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THE ORDERING OF LOCALIZED ELECTRON PAIRS IN MIXED-VALENCE CRYSTALS

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ABSTRACT

The aim of this article is to describe the factors that determine the types of ground states in crystals with localized electron pairs, or bipolarons. We consider the concentration of the electron pairs and parameters describing the lattice polarization due to the bipolaron-phonon interaction, together with parameters for the possible ground states. All the parameters and the bipolaron concentration must be self-consistently related. The conditions that favour the disordered and superconducting states, and the charge-ordered states, of such crystals are presented.

1. INTRODUCTION

The last decade has seen rapid progress in the theory of localization-delocalization processes of electron pairs in mixed-valence crystals [see papers by Ionov *et al.* (1970, 1975, 1981); Anderson (1975); Chackraverty and Schlenker (1976); Wilson (1978); Toyzawa (1981); Lubimov *et al.* (1978); Alexandrov and Ranninger (1981)].

The existence of localized electron pairs (or bipolarons, as they were first named by Anderson (1975)) was experimentally established in the crystals formed by cube-octahedron complexes, such as M_2SbHal_6 (where $M = Rb^+, Cs^+, NH_4^+$; $Hal = Cl, Br$) (Ionov *et al.*, 1970, 1975), as well as in $BaBiO_3$ and $BaPb_{1-x}Bi_xO_3$ crystals (Raub *et al.*, 1964). Electron pairs in such crystals are localized in the outer shells of the cube-octahedron complexes located in lattice sites. A typical size of such a pair is $\sim 5 \times 10^{-8}$ cm and its binding energy is ~ 1 eV.

A quasi-chemical mechanism of stabilization of the electron pair in the site was introduced by Ionov *et al.* (1970, 1975, 1981) using the following disproportionation reaction as the basis:



where M' is the central atom of the group of atoms and X is the ligand.

An equilibrium displacement of this reaction to the right corresponds to the formation of an effective attraction between electrons in the complex. The disproportionation equilibrium displacement to the right or, in other words, the instability of the electron configuration of the complex relative to the mixture of valencies, implies that noninteracting complex energies with a different number of electrons in the s -shell satisfy the inequality (Makarov *et al.*, 1975)

$$2E_{(s^1)} > E_{(s^2)} + E_{(s^0)} \quad (1)$$

$E_{(s^1)}$ and $E_{(s^2)}$ are the energies of the complexes with one and two electrons, respectively; $E_{(s^0)}$ is its energy with an empty s -shell.

The experimental data point to the fact that, as to the mixture of valencies, not only elements with a valence s -shell (Sb^{3+} , Bi^{3+}) are found to be unstable, but also those with d - and f -electron configurations ($M_xV_2O_5$, where M is an alkali metal, Cu, Ag (Chackraverty *et al.*, 1978), Ti_4O_7 (Lakkis *et al.*, 1976), $(Ti_{1-x}V_x)_4O_7$, $Li_{1+x}Ti_{2-x}O_4$, $Na_{0.8}WO_3$ (Schlenker *et al.*, 1979; Johnston *et al.*, 1973; Sweedler *et al.*, 1965; Sleight, 1976; and Thanh *et al.*, 1980). Most of the above compounds are superconductors, some of them having a fairly high transition temperature; in $Li_{1-x}Ti_{2-x}O_4$, $T_c = 14$ K (Johnston *et al.*, 1973); in $BaPb_{0.75}Bi_{0.25}O_3$, $T_c = 11.7$ K (Rauls *et al.*, 1964).

The inequality (1) exhibits the presence of an effective electron attraction in the complex. In the appendix to this article (1) is expressed in terms of parameters of the complex which relate to the fact that the electrons interact with intracomplex oscillations. The form of the effective attraction giving rise to (1) turns out not to be commonplace. In particular, the terms of the complexes with s^1 and s^0 (see (3A) in the Appendix) contribute to the formation of a relative effective attraction in the complex with s^2 . This is a very distinct characteristic by which a quasi-chemical mechanism differs from a normal mechanism of attraction (Anderson, 1975; Chackraverty and Schlenker, 1976). Also note that the effective attraction, from the viewpoint of (1), can also be gained through the interaction between s -electrons and electrons of inner shells (Manakova, 1981).

Note that, as was shown with the help of the analysis of Ionov *et al.* (1981), the quasi-chemical approach is effective for analysing the possibilities of occurrence of bipolarons in compounds of every kind.

The ground states of the crystal formed by the complexes in which localized pairs—bipolarons—are to be found, or, in other words, the types of ordering of bipolarons in the crystal, are governed by the following factors: the interaction of bipolarons in different sites; their relation with the crystalline phonons; the bipolaron hopping between different sites; as well as their concentration.

At a given concentration (the number of electrons is equal to that of the sites) the types of ordering in crystals with bipolarons were determined according to the interaction parameters (Lubimov *et al.*, 1978), and according to the concentration (Alexandrov and Ranninger, 1981; Alexandrov, 1982).

But these papers neglected a decisive fact in considering the properties of crystals with bipolarons. The point is that in those crystals the bipolaron bandwidth (determined by bipolaron hopping), and the interaction between bipolarons on different sites and that between them and crystalline phonons have magnitudes of the same order. In this sense such crystals have a strong bipolaron–phonon interaction. That is why the degree of lattice polarization and the parameters of the ground state are self-consistently related and should be determined in combination, as will be demonstrated in the present article. But in the work of Alexandrov and Ranninger (1981), for example, the lattice polarization was the first to be determined, i.e. the Hamiltonian coefficients were renormalized with regard to polaron effects, followed by the determination of types of the ground states using the given polarization.

Thus, the aim of this work is to determine the types of ground states in crystals with localized pairs according to their concentration (density) and the values of parameters describing the lattice polarization due to the bipolaron–phonon interaction.

The structure of the paper is as follows. Section 2 deals with the formulation of the problem of determining the types of ground states. The chemical potential, energy and other features of the states with a superconducting correlation and those of a disordered state are calculated in Section 3. Again there are conditions for the

concentration which permit the state with a superconducting correlation to be realized. In Section 4 the chemical potential and energy for a charge-ordered state are calculated. The conditions for realizing a particular state depending on parameters and density are determined in Section 5. Section 6 is devoted to calculating the energy for a pair transfer from one site to its neighbour, controlled by density. Here one finds the conditions for the ground state occurring with pairs delocalized on neighbouring sites. The conclusions in Section 7 summarize the principal results.

The conditions permitting the inequality (1) to be realized in the complex are given in the Appendix.

2. FORMULATION OF THE PROBLEM

If the energy of isolated complexes with different numbers of electrons in the s -shell satisfies Eq. (1) (see also Eq. (3A) in the Appendix), then in the complex (site) a pair of electrons is stabilized or, in other words, a bipolaron forms there. The bipolaron formation also occurs under the conditions suggested by Anderson (1975) and Chackraverty and Schlenker (1976).

The ground state of the crystal, on whose sites there are complexes with a pair of electrons in the outer shell, is determined by the intersite relation of the electron pairs, by their interactions with crystalline phonons, and by the bipolaron (electron) density. If one assumes that the binding energy of the electron pair on the site is much greater than both the interactions mentioned and kT , then the Hamiltonian describing the bipolaron behaviour in the crystal may be given as follows:

$$H = -\mu \sum_i B_i^+ B_i - \sum_{i \neq j} \varepsilon_{ij} B_i^+ B_j + \sum_{i \neq j} V_{ij} B_i^+ B_i B_j^+ B_j + \sum_{\mathbf{q}} F(\mathbf{q}) (C_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}_i} + C_{\mathbf{q}}^+ e^{-i\mathbf{q} \cdot \mathbf{r}}) B_i^+ B_i + \sum_{\mathbf{q}} \omega_{\mathbf{q}} C_{\mathbf{q}}^+ C_{\mathbf{q}} \quad (2)$$

where $B_i = a_{i\uparrow} a_{i\downarrow}$ is the bipolaron operator on site i ; $C_{\mathbf{q}}^+$, $C_{\mathbf{q}}$ are the phonon operators, $F_{\mathbf{q}}$ being the parameter describing the magnitude of the electron-phonon interaction; V_{ij} is the intersite Coulomb interaction; ε_{ij} describes bipolaron hopping energy to the adjacent sites (it is associated with a one-electron hopping t_{ij} in the following way: $\varepsilon_{ij} = t_{ij}^2/J$, J being the intrasite Coulomb interaction); $\omega_{\mathbf{q}}$ is the phonon energy; and μ is the chemical potential. We shall consider all the Hamiltonian parameters (V_{ij} , $F_{\mathbf{q}}$, ε_{ij}) to have the same order of magnitude. The bipolaron-phonon interaction is found to be strong in this case.

Our purpose is to ascertain the types of bipolaron ordering in the crystal according to the interaction parameters V_{ij} , $F(\mathbf{q})$, the hopping energy ε_{ij} , as well as the bipolaron density. In this case we shall, and this is the most important thing, demonstrate that the degree of lattice polarization due to the bipolaron-phonon interaction and the parameters of the ground state are self-consistently related.

It should be apparent that the following states of bipolarons are possible in the crystal.

1. The disordered (by electron pairs) state without a superconducting correlation.
2. The state with a superconducting correlation (s-state).
3. The charge-ordered state when electron pairs fill every next-but-one lattice site (co-state).

A homogeneous bipolaron distribution over the lattice corresponds to states (1) and

(2), and in such a distribution the number of bipolarons on neighbouring sites over the lattice is the same on average.

The ground state will be determined by a variation method. The trial functions are chosen in the following way. For states (1) and (2) with a homogeneous bipolaron distribution over the lattice, a trial function of the form

$$|\psi_s\rangle = \sum_i |\psi_i\rangle = \sum_i (u_i + v_i S_i^2 B_i^+) |0\rangle \quad (3)$$

is taken, where u_i, v_i are the variable parameters satisfying the condition

$$u_i^2 + v_i^2 = 1 \quad (3a)$$

The average number of electrons on the adjacent sites i and j is then the same: $\langle n_i \rangle = \langle n_j \rangle = n$, $n = 2v$ where v is the electron density. The parameter of the superconducting correlation Δ is proportional to the product uv and is different from zero in the s-state (a precise definition of the parameter Δ is given in Eq. (11)). In the disordered state $\Delta = 0$.

