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Theory of bipolarons and bipolaronic bands

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It is shown that in narrow-band crystals with sufficiently strong electron-lattice interaction a new energy band occurs. The tunneling motion of localized electron pairs (bipolarons), which is responsible for this band, is caused by virtual transitions of bipolarons to the polaron state. The electronic excitation spectrum of a bipolaronic crystal is examined. It is shown that in the low bipolaron-density limit the excitation spectrum is superfluidlike, so that bipolarons might be superconducting. In case of high density of bipolarons and their strong repulsion, a charge-density wave is predicted.

I. INTRODUCTION

It is well known that the strong electron-phonon interaction renormalizes the carrier mass and shifts the atomic level. In narrow-band crystals it leads to the well-defined polaron band ("small" polaron). As has been both postulated[1] and demonstrated,[2,3] if the lattice is soft enough to allow sufficient local deformation to overcome the near-neighbor Coulomb repulsion, the pairing of polarons on near-neighbor sites occurs. These Heitler-London bipolarons will generally lie energetically well below the on-site pairs or Anderson bipolarons.[4] In the case of a small dissociating bipolaron energy $\Delta \ll W$ (W is the polaron band halfwidth) the ground state is the BCS superconductor in which intersite pairing[5] plays the main role and the "large" bipolarons are the usual Cooper pairs.

In this paper, the theory of "small" bipolarons ($\Delta \gg W$) is developed. We first generalize the two-electron two-site model[1] for the crystal lattices to obtain the energy level of the localized bipolaron. In Sec. III, we derive the reduced Hamiltonian that describes the formation of the bipolaronic band and the interaction of bipolarons. We show that the tunneling motion of bipolarons, which is responsible for the bipolaronic band, is caused by virtual transitions to the polaron state, so that the bipolaronic bandwidth is proportional to W^2/Δ. In Sec. IV, the ground state of the interacting bipolarons is studied by using the well-known Anderson pseudospin analogy.[6] We show that the bipolaronic Hamiltonian is equivalent to the $S=\frac{1}{2}$ anisotropic Heisenberg Hamiltonian, which can be solved by the "semiclassical" (self-consistent-field) method of the theory of magnetism. For the sufficiently large density of bipolarons, the ground state may be spatially inhomogeneous (charge-density wave). The excitation spectrum is derived in Sec. V. We show that a range of bipolaron density exists where the excitation spectrum is similar to the one of superfluid Bose system, so that the "small" bipolarons may be superconducting. This is a new type of superconductivity, which is similar to the superfluidity of charged Bose particles and quite different from the BCS superconductivity where the Cooper pairs are spatially overlapping.

II. LOCALIZED BIPOLARON

Our starting point is a collection of crystalline electrons moving in a single narrow band and interacting with the lattice having two atoms in the cell:

$$H=\sum_{mm'} T_{mm'} c_m^\dagger c_{m'} + \sum_{mm',nn'} V_{mn}^{m'n'} c_{m'}^\dagger c_{n'}^\dagger c_n c_m + H_{ep} + H_p . \tag{1}$$

Here $m=(\vec{m},\alpha)$ are the quantum numbers in the site representation, $\vec{m}$ labels the cell, $\alpha=(\rho,\sigma)$ labels the atom in the cell ($\rho=1,2$) and the spin ($\sigma=\uparrow,\downarrow$), $T_{mm'}$ is the hopping integral, $V_{mn}^{m'n'}$ are the Coulomb correlations,

$$H_{ep}=\sum_{mm'\vec{q}} [U_{mm'}(q) c_m^\dagger c_{m'} d_{\vec{q}}^\dagger + \text{H.c.}] \tag{2}$$

is the electron-lattice interaction Hamiltonian,

$$H_p=\sum_{\vec{q}} \omega_{\vec{q}} d_{\vec{q}}^\dagger d_{\vec{q}} \tag{3}$$

denotes the phonon Hamiltonian, and $\omega_{\vec{q}}$ is the phonon frequency.

