

## Bipolaronic superconductivity

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Superconducting properties of narrow-band electrons are examined in the strong-coupling limit. It is shown that bipolarons (localized spatially nonoverlapping Cooper pairs) formed by strong electron-phonon interaction have under certain conditions superconducting properties which are characteristic of superfluid charged Bose systems. They represent an example of the "molecular" superconductivity proposed by Schafroth, Butler, and Blatt [Helv. Phys. Acta **30**, 93 (1957)]. The Meissner effect and the penetration depth of bipolaronic superconductors are examined. The relationship between Bardeen-Cooper-Schrieffer superconductors and bipolaronic ones is discussed.

### I. INTRODUCTION

The strong-coupling superconductivity is a subject of great theoretical and experimental interest primarily because of the high- $T_c$  problem.<sup>1</sup>

An extensive study of transition temperature of intermediate-coupling superconductors ( $\lambda \sim 1$ ) can be found in McMillan's work<sup>2</sup> based on the Eliashberg equations,<sup>3</sup> which were formulated in their finite-temperature form by Scalapino, Schrieffer, and Wilkins.<sup>4</sup>

The strong-coupling McMillan's expression for  $T_c$  shows saturation of  $T_c$  beyond  $\lambda \sim 2$ . Allen and Dynes<sup>5</sup> have shown that this  $T_c$  maximum is an artifact of McMillan's expression, and that Eliashberg theory gives  $T_c \sim \lambda^{1/2}$  for  $\lambda \gg 1$ .

On the other hand Anderson,<sup>6</sup> Chakraverty and Schlenker,<sup>7</sup> and Chakraverty<sup>8</sup> have pointed out that in large  $\lambda$  limit [ $\lambda \geq 2.5$  (Ref. 8)] the localization of Cooper pairs, i.e., bipolaron formation, occurs. A recent series of papers<sup>9</sup> shows the existence of a bipolaronic ground state in a great variety of nonmetallic transition-metal compounds.

Bipolarons form quite naturally in such systems due to the highly directional character of the  $3d$  wave functions and due to their particular lattice structures. This leads to a kind of molecular states for the electrons (bipolarons) which are broadened into narrow bands resulting from a small overlap between different molecules. As far as the lattice is concerned, these systems behave like weakly coupled oscillators of vibrating molecules. The number of electrons per molecule plays an important role in determining the interatomic distance of those molecules. Experimentally, changes of 10% of this distance and more have been observed upon adding or subtracting an electron at a given molecule. The effect of the electron-lattice coupling is therefore extremely important for such systems and any theory must necessarily take proper

account of this fact.

The theory of "small" bipolarons with a dissociation energy greater than the polaron bandwidth ( $\lambda \gg 1$ ) has been developed by the present authors in their previous work.<sup>10</sup>

In this paper, we use this theory to discuss the superconductivity of narrow-band electrons under the condition of bipolaron formation. By calculating the excitation spectrum and the Meissner effect, we show that the superconductivity in the strong-coupling limit has more common features with the superconductivity of nonoverlapping electron quasimolecules<sup>11</sup> than with the BCS superconductivity. The penetration depth is different from the London one and the critical temperature falls off with  $\lambda$ .

### II. BIPOLARONIC HAMILTONIAN

We start with the standard single-band electron-phonon Hamiltonian

$$\begin{aligned}
 H &= H_{\text{el}} + H_{\text{ph}} + H_{\text{el,ph}} , \\
 H_{\text{el}} &= \sum_{mm'} T_{mm'} c_m^\dagger c_{m'} + \sum_{mm'} V_{mm'}^{m'n'} c_m^\dagger c_n^\dagger c_n c_m , \\
 H_{\text{ph}} &= \sum_{\vec{q}} \omega_{\vec{q}} d_{\vec{q}}^\dagger d_{\vec{q}} , \\
 H_{\text{el,ph}} &= \sum_{mm' \vec{q}} [U_{mm'}(\vec{q}) c_m^\dagger c_{m'} d_{\vec{q}}^\dagger + \text{H.c.}] ,
 \end{aligned} \tag{1}$$

where  $m = (\bar{m}, \alpha)$ ,  $\bar{m}$  indicating the molecular site and  $\alpha$  labeling the internal degrees: the atomic site in the molecule and the spin of the electron of Wannier type which occupies this atom.  $T_{mm'}$  is the hopping integral,  $V_{mm'}^{m'n'}$  the Coulomb correlations,  $\omega_{\vec{q}}$  the phonon frequency of wave vector  $\vec{q}$ , and  $U_{mm'}(\vec{q})$  the Fourier transform of the electron-lattice coupling.