For the co-state, in which there is an inhomogeneous bipolaron distribution throughout the lattice, a trial function is chosen as

$$|\psi\rangle_{\text{co}} = \sum_{i \neq j} |\psi_{ij}\rangle = \sum_{i \neq j} (u_i + v_j S_j^2 B_j^+) |0\rangle \quad (4)$$

$i \neq j$ are the indices of the neighbouring lattice sites, u_i, v_j are the variable parameters obeying the condition

$$u_i^2 + v_j^2 = 1, \quad i \neq j \quad (4a)$$

and in this case $\langle n_j \rangle - \langle n_i \rangle = 2v$ where v is again the electron density.

The function S entering into Eqs. (3) and (4) assigns the lattice polarization to the electron-(bipolaron)-phonon interaction. It is determined as follows:

$$S_i = \exp \left\{ \sum_{\mathbf{q}} f_{\mathbf{q}} C_{\mathbf{q}} e^{-i\mathbf{q} \cdot \mathbf{r}_i} - h.c. \right\}, \quad S_i^+ = S_i^{-1} \quad (5)$$

$f_{\mathbf{q}}$ is an unknown function and it should be determined along with $u_i, v_i, h.c.$ is the hermitian conjugate. This is a mathematical expression of the fact that the degree of lattice polarization is self-consistently related to the parameters of the ground states. It is just this important physical fact which was ignored by Alexandrov and Ranninger (1981).

Since the chemical potential μ is also an unknown function, additional conditions for its determination should be provided. For the s-state the required condition is $\sum_i \langle \psi_s | n_i | \psi_s \rangle = N_0$, or, in the operators of the pairs,

$$\sum_i \langle \psi_s | B_i^+ B_i | \psi_s \rangle = N_0/2 \quad (6)$$

for the charge-ordered state:

$$\sum_{i \neq j} \langle \psi_{\text{co}} | n_i + n_j | \psi_{\text{co}} \rangle = N_0$$

or in the operators of the pair number:

$$\sum_{i \neq j} \langle \psi_{\text{co}} | B_i^+ B_i + B_j^+ B_j | \psi_{\text{co}} \rangle = N_0/2 \quad (7)$$

N_0 is the number of electrons in the system.

For the disordered and s-states the following functions are unknown: u_i (or v_i), f_q , μ ; for the co-states: u_i , v_i , f_q , μ .

Below we calculate functionals $\langle \psi_s | H | \psi_s \rangle$ and $\langle \psi_{co} | H | \psi_{co} \rangle$ and, minimizing them with regard to the additional Eqs. (3a), (4a), (6) and (7), obtain systems of equations for u_i , v_i , f_q , μ in the s-state and in the co-state. The solution of these equations enables one to define the chemical potentials and energies of all the states as functions of the Hamiltonian parameters and the electron density.

3. DETERMINATION OF CHEMICAL POTENTIALS AND ENERGIES FOR THE DISORDERED AND s-STATES

Here we calculate the functional

$$E_s = \langle \psi_s | H | \psi_s \rangle = \sum_{mm'} \langle 0 | (u_m + v_m S_m^{*2} B_m) H (u_{m'} + v_{m'} S_{m'}^2 B_{m'}^+) | 0 \rangle \quad (8)$$

Minimizing E_s over u_i , v_i , f_q , with the additional Eqs. (3a) and (6), we obtain a system of equations for u_i , f_q , μ .

Correlators of fourth and higher orders from the operators B_i and B_i^+ are reduced to the product of pair correlators of these operators in calculating different averages in Eq. (8), that is to say, the calculations are made in the mean-field approximation with respect to the operators B_i . This approximation is valid at temperatures which are much smaller than the interaction parameters in the Hamiltonian Eq. (2) since at such temperatures fluctuation corrections dictated by correlators of higher orders are exponentially small (Kulik and Pedan, 1980). Also, when calculating the averages, the following relation between the number of pairs (bipolarons) and the number of electrons is used: $2 \langle B_i^+ B_i \rangle = \langle n_i \rangle = \sum_{\sigma} \langle a_{i\sigma}^+ a_{i\sigma} \rangle$, $\langle n_i \rangle$ is the number of electrons on site i . The relation is valid at temperatures much lower than the binding energy of bipolarons on the site (i.e. it is more accurate at temperatures at which the mean-field approximation is valid). Commutators for pair operators have the form:

$$[B_i, B_i^+]_- = 1 - n_i \quad (9)$$

Based on the above, the following expressions are derived for the expectation values appearing in Eq. (8):

$$\begin{aligned} -\mu \sum_i \langle \psi_s | B_i^+ B_i | \psi_s \rangle &= -\mu \sum_{i \neq j} \left\langle \psi_s \left| \frac{B_i^+ B_i + B_j^+ B_j}{2} \right| \psi_s \right\rangle \\ &= -\mu \sum_{i \neq j} \left[\frac{1}{4} (u_i^2 + u_j^2 + 2u_i u_j) (n_i + n_j) + v_i^2 \left(1 - \frac{n_i}{2} \right)^2 \right. \\ &\quad \left. + v_j^2 \left(1 - \frac{n_j}{2} \right)^2 + v_i^2 \left(1 - \frac{n_i}{2} \right) \cdot \frac{n_j}{2} + v_j^2 \cdot \left(1 - \frac{n_j}{2} \right) \frac{n_i}{2} \right] \end{aligned}$$

The operator of a number of pairs is written here in a symmetrical form in i, j for convenience. Summing up is performed over the nearest neighbours (here and below):

$$\begin{aligned} \langle \psi_s | H_{et,ph} | \psi_s \rangle &= -2 \sum_{q, i \neq j} F_q f_q \left[v_i^2 \left(1 - \frac{n_i}{2} \right) \left(2 - n_i + \frac{n_j}{2} \right) \right. \\ &\quad \left. + v_j^2 \cos(\mathbf{q} \cdot \mathbf{R}_{ij}) \left(1 - \frac{n_j}{2} \right) \left(2 - n_j + \frac{n_i}{2} \right) \right] \end{aligned}$$

To calculate this result the following relations were used:

$$S_i^{*2} C_q S_i^2 = C_q - 2\beta_i(\mathbf{q})$$

$$S_i^{*2} C_q^+ S_i^2 = C_q - 2\beta_i^*(\mathbf{q})$$

where

$$\beta_i(\mathbf{q}) = f_q e^{-i\mathbf{q} \cdot \mathbf{r}_i}$$

These relations follow from the transformation of the operator C_q (Davydov, 1976):

$$\begin{aligned} S_i^* C_q S_i &= C_q - [S_i, C_q] - \\ \langle \psi_s | H_{ph} | \psi_s \rangle &= 2 \sum_{\mathbf{q}, m=j, i} \omega_q v_m^2 f_q^2 \left(1 - \frac{n_m}{2}\right) \\ \langle \psi_s | H_{el} | \psi_s \rangle &= - \sum_{i \neq j} \langle \psi_s | B_i^+ B_j | \psi_s \rangle \cdot \varepsilon_{ij} \\ &= - \sum_{i \neq j} \varepsilon_{ij} (u_i u_j v_i v_j + v_i v_j) \left(1 - \frac{n_i}{2}\right) \left(1 - \frac{n_j}{2}\right) \langle S_i^{*2} \cdot S_j^2 \rangle \end{aligned}$$

here

$$\langle S_i^{*2} \cdot S_j^2 \rangle \equiv e^{-\xi_{ij}}, \quad \xi_{ij} = \xi(\mathbf{R}_{ij}) = 8 \sum_{\mathbf{q}} f_q^2 \cdot \sin^2 \left(\frac{\mathbf{q} \cdot \mathbf{R}_{ij}}{2} \right)$$

\mathbf{R}_{ij} is the spacing between nearest neighbours.

$$\langle \psi_s | H_{el-el} | \psi_s \rangle = \sum_{i \neq j} V_{ij} \left\{ \frac{1}{2} n_i n_j (u_i^2 u_j + \frac{1}{2} u_i^2 + \frac{1}{2} u_j^2) + v_i^2 n_j \left(1 - \frac{n_i}{2}\right)^2 + v_j^2 \cdot n_i \left(1 - \frac{n_j}{2}\right)^2 \right\}$$

Using the condition $\langle n_i \rangle = \langle n_j \rangle = n$, we obtain the following expression for the energy functional E_s :

$$\begin{aligned} E_s &= -\frac{1}{2} \mu \sum_{i \neq j} \left[(u_i^2 + u_j^2 + 2u_i u_j) n + 2(v_i^2 + v_j^2) \left(1 - \frac{n}{2}\right)^2 \right. \\ &\quad \left. + \frac{n}{2} \left(1 - \frac{n}{2}\right) (v_i^2 + v_j^2) \right] - \sum_i \Delta_i u_i v_i \left(1 - \frac{n}{2}\right) - \sum_{i \neq j} t_{ij}^p v_i v_j \\ &\quad \times \left(1 - \frac{n}{2}\right)^2 - 4 \sum_{\mathbf{q}, i \neq j} F_{\mathbf{q}} f_{\mathbf{q}} [v_i^2 + v_j^2 \cos(\mathbf{q} \mathbf{R}_{ij})] \left(1 - \frac{n}{2}\right) \left(1 - \frac{n}{4}\right) \\ &\quad \left. + 2 \sum_{\mathbf{q}, i \neq j} \omega_{\mathbf{q}} f_{\mathbf{q}}^2 \left(1 - \frac{n}{2}\right) (v_i^2 + v_j^2) + \sum_{i \neq j} V_{ij} \left[\frac{n^2}{4} (u_i^2 + u_j^2 + 2u_i u_j) + (v_i^2 + v_j^2) n \left(1 - \frac{n}{2}\right)^2 \right] \right) \quad (10) \end{aligned}$$

In Eq. (10) we introduce the superconducting order parameter Δ_i , which is defined as follows:

$$\Delta_i = \sum_j \varepsilon_{ij} e^{-\xi_{ij}} \cdot v_j \cdot u_j \left(1 - \frac{n_j}{2}\right) \quad (11)$$

The parameter t_{ij}^p is the effective bipolaron hopping:

$$t_{ij}^p = \varepsilon_{ij} e^{-\xi_{ij}}$$

Because of the translational symmetry the order parameter Δ_i is independent of the site index i . Hence the parameters u_i, v_i have the same property, i.e. $u_i = u_j \equiv u, v_i = v_j \equiv v; i \neq j$.

