Phase dependent differential thermopower of *s***-wave-superconductor–normal-metal–** *d***-wave-superconductor junctions: Pair-breaking effects and Gaussian fluctuations**

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We start with revisiting our previous results on thermoelectric response of *s*-wave-superconductor–normalmetal–*s*-wave-superconductor (*SNS*) configuration in a C-shaped $Bi_rPb_{1-r}Sr_2CaCu_2O_v$ sample in order to include strong fluctuation effects. Then, by appropriate generalization of the Ginzburg-Landau theory based on admixture of *s*-wave (*S*) and *d*-wave (*D*) superconductors, we consider a differential thermoelectric power ~TEP! of *s*-wave-superconductor–normal-metal–*d*-wave-superconductor (*SND*) junction. In addition to its strong dependence on the relative phase $\theta = \phi_s - \phi_d$ between the two superconductors, two major effects are shown to influence the behavior of the predicted TEP. One, based on the chemical imbalance at *SD* interface, results in a pronounced maximum of the TEP peak near $\theta = \pi/2$ (where the so-called $s + id$ mixed pairing state is formed) for two identical superconductors with $T_{cd} = T_{cs} = T_c$. Another effect, which should manifest itself at *SD* interface comprising an *s*-wave low- T_c superconductor and a *d*-wave high- T_c superconductor with $T_{cd} \neq T_{cs}$, predicts $S_p \propto T_{cd} - T_{cs}$ for the TEP peak value. The experimental conditions under which the predicted behavior of the induced differential TEP can be measured are discussed. [S0163-1829(99)09617-4]

I. INTRODUCTION

During the last few years the order-parameter symmetry has been one of the intensively debated issues in the field of high- T_c superconductivity (HTS). A number of experiments points to its $d_{x^2-y^2}$ -wave character.¹ Such an unconventional symmetry of the order parameter has also important implications for the Josephson physics because for a *d*-wave (*D*) superconductor the Josephson coupling is subject to an additional phase dependence caused by the internal phase structure of the wave function. The phase properties of the Josephson effect have been discussed within the framework of the generalized Ginzburg-Landau (GL) $(Ref. 2)$ as well as the tunneling Hamiltonian approach.³ It was found⁴ that the current-phase relationship depends on the mutual orientation of the two coupled superconductors and their interface. This property is the basis of all the phase sensitive experiments probing the order-parameter symmetry. In particular, it is possible to create multiply connected *d*-wave superconductors which generate half integer flux quanta as observed in experiments.⁵ Various interesting phenomena occur in interfaces of *d*-wave superconductors. For example, for an interface to a normal metal a bound state appears at zero energy giving rise to a zero-bias anomaly in the *I*-*V* characteristics of quasiparticle tunneling^{6,7} while in such an interface to an *s*-wave (*S*) superconductor the energy minimum corresponds to a Josephson phase different from 0 or π . By symmetry, a small *s*-wave component always coexists with a predominantly *d*-wave order parameter in an orthorhombic superconductor such as YBCO, and changes its sign across a twin boundary.8,9 Besides, the *s*-wave and *d*-wave order parameters can form a complex combination, the so-called $s \pm id$ state which is characterized by a local breakdown of time reversal symmetry T either near surfaces^{10–13} or near the twin boundaries represented by tetragonal regions with a reduced chemical potential.¹⁴ Both scenarios lead to a phase difference of $\pm \pi/2$, which corresponds to two degenerate states.^{15,16} Moreover, the relative phase oscillations between two condensates with different order parameter symmetries could manifest themselves through the specific collective excitations ("phasons").¹⁷

At the same time, a rather sensitive differential technique to probe sample inhomogeneity for temperatures just below T_c , where phase slippage events play an important role in transport characteristics has been proposed 18 and successfully applied¹⁹ for detecting small changes in thermoelectric power (TEP) of a specimen due to the deliberate insertion of a macroscopic *s*-wave-superconductor–normal-metal– *s*-wave-superconductor (*SNS*) junction made of a normalmetal layer *N*, used to force pair breaking of the superconducting component when it flows down the temperature gradient. Analysis of the thermoelectric effects provides reasonable estimates for such important physical parameters as the Fermi energy, Debye temperature, interlayer spacing, etc. In particular, a carrier-type dependent thermoelectric response of such a *SNS* configuration in a C-shaped $Bi_xPb_{1-x}Sr_2CaCu_2O_y$ sample has been registered and its temperature behavior below T_c has been explained within the framework of GL theory.19

In the present paper, we consider theoretically the behavior of induced TEP at *NS*, *ND*, and *SD* interfaces and discuss its possible implications for the above-mentioned type of experiments. The paper is organized as follows. In Sec. II we briefly review the experimental results for *SNS* configuration (with both holelike and electronlike carriers of the normal-metal *N* insert) and present a theoretical interpretation of these results, based on GL free-energy functional, both below and above T_c . The crucial role of the pairbreaking effects (described via the chemical balance $\Delta \mu$ between the quasiparticles and Cooper pairs) in understanding the observed phenomena is emphasized. In Sec. III, extending the early suggested^{11,14} GL theory of an admixture of

FIG. 1. Schematic view of the sample geometry with $S'NS''$ junction and contacts configuration. Here *S'* and *S''* stand for *s* wave- and/or *d* wave-type superconductor. The thermopowers S_R and S_L result from the thermal voltages detected by the contact pairs $4-5$ and $1-7$, respectively.