In case of weak overlap of the electron functions at different sites (narrow bands) the interaction terms with $m=m', n=n'$ are the largest and all the other interaction terms in (1) which involve the overlap factor may be neglected.[7,8] Moreover, if the temperature is low enough, so that the phonon occupation numbers do not change as the electron moves,[8] we can decouple the electrons and lattice by the familiar (displaced-oscillator) canonical transformation[8,9]

$$S_1=\sum_{\vec{m}\vec{q}} \omega_{\vec{q}}^{-1} n_m [d_{\vec{q}}^{\dagger} U_{mm}(\vec{q}) - d_{\vec{q}} U_{mm}^{*}(\vec{q})] \tag{4}$$

with the result for the electron part of the Hamiltonian

$$H=\sum_{mm'} (t_{mm'} c_m^{\dagger} c_{m'} + v_{mm'} n_m n_{m'}), \tag{5}$$

where $n_m = c_m^{\dagger} c_m$ and

$$t_{mm} \equiv \epsilon_0 = T_{mm} - E_p, \quad E_p = \sum_{\vec{q}} \omega_{\vec{q}}^{-1} |U_{mm}(\vec{q})|^2 \tag{6}$$

is the polaron atomic level shift;

$$t_{mm'} = T_{mm'} \exp\left(-\sum_{\vec{q}} \omega_{\vec{q}}^{-2} |U_{mm}(\vec{q})|^2 \times \{1-\cos[\vec{q}\circ(\vec{R}_{\vec{m}\rho} - \vec{R}_{\vec{m}'\rho'})]\}\right), \tag{7}$$

$\vec{R}_{\vec{m}\rho}$ denotes the radius vector characterizing the equilibrium position of the atom ρ in the cell $\vec{m}$ $(m \neq m')$;

$$v_{mm'} = V_{mm'}^{mm'} - \sum_{\vec{q}} \omega_{\vec{q}}^{-1} |U_{mm}(\vec{q})|^2 \exp[i\vec{q}\circ(\vec{R}_{\vec{m}\rho} - \vec{R}_{\vec{m}'\rho'})] \tag{8}$$

is the effective electron-electron interaction, which may be attractive. In what follows, we show that if the electron-lattice interaction is strong enough so that the condition

$$\Delta \gg z t_{\vec{m}\rho,\vec{m}'\rho'} \quad (\vec{m} \neq \vec{m}') \tag{9}$$

is satisfied, the bipolaronic band is the ground state of the Hamiltonian (5). Here

$$\Delta = -v_{\vec{m}_1,\vec{m}_2} - 2t_{\vec{m}_1,\vec{m}_2}\{1 - \tfrac{1}{4}[(x^2+16)^{1/2} - x]\} \tag{10}$$

is the energy required to dissociate the ground-state localized singlet bipolaron into two localized polarons,[3] $x = (v_{mm} - v_{\vec{m}_1,\vec{m}_2})/t_{\vec{m}_1,\vec{m}_2}$; z is the number of nearest-neighbor cells.

Let us separate the Hamiltonian (5) into the intracell H_0 and the intercell H_1 contributions

$$H = H_0 + H_1, \tag{11}$$

where

$$H_0 = \sum_{\vec{m}} H_{\vec{m}},$$

$$H_{\vec{m}} = \sum_{\alpha\alpha'} (t_{\vec{m}\alpha,\vec{m}\alpha'} c_{\vec{m}\alpha}^{\dagger} c_{\vec{m}\alpha'} + v_{\vec{m}\alpha,\vec{m}\alpha'} n_{\vec{m}\alpha} n_{\vec{m}\alpha'}), \tag{12}$$

$$H_1 = \sum_{mm'(\vec{m}\neq\vec{m}')} (t_{mm'} c_m^{\dagger} c_{m'} + v_{mm'} n_m n_{m'}).$$

We use the orthonormalized system of the eigenfunction of $H_{\vec{m}}$ as the basic functions. In the case of two electrons in the cell these functions were found earlier.[3] The corresponding energy levels are shown in Fig. 1, where the dashed line refers to the energy of two widely separated Heitler-London single polarons which is the low-energy state in the case of one electron in the cell.

