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Bipolarons and superconductivity

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Résumé. — Nous étudions de façon détaillée le problème de l'attraction électronique induite par une déformation entraînant une paire d'électrons localisés, appelée « bipolaron ». Nous explorons l'analogie entre les bipolarons et les paires de Cooper itinérantes dans un supraconducteur. Nous montrons que les deux types de paires résultent de la nature microscopique de l'interaction électron-phonon et que suivant la constante de couplage, l'état fondamental devient un isolant bipolaronique au-delà d'une certaine valeur critique. Nous proposons un diagramme de phase entre un métal, un supraconducteur et un isolant bipolaronique.

Abstract. — The problem of deformation induced attraction leading to localized pairs of electrons, the so-called bipolarons, is studied in detail. The analogy between bipolarons and itinerant Cooper pairs in a superconductor is explored. It is shown that the two types of pairing result from the microscopic nature of the electron-phonon Hamiltonian and that following the coupling constant the ground-state becomes a bipolaronic insulator beyond a critical coupling strength. A phase diagramme between a metal, superconductor and bipolaronic insulator is proposed.

Introduction. — In a series of recent papers [1], we have pointed out the fundamental interest of the bipolaronic ground-state defined as a localized pair of electrons coupled through lattice deformation. The experimentally observed bipolarons, the charge localization, their insulator-metal transition and other physical properties have been dealt with at length [2]. We have also recently [3] suggested that there is a fundamental symmetry between this bipolaronic ground-state and a superconducting ground-state because these bipolarons can be considered as localized Cooper pairs in the limit of large electron-phonon coupling constant. A phase diagramme between metal-superconductor and bipolaronic insulator has been proposed that reflects the increasing instability of the metallic electrons at the Fermi level to attractive pairing interaction due to strain-induced coupling.

In part 1 of this paper, we shall briefly recall the essential results of electron pairing due to static strain while in part 2 we shall describe in some detail the dynamic Hamiltonian and will show that the electron-phonon Hamiltonian contains within its very structure two complementary parts one of which gives rise to bipolaron formation while the other part leads to superconductivity. Part 3 will be a succinct discussion of some of the points still obscure.

1. **Pairing due to static strain.** — It is easy to see why strain is essential if one is to form a pair of localized electrons in a singlet ground-state out of two itinerant electrons in an empty band. In figure 1*a*, a one-dimensional chain of identically spaced atoms are indicated, with near-neighbour transfer integral t. The total energy for two electrons in an otherwise empty band is then

$$E_1 = 2\,\varepsilon_0 - 4\,t \qquad (1a)$$

where ε_0 is the single-site energy of an electron.

Were we to localize these two electrons in a pair of undeformed neighbouring atoms (Fig. 1*b*) into the singlet state, the ground-state energy will be

$$E_2 = 2\,\varepsilon_0 + v - 2\,t - J \qquad (1b)$$

where v is the near-neighbour Coulomb repulsion between the two electrons and J is the exchange integral between two sites.

We note that $v > J$, E_2 is larger than E_1 ($\Delta E = E_2 - E_1$ is positive) and hence E_2 can never be a ground-state for the two electrons. On the other hand, if we relax

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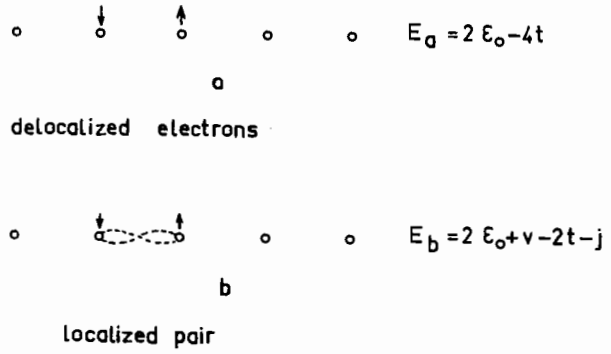

Fig. 1. — 2 electrons in an undeformed empty lattice : *a*) delocalized ; *b*) localized.

the condition of a rigid lattice and allow the two neighbouring sites to deform, it is easy to show [1] following the Anderson [4] Hamiltonian, that such a localized deformation gives rise to an effective total repulsion

$$V_{\text{eff}} = \frac{-g^2}{M\omega^2} + v \qquad (2)$$

where g is an electron-phonon coupling constant and ω is a vibration frequency.