s-wave and *d*-wave superconductors to incorporate strong pair-breaking effects, we calculate the differential thermopower ΔS of *SND* configuration near T_c . The main theoretical result of this section is the prediction of a rather specific dependence of ΔS on relative phase shift $\theta = \phi_s$ $-\phi_d$ between the two superconductors. Two independent mechanisms contributing to the peak value $S_p(\theta)$ $= \Delta S(T_c, \theta)$ of the differential thermopower are discussed. One, based on the chemical balance between *S* and *D* superconductors at an SD interface (and responsible for chargerelated interference effect), is discussed in Sec. III A. It results in a pronounced maximum of the peak $S_n(\theta)$ near θ $=$ $\pi/2$ (the so-called *s* + *id* mixed pairing state) for two identical superconductors with $T_{cd} = T_{cs} = T_c$. This mechanism can be realized, e.g., in a *d*-wave orthorhombic sample (like YBCO) with twin boundaries which are represented by tetragonal regions of variable width, with a reduced chemical potential. Another mechanism (discussed in Sec. III B), which is active in the absence of the normal-metal layer, takes place when two different superconductors with T_{cd} $\neq T_{cs}$ are used to form an *SD* interface. This situation can be realized for an s -wave low- T_c superconductor (like Pb) and a *d*-wave high- T_c superconductor (like orthorhombic YBCO) and is shown to yield $S_p(\theta) \propto T_{cd} - T_{cs}$ for predicted TEP peak value.

II. *SNS* **CONFIGURATION REVISITED**

A. Experimental setup and main results

Before turning to the main subject of the present paper, let us briefly review the previous results concerning a carriertype dependent thermoelectric response of *SNS* configuration in a C-shaped $Bi_xPb_{1-x}Sr_2CaCu_2O_y$ sample (see Ref. 19 for details). The sample geometry used is sketched in Fig. 1, where the contact arrangement and the position of the sample with respect to the temperature gradient $\nabla_r T$ is shown as well. Two cuts are inserted at 90° to each other into a ringshaped superconducting sample. The first cut lies parallel to the applied temperature gradient serving to define a vertical symmetry axis. The second cut lies in the middle of the right wing, normal to the symmetry axis, separating two similar superconductors with $S' = S'' = S$ or *D* and completely interrupting the passage of supercurrents in this wing. The pas-

FIG. 2. The temperature dependence of the observed differential thermopower of *SNS* configuration defined by Eq. (1). The upper (lower) part of the picture refers to In (Ag) normal-metal insert in the right wing (see Fig. 1). The asymmetric curved triangle shapes are approximated by linear shapes produced by the linear fit to the data points (see the text for details).

sage of any normal component of current density is made possible by filling up the cut with a normal metal *N*. The carrier type of the normal-metal insert *N* was chosen to be either an electronlike N_e (silver) or holelike N_h (indium). Thermal voltages resulting from the same temperature gradient acting on both continuous and normal-metal-filled halves of the sample were detected as a function of temperature around T_c . The measured difference between the thermopowers of the two halves $\Delta S = S_R - S_L$ was found to approximately follow the linear dependence

$$
\Delta S(T) \approx S_p \pm B^{\pm} (T_c - T), \tag{1}
$$

with slopes B^- and B^+ defined for $T < T_c$ and $T > T_c$, respectively. Here $S_p = \Delta S(T_c)$ is the peak value of $\Delta S(T)$ at $T=T_c$. The best fit of the experimental data with the above equation yields the following values for silver (Ag) and indium (In) inserts, respectively (see Fig. 2): (i) $S_p(Ag) = -0.26 \pm 0.01 \mu \text{V/K}, \quad B^-(Ag) = -0.16 \pm 0.1$ μ V/K², $B^{-}(Ag)/B^{+}(Ag)=1.9\pm0.1;$ (ii) $S_p(In)=0.83$ $\pm 0.01 \mu$ V/K, $B^{-}(\text{In})=0.17\pm0.1 \mu$ V/K², $B^{-}(\text{In})/B^{+}(\text{In})$ $=2.1\pm0.1.$

B. Interpretation

It is important to mention that, unlike the case of mixed *SND* configuration (considered in Sec. III), the suggested interpretation of the current experimental results for *SNS* configuration does not involve the phase of the order parameter and hence is not sensitive (at least near T_c) to the pairing symmetry of the two superconductors *S'* and *S''*. To describe the observed behavior of the differential TEP both below and above T_c , we can roughly present it in a two-term contribution form:19,20

 (9)

$$
\Delta S(T) = \Delta S_{av}(T) + \Delta S_{fl}(T),\tag{2}
$$

where the average term $\Delta S_{av}(T)$ is assumed to be nonzero only below T_c (since in the normal state the TEP of HTS is found to be very small^{21,22}) while the fluctuation term $\Delta S_f(T)$ should contribute to the observable $\Delta S(T)$ for *T* $\simeq T_c$. In what follows, we shall discuss these two contributions separately within a mean-field theory approximation.

1. Mean value of the differential thermopower: $\Delta S_{av}(T)$

Assuming that the net result of the normal-metal insert is to break up Cooper pairs that flow toward the hotter end of the sample and to produce holelike (In) or electronlike (Ag) quasiparticles, we can write the difference in the generalized GL free-energy functional $\Delta \mathcal{G}$ of the right and left halves of the C-shaped sample as

$$
\Delta \mathcal{G}[\psi] = \Delta \mathcal{F}[\psi] + \Delta \mu |\psi|^2, \tag{3}
$$

where

$$
\Delta \mathcal{F}[\psi] \equiv \mathcal{F}_R - \mathcal{F}_L = a(T) |\psi|^2 + \frac{\beta}{2} |\psi|^4 \tag{4}
$$

