Quartet Formation at (100)/(110) Interfaces of *d*-Wave Superconductors

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Across a faceted (100)/(110) interface between two $d_{x^2-y^2}$ superconductors the structure of the superconducting order parameter leads to an alternating sign of the local Josephson coupling. Describing the Cooper pair motion along and across the interface by a one-dimensional boson lattice model, we show that a small attractive interaction between the bosons strongly enhances their binding at the interface. As a consequence, we propose that electrons tunnel in quartets across an interface with a staggered sequence of 0- and π-junction contacts. We connect this finding to the recently observed $h/4e$ oscillations in bicrystalline (100)/(110) SQUIDs of cuprate superconductors.

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The $d_{x^2-y^2}$ symmetry of the superconducting state in high-T_c cuprates causes a wealth of phenomena at surfaces and grain boundaries in these materials. In particular, the sign change of the order parameter around the Fermi surface is the origin of the most compelling experimental evidence for the d-wave nature of superconductivity in cuprates, as became manifest in the observation of half-flux quanta at grain boundaries on tricrystal substrates [1,2]. Already prior to these experiments it was recognized that conventional Josephson junctions (0 junctions) as well as junctions with a sign reversal of the Josephson coupling—which we henceforth call π junctions [3,4]—can be realized in contacts between cuprate superconductors depending on the mutual orientation of their crystal lattice and the attached fourfold symmetry of the order parameters.

At (100)/(110) interfaces or grain boundaries of cuprate superconductors the CuO_2 lattices meet at 45°, such that the $d_{x^2-y^2}$-order parameter lobes of the two superconductors point from a nodal towards an antinodal direction (see also Fig. 1). As described in Ref. [5], for a perfectly flat interface a net weak supercurrent would arise not from individual pair tunneling processes but rather from multiple Andreev reflections. Microscopic roughness, however, allows for local Cooper pair supercurrents across interface facets [6]; the current direction at each facet is thereby determined by the relative phase of the clover leaf lobes pointing towards the facet's surface. This special situation at (100)/(110) interfaces leads to a variety of effects like spontaneous supercurrent loops [6], locally time-reversal symmetry breaking phases [7,8], or anomalous field dependencies of the critical current density [9]. Yet another peculiar experimental observation was recently reported for SQUIDs with (100)/(110) interfaces, where the flux periodicity of the I-V characteristics was found to be $h/4e$, which is half a flux quantum [10]. An intriguing possibility for the microscopic origin of the $h/4e$ periodicity is that Cooper pairs *tunnel in pairs* (i.e., quartets). This would also naturally explain the occurrence of a $\sin 2\varphi$ component for the supercurrent.

In this Letter we propose a possible mechanism for pair binding or quartet formation in the interface. The alternating sequence of superconducting 0 or π junctions is modeled by a bosonic lattice Hamiltonian with a staggered sign for the hopping amplitude. We show that the special staggered structure of the kinetic energy term strongly enhances the tendency towards boson-pair formation in the presence of a weak attractive interaction. In a closed loop Aharonov-Bohm SQUID geometry of the underlying bo-