The parameters u, v satisfy the relation $u^2 + v^2 = 1$ (see Eq. 3a). Taking into account these notions we obtain the final expression for the energy functional in the form

$$\begin{aligned} \frac{E_s}{N} = & -\frac{1}{2}\mu \left\{ 4n + v^2 \left[n \left(1 - \frac{n}{2} \right) - 4n + 4 \left(1 - \frac{n}{2} \right)^2 \right] \right\} \\ & + 4 \sum_q \omega_q f_q^2 v^2 \left(1 - \frac{n}{2} \right) - \Delta v \cdot \sqrt{1 - v^2} \cdot \left(1 - \frac{n}{2} \right) - t^p \cdot v^2 \cdot \left(1 - \frac{n}{2} \right)^2 \\ & - 4 \sum_q F_q f_q (1 + Z_q) v^2 \left(1 - \frac{n}{2} \right) \left(1 - \frac{n}{4} \right) + V_0 n \left\{ n - v^2 \left[n - 2 \left(1 - \frac{n}{2} \right)^2 \right] \right\} \end{aligned} \quad (12)$$

Here N is the number of sites,

$$\begin{aligned} t^p &= \sum_{\mathbf{R}_{ij}} \varepsilon(\mathbf{R}_{ij}) e^{-\xi(\mathbf{R}_{ij})} \\ \Delta &= t^p \cdot uv \left(1 - \frac{n}{2} \right); \\ Z_q &= \frac{1}{2} \sum_{\mathbf{R}_{ij}} \cos(\mathbf{q} \cdot \mathbf{R}_{ij}) \end{aligned}$$

is the configuration sum.

Now we must write down the condition for the definition of the chemical potential. Using the symmetrical form with respect to i, j , as in Eq. (7), we obtain

$$\sum_{i \neq j} \left[(u_i^2 + u_j^2 + 2u_i u_j) n + 2(v_i^2 + v_j^2) \left(1 - \frac{n}{2} \right)^2 + \frac{n}{2} \left(1 - \frac{n}{2} \right) (v_i^2 + v_j^2) \right] = N_0$$

and using relations $u_i = u_j = u = \sqrt{1 - v^2}$, $v_i = v_j = v$ we have

$$4n - 4v^2 \left[n - \left(1 - \frac{n}{2} \right)^2 - \frac{n}{2} \left(1 - \frac{n}{2} \right) \right] = n \quad (13)$$

$n = 2v$, where $v = N_0/N$ is the electron density.

We minimize Eq. (12) with respect to v, f_q and obtain the following equations:

$$\lambda v - \Delta \sqrt{1 - v^2} \cdot \left(1 - \frac{n}{2} \right) + \frac{\Delta v^2}{\sqrt{1 - v^2}} \cdot \left(1 - \frac{n}{2} \right) = 0 \quad (14)$$

$$\begin{aligned} \lambda = & -4\mu \left[-n + \left(1 - \frac{n}{2} \right)^2 + \frac{n}{4} \left(1 - \frac{n}{2} \right) \right] + 8 \sum_q \omega_q f_q \left(1 - \frac{n}{2} \right) \\ & - 8 \sum_q F_q f_q (1 + Z_q) \left(1 - \frac{n}{2} \right) \left(1 - \frac{n}{4} \right) - 2V_0 n \left[-2 \left(1 - \frac{n}{2} \right)^2 + n \right] - 2t^p \cdot \left(1 - \frac{n}{2} \right)^2 \end{aligned} \quad (15)$$

$$f_q^s(n) = \frac{F_q (1 + Z_q) \left(1 - \frac{n}{4} \right)}{2 \left[\omega_q + 2t_1 \left(1 - \frac{n}{2} \right) \right]}; \quad t_1 = \sum_{\mathbf{R}_{ij}} \varepsilon_{ij} e^{-\xi_{ij}} \sin^2 \left(\frac{\mathbf{q} \cdot \mathbf{R}_{ij}}{2} \right) \quad (16)$$

From Eq. (13) we can find v and then substituting this into Eq. (14), we can get the expression for the chemical potential. Thus using Eq. (16) the solution of the system (13)–(15) leads to

$$v_{1,2}^2 = \frac{1}{2} [1 \pm \phi(n)] \quad (17)$$

where

$$\phi(n) = 1 - \frac{3n/2}{n - \left(1 - \frac{n}{2}\right)^2 - \frac{n}{4} \left(1 - \frac{n}{2}\right)} \tag{17a}$$

$$u_{1,2}^2 = \frac{1}{2} [1 \pm \phi(n)] \tag{18}$$

$$4\mu \left[n - \left(1 - \frac{n}{2}\right)^2 - \frac{n}{4} \left(1 - \frac{n}{2}\right) \right] + 8 \sum_q \omega_q f_q^2 \left(1 - \frac{n}{2}\right) - 2t^p \left(1 - \frac{n}{2}\right)^2 - 2V_0 n \left[n - \left(1 - \frac{n}{2}\right)^2 \right] - 8 \sum_q F_q f_q (1 + Z_q) \left(1 - \frac{n}{2}\right) \left(1 - \frac{n}{4}\right) = \frac{2\Delta \cdot \phi(n) \left(1 - \frac{n}{2}\right)}{[1 - \phi^2(n)]^{1/2}} \tag{19}$$

From Eqs. (17), (18) and (11) it follows that the superconducting order parameter is given as a function of electron density, by

$$\Delta(n) = t^p \cdot \left(1 - \frac{n}{2}\right) \cdot \sqrt{1 - \phi^2(n)} \tag{20}$$

Substituting Eqs. (16) and (20) into (19) we derive the dependence of μ on n for arbitrary densities, n .

Real solutions for v and u are found only in a certain density range. Accordingly, at those densities $\Delta \geq 0$. At other densities the only real solution conforms to the value $\Delta = 0$. In this case, either $u = 0, v = 1$, or $u = 1, v = 0$. The solution with $\Delta \neq 0$ is found at densities obeying the condition:

$$1 - \phi(n) \geq 0$$

which is reduced to two systems of inequalities:

$$1 - \phi(n) \geq 0, \quad 1 + \phi(n) \geq 0 \tag{21}$$

$$1 - \phi(n) \leq 0, \quad 1 + \phi(n) \leq 0 \tag{21a}$$

Condition (21) is satisfied at densities:

$$4 - 2\sqrt{2} < n < 4 + 2\sqrt{2}$$

Condition (21a) has no solution.

Inasmuch as the maximum possible value of n is equal to 2 in our problem, the solution $\Delta \neq 0$ is found in the range of densities satisfying the condition

$$n_{1c} < n < 2, \quad n_{1c} = 4 - 2\sqrt{2} \approx 1, 2 \tag{22}$$

We can also determine at which densities the chemical potential μ_s of the superconducting state is less than μ_H of the disordered (by pairs) state. Since in Eq. (19) f_q is independent of v , it can easily be done. Chemical potentials μ_s and μ_H differ in the right-hand side of Eq. (19): for μ_H the right-hand side equals 0, as $\Delta = 0$. This suggests that $\mu_s < \mu_H$ at those densities for which the right-hand side of Eq. (19), divided by

$$\left[n - \left(1 - \frac{n}{2}\right)^2 - \frac{n}{4} \left(1 - \frac{n}{2}\right) \right]$$

is negative. It is so under the condition

$$\frac{\phi(n)}{n - \left(1 - \frac{n}{2}\right)^2 - \frac{n}{4} \left(1 - \frac{n}{2}\right)} < 0$$

or using Eq. (17a), we find that $\mu_s < \mu_H$ when the following inequality is satisfied:

$$-\frac{\frac{n}{2} + \left(1 - \frac{n}{2}\right)^2 + \frac{n}{4} \left(1 - \frac{n}{2}\right)}{\left[n - \left(1 - \frac{n}{2}\right)^2 - \frac{n}{4} \left(1 - \frac{n}{2}\right)\right]^2} \leq 0$$

This inequality can be satisfied at all permissible densities. Thus, for all densities for which $\Delta \neq 0$, we have $\mu_s < \mu_H$. Hence, the superconducting state is realized at these electron densities. In the general case the expression for μ is unwieldy. Below we describe the density dependence of $\mu(n)$ in the following limiting cases:

1. Densities sufficiently close to $n=2$, i.e.

$$1 - \frac{n}{2} \ll 1 \quad (1 - v \ll 1)$$

2. Small densities: $n \ll 1$.

In case (1) $1 - n/2 \ll 1$ (or $1 - v \ll 1$). In the first order with respect to $1 - n/2 \ll 1$, we have

$$f_q^s(n) \approx f_q^{(0)}(n) \cdot \left[1 + \left(1 - \frac{2t_1}{\omega_q}\right) \left(1 - \frac{n}{2}\right) \right] \tag{23}$$

$$f_q^{(0)}(n) \equiv f_q(n=2) = \frac{F_q(1 + Z_q)}{4\omega_q} \tag{23a}$$

$$\mu_s \approx V_0 + \left(1 - \frac{n}{2}\right) \cdot \left[-\frac{3V_0}{4} + \sum_q \frac{F_q^2(1 + Z_q)^2}{16\omega_q} \right] \tag{24}$$

In the first order $\mu_s \approx \mu_H$, since $\Delta(n) \sim (1 - n/2)$. In the second order we obtain

$$\mu_H - \mu_s \approx \frac{t^p}{8} \cdot \left(1 - \frac{n}{2}\right)^2 \tag{25}$$

It follows from Eq. (24) that at $1 - n/2 \ll 1$ the chemical potential increases for $F_q/\omega_q \ll 1$ when the electron density decreases; for $F_q/\omega_q \gg 1$ the chemical potential decreases, when the density decreases.