In the strong-coupling limit the narrow-band electrons are coupled by the local lattice deformation into the intracell pairs—bipolarons—which by tunneling motion, caused by the virtual transitions into polaronic states, form a bipolaronic energy band.<sup>10</sup>

The bipolaronic Hamiltonian  $\tilde{H}$ , describing bipolaronic motion and their interaction is obtained by two successive canonical transformations  $S_1$  and  $S_2$ .  $S_1$  is the familiar<sup>12</sup> displaced oscillator transformation

$$S_1 = \sum_{m\bar{q}} \omega_{\bar{q}}^{-1} n_m [d_{\bar{q}}^\dagger U_{mm}(\bar{q}) - d_{\bar{q}} U_{mm}^\dagger(\bar{q})], \quad (2)$$

entirely decoupling the electrons from the molecular vibrations of the molecule which they occupy. This leads to a change in the interatomic distance of the molecule associated with a change of the electrons into small polaron operators and the appearance of an attractive interaction between two such polarons on the same molecule. On the other hand, it introduces a nonlocal short-range electron-lattice coupling leading to such mechanisms as an electron jumping from one molecule to another and carrying with it the molecular distortion manifest in the well-known polaronic band narrowing effect. Thus  $S_1$  is essentially different from the transformation employed in order to obtain the BCS Hamiltonian, in the case of which the linear electron-lattice coupling is eliminated for the entire lattice. Keeping only terms of second order in this coupling constant gives rise to long-range interaction between the electrons which in this case are of Bloch, rather than Wannier type.

The second transformation  $e^{(S_2)_{ik}}$

$$(S_2)_{ik} = \sum_{mm'} \frac{\sigma_{mm'}(c_m^\dagger c_{m'})_{ik}}{E_i - E_k} \quad (3)$$

is constructed such as to eliminate the individual intercell electron transitions which tend to destroy the bipolarons on creating real polarons.  $|i\rangle$ ,  $|k\rangle$ ,  $E_i$ , and  $E_k$  are the eigenvectors and energy levels of an isolated cell. The above procedure is useful where the bipolaronic binding energy is large compared to the polaronic band halfwidth permitting us to discard all the terms of  $\tilde{H}$  of higher than second order in  $(S_2)_{ik}$  and to keep only matrix elements of (3) which act between a polaronic state and bipolaronic state with  $E_i - E_k = \Delta$  defining the bipolaronic binding energy. This gives rise to the following bipolaronic Hamiltonian:

$$\tilde{H} = - \sum_{\bar{m}} \left[ \mu b_{\bar{m}}^\dagger b_{\bar{m}} + \sum_{\bar{m}' \neq \bar{m}} [t(\bar{m} - \bar{m}') b_{\bar{m}}^\dagger b_{\bar{m}'} - v(\bar{m} - \bar{m}') b_{\bar{m}}^\dagger b_{\bar{m}'} b_{\bar{m}}^\dagger b_{\bar{m}'}] \right] \quad (4)$$

$b_{\bar{m}}$ ,  $b_{\bar{m}}^\dagger$  are annihilation and creation bipolaron

operators defined as

$$b_{\bar{m}}^\dagger = \frac{1}{2\sqrt{\rho}} \sum_{\alpha\alpha'} A_{\alpha\alpha'} c_{\bar{m}\alpha}^\dagger c_{\bar{m}\alpha'}^\dagger, \quad (5)$$

$$b_{\bar{m}} = -\frac{1}{2\sqrt{\rho}} \sum_{\alpha\alpha'} A_{\alpha\alpha'} c_{\bar{m}\alpha} c_{\bar{m}\alpha'}$$

$\rho$  is the number of atoms in the cell.  $A_{\alpha\alpha'}$  is the unitary matrix, which determines the  $\psi$  function of the localized intracell bipolaron, and  $\mu$  is the bipolaron chemical potential.