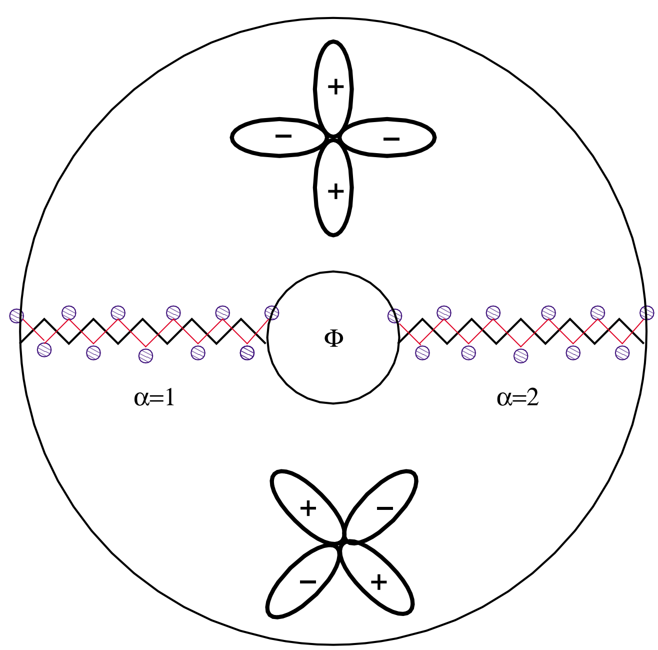

FIG. 1 (color online). SQUID geometry for two $d_{x^2-y^2}$ superconductors with two (100)/(110) interface contact regions (labeled $\alpha = 1, 2$) represented as bold sawtooth lines. The thin zigzag line, which crosses the interface sections and connects the circles, defines the chain for the model Hamiltonian Eq. (1).

son model, oscillations with a flux periodicity h/q are therefore expected, where q is the total charge of a boson pair. We interpret our results as a possible explanation of the observed $h/4e$ oscillations in high-T_c SQUIDS with (100)/(110) interfaces [10].

Josephson contacts or arrays and even granular superconductors are conveniently modeled by classical XY or extended quantum phase Hamiltonians [11]. These models can be derived from a purely bosonic description for the Cooper pair tunneling processes, if fluctuations in the bulk of the superconducting order parameter can be neglected [12]. By this means the boson kinetic energy translates directly into the Josephson coupling energy of the quantum phase Hamiltonian. The boson formulation allows for the advantage that in the hard-core limit an exact mapping to a spin-1/2 Hamiltonian is possible [13], so that preexisting knowledge for the spin model can be transferred to the boson problem.

We start from the disk-shape geometry shown in Fig. 1 and translate it into the Hamiltonian

$$H = \sum_{\alpha i}[-t(-1)^i a^+_{\alpha i+1}a_{\alpha i} - t' a^+_{\alpha i+2}a_{\alpha i} + \text{H.c.}] + H_\Phi + \sum_{\alpha i}[V a^+_{\alpha i}a_{\alpha i}a^+_{\alpha i+1}a_{\alpha i+1} + U(a^+_{\alpha i}a_{\alpha i} - 1)a^+_{\alpha i}a_{\alpha i}] \tag{1}$$

with boson creation (annihilation) operators $a^+_{\alpha i}$ ($a_{\alpha i}$) and $H_\Phi = -t_\perp \sum_j a^+_{1j}a_{2j}e^{i\Phi(-1)^j/2} + \text{H.c.}$ In Fig. 1 the (100)/(110) interface between the two d-wave superconductors is represented by a sawtooth line—assuming that the interface splits into a regular sequence of orthogonal facets. In a dc-SQUID setup a magnetic flux Φ may pass through the hole in the disk center, which separates the two interfaces labeled by $\alpha = 1, 2$. The circles mark chain sites, between which bosons (Cooper pairs) can hop with or without crossing the interface. The latter next-nearest-neighbor processes have the unique sign $-t'$ for their hopping amplitude, while the former have an amplitude with an alternating sign due to the 45° misalignment of the $d_{x^2-y^2}$-wave order parameter lobes on both sides of the interface. In Eq. (1) U and V denote the on-site and nearest-neighbor interaction strengths; in the following we explore, in particular, the effect of a weak attraction $V < 0$. The two interfaces $\alpha = 1, 2$ are connected by $t_\perp$, which contains the phase factor of the threading flux Φ. If Cooper pair binding occurs in the interface, oscillations with flux periodicity $h/4e$ are expected.