In case (2) $n \ll 1$. There is some complication in this case. It is impossible to obtain analytical expressions for arbitrary interaction parameters, since the equation for $f_q^{(0)} \equiv f_q(n=0)$ is transcendental:

$$f_q^{(0)} = \frac{F_q(1 + Z_q)}{2(\omega_q + 2t_1)}, \quad t_1 = \sum_{R_{ij}} \varepsilon(R_{ij}) e^{-\xi^{(0)}(R_{ij})} \cdot \sin^2\left(\frac{\mathbf{q} \cdot \mathbf{R}_{ij}}{2}\right)$$

where

$$\xi^{(0)}(R_{ij}) = 8 \sum_q f_q^{(0)} \cdot \sin^2\left(\frac{\mathbf{q} \cdot \mathbf{R}_{ij}}{2}\right)$$

In the general case this equation can only be solved numerically. Therefore we restrict ourselves to the following cases:

- (a) the phonon dispersion is absent: $\mathbf{q} = \mathbf{0}$;
- (b) the weak-coupling limit: $F_q/\omega_q \ll 1$, i.e.

$$V_0 \gg F_q^2/\omega_q (V_0 \sim F_q)$$

- (c) the extremely strong coupling limit: $F_q/\omega_q \gg 1$, i.e.

$$V_0 \ll F_q^2/\omega_q$$

In case (a) we obtain

$$f^{(0)} = \frac{F_0}{\omega_0}, \quad \mu^{(0)} \approx -\frac{2F_0^2}{\omega_0} - \frac{\varepsilon_0}{2} \tag{26}$$

We used, for

$$\mathbf{q} = \mathbf{0}: t_1 = 0, \xi(\mathbf{R}_{ij}) = 0, Z_q = 1, t^p = \sum_{\mathbf{R}_{ij}} \varepsilon(\mathbf{R}_{ij}) \exp[-\xi(\mathbf{R}_{ij})] = \sum \varepsilon(\mathbf{R}_{ij}) \equiv \varepsilon_0$$

In case (b) the parameters t_1, t^p are independent of f_q in the first order for $n \ll 1$. Therefore in the first order we obtain

$$f_q^{(0)} = \frac{F_q(1+Z_q)}{2(\omega_q+2t_1)}; \mu \approx -\frac{t^p}{2} + \left(\frac{3t^p}{14} + V_0\right)n \tag{27}$$

In the case (c) $t_1 t^p \rightarrow 0$ exponentially. Therefore we have

$$f_q^{(0)} \approx \frac{F_q(1+Z_q)}{2\omega_q}$$

$$\mu \approx -\sum_q \frac{F_q^2(1+Z_q)^2}{2\omega_q} + n \cdot \sum_q \frac{F_q^2(1+Z_q)(5-Z_q)}{2\omega_q} \tag{28}$$

Thus, at $n \ll 1, \mu^{(0)} < 0$ for all the parameter values. And the chemical potential $\mu(n)$ increases with the electron density. Now we write down the asymptotic expressions for the energy E_s at $1 - n/2 \ll 1$ and $n \ll 1$. In the case $1 - n/2 \ll 1$ we obtain in the first order

$$E_s \approx \left[-\mu^{(0)} \cdot v^{(0)2} + 4 \sum_q \omega_q f_q^{(0)2} \cdot v^{(0)2} - 2 \sum_q F_q f_q^{(0)} \cdot v^{(0)2} (1+Z_q) \right] \left(1 - \frac{n}{2} \right) + 8\mu^{(0)} \cdot v^{(0)} \cdot v^{(1)} - 8\mu^{(1)} \cdot (1 - v^{(0)2}) \tag{29}$$

Here $\mu^{(1)}, v^{(1)}$ are the first-order corrections for μ and v . The value of $\mu^{(1)}$ is given in Eq. (24). The correction $v^{(1)}$ can be found from Eq. (17); it is given by

$$v_1^2 \approx \frac{1}{4} - \frac{3}{16} \left(1 - \frac{n}{2} \right), v_1^{(0)2} = \frac{1}{4} \tag{30a}$$

$$v_2^2 \approx \frac{3}{4} + \frac{3}{16} \left(1 - \frac{n}{2} \right), v_2^{(0)2} = \frac{3}{4} \tag{30b}$$

Substituting $\mu^{(1)}, v^{(1)}$, into the approximation Eq. (29) we obtain

$$E_{s1} = \left[-\frac{11}{8}V_0 - \sum_q \frac{F_q^2(1+Z_q)^2}{2\omega_q} \right] \left(1 - \frac{n}{2} \right)$$

for the solution (30a)

$$E_s^2 = \left[-\frac{5}{8}V_0 - \sum_q \frac{17F_q^2(1+Z_q)^2}{16\omega_q} \right] \left(1 - \frac{n}{2} \right)$$

for the solution (30b).

Since the chemical potentials for the solutions (30a) and (30b) are equal to each other in the second order (with respect to $1 - n/2 \ll 1$), then near the value $n=2$ for $E_{s1} < E_{s2}$ the solution (30a) is realized, and for $E_{s1} > E_{s2}$ the solution (30b) is realized. The inequality $E_{s1} < E_{s2}$ is valid under the condition $V_0 > 6F_0^2/\omega_0$ (without phonon dispersion). On the contrary, when $V_0 < 6F_0^2/\omega_0$ the inequality $E_{s1} > E_{s2}$ applies.

In the case $n \ll 1$ the following solutions are found:

- (a) $v = 1, u = 0$
- (b) $v = 0, u = 1$

For solution (a) in the first order we have

$$E_{s1} = - \left[\frac{3\mu^{(0)}}{2} + t^p - \sum_q \frac{F_q^2(1+Z_q)^2}{\omega_q} - 2V_0 \right] n - 2\mu^{(1)} \tag{31a}$$

The correction $\mu^{(1)}$ is determined from the approximations (27) and (28). For solution (b) we obtain

$$E_{s2} = -2\mu^{(0)} \cdot n \tag{31b}$$

In the weak-coupling limit ($F_q/\omega_q \ll 1$), substituting $\mu^{(0)}, \mu^{(1)}$ into (31a) and (31b), we obtain the expressions

$$E_{s1} = -\frac{19}{28}t^p \cdot n, \quad E_{s2} = t^p \cdot n$$

Thus, the state with $v = 1, u = 0$ is realized. In the extremely strong coupling limit ($F_q/\omega_q \gg 1$), using the approximation (28), we obtain

$$E_{s1} = - \sum_q \frac{F_q^2 \cdot (1+Z_q)^2}{\omega_q} \cdot n; \quad E_{s2} = \sum_q \frac{F_q^3 \cdot (1+Z_q)^3}{2\omega_q} \cdot n$$

The same solution is realized here (i.e. $v = 1, u = 0$).

The qualitative behaviour of the functions $\mu_s(n), f_q^s(n), E_s(n)$ is shown in Figures 1, 2 and 3.

4. THE CHEMICAL POTENTIAL AND THE ENERGY FOR THE CHARGE-ORDERED STATE

In this section we introduce the functional

$$E_{co} = \sum_{\substack{m \neq n \\ m' \neq n'}} \langle 0 | (u_m + v_n S_n^{*2} B_n) H (u_{m'} + v_{n'} S_{n'}^2 B_{n'}) | 0 \rangle$$

which we minimize with respect to u_i, v_i, f_q under the conditions

$$\begin{aligned} \langle n_i \rangle + \langle n_j \rangle &= 2v \\ \langle n_j \rangle - \langle n_i \rangle &= 2v \end{aligned} \tag{32}$$

or

$$\langle n_j \rangle = 2v, \quad \langle n_i \rangle = 0$$

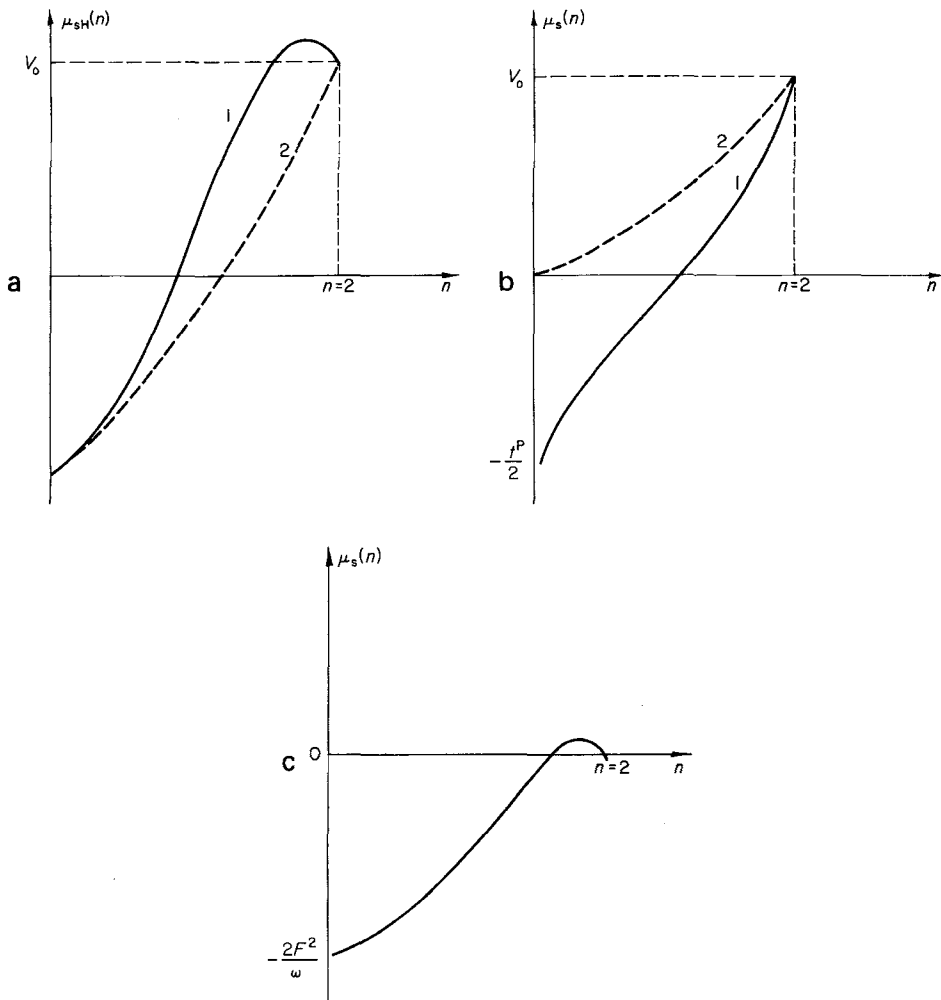


FIG. 1. The qualitative behaviour of the chemical potential vs electron density for the ground states (1) and (2) with the homogeneous pair distribution. (a) $\mu_s(n)$ for the intermediate parameter values: for curve 1: $V_0 < F^2/3\omega$; for curve 2: $V_0 > F^2/3\omega$. (b) $\mu_s(n)$ in the weak coupling limit: $F/\omega \ll 1$; for curve 1: $V_0 \sim t^p$; for curve 2: $V_0 \gg t^p$. (c) $\mu_s(n)$ in the extremely strong coupling limit: $F/\omega \gg 1$.