and

$$
\Delta \mu \equiv \mu_R - \mu_L. \tag{5}
$$

Here $\psi = |\psi|e^{i\phi}$ is the superconducting order parameter, $\Delta \mu$ accounts for the chemical balance between quasiparticles and Cooper pairs; $a(T) = \alpha(T - T_c)$ and the GL parameters α and β are related to the critical temperature T_c , zerotemperature BCS gap $\Delta_0 = 1.76 k_B T_c$, the in-plane Fermi energy $E_F^{ab} = p_F^2 / m_{ab}^*$, and the total particle number density *n* as $\alpha = \beta n / 2T_c = (4\Delta_0 k_B / E_F^{ab})(m_e / m_{ab}^*)$. In fact, in layered superconductors, $\Delta \mu \simeq E_F^c \simeq J_c^2/E_F^{ab}$, where $E_F^c = E_F^{ab}/\gamma_m^2$ is the out-of-plane Fermi energy and J_c the interlayer coupling energy within the Lawrence-Doniach model ($\gamma_m = m_c^*/m_{ab}^*$ is the mass anisotropy ratio, and $m_{ab}^* \approx 8 m_e$ for this material).

As usual, the equilibrium state of such a system is determined from the minimum-energy condition $\partial \mathcal{G}/\partial |\psi|=0$ which yields for $T < T_c$

$$
|\psi_0|^2 = \frac{\alpha (T_c - T) - \Delta \mu}{\beta}.
$$
 (6)

Substituting $|\psi_0|^2$ into Eq. (3) we obtain for the average free-energy density

$$
\Delta \Omega(T) \equiv \Delta \mathcal{G}[\psi_0] = -\frac{[\alpha (T_c - T) - \Delta \mu]^2}{2\beta}.
$$
 (7)

In turn, the difference of thermopowers $\Delta S(T)$ can be related to the corresponding difference of transport entropies $\Delta \sigma = -\partial \Delta \Omega / \partial T$ as $\Delta S(T) = \Delta \sigma(T)/nq$, where *q* is the charge of the quasiparticles. Thus finally the mean value of thermopower associated with a pair-breaking event reads (below T_c)

$$
\Delta S_{av}(T) = S_{p,av} - B_{av}(T_c - T),\tag{8}
$$

and

$$
B_{av} = \frac{\Delta_0 k_B}{2qE_F^{ab}T_c}.
$$
\n(10)

Before we proceed to compare the above theoretical findings with the available experimental data (see Fig. 2), we first have to estimate the corresponding fluctuation contributions to the observable TEP difference, both above and below T_c .

 $S_{p,av} = \frac{\Delta \mu}{2qT_c}$

2. Mean-field Gaussian fluctuations of the differential thermopower: $\Delta S_{fl}(T)$

The influence of superconducting fluctuations on transport properties of HTS (including TEP and electrical conductivity) has been extensively studied for the past few years (see, e.g., Refs. $23-32$ and further references therein). In particular, it was found that the fluctuation-induced behavior may extend to temperatures more than 10 K higher than the respective T_c . Let us consider now the region near T_c and discuss the Gaussian fluctuations of the pair-breaking induced differential TEP $\Delta S_{fl}(T)$. Recall that according to the theory of Gaussian fluctuations, 33 the fluctuations of any observable, which is conjugated to the order parameter ψ (such as heat capacity, susceptibility, etc.) can be presented in terms of the statistical average of the square of the fluctuation amplitude $\langle (\delta \psi)^2 \rangle$ with $\delta \psi = \psi - \psi_0$. Then the differential TEP above (+) and below (-) T_c have the form of

$$
\Delta S_{fl}^{\pm}(T) = A \langle (\delta \psi)^2 \rangle_{\pm}, \qquad (11)
$$

where

$$
\langle (\delta \psi)^2 \rangle = \frac{1}{Z} \int d|\psi| (\delta \psi)^2 e^{-\Sigma[\psi]}.
$$
 (12)

Here $Z = \int d|\psi| e^{-\Sigma[\psi]}$ is the partition function with $\Sigma[\psi]$ $\equiv (\Delta \mathcal{G}[\psi] - \Delta \mathcal{G}[\psi_0])/k_B T$. *A* is a coefficient to be defined below. Expanding the free-energy density functional $\Delta \mathcal{G}[\psi]$

$$
\Delta \mathcal{G}[\psi] \approx \Delta \mathcal{G}[\psi_0] + \frac{1}{2} \left[\frac{\partial^2 \Delta \mathcal{G}}{\partial \psi^2} \right]_{|\psi| = |\psi_0|} (\delta \psi)^2, \quad (13)
$$

around the mean value of the order parameter ψ_0 , which is defined as a stable solution of equation $\partial \mathcal{G}/\partial |\psi|=0$ we can explicitly calculate the Gaussian integrals. Due to the fact that $|\psi_0|^2$ is given by Eq. (6) below T_c and vanishes at T $\geq T_c$, we obtain finally

$$
\Delta S_{fl}^-(T) = \frac{Ak_BT_c}{4\alpha(T_c - T) - 4\Delta\mu}, \quad T \le T_c,
$$
 (14)

and

$$
\Delta S_{fl}^+(T) = \frac{Ak_BT_c}{2\alpha(T - T_c) + 2\Delta\mu}, \quad T \ge T_c. \tag{15}
$$

with

As we shall see below, for the experimental range of parameters under discussion, $\Delta \mu (E_F / \Delta_0) \gg k_B |T_c - T|$. Hence, with a good accuracy we can approximate Eqs. (14) and (15) as follows:

$$
\Delta S_{fl}^{\pm}(T) \simeq S_{p,fl}^{\pm} \pm B_{fl}^{\pm}(T_c - T), \tag{16}
$$

where

$$
S_{p,fl}^- = -\frac{Ak_B T_c}{4\Delta \mu}, \quad B_{fl}^- = \frac{Ak_B T_c \alpha}{(2\Delta \mu)^2}, \quad (17)
$$

and

$$
S_{p,fl}^+ = -2S_{p,fl}^-, \quad B_{fl}^+ = 2B_{fl}^-.
$$
 (18)