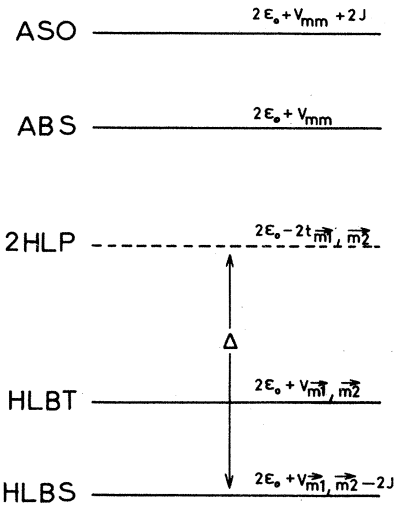

FIG. 1. Two-electron energy levels of intracell Hamiltonian. Ground state is the Heilter-London bipolaronic singlet HLBS (the bonding singlet orbital) followed by the triplet state HLBT and the Anderson bipolaronic singlet ABS (the singlet ionic state), the highest being the antibonding singlet orbital ASO. The dashed line refers to the energy of two polarons in different cells.

It becomes clear that if $\Delta > 0$, the separated polarons are unstable versus the formation of the bipolarons. Moreover, if the polaronic band is narrow or the electron-lattice interaction is strong, a well-defined bipolaronic band is generated by the interaction H_1.

III. THE SECOND CANONICAL TRANSFORMATION, BIPOLARON OPERATORS, AND REDUCED HAMILTONIAN

The effect of the intercell interaction H_1 tends to destroy the bipolarons in the first order and delocalizes them in the second order. It is clear that if $\Delta \gg W \sim z t_{mm'} (\vec{m} \neq \vec{m}')$, the ground state of the system does not involve the real polarons. In the second order, H_1 describes the processes in which the bipolaron dissociates virtually into two polarons and then recombines to a new bipolaron in the same or in a neighboring cell. Hence the second order of H_1 gives rise to the tunneling motion of bipolarons "dressed" in the virtual polaron "cloud." This motion may be described by a new canonical transformation S_2, which is similar to the electron-polaron transformation S_1,

$$\tilde{H} = e^{S_2} H e^{-S_2}, \tag{13}$$

where

$$(S_2)_{ik}=\sum_{mm'(\vec{m}\neq\vec{m}')}\frac{t_{mm'}(c_m^\dagger c_{m'})_{ik}}{E_i-E_k}, \tag{14}$$

$|i\rangle, |k\rangle$ and E_i, E_k are the eigenfunctions and the energy levels of the Hamiltonian H_0.

The transformed Hamiltonian is given by

$$\tilde{H}=H_0+\sum_{mm'(\vec{m}\neq\vec{m}')}v_{mm'}n_{m'}n_{m'}-2\sum_{mm'(\vec{m}\neq\vec{m}'),nn'(\vec{n}\neq\vec{n}')}\frac{t_{mm'}t_{nn'}}{\Delta}c_m^\dagger c_{m'}c_n^\dagger c_{n'}. \tag{15}$$

In the derivation of (15), we consider the ground state of H_0 [Heilter-London bipolaronic singlet (HLBS)] as the zeroth-order perturbation and neglect all the terms of higher order than $(W/\Delta)^2\ll 1$. In this case, the only nonzero matrix element of S_2 is the matrix element between the states HLBS and 2HLP (Heilter-London polarons) (Fig. 1), so that $|E_i-E_k|=\Delta$.