In Eq. (32), $n = 2v$, where v is the electron density. Rewriting the first condition in (32) by the pair operators and calculating the averages, we obtain the condition for the definition of the chemical potential in the form

$$\sum_{i \neq j} \left\{ (u_i^2 + u_j^2) \frac{n_i + n_j}{2} + 2v_j^2 \cdot \left(1 - \frac{n_j}{2}\right)^2 + 2v_i^2 \cdot \left(1 - \frac{n_i}{2}\right)^2 + v_j^2 \cdot \left(1 - \frac{n_j}{2}\right) \cdot \frac{n_i}{2} + v_i^2 \left(1 - \frac{n_i}{2}\right) \frac{n_j}{2} + u_i u_j (n_i + n_j) \right\} = \frac{N_0}{2} \tag{33}$$

The left-hand part of this equation as well as the expression for E_{∞} is symmetrical with

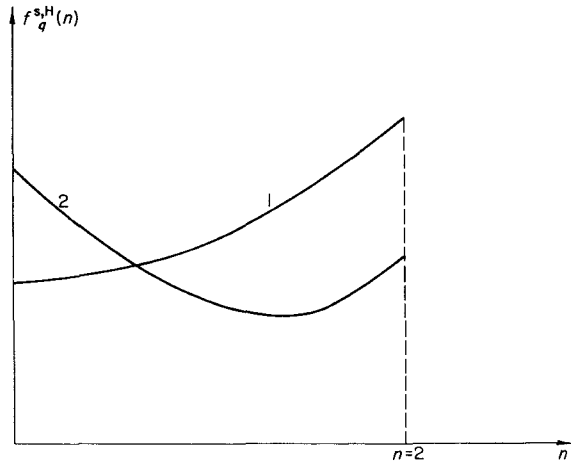


FIG. 2. The qualitative behaviour of the function $f_q^s(\omega)$ for curve 1: $2t_1 > \omega_q$; for curve 2: $2t_1 < \omega_q$

respect to i, j . Therefore our expression is valid in the case when in Eq. (32) the indices i and j are transposed.

The expression for E_{co} has the form

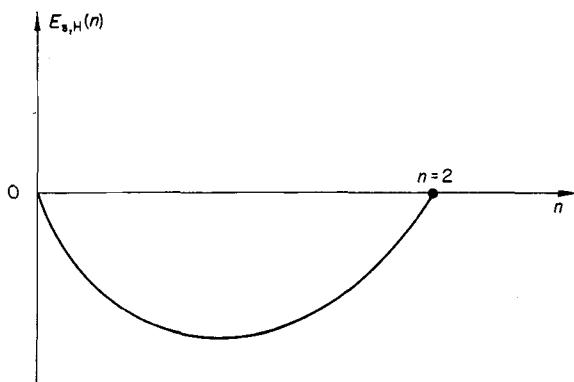
$$\begin{aligned}
 E_{co} = & -\mu \sum_{i \neq j} \left\{ (u_i^2 + u_j^2) \frac{n_i + n_j}{2} + 2v_j^2 \cdot \left(1 - \frac{n_j}{2}\right)^2 + 2v_i^2 \left(1 - \frac{n_i}{2}\right)^2 \right. \\
 & \left. + v_j^2 \cdot \left(1 - \frac{n_j}{2}\right) \frac{n_i}{2} + v_i^2 \left(1 - \frac{n_i}{2}\right) \frac{n_j}{2} + u_i u_j (n_i + n_j) \right\} \\
 & - \sum_{i \neq j} t_{ij}^p v_i v_j \left(1 - \frac{n_i}{2}\right) \left(1 - \frac{n_j}{2}\right) - 8 \sum_q F_q f_q \left\{ v_i^2 \left(1 - \frac{n_i}{2}\right) \left(1 - \frac{n_i + n_j}{4}\right) \right. \\
 & \left. + v_j^2 \cdot \left(1 - \frac{n_j}{2}\right) \left(1 - \frac{n_j + n_i}{4}\right) + v_j^2 \cos(\mathbf{q} \cdot \mathbf{R}_{ij}) \left(1 - \frac{n_i}{2}\right) \left(1 - \frac{n_j + n_i}{4}\right) \right. \\
 & \left. + v_i^2 \cos(\mathbf{q} \mathbf{R}_{ij}) \left(1 - \frac{n_i}{2}\right) \left(1 - \frac{n_i + n_j}{4}\right) \right\} + 4 \sum_q \omega_q f_q^2 \left[v_i^2 \left(1 - \frac{n_i}{2}\right) \right. \\
 & \left. + v_j^2 \left(1 - \frac{n_j}{2}\right) \right] + \sum_{i \neq j} V_{ij} \left\{ \frac{1}{2} (u_i^2 + u_j^2 + 2u_i u_j) n_i n_j \right. \\
 & \left. + v_i^2 \left(1 - \frac{n_i}{2}\right)^2 \cdot n_j + v_j^2 \left(1 - \frac{n_j}{2}\right)^2 \cdot n_i \right\} \tag{34}
 \end{aligned}$$

In Eqs. (33) and (34) we rewrite:

(a) u_j, v_j by u_i, v_i according to the relations

$$u_i^2 + v_j^2 = 1, \quad u_j^2 + v_i^2 = 1, \quad i \neq j \tag{35}$$

(b) $\langle n_i \rangle, \langle n_j \rangle$ by n according to the conditions in Eq. (32). The parameters u_i, v_i are independent of the site indices because of the translational symmetry.

FIG. 3. The energy $E_s(n)$ vs the electron density n .

Taking into account these notions, Eqs. (33) and (34) lead to

$$u^2 \cdot \left[\frac{n}{2} - 2 \left(1 - \frac{n}{2} \right)^2 \right] + 2v^2 + \frac{n}{2} + 2 \left(1 - \frac{n}{2} \right)^2 + u \sqrt{1-v^2} \cdot n = \frac{\dot{n}}{2} \quad (36)$$

$$\begin{aligned} \frac{E_{co}}{N} = & -\mu \left[(u^2 + 1 - v^2) \frac{n}{2} + 2(1-u^2) \left(1 - \frac{n}{2} \right)^2 + 2v^2 \left(1 + \frac{n}{4} \right) \right. \\ & \left. + u \cdot \sqrt{1-v^2} \cdot n \right] - t^p \cdot v \cdot \sqrt{1-u^2} \cdot \left(1 - \frac{n}{2} \right) - 8 \sum_q F_q f_q \left[v^2 \left(1 + \frac{n}{4} \right) \right. \\ & \left. + (1-u^2) \left(1 - \frac{n}{2} \right)^2 \right] (1 + Z_q) + 4 \sum_q \omega_q f_q^2 \left[v^2 + (1-u^2) \left(1 - \frac{n}{2} \right) \right] \\ & + V_0 v^2 \cdot n; \quad u, v = u_i, v_i; \quad V_0 = \sum_{R_{ij}} V(R_{ij}) \end{aligned} \quad (37)$$

We minimize the energy with respect to f_q and obtain the expression for f_q vs u, v and n :

$$f_q^{co} = \frac{F_q \left[v^2 \left(1 + \frac{n}{4} \right) + (1-u^2) \left(1 - \frac{n}{2} \right)^2 \right] (1 + Z_q)}{\omega_q \left[v^2 + (1-u^2) \left(1 - \frac{n}{2} \right) \right] + t_1 \cdot v \cdot \sqrt{1-u^2} \left(1 - \frac{n}{2} \right)} \quad (38)$$

Also we minimize the energy with respect to u, v and obtain the following equations:

$$\lambda_1 v + \mu \frac{uv}{\sqrt{1-v^2}} n - t^p \cdot \sqrt{1-u^2} \cdot \left(1 - \frac{n}{2} \right) = 0 \quad (39)$$

$$\lambda_2 u - \mu \cdot \sqrt{1-v^2} \cdot n + t^p \cdot \frac{uv}{\sqrt{1-u^2}} \left(1 - \frac{n}{2} \right) = 0$$

$$\lambda_1 = -4\mu n - 16 \sum_q F_q f_q \left(1 + \frac{n}{4} \right) (1 + Z_q) + 8 \sum_q \omega_q f_q^2 + 2V_0 n \quad (39a)$$

$$\lambda_2 = -\mu n + 4\mu \left(1 - \frac{n}{2}\right)^2 + 16 \sum_q F_q f_q \left(1 - \frac{n}{2}\right)^2 (1 + Z_q) - \sum_q \omega_q f_q^2 \left(1 - \frac{n}{2}\right) \quad (39b)$$

We shall find the solution of the system of Eqs. (36), (38) and (39) in the low-density limiting case ($n \ll 1$) and in the case of densities close to $n=2$, i.e. at $1 - n/2 \ll 1$. At $1 - n/2 \ll 1$ in the first order the solution of Eqs. (36), (38) and (39) has the form

$$\begin{aligned} v^2 &\approx \frac{1}{3} \left[1 - \frac{2}{3} \left(1 - \frac{n}{2}\right) \right]; \quad u^2 \approx \frac{2}{3} \left[1 + \frac{1}{\mu^{(0)}} \left(\frac{\mu^{(0)}}{3} - \sum_q \frac{18F_q^2}{\omega_q} + t^p \right) \right] \\ &\times \left(1 - \frac{n}{2}\right); \quad \mu^{(0)} \equiv \mu(n=2) = \frac{2}{3}V_0 - \sum_q \frac{3F_q^2}{\omega_q} \\ f_q^{co}(n) &\approx \frac{3F_q}{2\omega_q} \cdot \left[1 - \left(\frac{4}{3} + \frac{t}{\omega_q} \right) \left(1 - \frac{n}{2}\right) \right] \end{aligned} \quad (40)$$

$$\mu_{co}(n) \approx \frac{2}{3}V_0 - \sum_q \frac{3F_q^2}{\omega_q} + \left(1 - \frac{n}{2}\right) \left(-\frac{4V_0}{9} - \frac{t^p}{3} + \sum_q \frac{14F_q^2}{3\omega_q} \right) \quad (41)$$

At $n \ll 1$ we obtain in the first order

$$u^2 = \left(1 - \frac{n}{4}\right), \quad v^2 \approx \left(\frac{t^p}{4\lambda_1^{(0)}} \right)^2 \cdot n,$$

$$\lambda_1^{(0)} = -4\mu^{(0)} - 8 \sum_q f_q^{(0)} \cdot [2F_q - 2\omega_q f_q^{(0)}] = -4\mu^{(0)} - \sum_q \frac{8F_q^2}{\omega_q}$$

where

$$\mu_{co}^{(0)} = -\frac{t^p}{4} - \sum_q \frac{2F_q^2}{\omega_q}, \quad f_q^{(0)} = \frac{F_q}{\omega_q} \quad (42)$$

$$\mu_{co} \approx \mu_{co}^{(0)} + \left(-\frac{11}{8}t^p + \sum_q \frac{2F_q^2}{\omega_q} \right) n \quad (43)$$

Thus, according to the asymptotic expression (40)–(43) one can draw the following qualitative conclusions about the behaviour of μ_{co} at different densities and relative values of the parameters. In the weak-coupling limit ($F_q/\omega_q \ll 1$, $V_0, t^p \gg F_q^2/\omega_q$), $\mu_{co}(n)$ decreases both in the vicinity of $n=2$ (i.e. at $(1 - n/2) \ll 1$) and near $n=0$ (at $n \ll 1$). Here, $\mu_{co}(0) < 0$, $\mu_{co}(2) > 0$ (see Figure 4a). In the extremely strong coupling limit ($F_q/\omega_q \gg 1$, $V_0, t^p \ll F_q^2/\omega_q$) $\mu_{co}(0) < 0$, $\mu_{co}(2) < 0$, $|\mu_{co}(2)| > |\mu_{co}(0)|$. In this case $\mu_{co}(n)$ increases close to $n=2$ as well as close to $n=0$ (see Figure 4b). At intermediate values of the parameters one is likely to observe the curve $\mu_{co}(n)$ to behave differently depending on the ratio between V_0 , F_q^2/ω_q and t^p . Some versions of this behaviour are given in Figure 4c. Note, that at all values of the parameters $\mu_{co}(0) < 0$. Figure 5 exhibits qualitatively the behaviour of the function $f_q^{co}(n)$, attributing the lattice polarization to the interaction with bipolarons.