For sufficiently strong electron-lattice interaction,  $\Delta$  coincides with the electron-electron intracell attraction constant  $V_0$  (Refs. 8 and 10) and the condition  $\Delta \gg W$  is the same as  $\lambda = N(0)V_0 \gg 1$ . This condition leads to the high stability of the bipolarons and thus for sufficiently low temperature  $T \ll \Delta$ , only the subspace  $b_{\bar{m}}^\dagger |0\rangle$ ,  $|0\rangle_{\bar{m}}$  is important, where all the electrons are coupling into the bipolarons.

The effective bipolaron hopping  $t(\bar{m} - \bar{m}')$  is defined by<sup>10</sup>

$$t(\bar{m} - \bar{m}') = \frac{2}{\rho\Delta} \sum_{\substack{\alpha\alpha' \\ \beta\beta'}} A_{\alpha\beta} \sigma_{\alpha\alpha'}(\bar{m} - \bar{m}') \times A_{\alpha'\beta'} \sigma_{\beta\beta'}(\bar{m} - \bar{m}'), \quad (6)$$

where the value of  $\sigma_{\alpha\alpha'}(\bar{m} - \bar{m}') = \phi T_{\alpha\alpha'}(\bar{m} - \bar{m}')$  determines the polaron band halfwidth  $W$  and  $T_{\alpha\alpha'}(\bar{m})$  is the bare-electron hopping integral.

$$\phi = \exp \left[ - \sum_{\bar{q}} \omega_{\bar{q}}^{-2} |U_{mm}(\bar{q})|^2 [1 - \cos \bar{q}(\bar{R}_{\bar{m}\alpha} - \bar{R}_{\bar{m}\alpha'})] \right] \quad (7)$$

is the polaronic band narrowing factor.<sup>12</sup>

The expressions (4) and (6) are obtained for the case of the small overlap of the atomic functions. In the other cases, the contribution to Eq. (6) from the simultaneous two electron intercell transitions may be important, so in general one can consider the values  $t$  and  $v$  as phenomenological constants.

The ground state of the Hamiltonian (4) depends on the ratio of the effective bipolaron interaction  $v$  to the halfwidth of the bipolaronic band  $t$  and on the number of electrons  $n$ . Under the condition  $v > t$  and  $n > n_c = N \{1 - [(v-t)/(v+t)]^{1/2}\}$  the ground state is a charge-density wave (CDW) of bipolarons.<sup>10</sup> Here  $v = zv(a)$ ,  $t = zt(a)$ ,  $z$  is the number of nearest-neighbor cells,  $N$  is the total number of cells, and  $a$  is the lattice constant. Since  $t$  decreases with  $\lambda$  [Eq. (6)] and  $v$ , in particular, depends on the direct Coulomb repulsion which does not involve  $\lambda$  we have

in general  $v > t$  in the very strong-coupling limit. In this sense, the ground state of narrow-band electrons in the limit  $\lambda \rightarrow \infty$  is CDW insulator.

### III. SUPERFLUIDLIKE EXCITATION SPECTRUM OF BIPOLARONS

In what follows we discuss the properties of the homogeneous state, which is the ground state for all values of  $n$  in the case of  $v < t$  or for  $n < n_c$  if  $v > t$ . Previously<sup>10</sup> using the Anderson semiclassical pseudospin approach,<sup>13</sup> we have shown that the excitation spectrum of this ground state is superfluidlike for zero temperature. In order to estimate  $T_c$  and to calculate the Meissner effect, we first of all generalize the pseudospin approach to the finite temperature with the aid of Holstein-Primakoff transformation.

