Bipolaronic superconductivity: Thermodynamics, magnetic properties, and possibility of existence in real substances

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We examine systems where narrow-band electrons strongly couple to the lattice, resulting in the formation of locally bound pairs of small polarons, so-called bipolarons. Such systems present a hard-core charged Bose gas on a lattice. We study the strong dependence of the mass of these bosons and the interaction among themselves as a function of the characteristic phonon frequency. The conditions under which a phenomenological negative-U Hubbard model is applicable to such systems are established. We derive the phase diagram and excitation spectrum, fully taking fluctuations into account. It turns out that quantum fluctuations stabilize the homogeneous superconducting phase and suppress charge order. The specific heat in the superconducting phase shows a power-law behavior: $C_s \sim T^{\alpha}$, with $\frac{3}{2} \leq \alpha \leq 3$, depending on the temperature. The specific heat in the normal phase for such heavy bosons on a lattice shows linear T dependence at low temperature and a T^{-2} behavior for high temperature. We demonstrate that the specific heats in the normal state for narrow-band bosons and fermions on a lattice are practically identical. The spin susceptibility of triplet-bipolarons shows Curie behavior at high temperature, but differs qualitatively from the Pauli susceptibility of narrow-band electrons at low temperature. We examine the electrodynamics of the superconducting phase. The equivalent of the Ginzburg-Landau theory for the narrow-band strong-coupling electron-lattice system is derived; this represents an equation of the order parameters of the charged interacting Bose gas which determines the upper critical field and coherence length, which are strongly dependent on the scattering mechanism for the bosons. In the case of impurity scattering they show unusual temperature dependence: $d^2H_{c2}/dT^2 > 0$. The possible application of our picture of heavy bosons to the description of certain $A15$ compounds, Chevrel phases, heavy-fermion systems, and $BaBi_xPb_{1-x}O_3$ is discussed.

I. INTRODUCTION

Over the last twenty years a great number of strong-coupling d-and f-band superconducting compounds have been discovered,[1] in particular, $A15$, $C15$, Chevrel phases and heavy-fermion superconductors. All of them have narrow electron bands and large values of electron-phonon interaction, which results in poor metallic properties in the normal state but rather high values for the superconducting transition temperatures. Similar properties have been observed in some semiconductors and semimetals such as $BaBi_xPb_{1-x}O_3$, PbTe(Tl), $SrTiO_3$, ... which show superconducting behaviors which are quite different from those of standard BCS ones.[2]

The strong-coupling narrow-band superconductivity is a subject of great theoretical interest. As we have previously noted,[3] the strong-coupling condition

$$\lambda = VN(0) > 1 \tag{1.1}$$

is practically identical to the one for small polaron formation,[4]

$$2zg^2\omega/D > 1 \ . \tag{1.2}$$

$V = 2zg^2\omega$ represents the phonon-mediated attraction and $N(0) \sim D^{-1}$ is the density of states at the Fermi level. g is a dimensionless constant representing the strength of the electron-phonon interaction in the standard Fröhlich Hamiltonian. D denotes the bandwidth, ω is the characteristic phonon frequency in the system, and z is the number of nearest neighbors. It is well known[4,5] that under the condition of Eq. (1.2) a strong renormalization of the electron spectrum occurs, which results in an exponential reduction of the initial electronic bandwidth to an extremely narrow polaronic band with a half width:

$$W = (D/2)\exp(-g^2) \ . \tag{1.3}$$

In such a way the well-known Migdal theorem on which the Eliashberg theory[6] is based breaks down in narrow-band superconductors. Here, one is in the so-called antiadiabatic limit

$$\omega \gtrsim \epsilon_F \sim W \ , \tag{1.4}$$

where ϵ_F is the characteristic kinetic electron energy.

An instability in the many-polaron system occurs if the interaction between two polarons becomes attractive. This happens if the attractive interaction due to the quasistatic deformation which surrounds each polaron overcompensates for the Coulomb repulsion acting between them. This occurs for $2\epsilon_p = 2g^2\omega > V_0$, where ϵ_p denotes the polaronic level shift and V_0 the Coulomb repulsion. This instability in the many-polaron system leads to pairing between polarons and results in a condensate state at low temperature. The properties of this condensate are strongly dependent on the value of the bipolaron binding energy:

$$\Delta \simeq 2\epsilon_p - V_0 \ . \tag{1.5}$$

If the polaron-polaron interaction is attractive but small,

$$\Delta \lesssim W \ . \tag{1.6}$$

Alexandrov[7] has shown that the small polarons form spatially overlapping Cooper pairs with superconducting properties similar to ordinary BCS superconductivity. There are nevertheless differences in the gap equations as well as in the expressions for the critical temperature T_c. Analogous conclusions[8] were also obtained by Robaszkiewicz, Micnas, and Chao and by Nozières and Schmitt-Rink, who considered the extended Hubbard model in the case of weak interaction. The origin of these differences between this polaronic superconductivity (PS) and BCS lies in the violation of the adiabatic condition Eq. (1.4) for the polaronic case. As a consequence, all the electron states in the Fermi sea are strongly coupled to the phonons, and not only those on the Fermi sphere, as in BCS superconductors.

In the case of strong polaron-polaron coupling,

$$\Delta \gg W \ , \tag{1.7}$$

local small bipolarons occur. We must stress here what we mean by bipolarons. They are bound states of two polarons which can exist either on single atomic sites, on sites involving two adjacent metal atoms, or, more generally, sites describing clusters of a small number of metal atoms. In each case the characteristic Coulomb repulsion V_0 has to be interpreted accordingly. While in general V_0 will be fairly large for bipolarons located on single atoms, it will be considerably weaker for the case where bipolarons are located on adjacent metal ions or in atomic clusters.

The so-called on-site bipolarons have previously been proposed by Anderson[9] in connection with the anomalous behavior of amorphous semiconductors (see also Ref. 10). The picture of mobile bipolarons[11] made Alexandrov and Ranninger[3] (AR) realize its similarity with liquid ^{4}He, whose superfluid properties had been studied previously on the basis of a quantum lattice gas model by Matsubara and Matsuda.[12] The AR effective Hamiltonian which describes the tunneling and interaction between bipolarons is equivalent to a pseudo-spin-$\frac{1}{2}$ anisotropic Heisenberg Hamiltonian with a fixed total magnetization. In that sense the bipolaronic system is an even better candidate than ^{4}He for such a lattice gas model.

As it turns out, at zero temperature, two coherent states exist. At a low concentration of bipolarons ($n \ll 1$), the spatially homogeneous superconducting phase with off-diagonal long-range order (ODLRO) exists and shows a Meissner effect.[13] At a high concentration ($n \sim 1$), a mixed phase occurs in which ODLRO coexists with diagonal long-range order (DLRO) characterizing a charge-density wave.

Differing from BCS superconductors as well as from PS (Ref. 7), bipolaronic superconductors have low-lying excitations without a gap which are of a collective nature.[3] For short-range interaction they have a linear dispersion law for long wavelength, similar to that of a Bose liquid.

These excitations correspond to coherent fluctuations of the phase of the local bipolaronic wave functions defined on the different sites of the lattice. These phase fluctuations couple to the charge fluctuations of such a bipolaronic system. Provided that the interaction between bipolarons is short ranged, the zero-sound-like character of these charge fluctuations is responsible for producing the linear spectrum in the collective excitation spectrum which has coupled phase-density fluctuations. We want simply to remark that in the case of long-range interaction between bipolarons, charge-density fluctuations are plasmonlike—but with a plasma frequency determined by the very heavy mass m^{**} of bipolarons. In that case the collective excitation spectrum has a gap

$$\omega_{pl} = [32\pi e^2 n(1-n)/m^{**}]^{1/2}$$

in the long-wavelength limit, at zero temperature. This will modify the thermodynamic properties of the superconducting phase as compared to the short-range interacting case. In real systems we generally have a mixture of light electrons and bipolarons. Under these conditions the light electrons will lead to a screened short-range Coulomb interaction between bipolarons and hence in real materials we shall expect the linear dispersion for the fluctuations of the superconducting order parameter to hold.

Results similar to those of Alexandrov and Ranninger[3] were obtained independently and at the same time by Robaszkiewicz, Micnas, and Chao[14] starting from a phenomenological "negative-U" extended Hubbard model for the case of strong on-site attraction: $|U| \gg D$. These authors derived the "T-n" phase diagram. Using RPA (random-phase approximations) for magnetic systems, they obtained the same gapless, low-temperature excitation spectrum, as AR. Moreover, these authors found two high-temperature phases: one corresponding to dynamically disordered bipolarons and the other to a charge-ordered state.

Quite different results were obtained by Kulik and Pedan[15] also using the negative-U Hubbard Hamiltonian in the strong-coupling limit ($|U| \gg D$). Using a mean-field approximation (MFA), they found a gap in the excitation spectrum of the ODLRO phase and a gap over T_c ratio close to the BCS one.

Using the same MFA, Bulaevskii, Sobyanin, and

Khomskii[16] derived the upper critical field H_{c2} for local pair superconductors. They obtained a surprisingly small coherence length $\xi \sim a$ (a denoting the interatomic distance) as well as extremely high values and unusual temperature dependence of H_{c2}. As a result of their findings these authors expressed the opinion "that none of the compounds known at present is a superconductor of local pair type."

In this paper we derive the thermodynamics and magnetic properties of bipolaronic superconductors (BS) (by which we mean a superconductor of local pairs of fermionic carriers which are bound together by either a polaronic mechanism or any other which could lead to such bound states). We shall fully take into account quantum as well as thermal fluctuations, within a RPA scheme, and show that they are of *qualitative* importance throughout the whole range of the BS phase.

In Sec. II we generalize the AR approach using the Lang-Firsov technique[17] to obtain the bipolaronic Hamiltonian for all values of Δ/ω. We discuss the applicability of the phenomenological negative-U Hubbard Hamiltonian to strong narrow-band superconductors. In Sec. III we discuss the T-n phase diagram and thermodynamics of the BS on the basis of the RPA formulated for this problem by Robaskiewicz *et al.*[14] We show that the fluctuations give a gapless spectrum of excitations and as a result of power-law behavior for the specific heat at low temperature. We also demonstrate the insufficiency of the MFA, which is of a qualitative nature and which can lead to physically erroneous results.[15] The thermodynamics of the bipolaronic system above the superconducting transition is studied in Sec. IV. There we show that the narrow-band Bose gas on a lattice has the temperature dependence of the specific heat in the normal state which is extremely similar to the one for the electron gas in an equally narrow band. On the contrary, the magnetic susceptibility of triplet bosons on a lattice (in the normal phase) is qualitatively different from that for electrons at low temperature. In Sec. V we consider the magnetic properties of a BS based on the idea of Alexandrov and Kagan[18] that they ought to be equivalent to the magnetic properties of a charged Bose gas. We present unpublished results by one of us,[19] which show that the upper critical field of a charged Bose gas (which is strictly zero in the ideal charged Bose gas) is determined by either the interaction of the bosons with impurities or among themselves. We derive the coherence length which turns out to be much greater than the interatomic distance and we show the origin of the qualitative insufficiency of the MFA.[16]

The comparison between BCS and BS and an analysis of the anomalous properties of real d- and f-band compounds lead us to the conclusion that some of them could possibly be examples of BS's. This will be the subject of Sec. VI.

II. BIPOLARONIC HAMILTONIAN, MASS OF THE SMALL BIPOLARON

We start with the ordinary one-band Hamiltonian, including the Fröhlich electron-phonon U and Coulomb V interactions:

$$\begin{aligned} H &= \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} C^{\dagger}_{\mathbf{k}\sigma} C_{\mathbf{k}\sigma} + \sum_{\mathbf{k},\mathbf{q}\sigma} [U(\mathbf{q}) C^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma} C_{\mathbf{k}\sigma} d_{\mathbf{q}} + \text{H.c.}] \\ &\quad + \sum_{\substack{\mathbf{k},\mathbf{k}',\mathbf{q} \\ \sigma,\sigma'}} V(\mathbf{q}) C^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma} C^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma'} C_{\mathbf{k}'\sigma'} C_{\mathbf{k}\sigma} + H_{\text{ph}} , \\ H_{\text{ph}} &= \sum_{\mathbf{q}} \omega_{\mathbf{q}} d^{\dagger}_{\mathbf{q}} d_{\mathbf{q}} . \end{aligned} \tag{2.1}$$

Here, $\epsilon_{\mathbf{k}}$ denotes the bare initial electron dispersion in a rigid lattice, $C_{\mathbf{k}\sigma}$ and $d_{\mathbf{q}}$ are the electron and phonon operators, respectively, $\omega_{\mathbf{q}}$ represents the phonon dispersion, $\mathbf{k},\mathbf{k}',\mathbf{q}$ the wave vectors, and σ the spin of the electrons.

