It is important to notice that for zero external field, $\Phi_{\rm ex} = 0$, the frustrated loop ($\alpha = \pi$) carries a *spontaneous current*, $\pm I$ if $\gamma > 1$. This time-reversal-symmetry-breaking state appears through a continuous transition when the parameter γ exceeds 1.

Let us briefly consider the response of the system to a small external field in different regimes. If $\gamma < 1$, the response is linear,

$$I = -\frac{2\pi I_c \cos\alpha}{\Phi_0(1+\gamma\cos\alpha)}\Phi_{\rm ex}, \tag{11}$$

and diamagnetic for $\alpha = 0$ (unfrustrated), but paramagnetic for $\alpha = \pi$ (frustrated). The situation does not change for $\alpha = 0$ when γ exceeds 1. On the other hand, for $\alpha = \pi$, we enter the regime of nonlinear paramagnetic response if $\gamma \geq 1$, because of the presence of a spontaneous current; i.e., the right-hand side of Eq. (11) diverges at $\gamma = 1$.

Our simple example demonstrates an effect that we may consider typical for this kind of frustrated system. If the Josephson coupling is weak, it is favorable for the system to keep the phases constant everywhere and to pay the maximal energy loss at the junction. However, as the junction grows stronger, the system enters the regime where it pays to lower the junction energy at the expense of a phase gradient in the superconductor. Physically, a phase gradient means the existence of a finite current. For very large I_c, this spontaneous current generates a flux $\Phi \approx \pm\Phi_0/2$ (in zero external field) which originates from the winding of the order-parameter phase by π's going once around the loop. Note that in conventional superconductors, winding only as a multiple of 2π is possible.

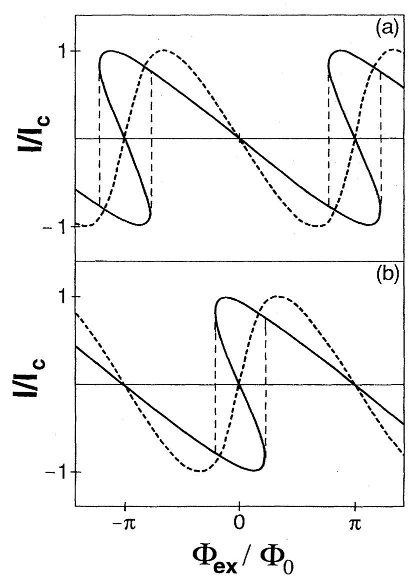

FIG. 7. Current I as a function of the external flux $\Phi_{\rm ex}$: (a) for an unfrustrated loop and (b) for a frustrated loop. Dashed lines indicate characteristics for $\gamma < 1$ and solid lines for $\gamma > 1$.

V. FRUSTRATED GRANULAR SUPERCONDUCTORS

Granular superconductors as frustrated networks can have very complex properties. Models for describing them, like the Josephson network model, are, in general, very difficult to handle. Therefore we shall introduce here a model that can be quite easily analyzed. It captures most of the essential physics and is remarkably successful in reproducing various features observed in the experiments discussed in Sec. II.

Our model is based on the single loop studied in the previous section. We consider now an ensemble of independent loops of this kind, each characterized by the critical current I_c, the self-inductance L, the area S, and their orientation Ω in space relative to the direction of the external field. There are N_0 unfrustrated and N_π frustrated loops. The unfrustrated loops produce, among other properties, the diamagnetic response of the system. The shortcomings of our model are obvious. We neglect the interaction among the loops, and volume and network effects such as flux trapping cannot be included here. The diamagnetic response obtained from the unfrustrated loops cannot completely account for the Meissner effect, which is the screening of the magnetic field out of the interior of a sample by means of surface currents. Nevertheless, as we shall see below, various other important features of the system are included in this model.