In the subspace involving only the bipolaronic or empty states of the cell the Hamiltonian (4) is fully equivalent to the anisotropic Heisenberg one

$$\begin{aligned} \hat{H} = & - \sum_{\bar{m}} \left( -\mu S_{\bar{m}}^z \right. \\ & + \sum_{\bar{m}' \neq \bar{m}} t(\bar{m} - \bar{m}') (S_{\bar{m}}^x, S_{\bar{m}'}^x + S_{\bar{m}}^y, S_{\bar{m}'}^y) \\ & \left. - v(\bar{m} - \bar{m}') S_{\bar{m}}^z, S_{\bar{m}'}^z \right), \end{aligned} \quad (8)$$

where  $S^i$  are the set of Pauli  $\frac{1}{2}$ -spin matrices and

$$S_{\bar{m}}^x = \frac{1}{2}(b_{\bar{m}}^\dagger + b_{\bar{m}}), \quad S_{\bar{m}}^y = \frac{1}{2i}(b_{\bar{m}}^\dagger - b_{\bar{m}}).$$

The chemical potential  $\mu$  is determined by the condition  $\bar{S}_{\bar{m}} \parallel \bar{H}_{\bar{m}}$

$$\mu = -(v + t) \cos \theta, \quad (9)$$

where  $\bar{H}_{\bar{m}}$  is the local pseudofield and the angle  $\theta$  between  $\bar{S}_{\bar{m}}$  and the  $z$  axis is determined by the number of electrons:

$$\left\langle \sum_{\bar{m}} S_{\bar{m}}^z \right\rangle = \frac{N - n}{2}. \quad (10)$$

Provided the number of excited pseudomagnons is small, the anisotropic Heisenberg Hamiltonian (8) can be diagonalized in three steps: (i) the rotation transformation

$$\begin{aligned} S^z &= \tilde{S}^z \cos \theta - \tilde{S}^x \sin \theta, \\ S^x &= \tilde{S}^x \cos \theta + \tilde{S}^z \sin \theta, \\ S^y &= \tilde{S}^y; \end{aligned} \quad (11)$$

(ii) the Holstein-Primakoff transformation

$$\begin{aligned} \tilde{S}_{\bar{m}}^z &= \frac{1}{2} - \frac{1}{N} \sum_{\bar{k}, \bar{k}'} \exp[i(\bar{k} - \bar{k}') \cdot \bar{m}] b_{\bar{k}}^\dagger b_{\bar{k}'}, \\ \tilde{S}_{\bar{m}}^x &= \frac{1}{2\sqrt{N}} \sum_{\bar{k}} e^{-i\bar{k} \cdot \bar{m}} (b_{\bar{k}} + b_{-\bar{k}}^\dagger), \\ \tilde{S}_{\bar{m}}^y &= \frac{1}{2i\sqrt{N}} \sum_{\bar{k}} e^{-i\bar{k} \cdot \bar{m}} (b_{\bar{k}} - b_{-\bar{k}}^\dagger); \end{aligned} \quad (12)$$

(iii) the Bogolubov transformation

$$\begin{aligned} b_{\bar{k}} &= u_{\bar{k}} \beta_{\bar{k}} + v_{\bar{k}} \beta_{-\bar{k}}^\dagger, \\ b_{-\bar{k}} &= u_{\bar{k}} \beta_{-\bar{k}} + v_{\bar{k}} \beta_{\bar{k}}^\dagger, \end{aligned} \quad (13)$$

with the result

$$\hat{H} = E_f + \sum_{\bar{k}} \omega_{\bar{k}} \beta_{\bar{k}}^\dagger \beta_{\bar{k}}, \quad (14)$$

where

$$\begin{aligned} \omega_{\bar{k}}^2 &= t^2 - \xi_{\bar{k}}^2 t (v \sin^2 \theta - t \cos^2 \theta) \\ &+ \xi_{\bar{k}} t (v \sin^2 \theta - t(1 + \cos^2 \theta)), \end{aligned} \quad (15)$$