In strong-coupling narrow-band superconductors the second term in Eq. (2.1) is the dominant one due to the condition given by Eq. (1.2). In this case, the site representation is more convenient:

$$\begin{aligned} H &= \sum_{i,i'} T_{ii'} C^{\dagger}_i C_{i'} + \sum_{i\mathbf{q}} [U_i(\mathbf{q}) C^{\dagger}_i C_i d_{\mathbf{q}} + \text{H.c.}] \\ &\quad + \sum_{i,i'} V^{ii'}_{ii'} C^{\dagger}_i C^{\dagger}_{i'} C_{i'} C_i + H_{\text{ph}} , \end{aligned} \tag{2.2}$$

where $T_{ii'}$ denotes the hopping integral, $U_i(\mathbf{q}) = U(\mathbf{q}) \exp(i\mathbf{q}\cdot\mathbf{m})$, $i \equiv (\mathbf{m},\sigma)$ where $\mathbf{m}$ labels the site. For simplicity we restrict ourselves to direct Coulomb interactions.

Using λ^{-1} as a small parameter, one can treat the kinetic energy as a perturbation. The unperturbed Hamiltonian, including electron-phonon and Coulomb interactions and the phonon Hamiltonian H_{ph}, is diagonalized by the familiar Lang-Firsov transformation $\hat{S}_1$,[17] yielding the following exact result:

$$\begin{aligned} H_p &= \hat{S}_1 H \hat{S}_1^{-1} = H_0 + H_1 , \\ \hat{S}_1 &= \exp\left[\sum_{i\mathbf{q}} [\omega_{\mathbf{q}}^{-1} C^{\dagger}_i C_i d^{\dagger}_{\mathbf{q}} U_i(q) - \text{H.c.}] \right] , \end{aligned} \tag{2.3}$$

with

$$\begin{aligned} H_0 &= \sum_i (T_{ii} - \epsilon_p) C^{\dagger}_i C_i + \sum_{ii'} v_{ii'} C^{\dagger}_i C^{\dagger}_{i'} C_{i'} C_i + H_{\text{ph}} , \\ H_1 &= \sum_{\substack{ii' \\ (\mathbf{m}\neq\mathbf{m}')}} \hat{\sigma}_{ii'} C^{\dagger}_i C_{i'} , \end{aligned} \tag{2.4}$$

where

$$\begin{aligned} \epsilon_p &= \sum_{\mathbf{q}} \omega_{\mathbf{q}}^{-1} |U(\mathbf{q})|^2 , \\ v_{ii'} &= V^{ii'}_{ii'} - \sum_{\mathbf{q}} \omega_{\mathbf{q}}^{-1} |U(\mathbf{q})|^2 e^{i\mathbf{q}\cdot(\mathbf{m}-\mathbf{m}')} . \end{aligned} \tag{2.5}$$

ϵ_p measures the polaronic level shift and $v_{ii'}$ represents the polaron-polaron interaction which for superconductors has to be attractive. The kinetic energy of the small polaron H_1 is an operator in the phonon variables:

$$\hat{\sigma}_{ii'} = T_{ii'} \exp\left[\sum_{\mathbf{q}} \omega_{\mathbf{q}}^{-1} \{ d_{\mathbf{q}} [U_i(\mathbf{q}) - U_{i'}(\mathbf{q})] \} - \text{H.c.} \right] . \tag{2.6}$$

Averaging Eq. (2.5) with the equilibrium phonon density

matrix

$$\rho = \exp(-H_{\rm ph}/T)/[\,{\rm Tr}\exp(-H_{\rm ph}/T)]\,, \tag{2.7}$$

yields a narrow small-polaron band:[4,5]

$$\sigma_{ii'} = \langle \hat{\sigma}_{ii'} \rangle = T_{ii'} \exp(-g^2)\,,$$
$$g^2 \equiv \sum_{\mathbf{q}} \omega_{\mathbf{q}}^{-2} \coth\left[\frac{\omega_{\mathbf{q}}}{2T}\right] |\, U(\mathbf{q})\,|^2 [1-\cos\mathbf{q}\cdot(\mathbf{m}-\mathbf{m}')]\,. \tag{2.8}$$

Usually, small-polaron theory[4,5] deals with one single electron in the lattice. This is quite sufficient for semiconductors. In the case of narrow-band superconductors the polaron-polaron attraction $v_{ii'}$ is crucial and was first considered by Alexandrov and Ranninger[3] in the strong-coupling limit, $|v_{ii'}| \gg \sigma_{ii'}$, and by Alexandrov[7] in the opposite limit of weakly interacting polarons, $|v_{ii'}| \lesssim \sigma_{ii'}$. As long as the polaron bandwidth is small enough, Eq. (2.8), the weak-coupling condition is satisfied in a small region of parameters, where the Coulomb repulsion is practically completely compensated for by the attraction coming from the lattice distortion.

In this paper we concentrate on the properties of strongly coupled bipolarons. Using $\sigma/|v|$ as a small parameter, we can treat H_1 as a perturbation. In the ground state of H_0 all the polarons are coupled into small bipolarons with atomiclike wave functions centered on effective lattice sites—discussed in detail in the Introduction.

Since we are only interested in bipolarons, with no single polarons existing in our system, we shall eliminate the latter ones by a second transformation $\hat{S}_2$ (Ref. 3) which eliminates H_1 to first order yielding the following result to second order:

$$\tilde{H} = \exp(\hat{S}_2) H_p \exp(-\hat{S}_2),\quad \langle f|\hat{S}_2|p\rangle = \sum_{\substack{ii'\\(\mathbf{m}\neq\mathbf{m}')}} \langle f|\hat{\sigma}_{ii'} C_i^\dagger C_{i'}|p\rangle (E_f - E_p)^{-1}\,,$$
$$\tilde{H}_{ff'} = E_f \delta_{ff'} - \tfrac{1}{2} \sum_{\substack{ii'(\mathbf{m}\neq\mathbf{m}')\\jj'(\mathbf{n}\neq\mathbf{n}')}} \sum_{p} \frac{\langle f|\hat{\sigma}_{ii'} C_i^\dagger C_{i'}|p\rangle\langle p|\hat{\sigma}_{jj'} C_j^\dagger C_{j'}|f'\rangle}{(E_f - E_p)(E_p - E_{f'})} (E_f + E_{f'} - 2E_p)\,. \tag{2.9}$$

$|f\rangle$, $|f'\rangle$, and $|p\rangle$ are eigenstates of H_0 with energies E_f, $E_{f'}$, and E_p. At low enough temperature, $T \ll \Delta$, only the subspace of H_0 with either doubly occupied or empty sites is of importance. In that case the intermediate states $|p\rangle$ [appearing in Eq. (2.9)] refer to configurations involving two polarons on adjacent sites. It is now convenient to change the representation involving polaron operators into one pertaining to bipolarons,

$$b_{\mathbf{m}}^\dagger = C_{\mathbf{m}\uparrow}^\dagger C_{\mathbf{m}\downarrow}^\dagger,\quad b_{\mathbf{m}} = C_{\mathbf{m}\downarrow} C_{\mathbf{m}\uparrow}\,, \tag{2.10}$$

and average Eq. (2.9) with the phonon density matrix Eq. (2.7).[20] In that way we can take, in Eq. (2.9),

$$E_f - E_p = E_{f'} - E_p = -\Delta + \sum_{\mathbf{q}} (n_{\mathbf{q}}^f - n_{\mathbf{q}}^p)\omega_{\mathbf{q}}\,, \tag{2.11}$$

where $n_{\mathbf{q}}^f, n_{\mathbf{q}}^p$ denote the occupation number of phonons of wave vector $\mathbf{q}$ in the states $|f\rangle$ and $|p\rangle$, respectively. This leads finally to the following result for the electronic part of the total Hamiltonian:

$$\tilde{H} = \sum_{\mathbf{m}\neq\mathbf{m}'} [\tilde{v}_{\mathbf{m}\mathbf{m}'} b_{\mathbf{m}}^\dagger b_{\mathbf{m}} b_{\mathbf{m}'}^\dagger b_{\mathbf{m}'} - t(\mathbf{m}-\mathbf{m}') b_{\mathbf{m}}^\dagger b_{\mathbf{m}'}]\,, \tag{2.12}$$

where we have put the renormalized site energy equal to zero:

$$t(\mathbf{m}-\mathbf{m}') = 2i \int_0^\infty d\tau\, e^{-(i\Delta+\delta)\tau} \langle \hat{\sigma}_{\mathbf{m}\mathbf{m}'}(\tau)\hat{\sigma}_{\mathbf{m}\mathbf{m}'}(0)\rangle \tag{2.13}$$

is the bipolaronic hopping integral and

$$\tilde{v}(\mathbf{m}-\mathbf{m}') = 4v(\mathbf{m}-\mathbf{m}') + 2i \int_0^\infty d\tau\, e^{-(i\Delta+\delta)\tau} \langle \hat{\sigma}_{\mathbf{m}\mathbf{m}'}(\tau)\hat{\sigma}_{\mathbf{m}'\mathbf{m}}(0)\rangle \tag{2.14}$$

is the effective bipolaronic interaction; $\delta = +0$. In Eqs. (2.13) and (2.14) we introduced the time-dependent phonon operators

$$\hat{\sigma}(\tau) = \exp(iH_{\rm ph}\tau)\hat{\sigma}\exp(-iH_{\rm ph}\tau)\,. \tag{2.15}$$

If the tunneling of bipolarons happens without emission or absorption of phonons in the intermediate states $|p\rangle$, we find

$$\langle \hat{\sigma}\hat{\sigma}\rangle \simeq \sigma^2\,, \tag{2.16}$$

which is our previous result.[3] As we shall see, this approximation is satisfied provided that the binding energy for small bipolarons is sufficiently small ($\Delta \ll \omega$), where

$$\omega = \epsilon_p/g^2 \tag{2.17}$$

is the characteristic phonon frequency in our system.

Let us consider the general case where in the intermediate state phonon emission and absorption processes take place. This will, in general, give rise to an effective bipolaronic mass $m^{**} \sim t^{-1}$ as well as to an effective bipolaron-bipolaron repulsion [second term in Eq. (2.14)].

Again, using the Lang-Firsov technique[17] we obtain

$$\langle \hat{\sigma}_{\mathbf{m}\mathbf{m}'}(\tau)\hat{\sigma}_{\mathbf{m}\mathbf{m}'}(0)\rangle = T_{\mathbf{m}\mathbf{m}'}^2 e^{-2g^2} \exp - \left\{ \sum_{\mathbf{q}} \frac{|\,U(\mathbf{q})\,|^2}{\sinh(\omega_{\mathbf{q}}/2T)} \frac{2}{\omega_q^2} [1-\cos\mathbf{q}(\mathbf{m}-\mathbf{m}')] \cos\left[\omega_{\mathbf{q}}\left[\tau + \frac{i}{2T}\right]\right] \right\}, \tag{2.18}$$

and $\langle \hat{\sigma}_{\mathbf{mm}'}(\tau)\sigma_{\mathbf{m}'\mathbf{m}}(0)\rangle$ which is given by the expression, Eq. (2.18), upon replacing the minus sign in the exponent, given before the first bracket, by a plus sign. Substituting these expressions into Eqs. (2.13) and (2.14), we hence obtain in the limit $\Delta \gg \omega$,

$$t(\mathbf{m}-\mathbf{m}')=(2T^2_{\mathbf{mm}'}/\Delta)\exp(-4g^2)\ ,$$
$$\tilde{v}(\mathbf{m}-\mathbf{m}')=4v(\mathbf{m}-\mathbf{m}')+(2T^2_{\mathbf{mm}'}/\Delta)\ . \tag{2.19}$$

In the opposite limit, $T \lesssim \Delta \ll \omega$, the calculation of the integrals, Eqs. (2.13) and (2.14), with the expansion of the exponents in Eq. (2.18) in a series of Bessel functions finally yields

$$t(\mathbf{m}-\mathbf{m}')=(2T^2_{\mathbf{mm}'}/\Delta)\exp(-2g^2)\ ,$$
$$\tilde{v}(\mathbf{m}-\mathbf{m}')=4v(\mathbf{m}-\mathbf{m}')+(2T^2_{\mathbf{mm}'}/\Delta)\exp(-2g^2)\ . \tag{2.20}$$

One can see from a comparison of Eqs. (2.19) and (2.20) that the effective bipolaronic mass and effective bipolaronic repulsion are strongly dependent on the ratio Δ/ω. Both of them increase rapidly with increasing Δ/ω.

