The thermoelectric response of \textit{SND} configuration is considered within the generalized Ginzburg-Landau theory for a homogeneous admixture of \textit{s}-wave and \textit{d}-wave superconductors. The resulting thermopower \( \Delta S(T, \theta, t_e) = S_p(\theta, t_e) - B(\theta, t_e)(T_{cs} - T) \) is found to strongly depend on the relative phase \( \theta = \phi_s - \phi_d \) between the two superconductors \( (t_e \equiv T_{cd}/T_{cs} \text{ where } T_{cs} \text{ and } T_{cd} \text{ are the corresponding critical temperatures}) \). Two independent mechanisms are shown to contribute to the peak value \( S_p(\theta, t_e) \). One, based on the charge imbalance between the quasiparticles and Cooper pairs (described by the corresponding chemical potentials, \( \mu_s \) and \( \mu_d \)) due to the normal metal insert, results in a pronounced maximum of the peak near \( \theta = \pm \pi/2 \) (the so-called \( s \pm id \) mixed pairing state) for two identical superconductors with \( T_{cd} = T_{cs} \). This mechanism can be realized in a \textit{d}-wave orthorhombic sample (like \textit{YBCO}) with twin boundaries which are represented by tetragonal regions of variable width, with a reduced chemical potential. Another mechanism (not related to the charge imbalance effects) occurs when two different superconductors with \( T_{cd} \neq T_{cs} \) are used for \textit{SND} junction. It gives rise to \( S_p(\theta, t_e) \propto 1 - t_e \) and can be realized via the junction comprising an \textit{s}-wave low-\textit{Tc} superconductor (like \textit{Pb}) and a \textit{d}-wave high-\textit{Tc} superconductor (like orthorhombic \textit{YBCO}). The experimental conditions (based on the previous experience with \textit{SNS} junctions) under which the predicted behavior of the induced differential thermopower can be measured are discussed.

I. INTRODUCTION

During the last few years the order parameter symmetry has been one of the intensively debated issues in the field of high-\textit{Tc} superconductivity (HTS). A number of experiments points to its \textit{d}_{x^2-y^2}\textit{-wave} character. Such an unconventional symmetry of the order parameter has also important implications for the Josephson physics because for a \textit{d}-wave 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) approach as well as the tunneling Hamiltonian approach. It was found 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 \textit{d}-wave superconductors which generate half-integer flux quanta as observed in experiments. Various interesting phenomena occur in interfaces of \textit{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 \textit{I-V}-characteristics of quasiparticle tunneling while in such an interface to an \textit{s}-wave superconductor the energy minimum corresponds to a Josephson phase different from 0 or \( \pi \). By symmetry, a small \textit{s}-wave component always coexists with a predominantly \textit{d}-wave order parameter in an orthorhombic superconductor such as \textit{YBCO}, and changes its sign across a twin boundary. Besides, the \textit{s}-wave and \textit{d}-wave order parameters can form a complex combination, the so-called \textit{s} \pm \textit{id}-state which is characterized by a local breakdown of time reversal symmetry \( T \) either near surfaces or near the twin boundaries represented by tetragonal regions with a reduced chemical potential. Both scenarios lead to a phase difference of \( \pm \pi/2 \), which corresponds to two degenerate states. Moreover, the relative phase oscillations between two condensates with different order parameter symmetries could manifest themselves through the specific collective excitations ("phasons")