Furthermore, it is quite reasonable to assume that $S_p^- = S_p^+$ $\equiv S_p$, where $S_p = S_{p,av} + S_{p,fl}$ and $S_p^+ = S_{p,fl}^+$. Then the above equations bring about the following explicit expression for the constant parameter *A*, namely $=$ $(4\Delta \mu/3k_BT_c)S_{p,av}$. This in turn leads to the following expressions for the fluctuation and total contributions to peaks and slopes through their average counterparts [see Eqs. (9) and (10) : $S_{p,fl}^+ = S_p = (2/3)S_{p,av}$, $S_{p,fl}^- = -(1/3)S_{p,av}$, B_{fl}^- = (1/3) B_{av} , B_{fl}^+ = (2/3) B_{av} , B^- = B_{av}^- + B_{fl}^- = (4/3) B_{av} , and $B^+=B_f^+ = (2/3)B_{av}$. Thus, in agreement with the observations, $B^{-}/B^{+}=2$ independent of the carrier type of the normal-metal insert. Let us proceed to discuss separately the case of In and Ag inserts.

(a) $N=$ In (holelike metal insert). In this case, the principal carriers are holes, therefore $q=+e$. Let the holelike quasiparticle chemical potential (measured relative to the Fermi level of the free-hole gas) be positive, then $\mu_q = +\mu$ and $\Delta \mu = \mu + 2\mu = 3\mu$ (two holes come from condensate and one hole is brought by normal metal). Therefore for this case Eq. (1) takes the form

$$
\Delta S^h(T) = S_p(\text{In}) \pm B^{\pm}(\text{In})(T_c - T),\tag{19}
$$

where

$$
S_p(\text{In}) = \left(\frac{k_B}{e}\right) \left(\frac{\mu}{k_B T_c}\right),\tag{20}
$$

and

$$
B^{-}(\text{In}) = \frac{2\Delta_0 k_B}{3eE_F^{ab}T_c}, \quad B^{+}(\text{In}) = \frac{1}{2}B^{-}(\text{In}).
$$
 (21)

(b) $N = Ag$ (electronlike metal insert). The principal carriers in this case are electrons, therefore $q=-e$. The electronlike quasiparticle chemical potential $\mu_q = -\mu$. Then $\Delta \mu = -\mu + 2\mu = \mu$ (plus one electron means minus one hole). For this case Eq. (1) takes the form

$$
\Delta S^{e}(T) = S_p(\text{Ag}) \pm B^{\pm}(\text{Ag})(T_c - T), \tag{22}
$$

where

$$
S_p(\text{Ag}) = -\left(\frac{k_B}{e}\right)\left(\frac{\mu}{3k_B T_c}\right),\tag{23}
$$

$$
B^{-}(Ag) = -\frac{2\Delta_0 k_B}{3eE_F^{ab}T_c}, \quad B^{+}(Ag) = \frac{1}{2}B^{-}(Ag). \quad (24)
$$

By comparing the obtained theoretical expressions with the above-mentioned experimental findings for the slopes B^{\pm} and the peak S_p values for the two normal-metal inserts (see Fig. 2), we can estimate the order of magnitude of the inplane Fermi energy E_F^{ab} and interlayer coupling energy J_c . The result is: $E_F^{ab} \approx 0.16$ eV and $J_c \approx 4$ meV, in reasonable agreement with the other known estimates of these parameters. 30 In turn, using these parameters (along with the critical temperature), we find that $\bar{J}_c^2 / k_B \Delta_0 \simeq 100$ K. This justifies the use of the linearized Eq. (16) for the temperature interval $|T_c-T| \le 100$ K. As is seen in Fig. 2, the observed differential TEP practically disappears already for $|T_c-T|$ ≥ 10 K. Moreover, as it follows from Eqs. (20) and (23), the calculated ratio for peaks $|S_p(\text{In})/S_p(\text{Ag})|=3$ is very close to the corresponding experimental value $|S_p^{exp}(\text{In})/S_p^{exp}(\text{Ag})|=3.2\pm0.2$ observed by Gridin *et al.*¹⁹ Finally, as it follows from the above analysis, the calculated slopes B^- below T_c for the two metal inserts coincide with each other, namely $B^{-}(\text{In})=-B^{-}(Ag)$, and are twice their counterparts above T_c , i.e., B^- (In)=2*B*⁺(In) and *B*⁻(Ag) $=2B^+(Ag)$, in a good agreement with the observations. It is worthwhile to note that a very similar behavior of the induced TEP (including peaks and slopes both above and below T_c) has been observed in strong applied magnetic fields.²⁰ In fact, replacing the chemical potentials difference $\Delta \mu$ (responsible for pair-breaking effects in *SNS* junction) in the above equations by $\mu_B H$ term (where μ_B is the Bohr magneton and H the applied magnetic field) we recover most of the formulas presented in Ref. 20 where magneto-TEP of Bi₂Sr₂CaCu₂O_y superconductors was studied.