The approximate relation, Eq. (2.16), corresponds to bipolaron hopping via a virtual process involving incoherent hopping of each of the two polarons which constitute the bipolaron. This result is obtained therefore if one averages the polaronic Hamiltonian, Eq. (2.4), with the phonon density matrix, Eq. (2.7). In this case H_p will be equivalent to the negative-U Hubbard Hamiltonian but with a temperature-dependent extremely narrow band W. We hence conclude that the phenomenological negative-U Hubbard Hamiltonian is applicable to polaronic systems only in the limit $\omega \gg U$ and with D being replaced by a temperature-dependent W. In the limit $\omega \ll \Delta$ the bipolaronic Hamiltonian can be parametrized by an extended negative-U Hubbard model in the strong-coupling limit.

Starting from the usual Fröhlich interaction, we derived in this section the effective Hamiltonian, Eq. (2.12), describing mobile bipolarons which obey the mixed commutation rules (Pauli statistics)

$$[b_{\mathbf{m}},b^{\dagger}_{\mathbf{m}}]_+=1,\ \ [b_{\mathbf{m}},b^{\dagger}_{\mathbf{m}'}]=0\ (\mathbf{m}\neq\mathbf{m}')\ . \tag{2.21}$$

So far we assumed singlet bipolarons with spin $s=0$ [Eq. (2.10)]. Triplet bipolarons can exist quite naturally in real narrow-band d- and f-band materials due to the orbital degeneracy of the effective bipolaronic sites which in general may be considered as clusters of a small number of metal ions surrounded by their ligand environment. In the strong-coupling limit these triplet bipolarons again form very narrow bands and can be described by the same Hamiltonian [Eq. (2.12)] as for singlet bipolarons—generalized to three degenerate bands. This is possible since due to the polaronic character of bipolarons the exchange interaction between triplet bipolarons with different values for s_z will be negligible. We shall show in the following section that in a dilute system with small enough atomic concentrations of bipolarons ($n \lesssim 0.1$), their properties are equivalent to the free heavy-boson liquid on a lattice.

III. THERMODYNAMICS OF A BIPOLARONIC SUPERCONDUCTOR

The Pauli commutation rules, Eq. (2.21), lead us to adopt the following pseudospin language for the bipolaronic Hamiltonian, Eq. (2.12):[3]

$$\tilde{H}=\sum_{\mathbf{m}} S^z_{\mathbf{m}}\left[\mu+\sum_{(\mathbf{m}'\neq\mathbf{m})}\tilde{v}(\mathbf{m}-\mathbf{m}')S^z_{\mathbf{m}'}\right]$$
$$-\sum_{(\mathbf{m}\neq\mathbf{m}')} t(\mathbf{m}-\mathbf{m}')(S^x_{\mathbf{m}}S^x_{\mathbf{m}'}+S^y_{\mathbf{m}}S^y_{\mathbf{m}'})\ , \tag{3.1}$$

where

$$S^z_{\mathbf{m}}=\tfrac{1}{2}-b^{\dagger}_{\mathbf{m}}b_{\mathbf{m}},\ \ S^x_{\mathbf{m}}=\tfrac{1}{2}(b_{\mathbf{m}}+b^{\dagger}_{\mathbf{m}}),\ \ S^y_{\mathbf{m}}=\frac{i}{2}(b_{\mathbf{m}}-b^{\dagger}_{\mathbf{m}})$$

are the Pauli spin-$\frac{1}{2}$ matrices and μ denotes the chemical potential of the bipolarons.

In this section we discuss the phase diagram and derive the thermodynamics of the low-temperature phase of this anisotropic Heisenberg Hamiltonian with fixed total magnetization, which follows from the conservation of the number of bipolarons:

$$\frac{1}{N}\sum_{\mathbf{m}}\langle S^z_{\mathbf{m}}\rangle=\tfrac{1}{2}-n\ . \tag{3.2}$$

N is the number of sites (in the larger sense as discussed above) in a crystal volume Ω, which is supposed to be equal to unity, $\Omega=1$.

We use the RPA approach, formulated in terms of the standard basis operators,[21,22] developed for this problem by Robaszkiewicz *et al.*[14] in their analysis of the elementary excitation spectrum. This treatment allows us to take into account quantum as well as thermal fluctuations.

The Hamiltonian Eq. (3.1) has been investigated in detail in the context of magnetic materials[23–25] and quantum solids.[12,25] In those cases the magnetic field, or pressure, is one of the independent thermodynamic variables and the magnetization (or the molar volume) is determined such as to minimize the free energy. In our case, on the contrary, the average electron density is fixed and thus μ is not an independent variable and has to be determined self-consistently via the constraint, Eq. (3.2). Therefore, we are essentially dealing with a problem of an antiferromagnet in a temperature-dependent magnetic field.

Let us first of all briefly discuss the MFA results. The MFA ground state was obtained in our previous work.[3] Below the critical concentration n_c,

$$n_c=\tfrac{1}{2}\{1-[(\tilde{v}-t)/\tilde{v}+t)]^{1/2}\}\ , \tag{3.3}$$

where $\tilde{v}=zv(\mathbf{m}-\mathbf{m}')$, $t=zt(\mathbf{m}-\mathbf{m}')$, and nearest-neighbor interaction is assumed ($|\mathbf{m}-\mathbf{m}'|=a$); the MFA yields a homogeneous coherent phase BS with $S^x\neq 0$. For $-t<\tilde{v}<t$, this phase is the ground state for all concentrations. For $\tilde{v}<-t$, the system is unstable versus bipolaron droplet formation (see Fig. 1).

In the high-concentration region $n>n_c$ the mixed (ODLRO plus DLRO) phase (M) exists. The complete MFA (T-n) phase diagram of the Hamiltonian Eq. (3.1),

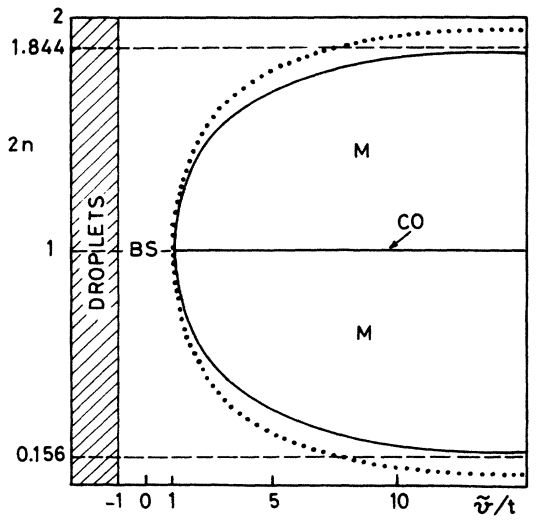

FIG. 1. Ground-state phase diagram ($T=0$). RPA (solid line), MFA (dotted line). The ground state at $n=0.5$ is a charge-ordered state without ODLRO.

together with the condition Eq. (3.2), was obtained by Robaszkiewicz *et al.*[14] (Fig. 2). It shows two additional nonsuperconducting phases, one of which is charge ordered (DLRO) (see also Ref. 26).

The excitation spectrum of the Hamiltonian Eq. (3.1) was found at $T=0$ (Refs. 3 and 13) as well as for finite T (Refs. 14 and 26). It is magnonlike with a linear dispersion law in the long-wavelength limit both for the BS and for the M phase. In the latter case, MFA-RPA gives linear behavior[14,26] for the entire temperature regime of the M phase, except at $T=0$.[3] However, it turns out that if one takes into account quantum zero-point fluctuations, one obtains a linear dispersion for the excitation spectrum of the M phase for $T=0$ also.[26]

If one uses MFA to obtain the excitation spectrum[15] with the classical pseudomagnetic field $\mathbf{H}_\mathbf{m}$

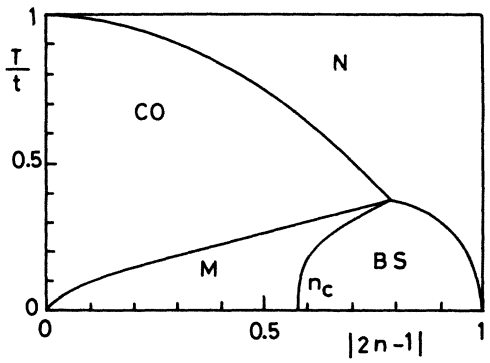

FIG. 2. MFA phase diagram (Ref. 14) for $\tilde{v}/t=2$ as a function of T and bipolaron concentration n.

$$H=-\sum_{\mathbf{m}} \mathbf{S}_\mathbf{m}\mathbf{H}_\mathbf{m} , \tag{3.4}$$

where

$$H_\mathbf{m}=-\mu-2\sum_{\mathbf{m}\neq\mathbf{m}'}[\langle S^z_{\mathbf{m}'}\rangle\tilde{v}(\mathbf{m}-\mathbf{m}')-t(\mathbf{m}-\mathbf{m}')\langle \mathbf{S}^\perp_{\mathbf{m}'}\rangle] , \tag{3.5}$$

one obtains a gap in the spectrum proportional to t, which corresponds to local spin flips ($\mathbf{S}^\perp_\mathbf{m}$ denotes the projection of $\mathbf{S}_\mathbf{m}$ onto the x-y plane). This is an artifact of the MFA which leads to exponential dependence of the specific heat. The true excitations of the spectrum are pseudomagnons with a gapless dispersion.

We shall now generalize the RPA results[3,14] concerning the excitation spectrum by taking into account quantum fluctuations, and determine the thermodynamics of the BS phase within this scheme. It turns out that this leads to qualitative changes in the phase diagram as compared to previous MFA results (see Figs. 1 and 2).

Using the RPA equations of motion for double time-retarded Green's functions, one obtains the following temperature-dependent excitation spectrum of the BS (see Appendix A):

$$\omega_\mathbf{k}=R[(t-t_\mathbf{k}\cos^2\theta+\tilde{v}_\mathbf{k}\sin^2\theta)(t-t_\mathbf{k})]^{1/2} , \tag{3.6}$$

where $t_\mathbf{k},\tilde{v}_\mathbf{k}$ are the Fourier components of $t(\mathbf{m})$ and $v(\mathbf{m})$, respectively, and R is the occupation probability which obeys the following equation:

$$\frac{1}{R}=\frac{1}{N}\sum_\mathbf{k}\frac{A_\mathbf{k}}{\omega_\mathbf{k}}\coth\frac{\omega_\mathbf{k}}{2T} , \tag{3.7}$$

where

$$A_\mathbf{k}=R[t-t_\mathbf{k}\cos^2\theta-\tfrac{1}{2}(t_\mathbf{k}-\tilde{v}_\mathbf{k})\sin^2\theta] \tag{3.8}$$

and

$$\cos\theta=(2n-1)/R \tag{3.9}$$

determine the angle between $\mathbf{S}_\mathbf{m}$ and $\mathbf{H}_\mathbf{m}$. The superconducting order parameter is given by

$$S^x=\langle S^x_\mathbf{m}\rangle,\quad S^x=\tfrac{1}{2}R\sin\theta=\tfrac{1}{2}[R^2-(2n-1)^2]^{1/2} . \tag{3.10}$$

The quantity R is determined in such a way, Eq. (3.7), that it includes quantum as well as thermal fluctuations. Remember that MFA gives $R=1$ at $T=0$.