$\omega_{\bar{k}}$  is the pseudomagnon energy,

$$E_f = - \left\{ \frac{Nt}{4} \left[ 1 + \left( 1 + \frac{v}{t} \right) \cos^2 \theta \right] + 2 \sum_{\bar{k}} \omega_{\bar{k}} v_{\bar{k}}^2 \right\},$$

$$u_{\bar{k}}^2 = 1 + v_{\bar{k}}^2$$

$$= \frac{1}{2} \left[ 1 + \frac{t + \frac{1}{2} \xi_{\bar{k}} [v \sin^2 \theta - t(1 + \cos^2 \theta)]}{\omega_{\bar{k}}} \right], \quad (16)$$

and

$$\xi_{\bar{k}} = Z^{-1} \sum_{|\bar{n}|=a} e^{i\bar{k} \cdot \bar{n}}.$$

From Eq. (10) we obtain for the angle  $\theta$  using Eqs. (11)–(13)

$$\cos \theta = \frac{1 - \frac{n}{N}}{1 - \frac{2}{N} \sum_{\bar{k}} v_{\bar{k}}^2 - \frac{2}{N} \sum_{\bar{k}} (u_{\bar{k}}^2 + v_{\bar{k}}^2) f_{\bar{k}}}, \quad (17)$$

where  $f_{\bar{k}} = (\exp \omega_{\bar{k}} / T - 1)^{-1}$  is the energy distribution of pseudomagnons, which are described by the Bose operators  $\beta$  and  $\beta^\dagger$ .

We see that the quantum-mechanical treatment of the bipolaronic Hamiltonian gives two additional contributions to the definition of  $\cos \theta$  Eq. (17): the quantum-mechanical zero-point fluctuations, which are small just as for the Heisenberg antiferromagnets (second term in the denominator) and the temperature-dependent pseudomagnons contribution

(the third term).

The spectrum Eq. (15) is superfluidlike with the linear dispersion in the long-wavelength limit

$$\omega_{\vec{k}} = s |\vec{k}|, \quad (18)$$

where the "sound" velocity  $s$  is proportional to the value of  $\sin\theta$  ( $\hbar = c = 1$ )

$$s = \left[ \sin^2\theta \frac{t(v+t)}{Z} \sum_{|\vec{n}|=u} \left( \frac{\vec{k} \cdot \vec{n}}{k} \right)^2 \right]^{1/2} \quad (19)$$

Hence  $\sin^2\theta$  plays the role of the density of condensed bosons. The critical temperature of superfluid (superconducting) transition  $T_c$  is determined by

$$\sin\theta(T_c) = 0, \quad (20)$$

at which point the spectrum [Eq. (15)] becomes identical to the electron spectrum in the tight-binding approximation:

$$\omega_{\vec{k}} = t(1 - \xi_{\vec{k}}) \quad (21)$$

with a critical velocity  $v_c = \min(\omega/k) = 0$ .

It will be shown below that the Meissner effect vanishes under the same condition. Hence, from Eqs. (17) and (20), we obtain for  $T = T_c$

$$-\int d\xi \frac{N(\xi)}{\exp[t(1-\xi)/T_c] - 1} = \frac{n}{2}, \quad (22)$$

$$\chi = \frac{K}{1 - 4\pi K},$$

$$K(q) = \frac{e^2}{2m^2 q^2} \sum_{mm'} \int d\vec{x} \int d\vec{x}' \exp[i\vec{q} \cdot (\vec{x} - \vec{x}')] F_{mm'}^{nn'}(\vec{x}, \vec{x}') \sum_i \rho_i \frac{\langle i | c_m^\dagger c_m | z \rangle \langle z | c_n^\dagger c_n | i \rangle}{E_i - E_z}, \quad (24)$$

where in the site representation

$$F_{mm'}^{nn'}(\vec{x}, \vec{x}') = \frac{3}{q^2} [\vec{q} \vec{p}_{mm'}(\vec{x})][\vec{q} \vec{p}_{nn'}(\vec{x}')] - \vec{p}_{mm'}(\vec{x}) \vec{p}_{nn'}(\vec{x}'), \quad (25)$$

$$\vec{p}_{mm'}(\vec{x}) = u_{m'}(\vec{x}) \vec{\nabla} u_m(\vec{x}) - u_m(\vec{x}) \vec{\nabla} u_{m'}(\vec{x}).$$

$u_m(\vec{x})$  is the Wannier function and the average is made over a grand canonical ensemble  $\rho_i$ .

In a superconductor  $K = -1/4\pi\lambda_H^2 q^2$  for  $q \rightarrow 0$ , where  $\lambda_H$  is the magnetic penetration depth. We show that the bipolaronic contribution to Eq. (24) has precisely that behavior, hence the bipolaronic Meissner effect exists.