It is clear that the lowest eigenstates of the Hamiltonian (15) are in the subspace, which involves only the HLBS $|1\rangle_{\vec{m}}$ or empty $|0\rangle_{\vec{m}}$ states of the cell:

$$|1\rangle_{\vec{m}}=\frac{1}{2\sqrt{2}}\sum_{\alpha\alpha'}A_{\alpha\alpha'}c_{\vec{m}\alpha}^\dagger c_{\vec{m}\alpha'}^\dagger|0\rangle, \quad |0\rangle_{\vec{m}}, \tag{16}$$

where the unitary matrix A is given by[3]

$$A=\{1+\tfrac{1}{16}[x+(x^2+16)^{1/2}]^2\}^{-1/2}\times\begin{pmatrix}0 & \frac{1}{4}[x+(x^2+16)^{1/2}] & 0 & 1\\ -\frac{1}{4}[x+(x^2+16)^{1/2}] & 0 & 1 & 0\\ 0 & -1 & 0 & \frac{1}{4}[x+(x^2+16)^{1/2}]\\ -1 & 0 & -\frac{1}{4}[x+(x^2+16)^{1/2}] & 0\end{pmatrix}. \tag{17}$$

Let us introduce the bipolaron creation $b_{\vec{m}}^\dagger$ and annihilation $b_{\vec{m}}$ operators

$$b_{\vec{m}}^\dagger=\frac{1}{2\sqrt{2}}\sum_{\alpha\alpha'}A_{\alpha\alpha'}c_{\vec{m}\alpha}^\dagger c_{\vec{m}\alpha'}^\dagger,$$
$$b_{\vec{m}}=-\frac{1}{2\sqrt{2}}\sum_{\alpha\alpha'}A_{\alpha\alpha'}c_{\vec{m}\alpha}c_{\vec{m}\alpha'}, \tag{18}$$

which satisfy the mixed Bose-Fermi commutation rules

$$[b_{\vec{m}}^\dagger,b_{\vec{m}}]_+=1, \quad [b_{\vec{m}}^\dagger,b_{\vec{m}'}]_-=0 \quad (\vec{m}\neq\vec{m}'). \tag{19}$$

In what follows, we show that while the bipolarons do not have the Bose properties, the excitations of the Hamiltonian (15) are Bose quasiparticles.

In the subspace (16) we have

$$b_{\vec{m}}=\begin{pmatrix}0&1\\0&0\end{pmatrix}, \quad b_{\vec{m}}^\dagger=\begin{pmatrix}0&0\\1&0\end{pmatrix}, \quad b_{\vec{m}}^\dagger b_{\vec{m}}=\begin{pmatrix}0&0\\0&1\end{pmatrix} \tag{20}$$

and

$$c_m^\dagger c_{m'}=\tfrac{1}{2}\delta_{mm'}b_{\vec{m}}^\dagger b_{\vec{m}},$$
$$c_m^\dagger c_{m'}^\dagger=\frac{1}{\sqrt{2}}\delta_{\vec{m}\vec{m}'}A_{\alpha\alpha'}b_{\vec{m}}^\dagger, \tag{21}$$
$$c_m c_{m'}=-\frac{1}{\sqrt{2}}\delta_{\vec{m}\vec{m}'}A_{\alpha\alpha'}b_{\vec{m}}.$$

Using (21) we can rewrite the Hamiltonian (15) in terms of the bipolaron operators (18):

$$\tilde{H}=\tilde{\epsilon}_0\sum_{\vec{m}}b_{\vec{m}}^\dagger b_{\vec{m}}+\sum_{\vec{m}\vec{m}'\neq\vec{m}}(v_{\vec{m}\vec{m}'}b_{\vec{m}}^\dagger b_{\vec{m}}^\dagger b_{\vec{m}'}b_{\vec{m}'}-t_{\vec{m}\vec{m}'}b_{\vec{m}}^\dagger b_{\vec{m}'}), \tag{22}$$

where

$$v_{\vec{m}\vec{m}'}=\tfrac{1}{4}\sum_\alpha\left(v_{\vec{m}\alpha,\vec{m}'\alpha}+2\sum_{\alpha'}\frac{|t_{\vec{m}\alpha,\vec{m}\alpha'}|^2}{\Delta}\right) \tag{23}$$