With nearest-neighbor interaction we obtain from Eq. (3.6)

$$\omega^2_\mathbf{k}=(Rt)^2\left[1-\gamma_\mathbf{k}\left[\cos^2\theta-\frac{\tilde{v}}{t}\sin^2\theta\right]\right](1-\gamma_\mathbf{k}) \tag{3.11}$$

with

$$\omega_\mathbf{k}\simeq sk+O(k^2)\ \ (k\to 0),\quad \gamma_\mathbf{k}=t(\mathbf{k})/t=\frac{1}{z}\sum_{|\mathbf{m}|=a}e^{i\mathbf{k}\cdot\mathbf{m}} , \tag{3.12}$$

where the "sound" velocity s is temperature dependent (see also Ref. 13):

$$s(T)=R(\sin\theta)\delta[t(\tilde{v}+t)]^{1/2}\,,\qquad \delta^2=\frac{1}{6z}\sum_{|\mathbf{m}|=a}\left[\frac{\mathbf{k}\cdot\mathbf{m}}{k}\right]^2 . \tag{3.13}$$

The boundary line between the BS and the normal phase determining $T_c(n)$ is given by the condition

$$s(T_c)=0\,, \tag{3.14}$$

which is the same as

$$S^x=0\,. \tag{3.15}$$

The boundary with the mixed phase M is determined by the condition of the instability of the spectrum, Eq. (3.11), against doubling of the lattice periodicity, i.e.,

$$\omega_{\mathbf{Q}}=0\,, \tag{3.16}$$

where $2\mathbf{Q}$ is the smallest reciprocal-lattice vector.

Together with Eq. (3.11), Eq. (3.16) reduces to

$$\frac{R^2+(2n_c-1)^2}{R^2-(2n_c-1)^2}=\frac{\tilde{v}}{t}\,, \tag{3.17}$$

where $R(T,n,\tilde{v}/t)$ has to be determined from Eqs. (3.7)–(3.9). We should mention that s becomes imaginary for $\tilde{v}<-t$, which indicates that at $\tilde{v}/t=-1$ the system becomes unstable versus a phases of bipolaron "droplets" (see Fig. 1).

Let us first derive the critical concentration n_c as a function of $\tilde{v}/t$ at $T=0$. Substituting

$$R(0)=(1+2\psi_0)^{-1} \tag{3.18}$$

into Eq. (3.7), we obtain together with Eq. (3.9), the self-consistent equation for the zero-point fluctuation contribution ψ_0

$$2\psi_0=\frac{1}{N}\sum_{\mathbf{k}}\frac{1-\frac{1}{2}\{1+[(2n-1)^2(1+2\psi_0)^2(1+\tilde{v}/t)-\tilde{v}/t]\gamma_{\mathbf{k}}\}}{(\{1-\gamma_{\mathbf{k}}[(2n-1)^2(1+2\psi_0)^2(1+\tilde{v}/t)-\tilde{v}/t]\}(1-\gamma_{\mathbf{k}}))^{1/2}}-1\,. \tag{3.19}$$

The numerical solution of Eqs. (3.17)–(3.19) for a cubic lattice is shown in Fig. 1. One can notice the qualitative difference of the behavior of n_c determined in this way as compared to the MFA results.[3,14] The quantum fluctuations extend the region of stability of the homogeneous BS phase. In such a way, the BS phase exists even in the limit $\tilde{v}/t\to\infty$ provided

$$2n<0.156 \tag{3.20}$$

for a sc lattice, contrary to the MFA result, Eq. (3.3), which gives $n_c=0$ in this limit. The behavior of the order parameter S^x as a function of $\tilde{v}/t$, determined numerically from Eqs. (3.10), (3.18), and (3.19) is shown in Fig. 3. One can see that the bipolaron interaction suppresses the order parameter, contrary to MFA results in which the order parameter is independent of $\tilde{v}$.

From Eq. (3.7) one obtains the following temperature expansion for $R(T)$:

$$R(T)=\{4[S^x(0)]^2+(2n-1)^2\}^{1/2}-T^2/6^{5/2}(1+\tilde{v}/t)^{1/2}t^2[S^x(0)]^2+O(T^4)\,. \tag{3.21}$$

Let us now consider the low-temperature behavior for the internal energy and the specific heat C_s. The internal energy within our RPA is determined at low temperature by

$$E\simeq E_0+\sum_{\mathbf{k}}\omega_{\mathbf{k}}\left[\exp\frac{\omega_{\mathbf{k}}}{T}-1\right]^{-1}\,, \tag{3.22}$$

where E_0 is the ground-state energy. For sc lattices the direct calculation of Eq. (3.22) yields

$$E-E_0\simeq\pi^2T^4\frac{\{1+18T^2[S^x(0)t(t+\tilde{v})]^{-1}\}}{240\delta^{3/2}S^x(0)[t(t+\tilde{v})]^{3/2}}\,. \tag{3.23}$$

In the derivation of Eq. (3.23) we used the expansion of R, Eq. (3.21). In such a way we obtain the power-law temperature specific heat:

$$C_s=\pi^2[t(t+\tilde{v})S^x(0)]^{-3/2}(60\delta^{3/2})^{-1}\times[T^3+27T^5/S^x(0)t(t+\tilde{v})]\,. \tag{3.24}$$

We should mention that the temperature range of validity of Eq. (3.24) diminishes as $n\to0$. At fixed n at high enough temperature, the k^2 term in Eq. (3.12) will be dominant and will give rise to

$$C_s\sim T^{3/2}\,. \tag{3.25}$$

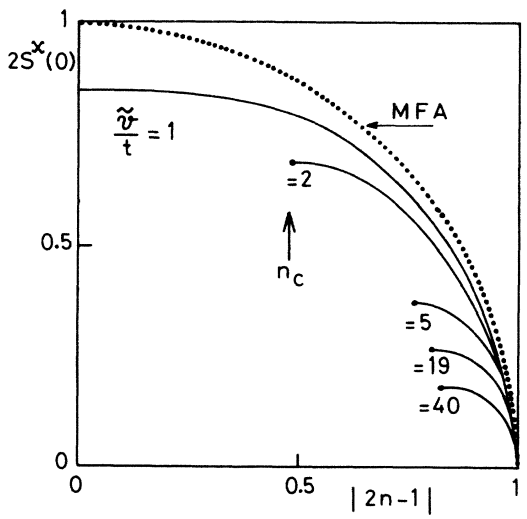

FIG. 3. Concentration dependence of the order parameter of BS at $T=0$ for different values of $\tilde{v}/t$. For $n>n_c$, a mixed phase with two order parameters exists.

In concluding this section, we shall derive T_c. Substituting Eq. (3.15) into Eqs. (3.7)–(3.9), we obtain

$$(2n-1)^{-1}=\frac{1}{N}\sum_{\mathbf{k}}\coth\left[\frac{(2n-1)}{2T_c}(t-t_{\mathbf{k}})\right]. \quad (3.26)$$

The numerical solution of Eq. (3.26) for sc lattices is plotted in Fig. 4.

For a dilute system ($n \ll 1$), we obtain from Eq. (3.26) the following analytic expansion:

$$T_c \simeq \frac{3.31(na^{-3})^{3/2}}{m^{**}}(1-0.54n^{2/3}), \quad (3.27)$$

where $m^{**}=3/ta^2$ is the bipolaronic effective mass for the case of a sc lattice. In the high-density limit,

$$|2n-1| \ll 1. \quad (3.28)$$

Equation (3.26) gives

$$T_c \simeq \frac{t}{2}\left[c^{-1}-\frac{(2n-1)^2}{3}\right], \quad (3.29)$$

where $c=1.5164$, 1.393, and 1.345 for sc, bcc, and fcc lattices, respectively. One can see from Fig. 4 that the region $2n \lesssim 0.2T_c$ is practically the same as for the ideal Bose gas. On the contrary, the MFA result[15]

$$T_c = t(2n-1)/\ln(n/1-n), \quad (3.30)$$

as well as the cluster approximation,[27] gives a qualitatively wrong concentration dependence of $T_c \sim [\ln(1/n)]^{-1}$ for low densities and overestimates T_c by a factor of about 1.5 for $2n=1$ (see Fig. 4). Moreover, in the cluster approximation[27] the $T_c(n)$ curve intersects the n axis not at $n=0$, but at $n=\exp(-z)$. We want to point out that this approach is questionable also for $2n \sim 1$ and $\tilde{v} > t$. This is connected with the well-known,[28] inherent pathologies of the cluster approximation such as unphysical anti-Néel and anti-Curie points.

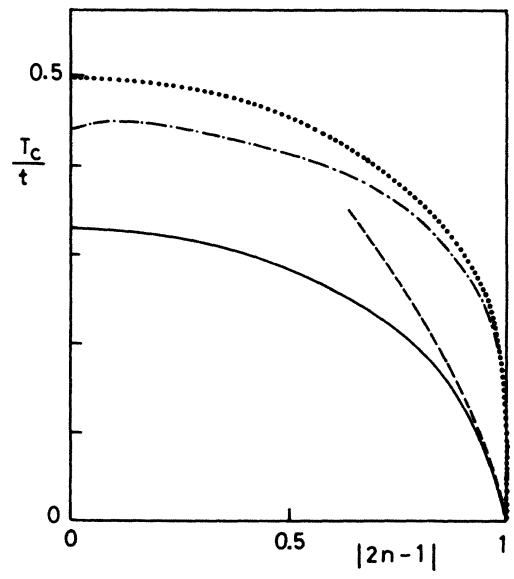

FIG. 4. Critical temperature of a BS as a function of concentration. RPA result—present work (solid line), MFA result (Refs. 14 and 15) (dotted line), cluster approximation result (Ref. 27) for $\tilde{v}/t=1$ (dashed-dotted line). The T_c for the ideal Bose gas is indicated by the dashed line.

We would like to stress that the RPA used in this paper has proven to be an excellent approximation in problems of magnetism.[22,24,29] In particular, it predicts the absence of long-range order in one and two dimensions for short-range interaction at finite temperature, in agreement with exact theorems.

In this section we examined the thermodynamics of the homogeneous BS phase. The thermodynamics of the M phase as well as the charge-ordered (CO) phase will be examined in a separate publication.[30]

IV. NORMAL-STATE PROPERTIES OF BIPOLARONIC SYSTEMS

One of the most striking features of bipolaronic systems is that above T_c the normal phase is characterized by an ensemble of bipolarons on a lattice, forming a very narrow bipolaronic band. This is hence quite different from an ordinary BCS superconductor which above T_c goes into a metallic state characterized by an ensemble of electrons on a lattice, generally forming a fairly large electron band.

We shall in the following consider some of the normal-state thermodynamic properties of such a bipolaronic system. This can be done very easily if the concentration of bipolarons is small. In this case, neither the hard core nor the effective interaction between bipolarons on different sites is important. Our initial Hamiltonian Eq. (2.12) thus reduces to

$$H=-\sum_{\mathbf{m}\neq\mathbf{m}'} t(\mathbf{m}-\mathbf{m}')b_{\mathbf{m}}^{\dagger}b_{\mathbf{m}'}, \quad (4.1)$$

where, moreover, the b's are simply boson operators. This is due to the fact that within the physically relevant subspace of either singly occupied or empty sites, the b's satisfy the commutation relation [Eq. (2.21)]

$$[b_{\mathbf{m}},b_{\mathbf{m}}]_-=1-2n.$$

For small bipolaron concentration ($n \ll 1$) the b's thus are ordinary boson operators.

We shall show in the following that as far as the temperature dependence of the specific heat is concerned, such bosonlike bipolarons behave in practically the same way as fermions (electrons) with a comparably narrow half bandwidth $t[\equiv zt(\mathbf{m}-\mathbf{m}')]$. This holds for the entire temperature regime.

In the present discussion we shall include triplet bipolarons and evaluate the specific heat and magnetic susceptibility for electrons ($s=\frac{1}{2}$), singlet bipolarons ($s=0$), and triplet bipolarons ($s=1$) (s denoting the spin).