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 and successfully applied for detecting small changes in thermopower of a specimen due to the
deliberate insertion of a macroscopic SNS junction made of a normal-metal layer N, used to force pair breaking of the superconducting component when it flows down the temperature gradient. In particular, a carrier-type-dependent thermoelectric response of such a SNS configuration in a C-shaped Bi$_2$Pb$_{1-x}$Sr$_2$CaCu$_2$O$_y$ sample has been registered and its $\Delta$-shaped temperature behavior around $T_c$ has been explained within the framework of GL theory. In the present paper, we consider theoretically the case of SND junction and discuss its possible implications for the above-mentioned type of experiments. The paper is organized as follows. In Section II we briefly review the experimental results for SNS configuration (with both holonlike and electronlike carriers of the normal-metal $N$ insert) and present a theoretical interpretation of these results, based on GL free energy functional. The crucial role of the difference between the quasiparticle $\mu_n$ and pair $\mu_p$, chemical potentials in understanding the observed phenomena is emphasized. In Section III, extending the early suggested GL theory of an admixture of s-wave and d-wave superconductors by taking into account pair-breaking effects with $\mu_n \neq \mu_p$, we calculate the differential thermopower $\Delta S$ of SND configuration near $T_c$. The main theoretical result of this Section is prediction of a rather specific dependence of $\Delta S$ on relative phase shift $\theta = \phi_s - \phi_d$ between the two superconductors. Two independent mechanisms contributing to the peak value of the thermopower are discussed. One, based on the charge imbalance between the quasiparticles and Cooper pairs due to the normal metal insert, is discussed in Section IIIA. It results in a pronounced maximum of the peak near $\theta = \pm \pi/2$ (the so-called $s \pm id$ mixed pairing state) for two identical superconductors with $T_{cd} = T_{cs} \equiv T_c$. 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 (not related to the charge imbalance effects), discussed in Section IIIB, occurs when two different superconductors with $T_{cd} \neq T_{cs}$ are used for SND junction. 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).

II. SNS CONFIGURATION: A REVIEW

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 carrier-type-dependent thermoelectric response of SNS configuration in a C-shaped Bi$_2$Pb$_{1-x}$Sr$_2$CaCu$_2$O$_y$ sample (see Ref. [13] 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 $\nabla_x T$ is shown as well. Two cuts are inserted at 90° to each other into a ring-shaped 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 an s-wave superconductor ($S' = S$) from another s-wave superconductor ($S'' = S$) and completely interrupting the passage of supercurrents in this wing. The passage 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

$$\Delta S(T) \simeq S_p - B(T_c - T),$$

where $S_p = \Delta S(T_c)$ is the peak value of $\Delta S(T)$ at $T = T_c$, and $B$ is a constant. The best fit of the experimental data with the above equation yields the following values for silver (Ag) and indium (In) inserts, respectively: (i) $S_p(\text{Ag}) = -0.26 \pm 0.01 \mu V/K$, $B(\text{Ag}) = -0.16 \pm 0.1 \mu V/K^2$; (ii) $S_p(\text{In}) = 0.83 \pm 0.01 \mu V/K$, $B(\text{In}) = 0.17 \pm 0.1 \mu V/K^2$.

FIG. 1. Schematic view of the sample geometry with $S' NS''$-junction and contacts configuration. The thermopowers $S_R$ and $S_L$ result from the thermal voltages detected by the contact pairs 4–5 and 1–7, respectively.

B. Interpretation

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
\[ \Delta G[\psi] = \Delta F[\psi] - \Delta \mu |\psi|^2, \quad (2) \]

where

\[ \Delta F[\psi] \equiv F_R - F_L = a(T)|\psi|^2 + \frac{\beta}{2}|\psi|^4 \quad (3) \]

and

\[ \Delta \mu = \mu_R - \mu_L. \quad (4) \]

Here \( \psi = |\psi|e^{i\phi} \) is the superconducting order parameter, \( \mu_p \) and \( \mu_q \) are the chemical potentials of quasiparticles and Cooper pairs, respectively; \( a(T) = a(T - T_c) \) and the GL parameters \( \alpha \) and \( \beta \) are related to the critical temperature \( T_c \), zero-temperature gap \( \Delta_0 = 1.76k_BT_c \), the Fermi energy \( E_F \), and the total particle number density \( n \) as \( \alpha = 2\Delta_0 k_B/E_F \) and \( \beta = \alpha T_c/n \).