is the effective bipolaron interaction,

$$t_{\vec{m}\vec{m}'}=\sum_{\alpha\alpha',\beta\beta'}A_{\alpha\beta}A_{\alpha\beta}\frac{t_{\vec{m}\alpha,\vec{m}'\alpha'}t_{\vec{m}\beta,\vec{m}'\beta'}}{\Delta} \tag{24}$$

is the effective bipolaron hopping,

$$\tilde{\epsilon}_0=2\epsilon_0+v_{\vec{m}_1,\vec{m}_2}-2J-\sum_{\alpha\alpha',\vec{m}'\neq\vec{m}}\frac{|t_{\vec{m}\alpha,\vec{m}'\alpha'}|^2}{\Delta} \tag{25}$$

is the renormalized HLBS energy, and

$$2J=\frac{t_{\vec{m}_1,\vec{m}_2}}{2}[(x^2+16)^{1/2}-x] \tag{26}$$

is the singlet-triplet exchange energy.[3]

As one can see from the Hamiltonian (22) the bipolaron interaction $v_{\vec{m}\vec{m}'}$ is the sum of the direct Coulomb repulsion, the phonon-exchange attraction, and the polaron-exchange repulsion. It may be repulsive or attractive. It is seen that in case of attraction, the spatially homogeneous state is unstable in relation to the formation of the bipolaron clusters (bipolaron drops). For this, among

other conditions, a strong dispersion of the phonon frequencies is needed, because in fact for an Einstein model the phonon intercell attraction (8) vanishes. In the following we restrict ourselves to the case of a repulsive interaction $v_{\vec{m}\vec{m}'}>0$, assuming that the intercell phonon attraction is dominated by the intercell Coulomb and polaron exchange repulsion.

IV. GROUND STATE

To find the ground state of the Hamiltonian (22) it is convenient to use the well-known Anderson pseudospin analogy,[6] as the bipolaron operators (18) are fully equivalent to the set of Pauli spin matrices

$$b_{\vec{m}}=S^x_{\vec{m}}-iS^y_{\vec{m}},\quad b^\dagger_{\vec{m}}b_{\vec{m}}=\tfrac{1}{2}-S^z_{\vec{m}}, \tag{27}$$

where

$$S^x=\frac{1}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix},\quad S^y=\frac{1}{2}\begin{pmatrix}0&i\\-i&0\end{pmatrix},\quad S^z=\frac{1}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}. \tag{28}$$

These S operators act in an imaginary space where the $\hat{z}$ component of spin-up means an "empty" cell, spin-down means a "full"one.

In terms of the pseudospins (27) the Hamiltonian has the Heisenberg form

$$\tilde{H}=\mu\sum_{\vec{m}}S^z_{\vec{m}}+\sum_{\vec{m}\vec{m}'\neq\vec{m}}v_{\vec{m}\vec{m}'}S^z_{\vec{m}}S^z_{\vec{m}}-\sum_{\vec{m}\vec{m}'\neq\vec{m}}t_{\vec{m}\vec{m}'}\vec{S}^\perp_{\vec{m}}\vec{S}^\perp_{\vec{m}}. \tag{29}$$

The "field" $\vec{H}_{\vec{m}}$ "seen" by $\vec{S}_{\vec{m}}$ is from (29):

$$\vec{H}_{\vec{m}}=-\left(\mu+2\sum_{\vec{m}'\neq\vec{m}}v_{\vec{m}\vec{m}'}S^z_{\vec{m}'}\right)\hat{z}+2\sum_{\vec{m}'\neq\vec{m}}t_{\vec{m}\vec{m}'}\vec{S}^\perp_{\vec{m}'}, \tag{30}$$

where $\vec{S}^\perp$ is that portion of $\vec{S}$ perpendicular to $\hat{z}$, μ is the chemical potential of bipolarons, which plays the role of the external field. It is determined by the condition