The corresponding expressions for the specific heat and the chemical potential which have to be evaluated self-consistently are the following:

$$C_{b,e}=-2(s+1)\int d\epsilon N(\epsilon)\partial f_{b,e}(\epsilon)/\partial T$$
$$=-2(s+1)T\int_{-t-\mu}^{t-\mu}d\xi N(\xi+\mu)\frac{\partial f_{b,e}(\xi)}{\partial\xi}\times\left[\left[\frac{\xi}{T}\right]^2+\left[\frac{\xi}{T}\right]\frac{\partial\mu}{\partial T}\right], \tag{4.2}$$

$$n=(2s+1)\int d\epsilon N(\epsilon)f_{b,e}(\epsilon)$$
$$=(2s+1)\int_{-t-\mu}^{t-\mu}d\xi N(\xi+\mu)f(\xi),$$

$f_{b,e}(\epsilon)$ denote, respectively, the Bose and the Fermi distribution function $f_{b,e}(\epsilon)=\{\exp[(\epsilon-\mu)/T]\mp1\}^{-1}$, and $N(\epsilon)$, the density of states of energy ϵ. μ denotes the chemical potential.

We are interested in the temperature dependence of the thermodynamic quantities on a temperature scale which is of the order of the bandwidth (a few meV in the systems of interest). Moreover, we restrict ourselves to a discussion of the normal-state properties, well above T_c—the transition temperature to the super-fluid phase. Under these conditions the fine structure of the density of states of the low-energy states is of no importance. Hence, we choose a square density of states

$$N(\xi)=(2t)^{-1}, \tag{4.3}$$

for which $T_c\equiv0$ and which permits us to treat the normal phase in a consistent fashion. In such a way we can compare self-consistently the thermodynamical behavior of electrons and bosons in the normal phase down to zero temperature.

Introducing the dimensionless parameters $\beta=t/T$ and $\mu^*=\mu/T$, we obtain for bosons using Eqs. (4.2) and (4.3),

$$C_b=\frac{2s+1}{8\beta}\int_{-\beta-\mu^*}^{\beta-\mu^*}dx\left[x^2+x\left[\mu^*-\beta\frac{\partial\mu^*}{\partial\beta}\right]\right]\times\sinh^{-2}\left[\frac{x}{2}\right], \tag{4.4}$$

$$\mu^*=\ln\left[\frac{1-\exp(-2n^*\beta)}{\exp\beta-\exp(-2n^*+1)\beta}\right],\quad n^*=\frac{n}{2s+1}. \tag{4.5}$$

In the high-temperature limit ($\beta\lesssim1$), we find from Eq. (4.5)

$$\mu^*\simeq\ln n^*/(n^*+1)-\beta^2\tfrac{1}{6}(1+2n^*). \tag{4.6}$$

Substituting Eq. (4.6) into Eq. (4.4), we obtain

$$C_b\simeq n[1+n/(2s+1)]\beta^2/3,\quad \beta\lesssim1. \tag{4.7}$$

The coefficient in the T^{-2} term in expression (4.7) is physically quite understandable. Specific heat is connected with the probability of the absorption of thermal energy, which is proportional to the numbers of occupied initial states (n^*) times (n^*+1) coming from the final states and reflecting the two contributions characteristic for Bose systems, i.e., processes connected with spontaneous as well as induced emission.

Let us next consider the low-temperature behavior of the specific heat. In this temperature regime ($\beta n,\beta\gg1$) we obtain from Eq. (4.5)

$$\mu^*\simeq-\beta-\exp(-2n^*\beta), \tag{4.8}$$

which shows that the chemical potential at low temperature is locked near the bottom of the band ($\mu\simeq-t$) and is practically temperature independent. Substituting (4.8) into Eq. (4.4), we thus obtain

$$C_b=(2s+1)\pi^2/6\beta\quad(\beta,\beta n\gg1). \tag{4.9}$$

This result shows that bosons in narrow bands at low temperature have a temperature-independent specific-heat coefficient $\gamma=C/T$, just as for electrons. The linear temperature dependence in fermion as well as boson systems is linked to the existence of a quasilocked chemical potential. For comparison we quote here the results for electrons in the two extreme temperature regimes. Based on the same square density of states as before [Eq. (4.3)], we obtain[31]

$$C_e\simeq n(1-n/2)\beta^2/3\quad(\beta\lesssim1),$$
$$C_e\simeq\pi^2/3\beta\quad(\beta,\beta n>1). \tag{4.10}$$

If $n\ll1$, an intermediary temperature region exists for $1/n\gg\beta\gtrsim1$ in which the boson and fermion specific heat shows logarithmic behavior,

$$C_{b,e}\simeq-2n\ln(n\beta). \tag{4.11}$$

In such a way bosons and electrons in narrow-band systems have extremely similar temperature dependences of their specific heat in the normal phase [see Figs. 5(a) and 5(b)] with the following ratio of γ at low temperature $\gamma_b/\gamma_e=s+\frac{1}{2}$. It is necessary to point out that the temperature region in which we expect the linear behavior of the specific heat can be very small if $n\ll1$. In this case, we find for γ a fairly sharp rise as one approaches $T=0$ which will abruptly turn over into a constant for extremely small temperature ($T\lesssim nt$). For real systems which show a transition to a superconducting phase, the region for the linear temperature behavior of C can practically disappear if the critical temperature is high enough. In particular, for ideal bosons we have[13] $T_c\sim n^{2/3}t$ with $n\ll1$. In this case, the low-temperature behavior will be given by Eq. (4.11) down to T_c.

The T^{-2} law for the specific heat at high temperature, common to both fermions and bosons originates from the finite value of the band for these particles, which is a direct consequence of the discreteness of the lattice. The classical value for the specific heat is only obtained for continuous media which have infinite bandwidth. Let us now briefly discuss the magnetic susceptibility for bipolarons in the normal phase. For singlet bipolarons evidently the spin susceptibility is zero due to the fairly large binding energy of those bipolarons (typically, $\Delta\sim0.1-1$ eV). For triplet bipolarons, however, the magnetic field couples to the spin of those bosons and the magnetic susceptibility is determined from the linear term of the induced magnetization

$$M(H)=2\mu_B\int d\epsilon N(\epsilon)[f_b(\epsilon-\mu_BH)-f_b(\epsilon+\mu_BH)], \tag{4.12}$$

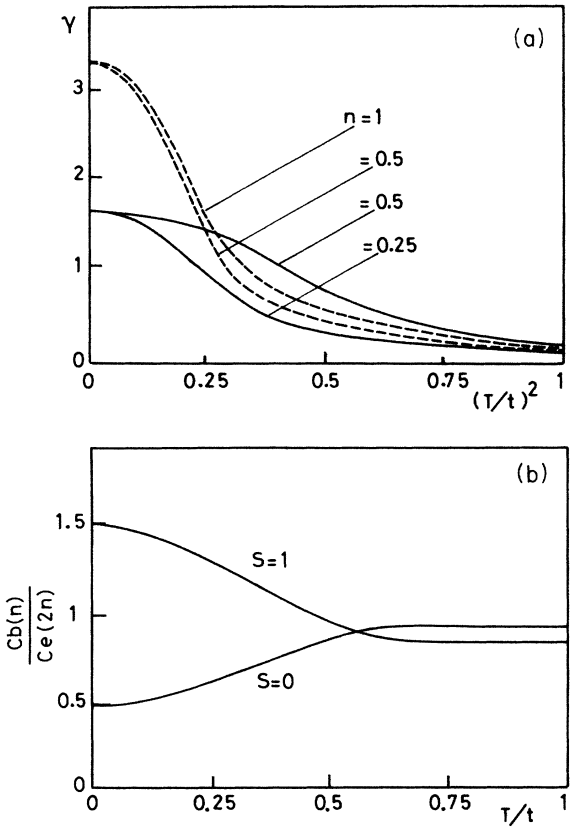

FIG. 5. (a) Temperature dependence of the specific-heat coefficient $\gamma = C\beta$ for electrons (dashed line) and for singlet bosons (solid line). (b) Ratio of the triplet ($s=1$) and singlet ($s=0$) boson specific heat to the electron one as a function of temperature ($n=0.25$).

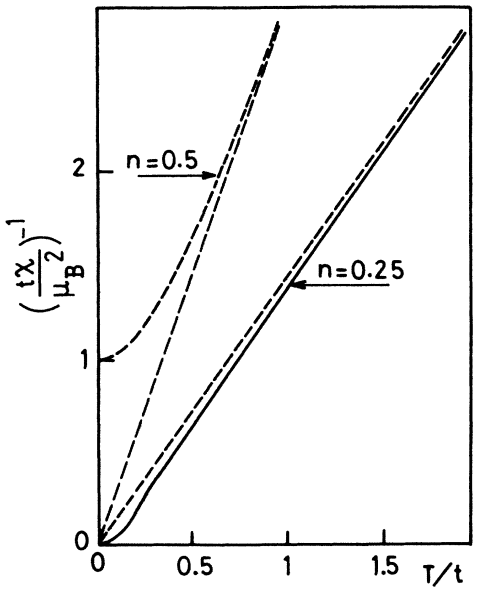

FIG. 6. Temperature dependence of the inverse magnetic susceptibility for electrons (dashed line) and for triplet bosons (solid line).

where H denotes the applied magnetic field and μ_B, the Bohr magneton. We thus obtain

$$\chi_t = -\frac{4\mu_B^2}{t}\int_{-t-\mu}^{t-\mu} d\xi \frac{\partial f_b}{\partial \xi}(\xi) = -\frac{4\mu_B^2}{t}[f_b(t-\mu)-f_b(-t-\mu)] , \tag{4.13}$$

which, together with the corresponding expression for the chemical potential of triplet bipolarons [Eq. (4.5)], finally gives us

$$\chi_t = \frac{4\mu_B^2}{t}\frac{(e^{2n\beta/3}-1)(e^{2\beta}-e^{-2n\beta/3})}{(e^{2\beta}-1)} . \tag{4.14}$$

At high temperatures ($n\beta, \beta \lesssim 1$) we obtain from Eq. (4.14) a Curie behavior (just as for narrow-band electrons [31] given below for comparison):

$$\chi_t \simeq (8\mu_B^2/3T)n(1+n/3) , \quad \chi_e \simeq (\mu_B^2/T)n(1-n/2) . \tag{4.15}$$

At low temperatures ($\beta n, \beta \gg 1$) the behavior of the susceptibility of triplet bosons differs significantly from that of electrons (see Fig. 6):

$$\chi_t = (4\mu_B^2/t)\exp(\tfrac{2}{3}n\beta) \sim \exp(2nt/3T) , \quad \chi_e = \mu_B^2/t \sim \text{const} . \tag{4.16}$$

In such a way, we have shown that while the specific heat for narrow-band systems is extremely similar for bosons and fermions; this is not true as far as the susceptibility is concerned. See for comparison Figs. 5(b) and 6.

V. ELECTRODYNAMICS AND MAGNETIC PROPERTIES OF BIPOLARONIC SUPERCONDUCTORS

We have shown above that in the dilute system ($n \lesssim 0.1$) the thermodynamical properties of bipolarons are identical to the ones for bosons on a narrow band. In this section we derive the electrodynamic equations for such a system following the ideas initially proposed by Alexandrov and Kagan[18] and some unpublished results by Alexandrov[19] concerning the determination of the upper critical field of a charged Bose gas.