III. *SND* **CONFIGURATION: PREDICTION**

Since Eqs. (3) – (5) do not depend on the phase of the order parameter, they will preserve their form for a *DND* junction (created by two *d*-wave superconductors, $S' = S''$ $=$ *D*, see Fig. 1) as well, bringing about the results similar to that given by Eqs. $(8)–(10)$. It means that the experimental method under discussion (and its interpretation) cannot be used to tell *SNS* and *DND* configurations apart, at least for temperatures close to T_c . As for low enough temperatures, the situation may change drastically due to a markedly different behavior of *s*-wave and *d*-wave order parameters at $T \ll T_c$ (where the node structure begins to play an important role). As we shall show below, this method, however, is quite sensitive to the mixed *SND* configuration (when *S'* $=$ *S* has an *s*-wave symmetry while $S'' = D$ is of a *d*-wave symmetry type, see Fig. 1) predicting rather specific relative phase $(\theta = \phi_s - \phi_d)$ dependencies of both the slope $B(\theta)$ and peak $S_p(\theta)$ of the observable thermopower difference $\Delta S(T,\theta)$.

Following Feder et al.,¹⁴ who incorporated chemical potential effects near twin boundaries into the approach suggested by Sigrist *et al.*, ¹¹ we can represent the generalized GL free-energy functional $\Delta \mathcal{G}$ for *SND* configuration of the C-shaped sample in the following form:

and

$$
\Delta \mathcal{G}[\psi_s, \psi_d] = \Delta \mathcal{G}[\psi_s] + \Delta \mathcal{G}[\psi_d] + \Delta \mathcal{G}_{int}, \qquad (25)
$$

where

$$
\Delta \mathcal{G}[\psi_s] = A_s(T) |\psi_s|^2 + \frac{\beta_s}{2} |\psi_s|^4, \tag{26}
$$

$$
\Delta \mathcal{G}[\psi_d] = A_d(T) |\psi_d|^2 + \frac{\beta_d}{2} |\psi_d|^4, \tag{27}
$$

and

$$
\Delta \mathcal{G}_{int} = \gamma_1 |\psi_s|^2 |\psi_d|^2 + \frac{\gamma_2}{2} (\psi_s^{*2} \psi_d^2 + \psi_s^2 \psi_d^{*2})
$$

- 2 \delta_1 |\psi_s| |\psi_d| - \delta_2 (\psi_s^* \psi_d + \psi_s \psi_d^*). (28)

Here $\psi_n = |\psi_n| e^{i\phi_n}$ is the *n*-wave order parameter (*n* $S = \{s, d\}$; $A_n(T) = a_n(T) + \Delta \mu_n$ where $a_n(T) = \alpha_n(T - T_{cn})$ with the corresponding parameters α_n , β_n , T_{cn} , and $\Delta \mu_n$ for *s*-wave and *d*-wave symmetries.

An equilibrium state of such a mixed system is determined from the minimum-energy conditions $\partial \mathcal{G}/\partial |\psi_s| = 0$ and $\partial \mathcal{G}/\partial |\psi_d|=0$ which result in the following system of equations for the two equilibrium order parameters ψ_{s0} and ψ_{d0}

$$
A_{s}(T)|\psi_{s0}| + \beta_{s}|\psi_{s0}|^{3} + \Gamma(\theta)|\psi_{s0}||\psi_{d0}|^{2} = \Delta(\theta)|\psi_{d0}|,
$$
\n(29)
\n
$$
A_{d}(T)|\psi_{d0}| + \beta_{d}|\psi_{d0}|^{3} + \Gamma(\theta)|\psi_{d0}||\psi_{s0}|^{2} = \Delta(\theta)|\psi_{s0}|,
$$
\n(30)

where we introduced relative phase $\theta = \phi_s - \phi_d$ dependent parameters

$$
\Gamma(\theta) = \gamma_1 + \gamma_2 \cos 2\theta, \tag{31}
$$

$$
\Delta(\theta) = \delta_1 + \delta_2 \cos \theta.
$$

Notice that unlike chemical potentials difference $\Delta \mu_n$ (which is responsible for pair-breaking effects in *SND* junction due to the normal-metal insert), the interference terms $\delta_{1,2}$ describe the chemical balance between *s*-wave and *d*-wave superconductors at *SD* interface in the absence of a normal-metal layer. Therefore the effects due to $\Delta \mu_n \neq 0$ should be distinguished from the interference effects due to $\Delta(\theta) \neq 0$. The latters are generically close to the interference effects between the two condensates and are described by the $\Gamma(\theta)$ term. Notice also that the $\Delta(\theta)$ term favors $\theta = l\pi$ (*l* integer), while the $\Gamma(\theta)$ term favors $\theta = n\pi/2$ ($n=1,3$, $5 \cdots$) which corresponds to a *T*-violating phase.¹⁴ In principle, we can resolve the above system [given by Eqs. (29) – (31)] and find ψ_{n0} for arbitrary set of parameters α_n , β_n , and T_{cn} . For simplicity, in what follows we restrict our consideration to the two limiting cases which are of the most importance for potential applications.

A. Twin boundaries in orthorhombic *d***-wave superconductors**

1. Mean value of the differential thermopower: $\Delta S_{av}(T,\theta)$

First, let us consider the case of similar superconductors comprising the *SND* junction with $|\psi_{s0}| = |\psi_{d0}| = |\psi_0|$, α_s $= \alpha_d \equiv \alpha$, $\beta_s = \beta_d \equiv \beta$, $\Delta \mu_s = \Delta \mu_d \equiv \Delta \mu$, and $T_{cs} = T_{cd}$ $\equiv T_c$. This situation is realized, for example, in a *d*-wave orthorhombic sample (like YBCO) with twin boundaries which are represented by tetragonal regions of variable width, with a reduced chemical potential.¹⁴ In this particular case, Eqs. (29) and (30) yield for $T < T_c$

$$
|\psi_0|^2 = \frac{\alpha (T_c - T) - \Delta \mu(\theta)}{\beta + \Gamma(\theta)},
$$
\n(32)