$$\left\langle\sum_{\vec{m}}S^z_{\vec{m}}\right\rangle=\frac{N-n}{2}, \tag{31}$$

where N and n are the numbers of cells and electrons, respectively. We assume that $n\leq N$. If $N<n\leq 2N$ holes may be used instead of electrons. In the "mean field" approximation the spin vector $\vec{S}_{\vec{m}}$ is parallel to the field acting upon them. Restricting ourselves to the nearest neighbors, we find for the angle $\theta\equiv\theta_{\vec{m}}$ between the new direction of the spin $\vec{m}$ and the $\hat{z}$ axis

$$\sin\theta=\frac{t\sin\theta'}{[(\mu+v\cos\theta')^2+t^2\sin^2\theta']^{1/2}},$$
$$\cos\theta=\frac{-(\mu+v\cos\theta')}{[(\mu+v\cos\theta')^2+t^2\sin^2\theta']^{1/2}}, \tag{32}$$
$$\cos\theta+\cos\theta'=2\left(1-\frac{n}{N}\right),$$

where θ' is the angle of the nearest neighbors of $\vec{m}$, $v=zv_{\vec{m}\vec{m}'}$, $t=zt_{\vec{m}\vec{m}'}$, and we assume $v,t>0$.

Two solutions to Eq. (32) are possible. The first one is the "ferromagnetic" solution (Fig. 2):

$$\cos\theta=\cos\theta'=1-n/N. \tag{33}$$

In this case, the bipolarons are distributed homogeneously over the crystal lattice. The probability of finding one bipolaron in the cell is $n/2N$. The energy (29) of the "ferromagnetic" state is

$$E_f=-\frac{tN}{4}\left[1+\left(1+\frac{v}{t}\right)\left(1-\frac{n}{N}\right)^2\right]. \tag{34}$$

The second solution to Eq. (32) is the "antiferromagnetic" one, where two sublattices (θ and θ') occur:

$$\cos\theta=1-\frac{n}{N}+\left[1+\left(1-\frac{n}{N}\right)^2-2\left(1-\frac{n}{N}\right)\left(1-\frac{t^2}{v^2}\right)^{-1/2}\right]^{1/2},$$
$$\cos\theta'=1-\frac{n}{N}-\left[1+\left(1-\frac{n}{N}\right)^2-2\left(1-\frac{n}{N}\right)\left(1-\frac{t^2}{v^2}\right)^{-1/2}\right]^{1/2}. \tag{35}$$

It is possible if $v>t$ and $n>n_c=N\{1-[(v-t)/(v+t)]^{1/2}\}$. This solution is a low-energy state in the range of its existence with energy

$$E_a=-\frac{vN}{4}<E_f \tag{36}$$

if $n>n_c$.

So we come to the conclusion that in the case of the sufficiently high density of bipolarons ($n>n_c$)

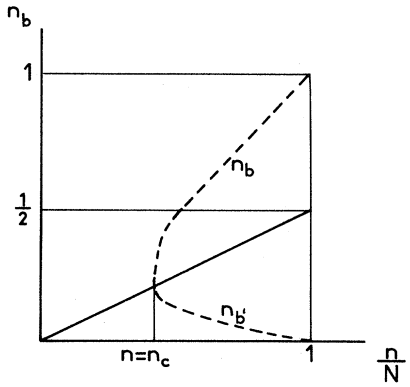

FIG. 2. Bipolaron distribution $n_b=\langle b^\dagger_{\vec{m}}b_{\vec{m}}\rangle=\frac{1}{2}(1-\cos\theta)$ as a function of the electron concentration n. The solid line refers to the "ferromagnetic" solution, the dashed line to the "antiferromagnetic" one. In the range $n>n_c$ and $v>t$ the "antiferromagnetic" solution with two sublattice ($n_b'\neq n_b$) is the ground state.

and their strong repulsion ($v > t$) two sublattices occur which have different densities of bipolarons (Fig. 2). This is the charge-density wave (CDW).