As usually assumed,[32] we take the magnetic field H with a vector potential $\mathbf{A}(\mathbf{r})$ to be small compared to the atomic field

$$(eH)^{-1} \gg a^2 . \tag{5.1}$$

This condition allows us to calculate the electronic hopping $\tilde{T}$ in the presence of the magnetic field as follows:[33]

$$\tilde{T}(\mathbf{m},\mathbf{m}') = T(\mathbf{m}-\mathbf{m}')\exp[-ie\mathbf{A}(\mathbf{m})\cdot(\mathbf{m}-\mathbf{m}')] . \tag{5.2}$$

In such a way, the bipolaron Hamiltonian $\tilde{H}$ in the magnetic field can be derived from the expression, Eq. (2.12), on substituting $t \sim \tilde{t}$ with

$$\tilde{t}(\mathbf{m},\mathbf{m}')=t(\mathbf{m}-\mathbf{m}')\exp[-2ie\mathbf{A}(\mathbf{m})\cdot(\mathbf{m}-\mathbf{m}')] . \quad (5.3)$$

The magnetic field breaks the translational symmetry, so that the real-space representation of $\tilde{H}$ is more adequately described by the field operators $\psi(\mathbf{r})$ and $\psi^{\dagger}(\mathbf{r})$ defined by

$$b_{\mathbf{m}}=\int d\mathbf{r}\,\psi(\mathbf{r})\delta(\mathbf{r}-\mathbf{m}) ,$$
$$b_{\mathbf{m}}^{\dagger}=\int d\mathbf{r}\,\psi^{\dagger}(\mathbf{r})\delta(\mathbf{r}-\mathbf{m}) . \quad (5.4)$$

Substituting Eqs. (5.3) and (5.4) into Eq. (2.12) we obtain, using the well-known Luttinger method[34] (see Appendix B),

$$\tilde{H}=\int d\mathbf{r}\,\psi^{\dagger}(\mathbf{r})\{\epsilon[-i\nabla-2ie\mathbf{A}(\mathbf{r})]-\mu\}\psi(r)$$
$$+\int d\mathbf{r}\int d\mathbf{r}'\tilde{v}(\mathbf{r}-\mathbf{r}')\psi^{\dagger}(\mathbf{r})\psi(\mathbf{r})\psi^{\dagger}(\mathbf{r}')\psi(\mathbf{r}') . \quad (5.5)$$

Here,

$$\epsilon(\mathbf{k})=-\sum_{\mathbf{m}}t(\mathbf{m})e^{i\mathbf{k}\cdot\mathbf{m}} \quad (5.6)$$

denotes the dispersion law of the bipolaronic band and

$$\tilde{v}(\mathbf{r})=\sum_{\mathbf{m}}\tilde{v}(\mathbf{m})\delta(\mathbf{r}-\mathbf{m}) \quad (5.7)$$

represents the real-space potential for bipolaron-bipolaron interaction.

The field operators, Eq. (5.4), obey the following commutation rules:

$$[\psi(\mathbf{r}),\psi^{\dagger}(\mathbf{r}')]_{-}=\delta(\mathbf{r}-\mathbf{r}')[1-2\hat{n}(\mathbf{r})] , \quad (5.8)$$

where $\hat{n}(\mathbf{r})=\sum_{\mathbf{m}}b_{\mathbf{m}}^{+}b_{\mathbf{m}}\delta(\mathbf{r}-\mathbf{m})$ is the bipolaron concentration operator which in the dilute system will have vanishingly small expectation values, and hence we can treat ψ and $\psi^{\dagger}$ as simple Bose operators. They obey the following equation of motion:

$$i\frac{\partial\psi(\mathbf{r})}{\partial t}=[\epsilon(-i\nabla-2ie\mathbf{A})-\mu]\psi(\mathbf{r})$$
$$+2\int d\mathbf{r}'\tilde{v}(\mathbf{r}-\mathbf{r}')\psi^{\dagger}(\mathbf{r}')\psi(\mathbf{r})\psi(\mathbf{r}') . \quad (5.9)$$

In the coherent superfluid phase (BS), the condensate wave function ψ_0 is a c number. Putting $\psi(r)=\psi_0(\mathbf{r})+\tilde{\psi}(\mathbf{r})$, where $\tilde{\psi}(\mathbf{r})$ represents the excited states, we obtain from Eq. (5.9)

$$i\frac{\partial\psi_0(\mathbf{r})}{\partial t}=[\epsilon(-i\nabla-2ie\mathbf{A})-\mu]\psi_0(\mathbf{r})$$
$$+2\int d\mathbf{r}'\tilde{v}(\mathbf{r}-\mathbf{r}')\{\psi_0(\mathbf{r})[n_0(\mathbf{r}')+\tilde{n}(\mathbf{r}')]$$
$$+\psi_0(\mathbf{r}')\langle\tilde{\psi}^{\dagger}(\mathbf{r}')\tilde{\psi}(\mathbf{r})\rangle\} , \quad (5.10)$$

where the condensate density and the concentration of excitations

$$n_0(\mathbf{r})=|\psi_0(\mathbf{r})|^2,\quad \tilde{n}(\mathbf{r})=\langle\tilde{\psi}^{\dagger}(\mathbf{r})\tilde{\psi}(\mathbf{r})\rangle \quad (5.11)$$

have to obey Eq. (3.3) requiring that the total number of bipolarons be fixed:

$$\int d\mathbf{r}[n_0(\mathbf{r})+\tilde{n}(\mathbf{r})]=n . \quad (5.12)$$

Throughout Sec. V we denote by n the density of bipolarons. Equation (5.10) is a direct generalization of the Ginzburg-Pitaevskii[35] equation for a neutral Bose gas. One can see that in the strong-coupling narrow-band superconductors the time-dependent Ginzburg-Landau (GL) theory exists [Eq. (5.10)]. In the case of BCS superconductors one can obtain[36] a simple generalization of the GL equations only if the excitation spectrum is gapless (magnetic impurities). In our BS system the excitation spectrum *is* gapless (see Sec. III), which permits us to derive the electrodynamics of strong-coupling superconductors starting from Eq. (5.10).

Up to now there have been very few results on the electromagnetic properties of the charged interacting Bose gas, which moreover have led to a rather confused picture on this subject. Contrary to the Fermi gas in a Bose condensed system, long-wavelength collective excitations are predominant. They are, however, strongly influenced by scattering processes. Moreover, the interaction can be long range, being of a Coulomb origin. These two facts render the problem of the charged Bose gas a rather intricate one.

In this section we restrict ourselves to the calculation of the upper critical field H_{c2} of a charged Bose gas, taking into account scattering by impurities.[19] We show that the value of the coherence length ξ is strongly dependent on the scattering of Bose particles and differs significantly from the interparticle distance $\sim n^{-1/3}$ as well as from the interatomic one. In such a way, the intuitive[37] estimation of $\xi(\xi\sim n^{-1/3})$ as well as the MFA result of Bulaevskii *et al.*[16] ($\xi\sim a$) are qualitatively wrong.

As usual[36] we determine H_{c2} as the field in which the first nonzero solutions of Eqs. (5.10) and (5.12) for ψ_0 appear. Approximating Eq. (5.10) to lowest order in ψ_0, one obtains

$$\tilde{\mu}\psi_0(\mathbf{r})=[(-i\nabla-2ie\mathbf{A})^2/2m^{**}+U_{\mathrm{imp}}(\mathbf{r})]\psi_0(\mathbf{r}) , \quad (5.13)$$

where $\tilde{\mu}=\mu+t-4\tilde{v}n$. In deriving Eq. (5.13) we restrict ourselves to short-range particle-particle interaction

$$\tilde{v}(\mathbf{r}-\mathbf{r}')=\tilde{v}\delta(\mathbf{r}-\mathbf{r}') \quad (5.14)$$

and use the effective-mass Eq. (3.28).

We introduce the random impurity potential $U_{\mathrm{imp}}(\mathbf{r})$ describing the scattering of bosons. The effective-mass approximation $[\epsilon(k)=-t+k^2/2m^{**}]$ is valid provided that H_{c2} is smaller than the atomic field, Eq. (5.1). Therefore, only low-energy states of the band ($\epsilon\ll\omega^{*}$) are relevant:

$$\omega^{*}=\frac{2eH_{c2}}{m^{**}}\ll t . \quad (5.15)$$

The chemical potential $\tilde{\mu}$ can be obtained from Eq. (5.12), which to lowest order in ψ_0 is given by

$$\int d\epsilon N(\epsilon,H_{c2})/[\exp(\epsilon-\tilde{\mu})/T-1]=n , \quad (5.16)$$

where $N(\epsilon,H_{c2})$ is the field-dependent one-particle density of states. It is, however, more convenient to derive $\tilde{\mu}$ directly from Eq. (5.13) and put it into Eq. (5.16). In such

a way we obtain at $H=H_{c2}$,

$$\tilde{\mu}=\epsilon_0(H_{c2}) , \tag{5.17}$$

where $\epsilon_0(H_{c2})$ is the lowest eigenvalue of the Schrödinger equation, Eq. (5.13).

Let us first consider the ideal charged Bose gas without scattering, $U_{\rm imp}\equiv 0$. In this case,

$$N(\epsilon,H)=\frac{\sqrt{2}(m^{**})^{3/2}\omega^*}{4\pi^2}\sum_{N=0}^{\infty}[\epsilon-\omega^*(N+\tfrac{1}{2})]^{-1/2} \tag{5.18}$$

and

$$\tilde{\mu}=\frac{\omega^*}{2} . \tag{5.19}$$

Substituting Eqs. (5.18) and (5.19) into Eq. (5.16), we obtain

$$\omega^*=\left[\frac{\sqrt{2}(m^{**})^{3/2}T}{4\pi^2 n}\int_0^{\infty}d\epsilon\,\epsilon^{-3/2}\right]^{-1}=0 \tag{5.20}$$

in such a way that the upper critical field of an ideal charged Bose gas

$$H_{c2}^{\rm ideal}=0 . \tag{5.21}$$

This result was obtained a long time ago by Schafroth,[38] who first showed that the charged ideal Bose gas does not condense in a homogeneous magnetic field similar to a one-dimensional neutral Bose gas. We shall now show why a simple MFA (Ref. 16) for this problem leads to erroneous results, predicting enormously high values for H_{c2}.

If one substitutes the MFA chemical potential (see Sec. III) into Eq. (5.19), one obtains for $n\ll 1$ and $|T-T_c|\ll T_c$ the results of Bulaevskii *et al.*:[16]

$$\tilde{\mu}_{\rm MFA}=2t\tau ,$$
$$H_{c2}=6\phi_0\tau/a^2\pi , \tag{5.22}$$

where $\tau=1-T/T_c^{\rm MFA}$ and ϕ_0 denotes the flux quantum. From this it is clear that the origin of the qualitatively wrong result, Eq. (5.22), is due to the choice of the chemical potential determined within the MFA.

In order to obtain a finite value for H_{c2}, one has to take into account the scattering of bosons due to particle-particle as well as particle impurity interaction, both of which destroy the one-dimensional character of low-energy excitations in a magnetic field and smear out the one-dimensional singularities of the ideal density of states, Eq. (5.18). For sufficiently "dirty" dilute Bose systems, one can neglect particle-particle scattering as compared to particle impurity scattering. Moreover, if the mean free path l is large enough,

$$l\gg n^{-1/3} , \tag{5.23}$$

as is usually in the case of BCS superconductors;[32] one can use the analytical "ladder" approximation for determining $N(\epsilon,H)$, which has been derived for semiconductors in a magnetic field.[39,40] For low energies it has the form[40]

$$N(\tilde{\epsilon},H)=\frac{\sqrt{6}(m^{**})^{3/2}\omega^*}{8\pi^2\Gamma_0^{3/2}}\left\{\left[\frac{\tilde{\epsilon}^3}{27}+\frac{\Gamma_0^3}{2}+\left[\frac{\Gamma_0^6}{4}+\frac{\tilde{\epsilon}^3\Gamma_0^3}{27}\right]^{1/2}\right]^{1/3}-\left[\frac{\tilde{\epsilon}^3}{27}+\frac{\Gamma_0^3}{2}-\left[\frac{\Gamma_0^6}{4}+\frac{\tilde{\epsilon}^3\Gamma_0^3}{27}\right]^{1/2}\right]^{1/3}\right\}, \tag{5.24}$$

where $\tilde{\epsilon}=\epsilon-\omega^*/2$, $\Gamma_0=(n_{\rm imp}8\pi f^2 eH)^{2/3}/2m^{**}$, $n_{\rm imp}$ is the impurity concentration, f is the scattering amplitude, and

$$\mu=\epsilon_0=-3\Gamma_0/2^{2/3}+\omega^*/2 . \tag{5.25}$$

Let us consider the rather large temperature region: $\omega^*\ll T\lesssim T_c$. In this case two contributions in the integral Eq. (5.16) are important. The first one arises from the low-energy regime $\epsilon\lesssim\omega^*$ described by the expression, Eq. (5.24); the second one arises from the high-energy regime, $\omega^*<\epsilon\lesssim T$, which is described by the classical density of states:

$$N_{cl}(\epsilon)=(m^{**})^{3/2}\sqrt{\epsilon}/\sqrt{2}\pi^2 . \tag{5.26}$$

Dividing the interval of integration in Eq. (5.16) into a low-energy part with a density of states Eq. (5.24), and into a high-energy part, described by $N_{cl}(\epsilon)$, Eq. (5.26), we finally obtain

$$H_{c2}=\phi_0/2\pi\xi^2(T) , \tag{5.27}$$

where

$$\xi(T)=K\left[\frac{l}{n}\right]^{1/4}\left\{\frac{T_c}{T}\left[1-\left[\frac{T}{T_c}\right]^{3/2}\right]\right\}^{-3/4} \tag{5.28}$$

is the coherence length

$$K^{4/3}=\frac{(3.31)3^{1/2}}{2^{8/3}\pi^2}\int_0^{\infty}\frac{dx}{x}\{[x^3+2+2(1+x^3)^{1/2}]^{1/3}-[x^3+2-2(1+x^3)^{1/2}]^{1/3}\}^{1/2}$$

$K\simeq 0.8$, $l=(4\pi n_{\rm imp}f^2)^{-1}$, and $T_c=3.31n^{2/3}/m^{**}$.