In the weak coupling limit and for the condition $t^p \gg \frac{2}{3}V_0$, the point n_0 where the $\mu_{co}(n)$ crosses the x-axis lies close to $n=2$, i.e. in the region $1 - n/2 \ll 1$. With increasing F_q^2/ω_q the condition proves to be more restrictive, namely,

$$\frac{2}{3}V_0 + \sum_q \frac{5F_q^2}{\omega_q} \ll t^p$$

i.e. it is likely that the point n_0 , where $\mu_{co}(n_0) = 0$, with increasing F_q/ω_q it abandons the

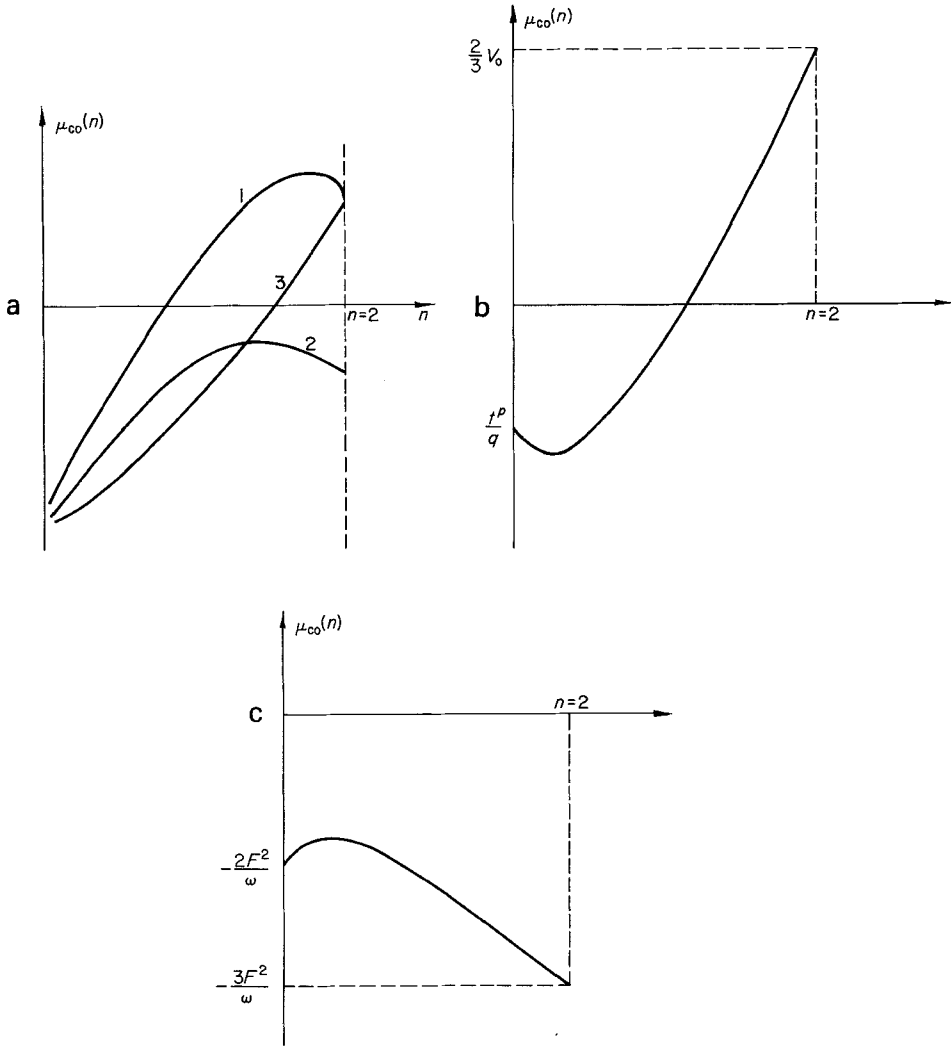
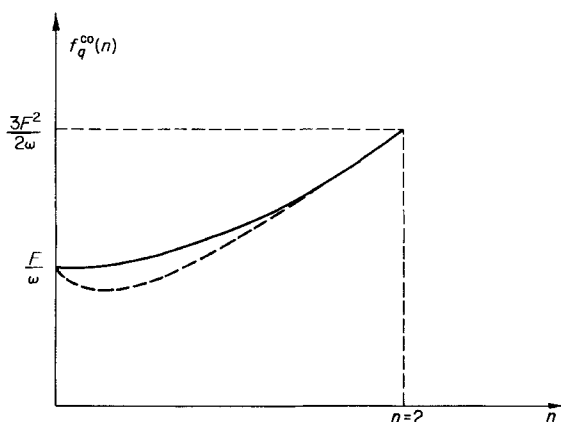


FIG. 4. The qualitative behaviour of $\mu_{co}(n)$ in the charge-ordered state. (a) $\mu_{co}(n)$ for the intermediate parameter values, for curve 1: $V_0 > \frac{9F^2}{2\omega}$, $V_0 < \frac{21}{2} \frac{F^2}{\omega} - \frac{3}{4} t^p$; for curve 2: $V_0 < \frac{9F^2}{2\omega}$, $V_0 < \frac{21}{2} \frac{F^2}{\omega} - \frac{3}{4} t^p$; for curve 3: $\frac{9F^2}{2\omega} < V_0 < \frac{21}{2} \frac{F^2}{\omega} - \frac{3}{4} t^p$. (b) $\mu_{co}(n)$ in the weak-coupling limiting case $F/\omega \ll 1$. (c) $\mu_{co}(n)$ in the extremely strong coupling limiting case: $F/\omega \gg 1$.

region $1 - n/2 \ll 1$, even if at $F_q/\omega_q \ll 1$ it occurred in the region mentioned. Again we shall write down the values of the energy E_{co} at $n \ll 1$ and $1 - n/2 \ll 1$. Accurate to linear terms we have

$$E_{co}(n) \approx - \left(\frac{t^p}{8} + \sum_q \frac{3F_q^2}{\omega_q} \right) n, \quad n \ll 1 \tag{44}$$

FIG. 5. The qualitative behaviour $f_q^{co}(n)$ in the charge-ordered state.

$$E_{co}(n) \approx \left(\frac{16}{27} V_0 - \sum_q \frac{10F_q^2}{3\omega_q} \right) \left(1 - \frac{n}{2} \right), \quad 1 - \frac{n}{2} \ll 1 \quad (45)$$

5. COMPARISON OF $\mu_s(n)$ AND $\mu_{co}(n)$. POSSIBLE TYPES OF ORDERING

Using the expressions for $\mu_{co}(n)$ derived in Section 4 and those for $\mu_s(n)$ from Section 3 we compare the chemical potentials of the co- and s-states. As follows from the Eqs. (24) and (41), at $n=2$ ($v=1$), $\mu_s(2) > \mu_{co}(2)$, hence at those densities the charge-ordered state is realized. With decreasing n the behaviour of curves $\mu_s(n)$ and $\mu_{co}(n)$ depends on the values of the interaction parameters and t^p . In the weak-coupling limit ($F_q/\omega_q \ll 1$), at $1 - n/2 \ll 1$, $\mu_s(n)$ decreases with n faster than $\mu_{co}(n)$, and at $n \ll 1$, as follows from comparing Eqs. (42), (43) and (27), (28), $\mu_s(0) = -t^p/2 < \mu_{co}(0) = -t^p/4$, with increasing n $\mu_{co}(n)$ decreases and $\mu_s(n)$ increases.

In the intermediate range of values of the parameters, for example at $\sum_q F_q^2/3\omega_q < V_0 < \sum_q 9F_q^2/2\omega_q$, with decreasing n μ_s decreases close to $n=2$ and μ_{co} increases, and here $\mu_{co}(2) < 0$, $\mu_s(2) > 0$. Other variants are also possible there. For example, at $V_0 < \sum_q F_q^2/3\omega_q$, $V_0 + 3t^p/2 > \sum_q 21F_q^2/2\omega_q$, μ_{co} and μ_s increase close to $n=2$, but $\mu_{co}(n) < 0$, $\mu_s(n) > 0$, etc. For the values of parameters satisfying the condition $\sum_q F_q^2/3\omega_q < V_0 < \sum_q 9F_q^2/2\omega_q$ at $n \ll 1$, $\mu_{co} > \mu_s$ and $\mu_s(n)$ increases with n , and $\mu_{co}(n)$ may both increase and decrease, as seen from Eq. (43). In the extremely strong coupling limit ($F_q/\omega_q \gg 1$) $\mu_s(2) \approx 0$, $\mu_{co}(2) \approx -\sum_q 3F_q^2/\omega_q$ and at $1 - n/2 \ll 1$, μ_s and μ_{co} increase with decreasing n , with $\mu_{co}(n)$ increasing faster. At $n \ll 1$, $\mu_s(0) \approx \mu_{co}(0) \approx -\sum_q 2F_q^2/\omega_q$ and $\mu_{co}(n)$ increases faster than $\mu_s(n)$ with n . From the comparison between $\mu_{co}(n)$ and $\mu_s(n)$ one can arrive at a conclusion on the realization of different states in the crystal at different densities and values of the parameters. At $n=2$, $\mu_s(2) > \mu_{co}(2)$ and the co-state is realized. The condition $\mu_s(2) > \mu_{co}(2)$ if fulfilled up to the densities $n=n_{2c}$ where the curves $\mu_s(n)$ and $\mu_{co}(n)$ intersect. The fact that they must intersect follows from their asymptotic behaviour described above. At $n < n_{2c}$, $\mu_s(n) < \mu_{co}(n)$. If $n_{2c} < n_{1c}$, where n_{1c} is given on page 244, then in the range $n_{1c} < n < n_{2c}$ the state with superconducting correlation is realized (it will be recalled that at $n_{1c} < n < 2$ the superconducting order