where $\Delta \mu(\theta) \equiv \Delta \mu - \Delta(\theta)$. After substituting the thus found $|\psi_0|$ into Eq. (25) we obtain for the generalized equilibrium free-energy density

$$
\Delta \Omega(T, \theta) = \Delta \mathcal{G}[\psi_0] = -\frac{\left[\alpha (T_c - T) - \Delta \mu(\theta)\right]^2}{\beta + \Gamma(\theta)} \quad (33)
$$

which in turn results in the following expression for the mean-field value of the thermopower difference in a C-shaped sample with *SND* junction (see Fig. 1):

$$
\Delta S_{av}(T,\theta) = S_{p,av}(\theta) - B_{av}(\theta)(T_c - T),\tag{34}
$$

where

$$
S_{p,av}(\theta) = \frac{\beta}{qT_c} \left[\frac{\Delta \mu(\theta)}{\beta + \Gamma(\theta)} \right],\tag{35}
$$

and

$$
B_{av}(\theta) = \frac{\alpha}{qT_c} \bigg[\frac{\beta}{\beta + \Gamma(\theta)} \bigg].
$$
 (36)

2. Mean-field Gaussian fluctuations of the differential thermopower: $\Delta S_{fl}(T,\theta)$

Following the lines of Sec. II, we can present the fluctuation contribution to the differential TEP above $(+)$ and below $(-)T_c$ as

$$
\Delta S_{fl}^{\pm}(T,\theta) = A(\theta) \left[\langle (\delta \psi_s)^2 \rangle_{\pm} + \langle (\delta \psi_d)^2 \rangle_{\pm} + 2 \langle \delta \psi_s \delta \psi_d \rangle_{\pm} \right],
$$
\n(37)

where, e.g.,

$$
\langle (\delta \psi_s)^2 \rangle = \frac{1}{Z} \int d|\psi_s| \int d|\psi_d| (\delta \psi_s)^2 e^{-\Sigma[\psi_s, \psi_d]}.
$$
 (38)

Here $Z = \int d|\psi_s| \int d|\psi_d| e^{-\Sigma[\psi_s, \psi_d]}$ is the corresponding partition function with $\Sigma[\psi_s, \psi_d] = {\Delta \mathcal{G}[\psi_s, \psi_d]}$ $\Sigma[\psi_s, \psi_d] \equiv {\Delta \mathcal{G}[\psi_s, \psi_d]}$ $-\Delta \mathcal{G}[\psi_{s0}, \psi_{d0}]}/k_B T$. *A*(θ) is a coefficient to be fixed later. Expanding the free-energy density functional $\Delta \mathcal{G}[\psi_s, \psi_d],$

$$
\Delta \mathcal{G}[\psi_s, \psi_d] \approx \Delta \mathcal{G}[\psi_{s0}, \psi_{d0}]
$$

+
$$
\frac{1}{2} \left\{ \left[\frac{\partial^2 \Delta \mathcal{G}}{\partial \psi_s^2} \right]_{|\psi_s| = |\psi_{s0}|} (\delta \psi_s)^2 + \left[\frac{\partial^2 \Delta \mathcal{G}}{\partial \psi_d^2} \right]_{|\psi_d| = |\psi_{d0}|} (\delta \psi_d)^2 \right\}
$$

+
$$
\left[\frac{\partial^2 \Delta \mathcal{G}}{\partial \psi_s \partial \psi_d} \right]_{|\psi_n| = |\psi_{n0}|} (\delta \psi_s \delta \psi_d), \quad (39)
$$

around the mean values of the order parameters ψ_{n0} , which are defined as stable solutions of equations $\partial \mathcal{G}/\partial |\psi_n|=0$ we can explicitly calculate the Gaussian integrals to obtain

$$
\langle (\delta \psi_s)^2 \rangle_{-} = \langle (\delta \psi_d)^2 \rangle_{-} = \frac{k_B T_c \beta}{4(\beta - \Gamma) [\alpha (T_c - T) - \Delta \mu(\theta)]},\tag{40}
$$

$$
\langle \delta \psi_s \delta \psi_d \rangle_{-} = -\frac{k_B T_c \Gamma}{4(\beta - \Gamma) [\alpha (T_c - T) - \Delta \mu(\theta)]} \quad (41)
$$

and

$$
\langle (\delta \psi_s)^2 \rangle_+ = \langle (\delta \psi_d)^2 \rangle_+ = \frac{k_B T_c}{2[\alpha (T - T_c) + \Delta \mu(\theta)]},
$$
\n(42)

$$
\langle \delta \psi_s \delta \psi_d \rangle_+ = 0, \tag{43}
$$

for the order parameters fluctuations below and above T_c , respectively. In principle, the above expressions completely determine the fluctuation contribution to the seeking TEP of *SND* contact in the presence of strong *N*-metal induced pair-breaking effects. However, in order to compare it with the earlier calculated mean-field values, let us assume that $[\Delta \mu(\theta)] (E_F / \Delta_0) \gg k_B |T_c - T|$. Then, with a good accuracy we can approximate Eqs. (40) – (42) as follows:

$$
\Delta S_{fl}^{\pm}(T,\theta) \simeq S_{p,fl}^{\pm}(\theta) \pm B_{fl}^{\pm}(\theta)(T_c - T), \tag{44}
$$

where

$$
S_{p,fl}^-(\theta) = -\frac{Ak_BT_c}{2\Delta\mu(\theta)},\tag{45}
$$

$$
B_{fl}^-(\theta) = \frac{Ak_BT_c\alpha}{2[\Delta\mu(\theta)]^2},\tag{46}
$$

and

$$
S_{p,fl}^+(\theta) = -2S_{p,fl}^-(\theta), \quad B_{fl}^+(\theta) = 2B_{fl}^-(\theta). \tag{47}
$$