We notice from Eq. (5.28) that the value of $\xi(T)$ is much higher than the interatomic distance and that its temperature dependence is different from the usual BCS expression. In particular, $H_{c2}(T)$ of a charged Bose gas has a positive second derivative

$$\frac{d^2H_{c2}}{dT^2}>0 \tag{5.29}$$

and nonlinear behavior near T_c (see Fig. 7). It is interesting to note that the interparticle distance ($\sim n^{-1/3}$) of a

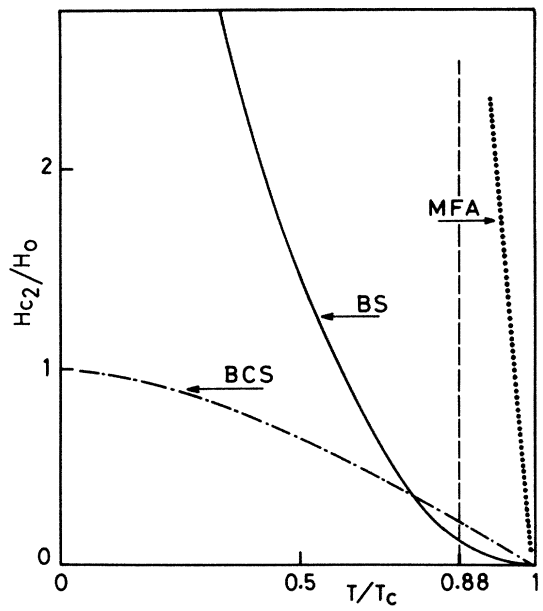

FIG. 7. Temperature dependence of the upper critical field of a charged Bose gas (BS), $H_0=\phi_0 n^{1/2}/2\pi l^{1/2}K^2$. H_{c2} for a BCS type-II superconductor with $H_{c2}(0)=H_0$ is shown for comparison. We also show the artifact of the MFA in which below $T=0.88T_c$ the magnetic field would be unable to destroy superconductivity (Ref. 16).

charged Bose gas represents the direct analogue of the coherence length ξ_0 of BCS:

$$\xi_0=\frac{V_c}{T_c}\simeq n^{-1/3} \tag{5.30}$$

if one takes for $V_c=2(T_c/m^{**})^{1/2}$ instead of the Fermi velocity. In the case of weak scattering [Eq. (5.23)], the physical coherence length ξ, Eq. (5.28), is greater than ξ_0 of Eq. (5.30):

$$\xi\sim l^{1/4}\xi_0^{3/4}\gg\xi_0 . \tag{5.31}$$

In a previous work[13] we have derived the Meissner effect of a BS and obtained a penetration depth

$$\lambda_H=(m^{**}/16\pi ne^2)^{1/2} , \tag{5.32}$$

which exceeds considerably the ordinary London penetration depth λ_L by a factor $(m^{**}/m)^{1/2}$. We are now in a position to estimate the GL parameter κ for a charged Bose gas

$$\kappa\sim\frac{1}{4\pi^{1/2}}(ln^{1/3})^{-1/4}(m^{**}/e^2n^{1/3})^{1/2} , \tag{5.33}$$

which is much greater than unity ($\kappa\gg1$) for all realistic values of n and l.

We conclude that a charged Bose gas is a type-II superconductor. For $T\to0$, Eq. (5.27) gives formally $H_{c2}=\infty$. However, for very low temperature, $T\tau\lesssim1$ (τ denoting the scattering time) the localization of bosons by random potential must be taken into account and this restricts the value for H_{c2} to a finite number. The ladder approximation giving rise to Eqs. (5.24) and (5.27) are not applicable in this region.

VI. DISCUSSION

The phenomenon of superconductivity in metallic compounds is based on the existence of Bose-like carriers which are able to form a condensate state. The usually considered mechanism to form such boson-like states of two fermions (electrons) is a phonon-mediated coupling between two electrons.

If this coupling is weak the pairing of two electrons will be in the form of resonant states. For wide bands there is a thin layer near the Fermi surface in which a compromise is reached between gaining maximal energy by involving as many pairs as possible within this layer without, however, violating the Pauli principle due to the overlap of these pairs. This leads to the well-known BCS ground-state wave function.

This situation changes qualitatively if the electron-lattice coupling increases to such an extent that it leads to instabilities (which may be local or of long range due to cooperative effects) in the many-electron-lattice system. The result is the formation of quasi-self-trapped electrons—so-called small polarons with extremely narrow bands as compared to the ones in which the lattice is treated as rigid. This reduction in bandwidth is typically of the order $10^{-2}-10^{-3}$.

Such systems are hence comprised of very heavy electrons which moreover are capable of forming boson-like states due to the overlap of the local lattice deformations that surround each one of them which leads to an attraction between them. Two situations are possible.

(i) These boson-like states are resonant states involving two small polarons. Contrary to the BCS picture, however, these resonant states will not only form within a thin layer near the Fermi surface but will cover the whole volume of the Fermi sea. A theory developed along these lines by Alexandrov[7] shows superconducting behavior which is formally very reminiscent of BCS, except that the characteristic frequency determining T_c is no longer the characteristic phonon frequency but rather the Fermi energy.

(ii) These boson-like states are real bound states involving two small polarons. These bound pairs—so-called bipolarons—behave like hard-core bosons on a lattice and hence lead to a superconductivity which is much more reminiscent of superfluid ^{4}HeII than BCS as far as its thermodynamics is concerned.

It was the purpose of this present work to investigate in some detail the thermodynamic as well as the electrodynamic properties of such bipolaronic systems in the superconducting as well as in the normal phase. We summarize first of all our main theoretical predictions for such systems and at the end discuss possible candidates in which bipolarons might determine their superconducting as well as normal-state properties.

A. Main characteristics of strong-coupling electron-lattice systems

The following are the main characteristics of strong-coupling electron-lattice systems.

(i) Narrow-band electrons (d- and f-band materials) strongly and locally coupled to lattice deformations form

bipolarons which behave like hard-core bosons on a *rigid* lattice.

(ii) The heavy bosons have a carrier charge $2e$ and because of their heavy mass $m^{**} \sim 100-1000m$ are in general poor conductors. Moreover, they will show a huge specific-heat coefficient $\gamma(T)$ and high Curie-like spin susceptibility for triplet bipolarons or diamagnetism for singlet ones in the normal state (Sec. IV).

(ii) The strong-coupling narrow-band superconductivity resulting from these local hard-core boson-like bipolarons (if the right conditions are met, see Sec. II) differs qualitatively from BCS. The main differences are the following.

(a) A gapless excitation spectrum (in the case of short-range interaction between the bipolarons) which has Bose statistics contrary to the single-particle Fermi-like excitations in BCS, which in general have a gap in their dispersion.

(b) A power-law behavior of the specific heat for singlet as well as triplet pairs with $C_s \sim T^{\alpha}$ ($\frac{3}{2} < \alpha \leq 3$), α depending on the temperature regime. Near the transition temperature we expect a λ-like behavior similar to ^{4}HeII.

(c) A large penetration depth $\lambda_H \sim (m^{**}/m)^{1/2}\lambda_L$.[13]

(d) Nonlinear behavior of $H_{c2}(T)$ near T_c with $d^2H_{c2}/dT^2 > 0$ (Sec. V).

(e) The upper critical field of a charged Bose gap exists which strongly depends on the scattering of the hard-core bosons by impurities[19] (Sec. V).

(f) T_c varies like $n^{2/3}$ (n denotes the bipolaron concentration) for small concentrations, $n \lesssim 0.1$. For higher values, T_c increases slower than the $n^{2/3}$ law on increasing n.

B. Application to real systems

Let us now discuss the possible application of the bipolaronic picture to real materials. Small polarons as well as small bipolarons have been seen in a great variety of substances; mostly, however, where they are in the form of localized states. For our picture to hold, coherent polaron and bipolaronic band states, respectively, are required. The question, whether what is observed experimentally—by, for instance, photoemission spectra—is indeed polarons or bipolarons, is difficult to answer. What favors a polaronic picture is the fact, that in the materials under consideration, band-structure calculations which do not take into account the coupling of electrons with the lattice, are in total disagreement with the experimentally produced extremely narrow bandwidth. Moreover, all the standard classic interpretations of explaining lattice instabilities, as well as high-γ values on the basis of peaks in the fine structure of the density of states, cannot avoid the inevitable problem of having to fix the Fermi level to within a few degrees K near such a peak in the density of states, with an overall energy width which is typically 1000—10 000 K. That such a coincidence would occur in such a large number of physical systems is totally unbelievable.

In this context the polaronic picture for $A15$ compounds[31] is a highly attractive and simple idea which automatically fixes the Fermi level near a peak in the density of states, which due to the polaronic bandwidth narrowing, generally shrinks the entire band into a single very narrow peak structure. In this way the polaronic picture can interpret most of the anomalous properties in the normal as well as the superconducting phase of those materials. We shall only mention the following: the anomalous T dependence of the magnetic susceptibility, the structural transition, the T^2 law for the low-temperature resistivity,[41] the nonlinear electronic specific heat,[42] as well as the violation of the Anderson theorem for irradiated samples which show a drastic change of T_c.[43] We believe that this polaronic picture applies to a variety of $A15$ compounds such as Nb_3Sn, V_3Ga, and V_3Si, and possibly to some Chevrel phases, in particular $PbMo_6S_8$.

As far as bipolarons are concerned, the situation is as follows. After the initially discovered cases[44] of Ti_4O_7 and $Na_xV_2O_5$, a large number of other compounds joined their rank. All of those materials for which direct unquestionable proof exists (as concerns their bipolaronic nature) have not shown superconductivity. The reason for that is known and is either related to the fact that they form half-filled bipolaronic bands and hence show a charge-ordered ground state (Ti_4O_7, $Na_xV_2O_5$) as predicted by theory[3,14], or are low dimensionality systems like polypyrol, polythiophen (Ref. 45), and KCP (Ref. 46), or else are structurally disordered or non stoichiometric systems like WO_{3-x}.[47] On the other hand, indirect experimental evidence strongly favors the bipolaronic picture for such systems as two of the $A15$ compounds Nb_3Ge and Nb_3Al (Refs. 1 and 31) which have estimated λ values above 1.5 and $BaBi_xPb_{1-x}O_3$ with an estimated $\lambda \sim 2$.[48] Similar to this last compound are PbTe(Tl) (Refs. 49 and 2) and $Li_{1-x}Ti_{2-x}O_4$ (Ref. 50), a class of materials in which bipolarons exist as mixed valence states $Bi^{3+}-Bi^{5+}$, $Ti^{1+}-Ti^{3+}$, and $Ti^{2+}-Ti^{4+}$ located on single cation sites.