A phase change for the boson operators at every second pair of adjacent sites according to $b^+_{\alpha 4i} = -a^+_{\alpha 4i}$, $b^+_{\alpha 4i+1} = -a^+_{\alpha 4i+1}$, $b^+_{\alpha 4i+2} = a^+_{\alpha 4i+2}$, $b^+_{\alpha 4i+3} = a^+_{\alpha 4i+3}$ transforms the kinetic energy part of the Hamiltonian for each interface into

$$H_{\text{kin}} = \sum_{\alpha i}[-t b^+_{\alpha i+1}b_{\alpha i} + t' b^+_{\alpha i+2}b_{\alpha i} + \text{H.c.}]; \tag{2}$$

all other terms remain unchanged. Importantly, for a sequence of ordinary 0 junctions the second term in Eq. (2) appears with a negative sign.

We now focus on the physics in *one* interface and consider the hard-core limit $U \to \infty$, in which the boson problem maps onto a spin-1/2 model by means of the transformation [13]

$$S^+_i = (-1)^i b_i, \quad S^-_i = (-1)^i b^+_i, \quad S^z_i = \tfrac{1}{2} - b^+_i b_i. \tag{3}$$

The resulting spin Hamiltonian reads

$$H_S = \sum_i [J_1(S^x_i S^x_{i+1} + S^y_i S^y_{i+1} + \Delta S^z_i S^z_{i+1}) + J_2(S^x_i S^x_{i+2} + S^y_i S^y_{i+2})] \tag{4}$$

with the spin exchange coupling constants $J_1 = 2t$, $J_2 = 2t'$, and the anisotropy parameter $\Delta = V/2t < 0$. This model has been studied before in the context of metamagnetic transitions [14]. Results for magnon binding (bosons in the original language) and cluster formation tendencies were obtained in specific parameter regimes. Because of its relevance for the quartet formation, we start to discuss the binding problem using the original bosonic language.

The results of the spin-chain model lead to the conclusion that for $t' > 0$ the partial frustration of the kinetic energy favors the binding of bosons. For each total momentum K of a pair of bosons, the bound state can be written as

$$|\psi_K\rangle = \sum_{j>0} A_j \sum_n e^{-iK(n+j/2)} b^+_{n+j} b^+_n. \tag{5}$$

The Schrödinger equation for the bound state, $H_1|\psi_K\rangle = \lambda_K|\psi_K\rangle$, with the Hamiltonian H_1 of one interface can be solved with the following ansatz:

$$A_j = (\gamma_1)^j - (\gamma_2)^j, \tag{6}$$

where γ_1 and γ_2 are the two solutions of the equation

$$-2t\cos\frac{K}{2}\left(\frac{1}{\gamma} + \gamma\right) + 2t'\cos K\left(\frac{1}{\gamma^2} + \gamma^2\right) = \lambda_K, \tag{7}$$

with $|\gamma_{1,2}| < 1$; the eigenvalue λ_K has to satisfy

$$\lambda_K = V + 2t'\cos K(\gamma_1^2 + \gamma_2^2 + \gamma_1\gamma_2 + 1) - 2t\cos\frac{K}{2}(\gamma_1 + \gamma_2). \tag{8}$$

The typical size of the pair is $\xi = -1/\ln[\max(|\gamma_1|, |\gamma_2|)]$, which decreases with increasing V.

The critical interaction V_b for binding is determined by the condition that the minimum of λ_K with respect to all possible pair momenta K equals twice the minimum of the one-particle energy $E_k = -2t\cos k + 2t'\cos(2k)$. In our analysis we find that the optimum two-particle wave vector is $K_{\min} = 0$ for $t'/t = \alpha \le 1/(2\sqrt{2})$ in agreement with previous results for the spin-chain model [14], and

$K_{\min} = 2k_{\min}$ for $\alpha \geq 1/(2\sqrt{2})$. The results for the minimum attraction necessary for binding are summarized as follows with $\Delta_b = V_b/2t$:

$$\Delta_b = \frac{V_b}{2t} = -\frac{1+\sqrt{1-4\alpha}}{2} \quad \text{for } \alpha = t'/t \leq 1/4,$$
$$\Delta_b = -2\alpha \quad \text{for } 1/4 \leq \alpha \leq 1/(2\sqrt{2}), \tag{9}$$
$$\Delta_b = -\frac{1}{8\alpha}(\sqrt{16\alpha^2 - 1} + 1) \quad \text{for } \alpha \geq 1/(2\sqrt{2}).$$