In the event V_{eff} become small or even negative, E_2 can be lower than E_1 and a localized pair of electrons (a bipolaron) can form. In figure 2, we plot that the total energy E_T of the electron pair plus the elastic energy involved in the deformation as a function of static strain ε for different coupling constants g. The zero of energy is taken to be the bottom of the band and one sees that a critical finite strain $\varepsilon = \varepsilon_0$ is needed to trap the two electrons into a bound localized state. The transition to the bound-state is sudden and is shown in the insert, as a function of temperature, the displacement involved in the mean field approximation. We note that bipolaron formation is not necessarily due to optical phonons and that a finite localized lattice strain is involved and in this the problem is analogous to polaron formation through finite acoustic deformation first treated by Toyozawa [5].

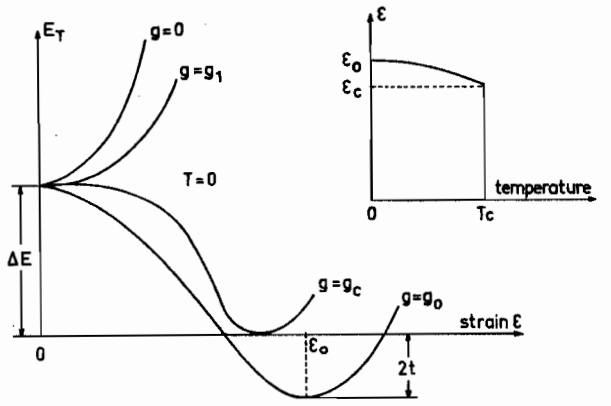

Fig. 2. — Electronic energy plus energy of deformation. In the inset : strain *versus* temperature.

2. **Electron-lattice Hamiltonian.** — The electron lattice term used in the Anderson Hamiltonian [4] and which we used for the results in part 1 is highly phenomenological and does not take into account the dynamical nature of the electron-lattice interaction or throw light on the origin of this coupling between the electrons. Furthermore the strain is taken in part 1 as a parameter and as a consequence the energy shift due to coupling was a first-order effect ; however, if strain is in reality a fluctuating quantity (varying in time and in space and alternating in sign) the ground-state energy of the coupled electron-lattice system will be perturbed due to second-order to begin with, first-order terms will be identically zero. To see these points clearly let us start with the tight-binding Hamiltonian elements relevant for narrow bands that we are interested in

$$H_0 = \sum_i V_i^c \,|\,\psi_i\rangle\langle\,\psi_i\,| + \sum_{i,j} V_i^c \,|\,\psi_i\rangle\langle\,\psi_j\,| \qquad (3)$$

where V_i^c is the crystal potential seen by electron at the site i given by $V_i^c = \sum_{j=i}^{j} v_j^a$, superscripts a signifying that the sum is over the atomic potentials v^a and includes all sites j, ψ_i's are the Wannier function on a given site i.

The first term in (3) corresponds to a shift of the atomic energy of a given electron due to crystal field seen at site i while the second term of the Hamiltonian refers to the spreading out of the atomic-like energy levels into a band due to transfer of electrons between different sites through overlap of the wavefunctions. The simplest perturbation due to some local deformation of the hamiltonian H_0 is seen in figures 3*a* and *b*, corresponding to a lattice of four sites. We can immediately see the two principal effects — first, the deepening of the potential well at the sites 2 and 3 and secondly, increased hopping or tunnelling probability between these two sites due to shortened distance. We can write in second quantization

$$H' = \sum_i \frac{1}{N} n_i \frac{\partial V_i^c}{\partial \varepsilon_i}\,\varepsilon_i + \sum_{i,j} \frac{1}{N} C_i^* C_j \frac{\partial T_{ij}}{\partial \varepsilon_{ij}}\,\varepsilon_{ij} \qquad (4)$$