Using the definition of the bipolaron operators (5), we find after the  $S_2$  canonical transformation

$$e^{S_2} c_m^\dagger c_m e^{-S_2} \approx \frac{\delta_{mm'}}{\rho} b_m^\dagger b_m - \frac{\sigma_{m'm}}{\Delta\rho} \left( b_m^\dagger b_m + b_m^\dagger b_{m'} - \frac{2}{\rho} b_m^\dagger b_m b_m^\dagger b_{m'} \right) - \frac{2}{\Delta\rho} \sum_{\beta\beta'} \sigma_{\beta\beta'}(\vec{m} - \vec{m}') A_{\alpha\beta} A_{\alpha'\beta'} b_m^\dagger b_{m'}. \quad (26)$$

Only the last term of Eq. (26) corresponding to the hopping of bipolarons gives a contribution to  $K$  since

$$F_{mm'}^{n'n} = F_{m'm}^{n'n} = -F_{mm'}^{nn'},$$

where  $N(\xi) = \sum_{\vec{k}} \delta(\xi - \xi_{\vec{k}})$  is the electron density of states.

It is well known that the Holstein-Primakoff transformation [Eq. (12)] is valid only if the number of excited magnons is small. Hence, we restrict ourselves to the low-density limit  $n \ll N$ . In the limit,  $T_c \ll t$  and only the long-wavelength region where  $\xi \sim 1$  and  $N(\xi) = C\sqrt{1-\xi}$  gives the main contribution to Eq. (22). With

$$\int_{-1}^1 d\xi N(\xi) = N$$

we find  $C = 3 \times 2^{-5/3} N$ . Substituting this density of states in Eq. (22), we obtain

$$T_c = \left( \frac{2^{5/3}}{3\sqrt{\pi}\xi(\frac{3}{2})} \right)^{2/3} t \left( \frac{n}{N} \right)^{2/3} \approx 0.4 t \left( \frac{n}{N} \right)^{2/3}. \quad (23)$$

Owing to the polaronic band narrowing effect contained in the expression for  $t$ , the critical temperature falls off with  $\lambda$ .

#### IV. BIPOLEARONIC MEISSNER EFFECT

Let us now come to illustrate the existence of the bipolaronic Meissner effect.

We use the gauge-invariant generalized form of the linear-response function obtained by Ranninger and Thirring<sup>14</sup> which gives for the static magnetic susceptibility  $\chi$

Finally, expressing the bipolaron operators in terms of pseudomagnon operators yields

$$K(q) = -\frac{e^2 \phi^2 \sin^2 \theta}{2 \Delta^2 \rho^2 m^2 q^2 N} \sum_{\substack{\bar{m}, \bar{m}' \neq \bar{m} \\ \bar{n}, \bar{n}' \neq \bar{n}}} \sum_{\bar{k}} \frac{(u_{\bar{k}} - v_{\bar{k}})^2}{\omega_{\bar{k}}} \exp[i \bar{k} \cdot (\bar{n} - \bar{m})] \Gamma_{\bar{m} \bar{m}'}^{\bar{n} \bar{n}'}, \quad (27)$$

where

$$\Gamma_{\bar{m} \bar{m}'}^{\bar{n} \bar{n}'} = \sum_{\substack{\alpha \alpha' \gamma \gamma' \\ \beta \beta' \delta \delta'}} \int d\bar{x} \int d\bar{x}' \exp[i \bar{q} \cdot (\bar{x} - \bar{x}')] F_{mm'}^{\bar{n} \bar{n}'}, (\bar{x}, \bar{x}') A_{\alpha \beta} A_{\alpha' \beta'} A_{\gamma \delta} A_{\gamma' \delta'} \sigma_{\beta \beta'}(\bar{m} - \bar{m}') \sigma_{\delta \delta'}(\bar{n} - \bar{n}'), \quad (28)$$

$m = (\bar{m}, \alpha)$ ,  $n = (\bar{n}, \gamma)$ , and the canonical transformation  $S_1$  is made which leads to the appearance of the polaron band narrowing factor  $\phi^2$  after averaging.