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

\[ |\psi_0|^2 = \frac{\alpha(T_c - T) + \Delta \mu}{\beta} \quad (5) \]

Substituting \( |\psi_0|^2 \) into Eq.(2) we obtain for the generalized free energy density

\[ \Delta \Omega(T) \equiv \Delta G[\psi_0] = -\frac{\alpha(T_c - T) + \Delta \mu}{2\beta} \quad (6) \]

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

\[ \Delta S(T) = \frac{\Delta \mu}{qT_c} - \frac{2\Delta_0 k_B}{qE_F T_c}(T_c - T), \quad (7) \]

where \( E_F = E_{F_p} - \mu_q \) accounts for the shift of the Fermi energy \( E_F \) due to the quasiparticle chemical potential \( \mu_q \). Let us discuss now separately the case of \( In \) and \( Ag \) normal-metal inserts.

1. \( N = In \) (holelike metal insert)

In this case, the principal carriers are holes, therefore \( q = +e \) in Eq.(7). Let the holelike quasiparticle chemical potential (measured relative to the Fermi level of the free-hole gas) be positive, then \( \mu_q = +\mu \) and \( \Delta \mu \equiv \mu_q - \mu_p = \mu - (-2\mu) = 3\mu \). Here \( \mu_p = -2\mu \) comes from the change of the pair chemical potential of the holelike condensate with respect to the holelike quasiparticle branch. Therefore, for this case Eq.(7) takes the form

\[ \Delta S^h(T) = 3 \left( \frac{k_B}{e} \right) \left( \frac{\mu}{k_BT_c} \right) - \frac{2\Delta_0 k_B}{eE_F T_c}(T_c - T), \quad (8) \]

where \( E_{F_p} = E_F - \mu \).

2. \( N = Ag \) (electronlike metal insert)

The principal carriers in this case are electrons, therefore \( q = -e \). The electronlike quasiparticle chemical potential (measured relative to the Fermi level of the free-hole gas) is \(-\mu\). Then \( \mu_q = -\mu \) and \( \Delta \mu = -\mu - (-2\mu) = \mu \). For this case Eq.(7) takes the form

\[ \Delta S^e(T) = -\left( \frac{k_B}{e} \right) \left( \frac{\mu}{k_BT_c} \right) + \frac{2\Delta_0 k_B}{eE_F T_c}(T_c - T), \quad (9) \]

where \( E_{F_p} = E_F + \mu \).

Using the above-mentioned experimental findings for the slope \( B \) and the peak \( S_p \) values for the two normal-metal inserts (see Eq.(1)), we can estimate the order of magnitude of the Fermi energy \( E_F \) and quasiparticle potential \( \mu \). The result is: \( E_F = 0.16eV \) and \( \mu = 5 \times 10^{-3}eV \), in reasonable agreement with the other known estimates of these parameters. Besides, as it follows from Eqs.(8) and (9), the calculated ratio for peaks \( S_p(\text{In})/S_p(\text{Ag}) \) is 3 very close to the corresponding experimental value \( S^{exp}(\text{In})/S^{exp}(\text{Ag}) \) = 3.2 ± 0.2 observed by Gridin et al [13].

### III. SND CONFIGURATION: PREDICTION

Since Eqs.(2)-(4) 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) bringing about the result similar to that given by Eqs.(7)-(9). It means that the experimental method under discussion (and its interpretation) can not be used to tell the difference between \( SNS \) and \( DND \) configurations, 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 \( T \ll T_c \). As we will show, this method, however, is quite sensitive to the mixed \( SNS \) configuration (when \( S' = S \) has an \( s \)-wave symmetry while \( S'' = D \) is of a \( d \)-wave symmetry type, see Fig.1) and predicts a rather specific relative phase \( (\theta = \phi_s - \phi_d) \) dependences of both the slope \( B(\theta) \) and peak \( S_p(\theta) \) of the observable thermopower difference \( \Delta S(T, \theta) \).