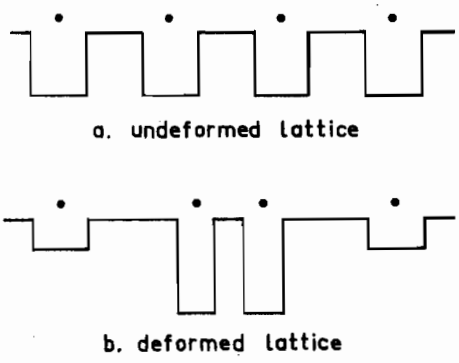

Fig. 3. — Crystal potential : *a*) undeformed lattice ; *b*) deformed lattice.

where n_i are the occupation operators at site i corresponding to c's which are the creation and annihilation operators for Fermions, ε's are the strains at sites or at bonds i-j. T_{ij}'s are the hopping integrals. It is worthwhile to look at the two terms of H' and see how they contribute. Calling the diagonal term of H' H_1, we write

$$H_1 = \sum_i \frac{1}{N} \frac{\partial V_i^c}{\partial \varepsilon_i} \varepsilon_i n_i . \qquad (4a)$$

Define a coupling constant $g_i = \frac{1}{N} \frac{\partial V_i^c}{\partial \varepsilon_i}$. We note that in H_1, ε_i is a fluctuating term and cannot contribute to first order due to averaging out of the effect but it will in second-order because the mean-square displacement of the atom is non-zero. Thus the second-order process will give a contribution proportional to g_i^2. Note $g_i^2 \sim |\overline{\psi_i^4}|$. If the electron is perfectly itinerant over N atomic sites we have $|\overline{\psi_i^2}| \simeq 1/N$ but we need to sum the interaction over *all* lattice sites to get

$$\Delta E_1 \simeq \frac{g^2}{N^2} N \left(\frac{\partial V^c}{\partial \varepsilon}\right)^2 \simeq 0\left(\frac{1}{N}\right) \to 0 \quad \text{as} \quad N \to \infty .$$

We thus see that for an itinerant electron the contribution of the diagonal term of the perturbation is infinitesimally small and hence is usually neglected. This is far from the case for a localized electron. Suppose the electron is localized over n-sites i.e. $|\overline{\psi_i^2}| \sim 1/n$. This gives $\Delta E_1 \sim \frac{g^2}{n}\left(\frac{\partial V^c}{\partial \varepsilon}\right)^2$ and as $n \to 1$, $\Delta \varepsilon_1$ becomes a very large quantity. This term in literature is known as the Franck-Condon shift, generally attributed to interaction with optical displacement but as it is seen here, it is really due to the diagonal contribution of the perturbed Hamiltonian. There are several points to be noted with respect to the diagonal term. First of all it is the very basis of Holstein [6] Molecular Crystal Model for polaron formation where all non-diagonal terms are generally neglected. Second of all, as Toyozawa [5] pointed out, the total pseudo-momentum is not conserved in the interaction process. This implies that either we are in the presence of recoiless transition as pointed out by Anderson [7] or must invoke Umklapp processes. The Umklapps imply short wavelength disturbances and any instability associated with them will be charge fluctuations of size quite small compared to the unit cell, associated with motions of the atoms. Such an object is a fair description of a covalent bond. The recoiless transition implies that the linear interaction term in the diagonal term of the Hamiltonian due to displacement of atomic position may induce a deformation of the electron orbital but not an electron jump from one site to another. This means that electrons follow the atomic motion adiabatically; electron and nuclear motion can be separated and the