V. EXCITATIONS

We can expect that the excitation spectrum is similar to the one of ferromagnetic ($n < n_c$) or antiferromagnetic ($n > n_c$) magnons, but the nature of excitations is different. In order to study the excitations we write down the equations of motion which are the usual spin ones[6]:

$$\frac{d\vec{S}_{\vec{m}}}{d\tau} = \vec{H}_{\vec{m}} \times \vec{S}_{\vec{m}} \,. \tag{37}$$

We allow each "spin" $\vec{S}_{\vec{m}}$ besides its static component $\vec{S}^{(0)}_{\vec{m}}$ to have a small increment

$$\vec{S} \exp(i\vec{k}\cdot\vec{m} - i\omega\tau) \,. \tag{38}$$

Then from (23) we obtain

$$\begin{aligned} -i\omega S_x &= -t \sin\theta' \cot\theta \, S_y + t\xi \cos\theta \, S'_y \,, \\ -i\omega S_y &= t \sin\theta' \cot\theta \, S_x - t\xi \cos\theta \, S'_x \\ &\quad - t \sin\theta' \, S_z - v\xi \sin\theta \, S'_z \,, \\ -i\omega S_z &= t \sin\theta' \, S_y - t\xi \sin\theta \, S'_y \,, \end{aligned} \tag{39}$$

where $\xi = (1/z)\sum_{|\vec{n}|=a} e^{i\vec{k}\cdot\vec{n}}$ is the sum over nearest-neighbor cells; a is the lattice constant. In the case of the "ferromagnetic" ground state ($n < n_c$) we find from Eq. (39)

$$\begin{aligned} \omega^2(\vec{k}) = t^2 - \xi^2 t \left[v - (v+t)\left(1 - \frac{n}{N}\right)^2 \right] \\ + \xi t \left[(v-t) - (v+t)\left(1 - \frac{n}{N}\right)^2 \right] \end{aligned} \tag{40}$$

with $\vec{k}$ varying in the first Brillouin zone

$$-\pi \leq \vec{k}\cdot\vec{a}_i < \pi \quad (-1 \leq \xi \leq 1), \quad i = x, y, z \,. \tag{41}$$

In the long-wavelength limit ($k \to 0$) we have from Eq. (40)

$$\omega(\vec{k}) = sk \,, \tag{42}$$

where

$$s = \left[t(v+t) \frac{n}{N}\left(1 - \frac{n}{2N}\right) z^{-1} \sum_{\vec{n}} \left(\frac{\vec{k}\cdot\vec{n}}{k}\right)^2 \right]^{1/2} \tag{43}$$

is the sound velocity.

The dispersion curve (40) is shown in Fig. 3, part "f". It is similar to the excitation spectrum of the Bose liquid,[10] so we are tempted to believe that in the low-density limit ($n < n_c$) the bipolarons have the superfluid (superconducting) properties of the Bose liquid.

When $n = n_c$

$$\omega(\vec{k}) = t(1 - \xi^2)^{1/2} \tag{44}$$

and the critical velocity $v_c = [\omega(k)/k]_{\min}$ reaches zero. In the range $n > n_c$ the ground state is the CDW and $\vec{S} \neq \vec{S}'$. In this case we obtain from (39) two branches of excitations[11]:

$$\omega^2_{1,2}(\vec{k}) = t^2(1 + \gamma^2 - \xi^2) \pm t^2\gamma^2 \left(1 + \frac{2(1-\xi^2)}{\gamma^2}\right)^{1/2} , \tag{45}$$

where

$$\gamma^2 = 2\,\frac{v^2 - t^2}{t^2}\left[1 + \left(1 - \frac{n}{N}\right)^2 - 2\left(1 - \frac{n}{N}\right)\left(1 - \frac{t^2}{v^2}\right)^{-1/2}\right], \tag{46}$$

and $\vec{k}$ varies now in the region $-\pi \leq \vec{k}\cdot\vec{a}'_i < \pi$, $\vec{a}'_i$ are the radius vectors of the cells of the second coordinating sphere (superlattice with double period).