Following Feder et al [13], who incorporated chemical potential effects near twin boundaries into the approach suggested by Sigrist et al [17], we can represent the generalized GL free energy functional \( \Delta G \) for \( SND \) configuration of the C-shaped sample in the following form

\[ \Delta G[\psi_s, \psi_d] = \Delta G[\psi_s] + \Delta G[\psi_d] + \Delta G_{int}, \quad (10) \]

where

\[ \Delta G[\psi_s] = \Delta F[\psi_s] - \Delta \mu |\psi_s|^2, \quad (11) \]

\[ \Delta G[\psi_d] = \Delta F[\psi_d] - \Delta \mu |\psi_d|^2, \quad (12) \]
and
\[ \Delta G_{\text{int}} = \gamma_1 |\psi_s|^2 |\psi_d|^2 + \frac{\gamma_2}{2} (\psi_s^2 \psi_d^2 + \psi_s^2 \psi_d^2) + 2\delta_1 |\psi_s| |\psi_d| - 2\delta_2 (\psi_s^* \psi_d + \psi_s \psi_d^*). \] (13)

Here \( \psi_n = |\psi_n| e^{i\phi_n} \) is the \( n \)-wave order parameter \((n = \{s, d\})\); \( \Delta \mathcal{F}[\psi_s, \psi_d] \) is given by Eq.(3) with the corresponding parameters \( a_s(T) = \alpha_s(T - T_{cs}) \), \( \beta_s \), \( a_d(T) = \alpha_d(T - T_{cd}) \), and \( \beta_d \) for \( s \)-wave and \( d \)-wave symmetry, respectively.

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 \( \psi_{s0} \) and \( \psi_{d0} \)

\[ A_s(T)|\psi_{s0}| + \beta_s|\psi_{s0}|^3 + \Gamma(\theta)|\psi_{s0}|^2 = \Delta(\theta)|\psi_{d0}| \] (14)
\[ A_d(T)|\psi_{d0}| + \beta_d|\psi_{d0}|^3 + \Gamma(\theta)|\psi_{d0}|^2 = \Delta(\theta)|\psi_{s0}| \] (15)

where \( A_s(T) = a_s(T) - \Delta \mu \), \( A_d(T) = a_d(T) - \Delta \mu \), and we introduced relative phase \( \phi_s - \phi_d \) depending on parameters \( \Gamma(\theta) = \gamma_1 + \gamma_2 \cos 2\theta \)
\[ \Delta(\theta) = \delta_1 + \delta_2 \cos \theta \] (16)

Notice that the \( \Delta(\theta) \) term favors \( \theta = l\pi \) \((l \text{ integer})\), while the \( \Gamma(\theta) \) term favors \( \theta = n\pi/2 \) \((n = 1, 3, 5 \ldots) \) which corresponds to a \( T \)-violating phase \( \Gamma \). In principle, we can resolve the above system (given by Eqs.(14)-(16)) and find \( \psi_{s0} \) for arbitrary set of parameters \( \alpha_n, \beta_s, \) and \( T_{cs} \). 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

First, let us consider the case of similar superconductors comprising the \( SND \) junction with \( |\psi_{s0}| = |\psi_{d0}| = |\psi_0| \), \( \alpha_s = \alpha_d \equiv \alpha \), \( \beta_s = \beta_d \equiv \beta \), 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 \( \tilde{\mu} \). In this particular case, Eqs.(14) and (15) yield for \( T < T_c \)
\[ |\psi_0|^2 = \frac{\alpha(T_c - T) + \Delta \mu + \Delta(\theta)}{\beta + \Gamma(\theta)} \] (17)

After substituting the thus found \( |\psi_0| \) into Eq.(10) we obtain for the generalized equilibrium free energy density
\[ \Delta \Omega(T, \theta) = \Delta \mathcal{G}[\psi_0] = -\frac{[\alpha(T_c - T) + \Delta \mu + \Delta(\theta)]^2}{\beta + \Gamma(\theta)} \] (18)

which in turn results in the following expression for the thermopower difference in a \( C \)-shaped sample with \( SND \) junction (see Fig.1)
\[ \Delta S(T, \theta) = S_p(\theta) - B(\theta)(T_c - T), \] (19)

where
\[ S_p(\theta) = -\frac{2\Delta \mu}{qT_c} \frac{(1 + \tilde{\delta} \cos \theta)}{1 + \tilde{\gamma} \cos 2\theta} \] (20)

and
\[ B(\theta) = \frac{4\Delta \mu k_B}{qE_F T_c} \frac{1}{1 + \tilde{\gamma} \cos 2\theta} \] (21)

Here, \( \tilde{\gamma} = \gamma_2/(\gamma_1 + \beta) \) and \( \tilde{\delta} = \delta_2/(\delta_1 + \Delta \mu) \) with \( \Delta \mu \) and \( \beta \) defined earlier.