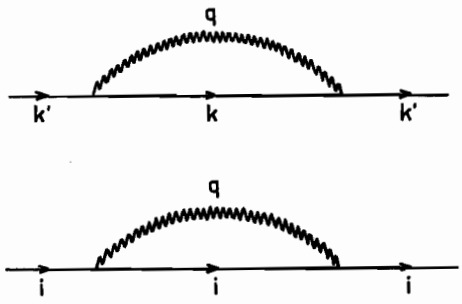

Fig. 4. — Electron scattering due to phonons : *a*) normal, *b*) recoiless.

electron eigenvalue for a given site serves as an adiabatic potential for the site or atomic displacement Hamiltonian. Here we are in the presence of strong electron-lattice coupling and which could lead to small-polaron formation. In this adiabatic regime the correct description is the Pekar wavefunction i.e. a composite particle of electron wavefunction centred about a static lattice distortion and it is known [8] to give correct ground-state energy in the limit of extreme strong-coupling. One can always define a non-adiabaticity parameter γ as the ratio of maximum phonon energy to electron bandwidth; when $\gamma \to 0$ electron motion is infinitely more rapid than phonon-motion and the former certainly follows the latter; the motion is adiabatic (we are in the acoustic regime). Hence we have the paradoxical result that the coupling is strongest when the energy-transfer is smallest (i.e. $h\omega \to 0$). In the limit of zero energy-transfer, the interaction becomes purely local, Franck-Condon and recoiless. We are suggesting that the recoiless transition is at the origin of a phonon-induced attractive interaction between two electrons at very short distances (of the order of interatomic distance).

Rewriting H_1 in the form $H_1 = \sum_i g_i n_i \varepsilon_i$ where g_i is the coupling constant at site i, and introducing phonon-operators for the strains ε_i and a canonical transformation [9, 10] that is standard (leading to displaced oscillator) we obtain the transformed Hamiltonian for the electrons

$$H_1 \to \tilde{H}_1 = \frac{-g_0^2}{M\omega^2} \sum n_i - \frac{g_0^2}{M\omega^2} \sum_i n_{i\uparrow} n_{i\downarrow} - \frac{g_1^2}{M\omega^2} \sum_{i,j}^{i \neq j} n_{i\sigma} n_{j\sigma'} \qquad (4b)$$

where M is the atomic mass,

ω is the lattice frequency,

g_0 on-site coupling constant assumed same for all sites i.

and $g_1 = g_0 \sum_q \exp\, iq.(R_i - R_j)$, R_i being the site coordinates with phonon wavevector q.

The first term of equation (4*b*) is just the polaronic shift to site energies ε_i, the second term is the contri-

bution to Mott-Hubbard U while the last term leads to overall diminution of near-neighbour Coulomb repulsion v_{ij}.

The non-diagonal part of the Hamiltonian is written as

$$H_2 = \sum_{i,j} \langle \psi_i^* \mid \psi_j \rangle C_i^* C_j \frac{\partial T_{ij}}{\partial \varepsilon_{ij}} \varepsilon_{ij} . \qquad (5)$$

It was shown first by Barisic-Labbé-Friedel [11] that it leads to the B.C.S. Hamiltonian, when transformed

$$H_2 \to \tilde{H}_2 = \frac{-g_s^2}{M\omega^2} \sum_{i,j} C_{i\uparrow}^* C_{i\downarrow}^* C_{j\downarrow} C_{j\uparrow} \qquad (6)$$

where

$$g_s = \langle \psi_i \mid \psi_i \rangle \frac{dT_{ij}}{d\varepsilon_{ij}} . \qquad (6a)$$

The unusual form of the B.C.S. Hamiltonian here is obtained quite trivially by Fourier transforming the standard B.C.S. Hamiltonian into real space and was written in this form amongst others by Bari [12]. This form and the nature of electron-electron interaction in real space in the case of Cooper pair formation with this Hamiltonian in narrow band solids was first investigated in detail by Appel and Kohn [13].