Again, requiring that $S_p^{\dagger}(\theta) = S_p^+(\theta) \equiv S_p(\theta)$, where S_p^{\dagger} $= S_{p,av} + S_{p,fl}^-$ and $S_p^+ = S_{p,fl}^+$, the above equations give

$$
A(\theta) = \frac{2\beta}{3qk_BT_c^2} \frac{[\Delta\mu(\theta)]^2}{[\beta + \Gamma(\theta)]}
$$
(48)

for the above-introduced parameter [see Eq. (37)]. This in turn leads to the following expressions for the fluctuation and total contributions to peaks and slopes through their average counterparts (cf. Sec. II): $S_{p,fl}^+ = S_p = (2/3)S_{p,av}$, $S_{p,fl}^- =$ $(1/3)S_{p,av}$, $B_{fl}^-=(1/3)B_{av}$, $B_{fl}^+=(2/3)B_{av}$, $B_{fl}^-B_{av}$ $+ B_{fl}^- = (4/3)B_{av}$, and $B^+ = B_{fl}^+ = (2/3)B_{av}$. Thus the ratio $B^{-}(\theta)/B^{+}(\theta)=2$ remains universal showing no dependence on the relative phase difference θ . As expected, completely neglecting the interference terms (when both $\Gamma(\theta) \rightarrow 0$ and $\Delta(\theta) \rightarrow 0$) we recover all the results of Sec. II for two independent order parameters. Finally, the differential TEP of *SND* junction consisting of two superconductors with similar critical parameters but markedly different pairing symme-

FIG. 3. Predicted phase dependent thermopower response of *SND* configuration in a C-shaped sample (see Fig. 1). Solid and dashed lines depict, respectively, the relative phase θ dependence of the normalized slope $B^{-}(\theta)/B^{-}(0)$ and peak value $S_p(\theta)/S_p(0)$ of the induced thermopower difference, according to Eqs. (50) and $(51).$

tries (like in a *d*-wave orthorhombic YBCO with *s*-wave tetragonal twin boundaries) reads

$$
\Delta S(T,\theta) = S_p(\theta) \pm B^{\pm}(\theta)(T_c - T), \tag{49}
$$

with

$$
S_p(\theta) = \frac{2\beta \delta_2}{3qT_c \gamma_2} \left(\frac{\tilde{\delta} + \cos \theta}{\tilde{\gamma} + \cos 2\theta} \right),
$$
 (50)

and

$$
B^{-}(\theta) = 2B^{+}(\theta) = \frac{4\alpha}{3qT_{c}\gamma_{2}} \left(\frac{\beta}{\tilde{\gamma} + \cos 2\theta}\right). \tag{51}
$$

Here $\tilde{\gamma} = (\beta + \gamma_1)/\gamma_2$ and $\tilde{\delta} = (\Delta \mu + \delta_1)/\delta_2$. Figure 3 shows the predicted θ -dependent behavior of the normalized slope $B^{-}(\theta)/B^{-}(0)$ (solid line) and the peak $S_p(\theta)/S_p(0)$ (dashed line) of the *SND*-induced thermopower difference $\Delta S(T,\theta)$ just below T_c , for $\tilde{\gamma} = \tilde{\delta} = 2$. As is seen, both the slope and the peak exhibit a maximum for the $s + id$ state (at θ $\sigma = \frac{\pi}{2}$ and a minimum for the *s*-*d* state (at $\theta = \pi$). Such sharp dependencies suggest quite an optimistic possibility to observe the above-predicted behavior of the induced thermopower, using the sample geometry and experimental technique described in Sec. II. Besides, when the pair-breaking effects (due to the normal-metal insert in *SND* junction) are negligible (so that $\Delta \mu$ =0), Eqs. (49)–(51) will describe the differential TEP at the *SD* interface where the pair-breaking interference effects [governed by the $\Delta(\theta)$ term] will dominate its peak behavior. This situation would allow one to get a more detailed information about the mixed pairing states and the introduced phenomenological parameters $\gamma_{1,2}$ and $\delta_{1,2}$.

B. Low- T_c *s*-wave superconductor and high- T_c *d*-wave **superconductor**

Let us turn now to another limiting case and consider an *SD* interface formed by two different superconductors (with $|\psi_{s0}| \neq |\psi_{d0}|$, $\alpha_s \neq \alpha_d$, $\beta_s \neq \beta_d$, and $T_{cs} \neq T_{cd}$) in the absence of a normal-metal layer (which is responsible for pairbreaking effects). We shall also assume that the chargerelated interference effects [governed by the $\Delta(\theta)$ term] are rather small and can be safely neglected. Thus in this section we consider the situation when $\Delta \mu_n = 0$ and $\Delta(\theta) = 0$. Such a situation can be realized for an s -wave low- T_c superconductor (like Pb) and a d -wave high- T_c superconductor (like orthorhombic YBCO).^{1,9} In fact, the solution for this particular case is well-known. It has been discussed by Sigrist $et al.¹¹$ in a somewhat different context. In principle, we can obtain both an average and fluctuation contributions to the resulting TEP for this case, following the recipes of the previous section. And in particular, it can be shown that the fluctuation contribution is still governed by expressions similar to the ones given by Eqs. $(40)–(43)$ with an evident change in parameters, $\alpha \rightarrow \alpha_n$ and $\beta \rightarrow \beta_n$ for *s*- and *d*-wave superconductors. Since, however, the correponding expressions are rather cumbersome, in what follows we restrict our analysis with the average values of the induced TEP only.