**FIG. 2.** 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 \( \theta \) 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.(20) and (21) with \( \tilde{\gamma} = \tilde{\delta} = 1/2 \). Fig.2 shows the predicted \( \theta \)-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 \( \Delta S(T, \theta) \) near \( T_c \), for \( \tilde{\gamma} = \tilde{\delta} = 1/2 \). As is seen, both the slope and the peak exhibit a maximum for the \( s \pm id \) state (at \( \theta = \pi/2 \)) 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 described in Section II sample geometry and experimental technique. Besides, by a controllable variation of the carrier type of the normal-metal insert, we can get a more detailed information about the mixed states and use it to estimate the 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 when the two superconductors of the SND junction are different, so that \( |\psi_{s0}| \neq |\psi_{d0}| \), \( \alpha_s \neq \alpha_d \), \( \beta_s \neq \beta_d \), and \( T_{cs} \neq T_{cd} \) but the charge imbalance effects are rather small and can be safely neglected. Thus, we assume \( \Delta \mu = 0 \), and \( \Delta(\theta) = 0 \). Such a situation can be realized for an s-wave low-\( T_c \) superconductor (like \( \text{Pb} \)) and a d-wave high-\( T_c \) superconductor (like orthorhombic \( \text{YBCO} \)). In fact, the solution for this particular case is well-known. It has been discussed by Sigrist et al. [10] in a somewhat different context. The corresponding expressions for the equilibrium order parameters read

\[
|\psi_{s0}|^2 = \frac{\beta_d a_s(T) - \Gamma(\theta)a_d(T)}{\Gamma(\theta) - \beta_s\beta_d}, \quad (22)
\]

\[
|\psi_{d0}|^2 = \frac{\beta_s a_d(T) - \Gamma(\theta)a_s(T)}{\Gamma(\theta) - \beta_s\beta_d}, \quad (23)
\]

where \( a_s(T) = \alpha_s(T - T_{cs}) \) and \( a_d(T) = \alpha_d(T - T_{cd}) \).

After substituting this solution into Eq.(10) we obtain for the the thermopower difference

\[
\Delta S(T, \theta, t_c) = S_p(\theta, t_c) - B(\theta, t_c)(T_{cs} - T), \quad (24)
\]

where \( t_c = T_{cd}/T_{cs} \) and both the peak

\[
S_p(\theta, t_c) = (1 - t_c)f(\theta, t_c) \quad (25)
\]

and the slope

\[
B(\theta, t_c) = 2\frac{f(\theta, t_c)}{T_{cs}} \quad (26)
\]

are governed by a universal function

\[
f(\theta, t_c) = \frac{2\Delta a_0 k_B \beta_s t_c}{qE_F[\Gamma(\theta) + \beta_s t_c]}. \quad (27)
\]

Notice that in this case (when changes in chemical potentials can be neglected) the peak’s amplitude \( S_p(\theta, t_c) \) will be entirely dominated by the critical temperatures difference \( T_{cd} - T_{cs} \) of the two superconductors because \( f(\theta, t_c) \) is a smooth function of \( t_c \). It would be interesting to test the predicted behavior of the induced thermopower in a C-shaped sample with an SND junction (see Fig.1) using a low-\( T_c \) s-wave and a high-\( T_c \) d-wave superconductors.

In summary, to probe into the mixed \( s \pm id \) pairing state of high-\( T_c \) superconductors, we calculated the differential thermopower \( \Delta S \) of SND junction in the presence of the strong charge imbalance effects (due to a nonzero difference between the quasiparticle \( \mu_q \) and Cooper pair \( \mu_p \) chemical potentials) using the generalized Ginzburg-Landau theory for a homogeneous 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 mixed \( s \pm id \) state with \( \theta = \pm \pi/2 \). The experimental conditions under which the predicted behavior of the induced thermopower could be observed were discussed.

(*) E-mail address: ssa@thsun1.jinr.dubna.su

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