Collecting all the electron terms including electron-electron repulsion of the total Hamiltonian, we get

$$H_T = H_0 + H' + H_{rep} \to \tilde{H}_T$$

$$\tilde{H}_T = \sum_i \varepsilon_i^{eff} n_i + U_{eff} \sum_i n_{i\uparrow} n_{i\downarrow} + V_{eff} \sum_{\substack{\sigma,\sigma' \\ i \neq j}} n_{i\sigma} n_{j\sigma'} + \sum_{ij} T_{ij} C_i^* C_j - \frac{g_s^2}{M\omega^2} \sum_{i,j} C_{i\uparrow}^* C_{i\downarrow}^* C_{j\downarrow} C_{j\uparrow} \qquad (7)$$

where

$$\varepsilon_i^{eff} = \varepsilon_i^0 - \frac{g_0^2}{M\omega^2}$$

$$U_{eff} = U - \frac{g_0^2}{M\omega^2}$$

$$V_{eff} = v_{ij} - \frac{g_1^2}{M\omega^2} .$$

We shall now solve $\tilde{H}_T$ for the case of 2-site 2-electrons. ε_i^{eff} terms can be dropped by redefining zero of the system. A further simplification results by observing that for 2-electrons in 2-sites we have

$$[(n_{i\uparrow} + n_{i\downarrow}) + (n_{2\uparrow} + n_{2\downarrow})]^2 = 4$$

and hence $n_{i\sigma} n_{j\sigma}$, terms can be amalgamated into U dropping a constant v_{ij} term to give us

$$\tilde{H}_{T'} = (U_{eff} - V_{eff}) \sum_{i=1,2} n_{i\uparrow} n_{i\downarrow} + \sum_{1,2} T_{ij} C_i^* C_j - \tilde{g}_s \sum_{i,j} C_{i\uparrow}^* C_{i\downarrow} C_{j\downarrow} C_{j\uparrow} \qquad (8)$$

where

$$\tilde{g}_s = \frac{g_s^2}{M\omega^2} .$$

For the two-sites 1 and 2 let us define the following basic vectors :

$$\mid a \rangle = \frac{1}{\sqrt{2}} (C_{1\uparrow}^* C_{1\downarrow}^* + C_{2\uparrow}^* C_{2\downarrow}^*) \mid 0 \rangle$$

$$\mid b \rangle = \frac{1}{\sqrt{2}} (C_{1\uparrow}^* C_{1\downarrow}^* - C_{2\uparrow}^* C_{2\downarrow}^*) \mid 0 \rangle$$

$$\mid c \rangle = \frac{1}{\sqrt{2}} (C_{1\uparrow}^* C_{2\downarrow}^* + C_{2\uparrow}^* C_{1\downarrow}^*) \mid 0 \rangle$$

$$\mid d \rangle = \frac{1}{\sqrt{2}} (C_{1\uparrow}^* C_{2\downarrow}^* - C_{2\uparrow}^* C_{1\downarrow}^*) \mid 0 \rangle .$$

We have the following 4 × 4 matrix

$\mid a \rangle$	$\mid b \rangle$	$\mid c \rangle$	$\mid d \rangle$
$U_0 - \tilde{g}_s$	0	$2t_0$	0
0	$U_0 + \tilde{g}_s$	0	0
$2t_0$	0	0	0
0	0	0	0

The matrix is easily diagonalized to give use the following eigenvalues

$$E_1 = 0$$

$$E_2 = U_0 + \tilde{g}_s \quad \text{where} \quad U_0 = U_{eff} - V_{eff} \qquad (9)$$

$$E_{+-} = \frac{U_0 - \tilde{g}_s}{2} \pm \frac{1}{2}\sqrt{(U_0 - \tilde{g}_s)^2 + 16 t_0^2}$$

where

$$t_0 = T_{ij} .$$

The E_+ level in the eigenvalues (9) is the superconducting level while the E_- level is the bipolaronic level. This is easy to see for the special case $t_0 = 0$ (Fig. 5). We get

$$E_+ = U_0 - \tilde{g}_s \qquad E_- = 0 .$$

The bipolaronic level is now a non-bonding level. The upper Hubbard level at U_0 is now split into two levels due to the superconducting interaction into $U_0 + \tilde{g}_s$ and $U_0 - \tilde{g}_s$. We note that the superconducting pair