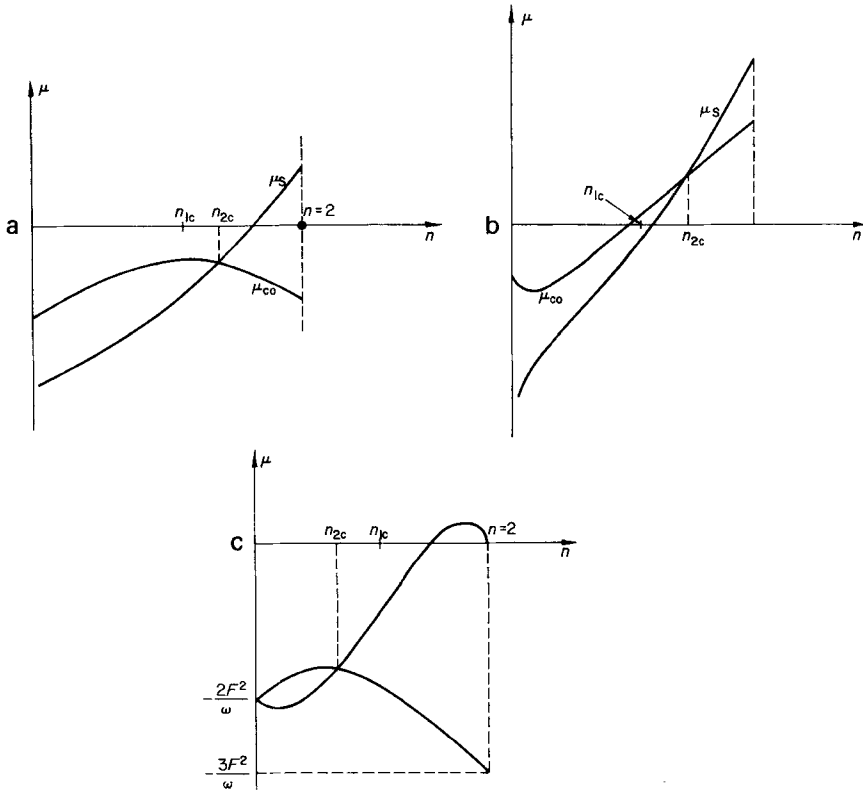


FIG. 6. The comparison of the functions $\mu_s(n)$ and $\mu_{co}(n)$ in the different limiting cases. (a) A possible situation for $\mu_s(n)$ and $\mu_{co}(n)$ at $F^2/3\omega < V_0 < 9F^2/2\omega$ (the intermediate parameter values), (b) at $F/\omega \ll 1$, i.e. $V_0 \gg F^2/\omega$, (c) at $F/\omega \gg 1$, i.e. $V_0 \ll F^2/\omega$.

parameter Δ differs from zero). At $n < n_{1c}$ the disordered (by pairs) state is realized. Then value n_{2c} depends on the relation between the parameters V_0 , t^p and F_q^2/ω_q . Since, as follows from Eq. (24), $\mu_s(n)$ does not intersect the x -axis in the region $1 - n/2 \ll 1$, so n_{2c} lies in any case in the region $n < 1.9$. That is why n_{2c} is only estimated numerically. Possible ways of intersecting $\mu_s(n)$ and $\mu_{co}(n)$ are qualitatively shown in Figure 6. For occurrence of the region $n_{1c} < n < n_{2c}$, where the state with superconducting correlation is realized, the following most favourable factors are: the weak-coupling limit $F_q^2/\omega_q \ll V_0$, t^p ; intermediate values of the parameters, for example, $\sum F_q^2/3\omega_q < V_0 < \sum 9F_q^2/2\omega_q$ (see Figures 6a and b). In the extremely strong coupling limit ($F_q/\omega_q \gg 1$), the intersecting point is $n_{2c} < 1$, therefore, only two states are possible: the co-state at $n > n_{2c}$ and the disordered one at $n < n_{2c}$ (see Figure 6c).

6. PAIR TRANSFER ENERGY. THE OCCURRENCE OF THE GROUND STATE WITH DELOCALIZED PAIRS

This section deals with the determination of the transfer energy of the electron pairs (bipolarons) from one site to the adjacent one, in the charge-ordered state. Within the

framework of the present paper, in which the types of the ground states of bipolarons in the crystal are defined, the calculation of the pair transfer energy is of interest for the following reason. Assume, that at some values of the parameters and density n the pair transfer energy becomes less than the ground-state energy E_{co} , the chemical potential remaining constant. Then in the given range of the parameter values and at the given density, the ground state of the system becomes that in which every electron pair is delocalized in neighbouring sites. Below we show that such a range of parameter values, in which this state is realized, is certain to occur. To calculate the pair transfer energy, we average the Hamiltonian (Eq. (2)) over the states with a wavefunction of the following form:

$$|\psi_{ij}\rangle = (S_i^{*2} \cdot B_i B_j^+ S_j^2) \sum_{m \neq n} (u_m + v_n S_n^2 B_n^+) |0\rangle, \quad i \neq j$$

Then the bipolaron transfer energy is

$$\omega_p = \frac{1}{2} \sum_{i \neq j} \langle \psi_{ij} | H | \psi_{ij} \rangle \quad (46)$$

here v_i, u_i, S_i are the functions determined in Section 4 for the charge-ordered state.

Omitting here commonplace but very cumbersome calculations of the expectation values in Eq. (46), we derive a final expression for $\omega_p(n)$. Here $\langle n_i \rangle, \langle n_j \rangle$ are expressed through n according to the conditions of Eq. (32):

$$\begin{aligned} \omega_p(n) = & -\frac{1}{2} \mu_{co}(n) \cdot \left\{ (u^2 + 1 - v^2 + 2u \cdot \sqrt{1 - v^2}) \left[n^2 + 2 \left(1 - \frac{n}{2} \right) \right] \right. \\ & + v^2 \left[4n - 2 \left(1 - \frac{n}{2} \right) + 3 \left(1 - \frac{3n}{2} + n^2 \right) + 2 \left(1 - \frac{n}{2} \right)^2 \right] \\ & + (1 - u^2) \left[\left(1 + \frac{5n}{2} \right) \left(1 - n + \frac{n^2}{2} \right) + \left(1 - \frac{n}{2} \right) \left(2 + \frac{n}{2} - \frac{n^2}{2} \right) \right] \left. \right\} \\ & - 2t^p \cdot v \cdot \sqrt{1 - u^2} \cdot \left[\frac{3}{2} \left(1 - n + \frac{n^2}{2} \right) + \left(1 - \frac{n}{2} \right) \left(\frac{3}{2} - n \right) \right] \\ & - \sum_q F_q f_q \left\{ (1 + Z_q) v^2 \left[4n - 2 \left(1 - \frac{n}{2} \right) + 3 \left(1 - \frac{3n}{2} + n^2 \right) \right. \right. \\ & + 2 \left(1 - \frac{n}{2} \right)^2 \left. \right] + (1 - u^2) (1 + Z_q) \left[\left(1 + \frac{5n}{2} \right) \left(1 - n + \frac{n^2}{2} \right) \right. \\ & + \left. \left. \left(1 - \frac{n}{2} \right) \left(2 + \frac{n}{2} - \frac{n^2}{2} \right) \right] - 2 \sum_q \omega_q f_q \left[(u^2 + 1 - v^2 + 2u \sqrt{1 - v^2}) \frac{n}{2} \right. \right. \\ & + \left. \left. \frac{3}{2} v^2 \cdot n + (1 - u^2) \left(1 - n + \frac{n^2}{2} \right) \right] + \frac{1}{2} V_0 [u^2 + 1 - v^2] \right. \\ & + 2u \cdot \sqrt{1 - v^2} \left[(n - 1) \left(n + 1 + \frac{n^2}{2} \right) + 3 \left(1 - \frac{n}{2} \right) + 2 \left(1 - n + \frac{n^2}{2} \right) \right. \\ & - \left. \left. 1 + \frac{3n}{2} - n^2 + 3 \left(1 - \frac{3n}{2} + n^2 \right) + 2 \left(1 - \frac{n}{2} \right)^2 \right] \right. \\ & + \left. \frac{1}{2} V_0 v^2 \left[8 \left(1 - \frac{3n}{2} + n^2 \right) - 4 \left(1 - \frac{n}{2} \right)^2 \right] + \frac{1}{2} V_0 (1 - u^2) \left\{ 4(1 - n) \right. \right. \end{aligned}$$

$$\begin{aligned} & \times \left(1 - \frac{n}{2}\right) \left(\frac{5}{2} - n\right) + \left(\frac{5n}{2} - 1\right) \left(1 - n + \frac{n^2}{2}\right) + \left(1 - \frac{n}{2}\right) \left(\frac{5n}{2} - 1 - \frac{n^2}{2}\right) \\ & + 2 \left[\left(\frac{5n}{2} - 1\right) \left(1 - n + \frac{n^2}{2}\right) + \left(1 - \frac{n}{2}\right) \left(\frac{5n}{2} - 1 - \frac{n^2}{2}\right) \right] \} \\ & u, v \equiv u_i, v_i \end{aligned} \quad (47)$$

At $n=2$, using the relation $u_0 = -\sqrt{1-v_0^2}$ and the parameter values $u_0^2 = \frac{2}{3}$, $v_0^2 = \frac{1}{3}$, we obtain

$$\omega_p(2) = \frac{22}{9}V_0 - t^p + \sum_q \frac{6F_q^2}{\omega_q} \quad (48)$$

It is interesting to note the following fact. As follows from (41), the interaction with phonons stabilizes the ground state (charge-ordered state), since the chemical potential $\mu_{\text{co}}^{(0)}$ decreases with increasing F_q^2/ω_q . Therefore the pair transfer energy must increase with F_q^2/ω_q as follows from Eq. (48). In section 4, E_{co} is shown to be equal to zero at $n=2$. Thus the density in question is responsible for the following form of the condition for transferring from the charge-ordered state to the state with delocalized pairs:

$$\omega_p(2) \leq E_{\text{co}}(2), \text{ or } t^p \geq \frac{22}{9}V_0 + \sum_q \frac{6F_q^2}{\omega_q} \quad (49)$$

The condition is more easily satisfied in the weak-coupling limit $F_q/\omega_q \ll 1$, when the inequality of Eq. (49) looks like

$$t^p \geq \frac{22}{9}V_0 \quad (50)$$

The condition in Eq. (50) has a clear physical meaning. Indeed, at a sufficiently great magnitude of the bipolaron bandwidth compared to the intersite repulsion, the pairs should be delocalized, and the state with localized pairs becomes thus unfavourable. Note, that t^p does not appear in the determination of $\mu_{\text{co}}(2)$ from Eq. (41). It is therefore a change in the pair transfer energy ω_p relative to the ground-state energy that may reveal the transition to the state with delocalized pairs.