Δ_b is represented by the full line in Fig. 2. A small to moderate attraction is enough to lead to pair binding for positive t', which represents the alternating sequence of 0 and π junctions, particularly for small hopping amplitudes t across the interface. Specifically, for the physically reasonable regime $t'/t > 1$ an attractive interaction of order t is sufficient for boson-pair formation; the energy scale for t is set by the Josephson coupling. Although ξ is very sensitive to V and diverges for $V \to V_b$, typical pair sizes for $V \sim t$ and $t' > 2t$ are an order of magnitude larger than the size of an individual facet.

It is known, particularly in models with strong correlations, that pairing competes with phase separation [15] and the tendency to bind in groups of more than two particles. To explore these possibilities, we have studied numerically the equivalent spin Hamiltonian Eq. (4) in a chain of $L = 16$ sites. For each total spin projection S_z, which translates into a number of flipped spins (i.e., magnons) $m = L/2 - S_z$ added to the fully polarized ferromagnetic ground state, we have calculated the ground-state energy $E(m)$. If the particles in the system (boson binding in the original language or magnons in the spin language) prefer to bind in groups of n particles, the quantity $e(m) = [E(m) - E(0)]/m$ is minimized for $m = n$. We argue that phase separation occurs, when the condition $E(m) > [mE(L) + (L-m)E(0)]/L$ holds for all m.

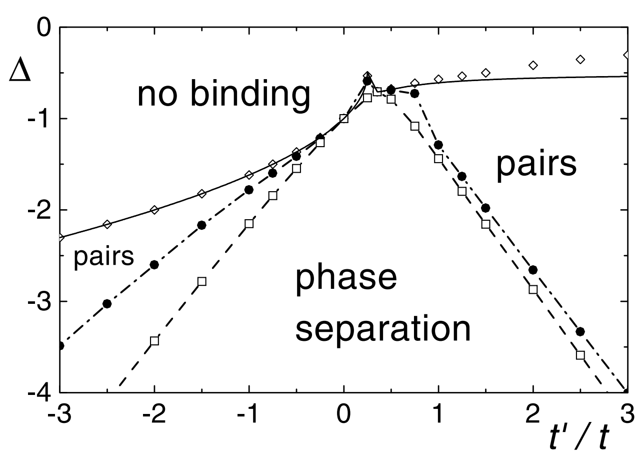

FIG. 2. Phase diagram of the interface model. The full line corresponds to the analytical solution Eq. (9). Open diamonds indicate the pair binding boundary, full circles correspond to the transition from $n = 2$ to $n > 2$, where n is the number of particles, which form bound composites; open squares denote the onset of phase separation. Here "pairs" means electronic quartets.

In Fig. 2 we show the resulting ground-state phase diagram. $\Delta = V/2t$ is the measure for the strength of the attractive interaction and $\alpha = t'/t$ is the ratio of hopping amplitudes for the motion along and across the interface. $\alpha > 0$ represents the alternating sequence of 0 and π junctions, while π junctions are absent for $\alpha < 0$. Four different regions are indicated in Fig. 2: the strong attraction regime, in which there is phase separation, a regime without binding, and two intermediate phases, in which the size of the optimum particle cluster is $n = 2$ or $n > 2$. In the latter region n increases in unit steps as the attraction increases, except for $t' > t$, where only even n appear. The asymmetry between positive and negative t' with respect to the stability of boson-pair binding is evident, underlining the importance of the existence of π junctions in the quartet formation. The numerical results for the border between $n = 1$ and $n = 2$ are in excellent agreement with the analytical results of Eq. (9)—except for the finite-size effects at $t' > t$.