Let us first give a rough outline of the properties of our model under different cooling procedures. Temperature enters here via the critical current $I_c = I_c(T)$, which vanishes when $T > T_c$ and grows for $T < T_c$. Hence, by cooling, I_c increases below T_c in each loop, so that gradually, in more and more loops, $\gamma(I_c)$ exceeds 1 and spontaneous currents start to flow in the frustrated ones. It is clear how we deal with the history of cooling in this model. In zero external field, these spontaneous currents nucleate randomly in a positive or negative direction, and their contribution to the total magnetization of the system averages to zero. At low temperatures, the direction of the currents is rigidly fixed, because the two current states are separated by a large energy barrier, and the response to a weak magnetic field is dominated by diamagnetism (Meissner effect in the real system). On the other hand, by cooling in a finite field, one can polarize all the spontaneous currents when they nucleate in each loop, and they will give rise to a nonlinear paramagnetic contribution to the magnetization. As the magnetization due to these currents is only weakly field dependent for small fields, the dc susceptibility has the form mentioned in Sec. II: $\chi_{\rm dc} = M_0/H_{\rm ex} + \chi_{\rm dia}$ where M_0 stays constant as $H_{\rm ex} \to 0$. Certainly, fluctuations and interaction effects would lead to a shrinking M_0 for very small $H_{\rm ex}$, as suggested in Sec. II.

We consider now the behavior of the ensemble model near T_c in more detail, using a specific form for the distribution of I_c, $\mathcal{P}(I_c,T) = (4I_c/\tilde{I}^2)\exp(-2I_c/\tilde{I})$, where $\tilde{I}$ is the average critical current $\propto (T_c - T)$ for $T < T_c$ near T_c. The orientational distribution is assumed to be completely random, while L and S shall be the same for all loops. We consider first the case of FC. The average magnetization is proportional to the average current projected to the axis of the external field,

$$\overline{M}(T) \propto \frac{1}{4\pi}\int d\Omega \int_0^\infty dI_c \mathcal{P}(I_c,T)\cos\theta \sum_{\alpha=0,\pi} n_\alpha I_\alpha(I_c, \Phi_{\rm ex} = SH\cos\theta), \tag{12}$$

where $n_\alpha = N_\alpha/V$ denotes the concentration of loops with $\alpha = 0$ or π (V: the volume of the system) and $d\Omega = d\phi d\cos\theta$. For I_α, we choose the current of the most stable state that the system would access were it cooled in a field; i.e., the currents are paramagnetically polarized. The dc susceptibility, $\chi_{\rm dc} = \overline{M}/H_{\rm ex}$, is plotted for T close to T_c in Fig. 8 for various values of the field and for a ratio $n_0/n_\pi = 3$. The comparison with Fig. 2 shows an overall qualitative agreement with experiment. For weak fields, we find a large paramagnetic response. The competition between the nonlinear paramagnetic and linear diamagnetic contributions leads to a weakly diamagnetic signal for larger fields. As an additional detail, we find that immediately below T_c the system develops a weak diamagnetic response, and only upon a further lowering of the temperature does the large paramagnetic signal develop. The reason for this feature lies in the fact that close to T_c the critical currents of most of the frustrated loops are too small to drive spontaneous currents. This initial diamagnetic drop is a typical feature of frustrated superconductors and is observed clearly in many experiments (Svedlindh *et al.*, 1989; Braunisch *et al.*, 1993; Niskanen *et al.*, 1993).

Now we turn to the situation in which the system is first cooled to low temperatures in zero field. Then a small field is applied to measure the dc susceptibility upon an increase in the temperature again. We can neglect here phase slip (flux creep) phenomena, which would modify the current distribution over longer time scales than that of the measurement. Therefore we work with the assumption that all states stable in zero field are occupied with equal probability even after the small field is applied, which turns some of these states into metastable ones. In this sense we perform an averaging in Eq. (12), where now I_π is the average over the two states (stable and metastable in a field) with opposite spontaneous current. Clearly, the averaged current, $\bar{I}_\pi$, is very small and the diamagnetic response of the unfrustrated loops dominated. Nevertheless, by considering the difference between the dc susceptibilities of a small and a larger field, we can essentially subtract the linear diamagnetic part in order to uncover a nonlinear response on $H_{\rm ex}$ due to the frustrated loops. The result in Fig. 9 shows a peak structure that is in good qualitative agreement with the experimental data shown in Fig. 3. It reproduces the behavior that the peak is higher the weaker the applied field, as well as the crossing of the curves at lower temperature. The peak is connected with the presence of a transition between the loop states, with and without spontaneous current. At very low temperatures, the spontaneous currents are "frozen" in a random configuration and are hardly affected by the application

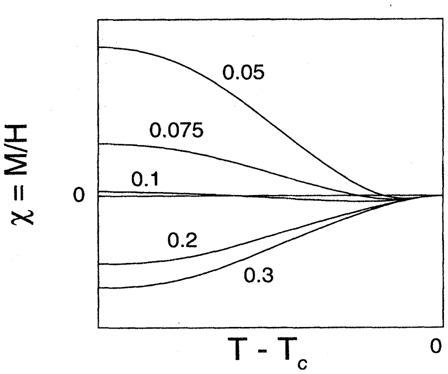

FIG. 8. FC dc susceptibility of the loop ensemble for the parameters given in the text. The fields are given in units of Φ_0/S (s: loop area). Arbitrary units on both axes.