Write down also expressions for $\omega_p(n)$ at densities $1 - n/2 \ll 1$. The value given below for $\omega_p^{(1)}(n)$ is derived from Eq. (47) with an accuracy to linear terms and using corrections $\mu^{(1)}$, $f_q^{(1)}$, $v^{(1)}$, $u^{(1)}$ from Section 4:

$$\begin{aligned} \omega_p^{(1)}(n) \approx & \left(1 - \frac{n}{2}\right) \left[-14V_0 + 3.7t^p - 9.7 \sum_q \frac{F_q^2}{\omega_q} \right. \\ & \left. + \left(-\frac{8}{9}V_0 + t^p + \sum_q \frac{28F_q^2}{\omega_q} \right) \cdot \frac{\frac{2}{9}V_0 - \sum_q \frac{19F_q^2}{\omega_q} + t^p}{\frac{2}{3}V_0 - \sum_q \frac{3F_q^2}{\omega_q}} \right] \end{aligned}$$

It follows from this expression that in the weak-coupling limit and at $t^p < \frac{22}{9}V_0$, $\omega_p^{(1)} < 0$. So $\omega_p(n)$ decreases with n close to $n=2$. Since in the weak-coupling limit $E_{\text{co}}(n)$ increases close to $n=2$ (see (45)), then at $n < 2$ the conditions for the inequality $\omega_p(n) \leq E_{\text{co}}(n)$ to be fulfilled become more favourable than at $n=2$.

With extremely strong coupling $\omega_p(n)$ increases and $E_{\text{co}}(n)$ decreases close to $n=2$. Note that in this case the occurrence of the state with delocalized pairs is impossible, as $t^p \rightarrow 0$ with an exponential limit.

7. CONCLUSIONS

It has been shown above that the function f_q characterizing the degree of lattice polarization due to the bipolaron-phonon interaction is strongly dependent on the type of the ground state and on the density. It is determined by Eq. (16) for states with a homogeneous bipolaron distribution (the s-state and the disordered one) and by Eq. (38) for the charge-ordered state. Its dependence on density in the various states is demonstrated in Figures 2 and 5. It is worth noting that in the absence of ordering in the bipolaron system at $n=0$, $f_q^H = F_q/\omega_q$. This is the actual value of f_q which was used in the calculations of Alexandrov and Ranninger (1981) and Alexandrov (1982). It is clear from the analysis carried out in this article that this function should be determined simultaneously with parameters of the ground states in place of a constant f_q value chosen in the absence of ordering. To put it differently, the function f_q (lattice polarization) and parameters of the ground states constitute self-consistent solutions of systems of equations like those obtained in Sections 3 and 4. Such an important change in the formulation of the problem is sure to modify significantly the physical behaviour of the bipolaron system. In particular, the dependence of various quantities (the chemical potential, the superconducting order parameter, etc) is considerably affected by the Hamiltonian parameters and by the density (compared to the data obtained by Alexandrov and Ranninger, 1981). Hence, the conditions for realizing a given ground state change as well.

It follows from Sections 3–6 that at sufficiently low temperatures crystals with bipolarons can be in the following ground states. These are the states realized at $n_{2c} < n_{1c}$:

- (a) the disordered (by pairs) at $n < n_{2c}$.
- (b) the charge-ordered states at $n > n_{2c}$.

n_{2c} is the intersecting point of the chemical potentials μ_{co} , μ_n (and $\mu_{co}(n) > \mu_s(n)$ at $n < n_{2c}$), n_{1c} is the density value from which the superconducting correlation parameter begins to differ from zero: $\Delta \neq 0$ at $n_{1c} < n < 2$.

At $n_{2c} > n_{1c}$ the following states are possible:

- (a) the disordered state at $n < n_{1c}$.
- (b) the superconducting correlation state (s-state) at $n_{1c} < n < n_{2c}$.
- (c) the charge-ordered state at $n_{2c} < n \leq 2$.

As is shown in Section 3, $n_{1c} = 1.2$. The value n_{1c} depends on the relation between the parameters V_0 , F_q^2/ω_q , t^p , and is defined only numerically from the equation $\mu_{co}(n_{2c}) = \mu_s(n_{2c})$; $\mu_{co}(n)$ and $\mu_s(n)$ are defined by Eqs. (39) and (19), respectively. In the weak-coupling limit ($F_q/\omega_q \ll 1$) and in the intermediate range of values of the parameters (see Figures 6a and 6b) the value of n_{1c} may lie in the range 1.2–1.9. Hence the maximum range of density values, where the s-state is realized, is 0.7: $1.2 < n < 1.9$.

In the extremely strong coupling limit ($F_q/\omega_q \gg 1$) $n_{2c} < 1$ (see Figure 6c) and the s-state is unrealizable.

The dependence of the order parameter on t^p and the density is expressed by Eq. (20). It is proportional to the bipolaron bandwidth. The density dependence is not straightforward, since at intermediate density values t^p itself depends on n : $t^p = \sum_{R_{ij}} \varepsilon(R_{ij}) e^{-\zeta(R_{ij})}$, $\zeta(R_{ij}) = \sum_q f_q^2(n) \sin^2(\mathbf{q}R_{ij}/2)$, f_q^s is determined by Eq. (16). At $F_q/\omega_q \ll 1$, $t^p = \varepsilon_0 \equiv t^p \sum_{R_{ij}} \varepsilon(R_{ij})$ and $\Delta(n) \simeq \varepsilon_0(1 - n/2) \cdot \sqrt{1 - \phi^2(n)}$; at $F_q/\omega_q \gg 1$, $t^p \rightarrow 0$ and

$\Delta \rightarrow 0$. Finally, note that under the conditions laid down in Section 5 it is possible to realize states with pairs delocalized on neighbouring sites. For example, at $n=2$ and $F_q/\omega_q \ll 1$, this state can be realized when $t^p > \frac{2}{9} V_0$.

All the states obtained here are to be found in compounds with bipolarons, such as those described in the Introduction. A quantitative application of the results of this work to particular compounds and comparison with experimental data are not given here, but will be presented elsewhere, with the help of numerical solutions of equations such as (19) and (39) over the whole density range.

APPENDIX

Here we obtain the condition for the site-complex parameters at which the inequality (1) is fulfilled. Taking into account the Coulomb interaction between the s -electrons of the complex, and interactions with the intracomplex oscillations, we write the Hamiltonian of a single complex in the form

$$H_i = J a_{i\sigma}^+ a_{i\sigma} a_{i-\sigma}^+ a_{i-\sigma} + \sum_{q_0} F_{q_0} (C_{q_0} e^{iq_0 z_i} + C_{q_0}^+ e^{-iq_0 z_i}) a_{i\sigma}^+ a_{i\sigma} \\ + \sum_{q_0} \omega_{q_0} C_{q_0}^+ C_{q_0} = H_{\text{el-el}} + H_{\text{el-ph}} + H_{\text{ph}}$$

J is the strength of the Coulomb interaction, $C_{q_0}^+$, C_{q_0} the operators of the oscillations of a_{1g} symmetry, \sum_{q_0} is the sum over the oscillations, ω_{q_0} is an oscillation frequency, F_{q_0} is the constant, characterizing the electron-oscillation interaction. The whole complex energy $E_{(s1)}$ with a single s -electron can be determined by

$$E_{(s1)} \equiv E_i(1) = \langle \psi_1 | H_i | \psi_1 \rangle \quad (1A)$$

We choose $|\psi_1\rangle$ in the form $|\psi_1\rangle = \sum_{m\sigma} f_m a_{m\sigma}^+ |0\rangle$, $S_m = \exp(\sum_{q_0} \beta^*(q_0) C_{q_0} + \text{h.c.})$, $\beta(q_0 i) = f_{q_0} e^{-iq_0 r_i}$, $E_i(1) = -2 \sum_{q_0} F_{q_0} f_{q_0} + \sum_{q_0} \omega_{q_0} f_{q_0}^2$. The function f_{q_0} is determined by the equation

$$\frac{E_0(1)}{f_{q_0}} = 0$$

from which we obtain

$$f_{q_0} = F_{iq_0} / \omega_{1q_0}$$

Using this expression, we can obtain the result

$$E_{(s1)} = - \sum_{q_0} \frac{F_{1q_0}^2}{\omega_{iq_0}}$$

The values F_{1q_0} , ω_{1q_0} correspond to the complex with a single s -electron.

The complex energy with two s -electrons is determined by

$$E_{(s2)} \equiv E_i(2) = \frac{1}{2} \langle \psi_2 | H_i | \psi_2 \rangle,$$

$$|\psi_2\rangle = \sum_{m\sigma} S_m^2 B_{m\sigma}^+ |0\rangle, \quad B_{m\sigma}^+ = a_{m\sigma}^+ a_{m-\sigma}^+$$

Calculating the expectation values, we obtain

$$f_{2q_0} = \frac{F_{2q_0}}{\omega_{2q_0}}, \quad E_i(2) = J_2 - \sum_{q_0} \frac{2F_{2q_0}}{\omega_{2q_0}} \quad (2A)$$

For the empty complex $E_i(0)=0$. Thus, the inequality Eq. (1),

$$2E_{(s^1)} > E_{(s^2)} + E_{(s^0)}$$

is equivalent to the condition

$$J_2 - \sum_{q_0} \left(\frac{2F_{2q_0}^2}{\omega_{2q_0}} - \frac{F_{1q_0}^2}{\omega_{1q_0}} \right) < 0 \quad (3A)$$

The inequality (3A) is the condition for the existence of the bipolaron in the complex. The bipolaron binding energy is the left-hand of (3A), with a minus sign. Following from the inequalities (1) and (3A), the form of the effective electron attraction differs from the usual results (Anderson, 1975) by the term in F_{1q_0} in (3A).

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