In the derivation of Eq. (27), we consider the contribution from the condensate which is proportional to  $\sin^2 \theta$ . The contribution from the uncondensed pseudomagnons shows only the normal diamagnetism. Note that the temperature dependence appears only through  $\sin^2 \theta(T)$ , as in the case of the weakly interacting bosons.<sup>14</sup>

The translational symmetry gives

$$\Gamma_{\bar{m} \bar{m}'}^{\bar{n} \bar{n}'} = \exp[i \bar{q} \cdot (\bar{m} - \bar{n})] \Gamma(\bar{m} - \bar{m}', \bar{n} - \bar{n}', \bar{q}). \quad (29)$$

Summing in Eq. (27) over  $\bar{m}'$  and  $\bar{n}'$  we finally obtain for  $q \rightarrow 0$

$$K(q) = -\frac{1}{4\pi \lambda_H^2 q^2} \quad (30)$$

with  $\lambda_H = \lambda_L \kappa$ , where

$$\frac{1}{\kappa} = \frac{\phi \sin \theta}{a \Delta \rho} \left( \frac{3N}{mN} \right)^{1/2} \sum_{\substack{\alpha \alpha' \\ \beta \beta'}} \sum_{\alpha \beta} A_{\alpha \beta} A_{\alpha' \beta'} \sigma_{\beta \beta'}(\bar{m}) \int d\bar{x} \left( \frac{2}{3} u_{\alpha}(\bar{x} + \bar{m}) \bar{x} \frac{\partial}{\partial \bar{x}} u_{\alpha}(\bar{x}) + u_{\alpha}(\bar{x} + \bar{m}) u_{\alpha}(\bar{x}) \right), \quad (31)$$

and  $\lambda_L = (m/4\pi n e^2)^{1/2}$  is the London penetration depth.

For simplicity, we suppose the cubic lattice symmetry. To estimate  $\kappa$  we take  $T = 0$  and:

$$\sigma_{\beta \beta'}(\bar{m}) = \sigma \delta_{\beta \beta'} \quad (|\bar{m}| = a).$$

In this case, we have from Eqs. (6) and (17)

$$t = \frac{4\sigma^2}{\Delta}, \quad \sin^2 \theta \approx \frac{2n}{N} \left( 1 - \frac{n}{2N} \right)$$

so that

$$\frac{1}{\kappa} = -\frac{\phi}{a} \left( \frac{6(1-n/2N)}{m\Delta} \right)^{1/2} \sum_{|\bar{m}|=a} \int d\bar{x} \left( \frac{2}{3} u(\bar{x} + \bar{m}) \bar{x} \frac{\partial}{\partial \bar{x}} u(\bar{x}) + u(\bar{x} + \bar{m}) u(\bar{x}) \right), \quad (32)$$

$$\frac{1}{\kappa} \sim \frac{\phi}{a} \left( \frac{1-n/2N}{m\Delta} \right)^{1/2} e^{-a/a_0},$$

where  $a_0$  is the size of the atomic function.

The corresponding estimations with the experimental value  $\Delta^9$  show that  $\kappa > 1$ . The penetration depth is proportional to  $(\sin \theta)^{-1}$  so the Meissner effect vanishes for  $T = T_c$ .

## V. CONCLUSION

To conclude, we have shown that the superconductivity of narrow-band electrons in the strong-coupling limit  $\lambda \gg 1$  is similar to the superfluidity of charged Bose particles and thus differs considerably from the BCS one. The main differences are: (i) the low-lying excitation (pseudomagnons) have Bose statistics and the gapless spectrum. (ii)  $T_c$  is determined by

the width of the bipolaronic band Eq. (20) and falls off with  $\lambda$ , and (iii) the penetration depth is different from the London one.

We would finally like to remark that the appropriate materials for the bipolaronic superconductivity are the nonmetallic transition-metal compounds, in particular  $M_x V_2 O_3$  ( $M$  is an alkali metal, Ag or Cu),  $LiTi_2 O_4$ ,  $Ti_4 O_7$ ,  $K_{0.3} MoO_3$ , and others, for which there is a strong experimental indication of bipolarons.<sup>9</sup>

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