In the long-wavelength limit ($\xi \to 1$) we have from Eq. (45)

$$\omega_1 = t\gamma\sqrt{2}, \quad \omega_2 = \frac{t}{2z\gamma} \sum_{\vec{n}} (\vec{k}\cdot\vec{n})^2 \sim k^2 \,. \tag{47}$$

So in the case of high bipolaron density and their strong repulsion there is no critical velocity ($V_c = 0$). On the edge of a new Brillouin zone ($\xi = 0$) the gap exists (Fig. 3, part "a"):

$$\begin{aligned} \omega_1 - \omega_2 = [t^2(1+\gamma^2) + t^2\gamma(\gamma^2+2)^{1/2}]^{1/2} \\ - [t^2(1+\gamma^2) - t^2\gamma(\gamma^2+2)^{1/2}]^{1/2} \,. \end{aligned} \tag{48}$$

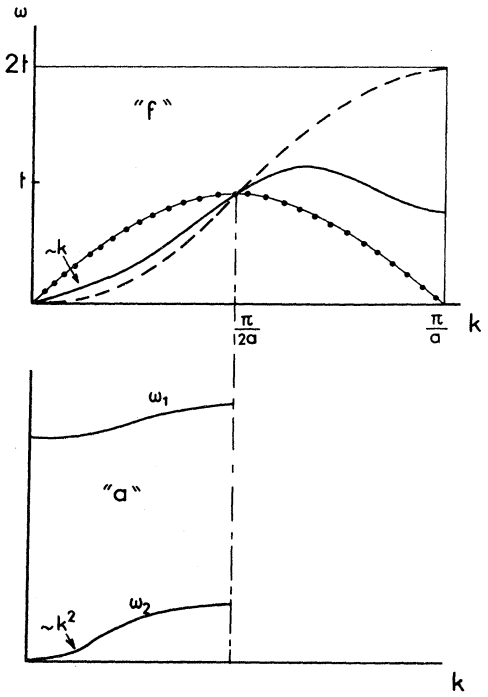

FIG. 3. The dispersion curves for excitations of the "ferromagnetic" ("f") ground state (dashed lines refers to $n = 0$, solid line to $0 < n < n_c$, dotted line to $n = n_c$) and "antiferromagnetic" ("a") ground state ($n > n_c$).

VI. DISCUSSION

In this paper, we considered a system of narrow-band electrons in a crystalline lattice which exhibits the formation of bipolarons. We have assumed that the dissociation energy of the bipolarons is large compared to the bandwidth of the polaronic motion, which tends to destroy the bipolarons. Under those assumptions, we were able to discuss certain stable ground-state configurations. They correspond, in particular, to (i) a long-range ordered state of bipolarons when the number of electrons is above a certain critical value n_c and to (ii) a state of homogeneously distributed bipolarons if the number of electrons is below n_c.

Examining the low-lying excitations of these ground states, we noticed that the low-density system exhibits features which are similar to the superfluid character of liquid helium. The excitations have a linear dispersion law and are of Bose character. We are currently[12] examining the superconducting properties of such a system of charged bosons[12] by examining its thermodynamics and the Meissner effect. It is shown that the system is indeed superconducting, representing an example of the Molecular Superconductivity proposed by Schafroth, Butler, and Blatt.[13] The corresponding critical temperature is found to fall off like the inverse electron-phonon coupling constant, and the penetration depth is essentially different from the London one. This new type of superconductivity is thus quite different from the usual BCS one.

On the other hand, the high-density system—ordered bipolarons—exhibits excitations analogous to magnons in a Heisenberg antiferromagnet, which correspond to a dynamical disorder of the ordered ground state.

The type of excitations studied here depends to a large extent on the assumption of the high degree of stability of the bipolarons. If this assumption is relaxed, then excitations of the bipolarons to real polarons become important. In a separate publication (Feinberg and Ranninger) this case has been investigated.

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