We recall that our model analysis so far is restricted to the special geometry of a faceted (100)/(110) interface. The boson binding phenomenon in this geometry tells us that the tunneling supercurrent flows in pairs of Cooper pairs. A discussion remains in order about the possible origin of the assumed attractive interaction. We first note that the idea of quartet formation has been put forward before in nuclear physics [16]; proposals exist that four-particle condensation may occur as a phenomenon alternative or complementary to nucleon pairing. In cuprates, a natural explanation for the source of attraction between pairs is an extension of the mechanism for binding between electrons. We also note the proposal, that due to strong phase fluctuations cuprates may be close to an exotic phase with quartet condensation [17].

There is a wide consensus that the pairing mechanism in the cuprates is most likely of magnetic origin [15,18]. It is an experimental fact that short-range antiferromagnetic (AFM) correlations are present also in the superconducting state. A simple picture for the source of binding in a system with short-range AFM correlations is obtained by thinking in terms of static holes added to a Néel antiferromagnet on a square lattice: if two separated holes are added, they break 8 AFM bonds. If instead they are added as nearest neighbors, only 7 bonds are broken. This picture serves even as the basis for quantitative estimates of the superconducting critical temperature T_c [19]. Naturally, this argument can be extended, suggesting that the binding mechanism is active also for more than two particles. The actual size of the composite object should be determined by the competition with the kinetic energy, in a similar way as it happens in our bosonic model for a single interface. Along the lines of these arguments the attraction between nearest-neighbor pairs is of order $J/4$, where J is the superexchange interaction.

Four-spin ring exchange, which arises in strong-coupling expansions around the atomic limit [20] and is necessary for a quantitative description of the spin dynamics in undoped cuprates [21], also adds a second-order contribution to the quartet binding (two ring exchanges are required to restore the Néel background). If two pairs of nearest-neighbor holes are added far apart, the contribution of the ring exchange to the total energy is lost in 12 square plaquettes. If instead the pairs are next to each other, only between 9 and 11 plaquettes are affected depending on the specific configuration.

In the context of frustrated Josephson junction networks an alternative mechanism of Cooper pair binding, based on a Z_2 symmetry of a particular geometry was reported for Aharonov-Bohm cages [22]. In this case 0 and π junctions are realized on plaquettes, which are threaded by one flux quantum. In a one-dimensional arrangement these plaquettes are interconnected in a geometry, which leads to perfectly flat bands and thus to particle localization. Interactions may then lead to delocalized two-particle bound states or mobile charge $4e$ composite objects, which in closed loop SQUIDs should also give rise to an elementary $h/4e$ period of flux. A common feature of this proposal and the mechanism discussed in this Letter is, indeed, the important role of the partial frustration of the kinetic energy.

A typical value of the Josephson coupling is $\sim$100 K or higher, while the value of the superexchange is of the order of 1000 K. Therefore, we expect that the parameters of our model are approximately $|V| \sim 250$ K, $t' > t > 100$ K. As seen in Fig. 2, these parameters favor quartet formation at (100)/(110) interfaces, but not in more conventional interfaces with 0 junctions only. The experimental observation of $h/4e$ flux periodicities in (100)/(110) SQUIDS of high-T_c superconductors follows as a natural consequence. The half-flux quantum periodicity does, indeed, tell that electrons tunnel in quartets across the interface. The previous results of a suppressed $\sin\varphi$ component and a dominant $\sin 2\varphi$ component of the Josephson current at (100)/(110) interfaces [5,23,24] should not necessarily be considered as a more conventional alternative explanation of the experimental findings. Rather, the $\sin 2\varphi$ phase dependence of the supercurrent can be the macroscopic consequence of the underlying microscopic quartet tunneling processes. This is consistent with the results of a phase fluctuation model [17], where an exotic superconductor with quartets was found in the parameter region for which the expectation value of the first harmonic is suppressed. Whether quartets exist also in the bulk of cuprate superconductors remains an intriguing open question [25,26]. Similarly the relation and mutual influence of quartets and Andreev states in the interface remains yet to be explored.

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