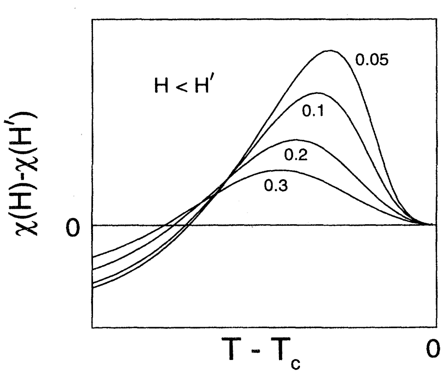

FIG. 9. Reduced ZFC dc susceptibility with subtracted linear diamagnetic signal: $\chi(H) - \chi(H')$ for $H < H'$ and $H' = 0.4\Phi_0/S$ (units of the field as in Fig. 9). Arbitrary units on both axes.

of an external field. (Due to the Meissner screening effect of a real system, an external field could in any case affect only a small region near the surface.) In the vicinity of the transition ($\gamma \approx 1$), currents in the frustrated loops are easier to polarize. In other words, the minima of the energy landscape of the currents are here rather flat and extended. Turning the temperature towards T_c, the polarizability of the currents is reduced again, because they are suppressed and have to vanish completely at T_c. (Note, that close to T_c the Meissner effect is reduced in the real system, and the applied field penetrates into a wider region.) The disorder (I_c distribution in our model) in the system leads to a broad peak, which has similarities with features observed in magnetic systems with quenched disorder.

Despite the simplicity and shortcomings of the model of an ensemble of independent loops, it describes consistently several details of the observed properties of granular $Bi_2Sr_2CaCu_2O_8$, in particular, in the vicinity of the superconducting transition temperature T_c. The reason for this success lies in the fact that close to T_c the distribution of frustrated loops contributing large spontaneous currents is rather sparse, so that interaction effects among them are of minor importance. Effects due to an external field, like screening and flux trapping in the voids of the system, are rather limited in this regime, too. However, they certainly have a strong influence on the low-temperature behavior. Meissner screening prevents drastic changes in the current pattern reached by zero-field cooling upon application of a small external field at low temperature. Furthermore, we should not forget that flux trapping in the FC case enhances the paramagnetic response by reducing the screening effects and supporting the polarization of the spontaneous currents in depth of the granular sample. It is, however, necessary to emphasize here that flux trapping alone cannot account for the Wohlleben effect, because in the superconducting state the (FC) magnetization exceeds the value of the normal state (see Fig. 2). In terms of flux trapping only, this would require that the granular superconductor attract magnetic field. Instead, from our discussion, a picture emerges in which paramagnetic degrees of freedom are created due to the presence of a frustrated superconducting state. The magnetic moments due to the spontaneous supercurrents can rise to large magnitudes. Estimates of order 10^8–$10^{10}\mu_B$ for a loop result from an assumption of 10 μm as a realistic diameter of a loop in a granular sample and an assumption that the circular current generates about half a flux quantum Φ_0, $LI/c \approx \Phi_0/2$. The existence of such large magnetic moments suggests that we interpret these systems as a new type of *superparamagnet*. A direct test of the existence of spontaneous orbital moments in ZFC samples, which is central to the model presented here, is, in principle, possible by scanning the surface with a magnetic microscope, e.g., scanning SQUID (superconducting quantum interference device) or Hall probes. Local variations in the magnetic field should be observed, although a ZFC sample has no net magnetic moment.