Assuming $T_{cs} < T_{cd}$, two temperature regions should be distinguished:

(a) $T \leq T^*(\theta)$. In this region, the corresponding expressions for the equilibrium order parameters read [see Eqs. (29)] and (30)

$$
|\psi_{s0}|^2 = \frac{\beta_d a_s(T) - \Gamma(\theta) a_d(T)}{\Gamma^2(\theta) - \beta_s \beta_d},
$$
\n(52)

and

$$
|\psi_{d0}|^2 = \frac{\beta_s a_d(T) - \Gamma(\theta) a_s(T)}{\Gamma^2(\theta) - \beta_s \beta_d},
$$
\n(53)

where the transition point $T^*(\theta)$, defined by the equation $\psi_{s0}(T^*)=0$, is strongly θ dependent and deviates from an s -wave critical temperature T_{cs} as follows:

$$
T^*(\theta) = T_{cs} - \frac{\alpha_d \Gamma(\theta) \Delta T_c}{\alpha_s \beta_d - \alpha_d \Gamma(\theta)},
$$
\n(54)

where $\Delta T_c \equiv T_{cd} - T_{cs}$.

After substituting the solution given by Eqs. (52) and (53) into Eq. (25) we obtain for the average thermopower difference

$$
\Delta S_{av}^{I}(T,\theta;\Delta T_{c}) = S_{p,av}^{I}(\theta;\Delta T_{c}) - B_{av}^{I}(\theta)[T^{*}(\theta) - T],
$$
\n(55)

where

$$
S_{p,av}^{I}(\theta; \Delta T_c) = \frac{\alpha_s}{2qN} \left[\frac{\alpha_d^2 \Delta T_c}{\alpha_s \beta_d - \alpha_d \Gamma(\theta)} \right],
$$
 (56)

and

$$
B_{av}^{I}(\theta) = \frac{2\alpha_{s}\alpha_{d}\Gamma(\theta) - \alpha_{s}^{2}\beta_{d} - \alpha_{d}^{2}\beta_{s}}{2qN[\Gamma(\theta)^{2} - \beta_{s}\beta_{d}]}.
$$
 (57)

Here $N = n_s n_d / (n_s + n_d)$ is a generalized carrier number density.

(b) $T^*(\theta) \leq T \leq T_{cd}$. In this region we obtain from Eqs. (29) and (30)

FIG. 4. The ratio $T^*(\theta)/T_{cs}$ as a function of T_{cd}/T_{cs} for different θ calculated according to Eq. (54). Solid, dotted, and dashed lines correspond to $\theta = \pi$ ($s - d$ state), $\theta = \pi/2$ ($s + id$ state), and $\theta = \pi/4$, respectively.

$$
|\psi_{s0}| = 0, \quad |\psi_{d0}|^2 = \frac{\alpha_d (T_{cd} - T)}{\beta_d}, \tag{58}
$$

for the equilibrium order parameters. The resulting meanfield thermopower difference in this region is

$$
\Delta S_{av}^{II}(T,\theta) = S_{p,av}^{II}(\theta, \Delta T_c) + B_{av}^{II}[T - T^*(\theta)], \quad (59)
$$

where

$$
S_{p,av}^{II}(\theta; \Delta T_c) = 2S_{p,av}^I(\theta; \Delta T_c), \quad B_{av}^{II} = \frac{\alpha_d^2}{qN\beta_d}.
$$
 (60)

Figure 4 depicts the ratio $T^*(\theta)/T_{cs}$ as a function of T_{cd}/T_{cs} for different θ . As we can see, for the chosen set of parameters ($\gamma_1 = \gamma_2 = \beta_s$ and $n_d = n_s$), in the mixed $s + id$ pairing state (with $\theta = \pi/2$, dashed line) $T^*(\pi/2) = T_{cs}$ for all T_{cd}/T_{cs} . As it follows from Eqs. (56) and (57), this state is described by the following dependencies of the TEP peak and slope (below T^*):

$$
S_{p,av}^I\left(\theta = \frac{\pi}{2}; \Delta T_c\right) = \frac{2\Delta_{d0}k_B}{qE_F^d}\left(1 - \frac{T_{cs}}{T_{cd}}\right),\tag{61}
$$

and

$$
B_{av}^I\left(\theta = \frac{\pi}{2}\right) = \frac{3.52k_B^2}{qE_F^s}\left(1 + \frac{E_F^s}{E_F^d}\right). \tag{62}
$$

As it is evident from the above equations, in this regime the peak's amplitude S_p is entirely dominated by the critical temperatures difference $T_{cd} - T_{cs}$ of the two superconductors while the slope *B* is governed by the corresponding Fermi energies. It would be interesting to test the predicted behavior of the induced thermopower at such *SD* interface using a low- T_c *s*-wave and a high- T_c *d*-wave superconductor (like, e.g., Pb and YBCO).

IV. CONCLUSION

In summary, to probe into the pairing state of high- T_c superconductors, we calculated the differential thermopower ΔS of *SND* junction in the presence of strong pair-breaking effects (due to the normal-metal layer N) and charge-related interference effects (due to the chemical imbalance at *SD* interface) using the generalized Ginzburg-Landau theory for an admixture of *s*-wave and *d*-wave superconductors near T_c . The calculated thermopower was found to strongly depend on the relative phase $\theta = \phi_s - \phi_d$ between the two superconductors (exhibiting a pronounced maximum near the

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mixed $s + id$ state with $\theta = \pi/2$) and their critical temperatures. The experimental conditions under which the predicted behavior of the induced thermopower could be observed were discussed.

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