Among those, $BaPb_{1-x}O_3$ is perhaps one of the most experimentally studied candidates and was initially suggested by Rice and Sneddon[51] to be of a bipolaronic nature in the insulating region. The superconducting properties of this material for $0.2 < x < 0.3$ pose some very intriguing problems, such as (i) anomalously high T_c (≥ 10 K) at low electron concentration ($n \sim 10^{21}$ cm^{-3}),[52] (ii) a very insignificant jump in the specific heat at the superconducting transition,[53] (iii) nonlinear behavior of H_{c2} with $d^2H_{c2}/dT^2 > 0$,[54] (iv) very high values for $\lambda_H \gtrsim 10^4$ Å (Ref. 55) and high values for $H_{c2}(4.2\text{ K}) = 53$ kOe (Ref. 54), and (v) a strong dependence of electrophysical properties and T_c on nonstoichiometry due to the lack of oxygen,[56] which leads to a weakening of bipolaron formation.

Our picture of small bipolarons is able to explain at least qualitatively the anomalous behavior described above. Let us fit the experimental values of $T_c \sim 10$ K and $n = 10^{21}$ cm^{-3} using Eq. (3.27) and we find $m^{**} \sim 300m$ for the heavy carriers in this system. With this value of m^{**} and the same concentrations as before, we obtain from the expression, Eq. (5.32), $\lambda_H \gtrsim 10^4$ Å. There is no specific-heat jump, compatible with the picture for an ideal Bose gas, which ought to be a fairly good description for such a low carrier concentration. The nonlinear behavior of H_{c2} near T_c with $d^2H_{c2}/dT^2 > 0$ is

similar to the one obtained in Sec. V (see Fig. 7). Moreover, recent Mössbauer and positron annihilation data[57] could be interpreted on the basis of mobile bipolarons in $BaPb_{1-x}Bi_xO_3$ for $0.2<x<0.3$. A determination as to whether finally $BaPb_{1-x}Bi_xO_3$ really is a bipolaronic superconductor will need further refined experimental as well as theoretical work in order to furnish the proof. As has been argued by Rice,[58] the observed $2\Delta/T_c \simeq 3.5$ (tunneling experiments by Batlogg *et al.*[59]) seems to favor a BCS rather than a bipolaronic superconductor. In this connection we think it would be fair to point out also that the same tunneling experiment gives a $\lambda \sim 1.5$ which is largely sufficient to form small bipolarons, Eq. (1.2). Moreover, the MFA calculations for the tunneling characteristics of a BS (Ref. 15) show the pseudogap (proportional to the bipolaronic bandwidth) and whence a value Δ/T_c, which again is close to the BCS one. However, we do not think that the results on bipolaronic Josephson tunneling are sufficiently developed and we think that once more the MFA for this problem[15] might perhaps not be correct. We shall conclude this discussion with a speculation that some of the "heavy-fermion" systems such as $CeAl_3$, $CeCu_6$, $CeCu_2Si_2$, UBe_{13}, UPt_3, and others,[1] might be bipolaronic in origin.

It remains an extremely controversial issue, how the Fermi-liquid nature arises from the bare f electrons and which mechanism could possibly lead to the drastic reduction of these bandwidths (down to about 0.001 eV) in order to explain the unusual properties observed in those materials. Possibly the answer to this problem could be in a rather strong electron-phonon interaction in those materials which could lead to Bose-like bipolarons that tunnel in very narrow bands. Let us for that purpose make some quantitative assessment of this situation. Let us take, for the initial bandwidth of f states in the rigid lattice, $D \lesssim 0.1$ eV and assume that the bipolaronic binding energy $\tilde{\Delta}$ is of the same order of magnitude. In that case we obtain the experimentally expected value for $t \lesssim 0.001$ eV for a reasonable value of $g^2 \simeq 2$. Within our picture of a heavy Bose liquid on a lattice—developed in this work—we obtain quite naturally the main anomalous properties of the specific heat and spin susceptibility (Sec. IV) in the normal phase, as well as the power-law behavior of C_s observed in the heavy-fermion superconductors, the fairly high value of H_{c2} ($T=0$), and a $d^2H_{c2}/dT^2>0$. In that sense it might not be too unreasonable to imagine that the heavy carriers in those materials are "heavy bosons". So far none of the existing experiments is direct enough to rule out this possibility.

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APPENDIX A

We define the standard basis operators as

$$L^{\mathbf{m}}_{\alpha\alpha'} = |\,\mathbf{m}\alpha\rangle\langle\mathbf{m}\alpha'|\ , \tag{A1}$$

where $|\,\mathbf{m}\alpha\rangle$ are the eigenstates of site $\mathbf{m}$ derived from the MFA. For the BS phase these states are given by[14]

$$\begin{aligned} |\,\mathbf{m}+\rangle &= \cos\left[\frac{\theta}{2}\right]|\,\mathbf{m}\tfrac{1}{2}\rangle + \sin\left[\frac{\theta}{2}\right]|\,\mathbf{m}-\tfrac{1}{2}\rangle\ , \\ |\,\mathbf{m}-\rangle &= -\sin\left[\frac{\theta}{2}\right]|\,\mathbf{m}\tfrac{1}{2}\rangle + \cos\left[\frac{\theta}{2}\right]|\,\mathbf{m}-\tfrac{1}{2}\rangle\ , \end{aligned} \tag{A2}$$

with the eigenenergies

$$E^{\pm}_{\mathbf{m}} \equiv -\frac{\mu}{2} \mp \left[\left[\frac{\mu}{2}-\tilde{v}\langle S_{\mathbf{m}}\rangle\right]^2 + (t\langle S^z_{\mathbf{m}}\rangle)^2\right]\ , \tag{A3}$$

θ is the angle between the pseudospin magnetization and its z component, $|\,\mathbf{m}\tfrac{1}{2}\rangle$ and $|\,\mathbf{m}-\tfrac{1}{2}\rangle$ are the two spin eigenstates, and

$$\tanh\theta = \frac{\langle S^x_{\mathbf{m}}\rangle}{\langle S^z_{\mathbf{m}}\rangle} = \frac{t\langle S^x_{\mathbf{m}}\rangle}{\frac{\mu}{2}-\tilde{v}\langle S^z_{\mathbf{m}}\rangle}\ . \tag{A4}$$

The ensemble average $D^{\mathbf{m}}_{\alpha} = \langle L^{\mathbf{m}}_{\alpha\alpha'}\rangle$ measures the probability that the state $|\,\mathbf{m}\alpha\rangle$ is occupied and satisfies the normalization condition $\sum_{\alpha=1}^{p} D^{\mathbf{m}}_{\alpha} = 1$, where p is the number of states.

The equation of motion for the double-time retarded Green's function

$$G^{\mathbf{m}\mathbf{m}'}_{\alpha\alpha'\beta\beta'} = \langle\langle L^{\mathbf{m}}_{\alpha\alpha'}(t); L^{\mathbf{m}'}_{\beta\beta'}(t')\rangle\rangle\ ,$$

derived within the RPA [see Eqs. (4.8) and (4.10) of Ref. 14] yield for the BS phase, the following result:

$$\begin{bmatrix} E-A_{\mathbf{k}} & -B_{\mathbf{k}} \\ +B_{\mathbf{k}} & E+A_{\mathbf{k}} \end{bmatrix} \begin{bmatrix} G_{+-\beta\beta'}(\mathbf{k},E) \\ G_{-+\beta\beta'}(\mathbf{k},E) \end{bmatrix} = \frac{1}{2\pi} D_{+-} \begin{bmatrix} \delta_{+\beta'} & \delta_{\beta-} \\ -\delta_{-\beta'} & \delta_{\beta+} \end{bmatrix}\ , \tag{A5}$$

where $(\beta\beta') = (+-)$ or $(-+)$, $D_{\alpha\alpha'} = D_{\alpha} - D_{\alpha'}$, and

$$\begin{aligned} A_{\mathbf{k}} &= 2\left[\left[\frac{\mu}{2}-\tilde{v}\langle S^z\rangle\right]^2 + t^2\langle S^x\rangle^2\right] \\ &\quad - \tfrac{1}{2} D_{+-}[t_{\mathbf{k}}(1+\cos^2\theta) - \tilde{v}_{\mathbf{k}}\sin^2\theta]\ , \end{aligned} \tag{A6}$$

$$B_{\mathbf{k}} = \tfrac{1}{2} D_{+-}(t_{\mathbf{k}} + \tilde{v}_{\mathbf{k}})\sin^2\theta\ .$$

The relationship between the occupation probability and the ensemble average of the pseudospin is obtained as

$$\langle S^x_m\rangle = \tfrac{1}{2} D_{+-}\sin\theta\ , \tag{A7a}$$

$$\langle S^z_{\mathbf{m}}\rangle = \tfrac{1}{2} D_{+-}\cos\theta = \tfrac{1}{2}(1-2n)\ , \tag{A7b}$$

the second equality in (A7b) follows from the condition (3.2).

The solution of Eq. (A5) determines the excitation spectrum of the BS phase

$$\omega^2_{\mathbf{k}} = A^2_{\mathbf{k}} - B^2_{\mathbf{k}}\ . \tag{A8}$$

The energies of the excitations are temperature dependent

via $D_{+-} \equiv R$ and θ.

The occupation probabilities $D_\beta = \langle L^{\mathbf{m}}_{\beta\alpha} L^{\mathbf{m}}_{\alpha\beta} \rangle = \langle L^{\mathbf{m}}_{\beta\beta} \rangle$ can be calculated from (A5) by use of the spectral theorem.[21,23] The result is

$$D_- = N^{-1} \sum_{\mathbf{k}} \tfrac{1}{2} R \left[\frac{A_{\mathbf{k}}}{\omega_{\mathbf{k}}} \coth \frac{\omega_{\mathbf{k}}}{2T} - 1 \right], \qquad D_+ = 1 - D_- \,. \tag{A9}$$

From Eq. (A4) one has

$$\frac{\mu}{2} = (t + \tilde{v}) \langle S^z \rangle \,. \tag{A10}$$

Taking into account the relation

$$R = D_+ - D_- = 1 - 2D_- \tag{A11}$$

and Eqs. (A7) and (A10), one obtains from Eqs. (A8) and (A9) Eqs. (3.6) and (3.7).

APPENDIX B

Substituting Eqs. (5.3) and (5.4) into Eq. (2.12), we obtain for the bipolaronic kinetic energy

$$\sum_{\mathbf{m}} \tilde{t}(\mathbf{m},\mathbf{m}') b^\dagger_{\mathbf{m}} b_{\mathbf{m}'} = \int d\mathbf{r} \int d\mathbf{r}' \psi^\dagger(\mathbf{r}) \tilde{t}(\mathbf{r},\mathbf{r}') \psi(\mathbf{r}') \tag{B1}$$

with

$$\tilde{t}(\mathbf{r},\mathbf{r}') = \sum_{\mathbf{n}} \delta(\mathbf{r}' - \mathbf{r} + \mathbf{n}) t(\mathbf{n}) e^{-2ie\mathbf{A}(\mathbf{r})\mathbf{n}} \,. \tag{B2}$$

One can see that the following relation holds:

$$\tilde{t}(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}') \equiv \tilde{t}(\mathbf{r},\mathbf{r}') e^{\nabla(\mathbf{r}'-\mathbf{r})} \psi(\mathbf{r}) = \sum_{\mathbf{n}} \delta(\mathbf{r}' - \mathbf{r} + \mathbf{n}) t(\mathbf{n}) e^{i[-i\nabla - 2e\mathbf{A}(\mathbf{r})]\mathbf{n}} \psi(\mathbf{r}) \,. \tag{B3}$$

The characteristic length $|\mathbf{r} - \mathbf{r}'|$ is of the order of the coherence length ξ, which is much greater than the interatomic distance a. Using a/ξ as a small parameter and the definition of $\epsilon(\mathbf{k})$, Eq. (5.6), one obtains

$$\tilde{t}(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}') \simeq -\delta(\mathbf{r}' - \mathbf{r}) \epsilon[-i\nabla - 2e\mathbf{A}(\mathbf{r})] \psi(\mathbf{r}) \,. \tag{B4}$$

Substituting Eq. (B4) into Eq. (B1), one obtains the first term of Eq. (5.5).

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