The nature of the large moments is essentially that of spontaneously created vortices with $\Phi \approx \Phi_0/2$ in a multiply connected system. Hence their properties are quite different from those of ordinary magnetic moments. The inversion of a moment here is connected with phase slip processes which are slow at low temperatures and, in many situations, energetically unfavorable. Therefore a moment (current) pattern, once generated, is rather inert to changes. In this respect, the environment of such half-quantized vortices is important. It was pointed out by Kusmartsev (1992a, 1992b) that neighboring frustrated loops in a network prefer to lock their fluxes in antiparallel directions. A sufficiently strong magnetic field may be able to align them by overcoming this interaction. Certainly such interaction effects lead to the reduction of the effective number of polarizable moments in very small fields. A recent numerical study of Josephson networks with π junctions confirms this view (Dominguez *et al.*, 1994). Interaction and network effects can also lead to properties related to glass behavior, in particular, if the concentration of frustrated loops is large. This aspect was recently investigated by Panyukov and Zaikin (1994), who explored the phase diagram of various possible states ranging from a weakly frustrated superconductor through glasslike phases to states where the percolation of superconductivity was suppressed due to strong frustration effects in the network. Following our discussion, we would locate the granular $Bi_2Sr_2CaCu_2O_8$ systems in the first rather than the last category. However, particular characteristics that would allow an unambiguous distinction among these categories have not yet been worked out.

VI. ARE HIGH-TEMPERATURE SUPERCONDUCTORS d-WAVE SUPERCONDUCTORS?

The discussion so far actually does not allow us to discriminate among the different origins proposed to cause intrinsic frustration, i.e., d-wave or other unconventional forms of superconductivity or π junctions arising from a very strong spin-flip channel. Recent progress in material preparation has given some indications, however. It has been found that samples with a strong Wohlleben effect consist of large grains (size ~ 10 μm) and are z-axis textured within small clusters, but have random mutual orientation in the basal plane (see Khomskii, 1994). This configuration provides, of course, optimal conditions for frustration in the case of a $d_{x^2-y^2}$-wave superconductor. In addition, the small clusters might be rather weakly connected to each other, a fact that would support our view of a system of independent entities (loops) that can be described in an ensemble model.

The mechanism of creating a frustrated superconductor based on unconventional superconductivity can provide a new scheme of testing the nature of the superconducting state beyond the study of granular systems. It is possible to create in a controlled way a frustrated system (e.g., a single loop), assuming a certain material has a superconducting order parameter with, for example, d-wave symmetry. There are essentially two types of measurements for testing whether a loop is frustrated. One method uses interference effects (SQUID) in order to detect a possible π-phase shift in a Josephson junction (Wollman *et al.*, 1993, 1994; Brawner and Ott, 1994; Iguchi and Wen, 1994; Mathai *et al.*, 1994). Another way is the observation of spontaneous currents in small frustrated loop structures (Tsuei *et al.*, 1994). The measurements performed so far consider exclusively $YBa_2Cu_3O_7$ and provide very strong support for the d-wave scenario, but we shall not go into that here, since they will be reviewed in an RMP Colloquium by Van Harlingen.

In closing we would like to comment on some other recent experiments, which have been interpreted as evidence against a d-wave symmetry. Two such experiments are the presence of a small but finite Josephson coupling between a conventional s-wave superconductor deposited on a c-axis film of $YBa_2Cu_3O_7$ (Sun *et al.*, 1994) and a finite Josephson coupling across interfaces between two $YBa_2Cu_3O_7$ regions with crystalline axis misoriented by 45° (Chaudhari and Lin, 1994). In both cases the application of Eq. (6) predicts $I_c \equiv 0$, contrary to the experimental results. The first point that we wish to make is that this vanishing by symmetry of I_c depends on strict d-wave symmetry, which in turn requires tetragonality. But $YBa_2Cu_3O_7$ superconductors have CuO chains oriented along one axis, and the magnitude of the superconducting order parameters differs substantially along directions in the ab plane parallel and perpendicular to the chains. As a consequence, the nodes of the order parameter do not lie along the $(1, \pm 1)$ directions in the plane, and there will be a finite overlap with an s-wave superconductor through Eq. (6). However, Sun *et al.* (1994) report observing similar effects on heavily twinned samples in which the chain axis rotates through 90° across a twin boundary, so that on the average the overlap with an s-wave superconductor vanishes. But the interface will be composed of regions with finite I_c whose sign varies. Millis (1994) has analyzed such problems in connection with the Chaudhari-Lin experiments. He showed that, if the magnitude of the Josephson coupling is strong but with spatially varying sign, then local vortices will appear to relieve the frustration. This class of problems is under active investigation and further progress can be expected.

By contrast, the frustration effects discussed here are more robust, since they do not depend on strict d-wave symmetry, only on the sign change of the order parameter when rotated through 90°. Therefore we believe that our conclusions regarding the unconventional nature of the superconductivity and the predominant $d_{x^2-y^2}$ character are on firm ground.

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