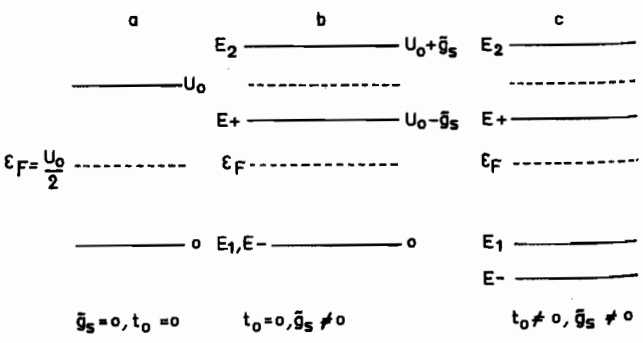

Fig. 5. — Energy levels of 2-electrons.

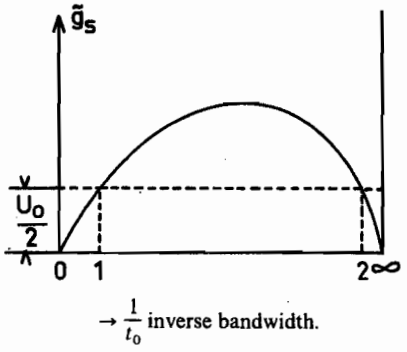

Fig. 6. — Superconducting coupling constant $\tilde{g}_s$.

appears as soon as the E_+ level goes below the Fermi level ε_F ($\varepsilon_F = U_0/2$) when $\tilde{g}_s$ achieves a critical value ($\tilde{g}_s = g_1$). A non-zero t_0 (Fig. 5*c*) does not alter this picture except the bipolaronic level E_- now makes its appearance as a bonding state for the two electrons. It should be realized that only when the two-electrons on a site E_+ level is occupied i.e. it is below ε_F that the average of the anormalous operator $\langle C^*_{i\uparrow} C^*_{i\downarrow} \rangle$ can be non-zero signifying onset of superconductivity. Note also that the attractive interaction parameter $\tilde{g}_s$ remains positive only as long as the sheath $\varepsilon_F - E_+$ is less than $\hbar\omega$. This indicates that the superconducting transition temperature $kT_c \sim \varepsilon_F - \varepsilon_+ \sim \varepsilon_F - U_0 + \tilde{g}_s$ will increase with $\tilde{g}_s$ only up to $kT_c \sim \hbar\omega_0$ must saturate beyond and fall if $\tilde{g}_s$ is arbitrarily increased. This is seen better if we write the condition for the appearance of superconductivity as

$$\Delta = \varepsilon_F - E_+ = \tilde{g}_s - \frac{U_0}{2} \geqslant 0 . \qquad (10)$$

The behaviour of $\tilde{g}_s$ as a function of bandwith t_0 is expected to be non-monotonic (Fig. 6) by definition from equation (6*a*). In the infinite bandwidth limit i.e. case of perfectly free electron $\tilde{g}_s = 0$ (they do not see crystal potential at all hence are unperturbed by phonons) $\partial T_{ij}/\partial \varepsilon_{ij}$ being zero. In the atomic limit $\tilde{g}_s$ is also zero, because the non-diagonal transfer $\tilde{g}_s$ implied in the overlap $\langle \psi_i \mid \psi_j \rangle$ vanishes. We thus see that superconductivity will appear at point 1 and will cease at point 2 as bandwidth decreases. Below point 2, the E_- remains the only occupied level and hence the system will become a bipolaronic insulator. As a function of the MacMillan [14] coupling constant $\lambda_s = \tilde{g}_s/2\, t_0$, the composite phase diagramme must look like figure 7 where λ_1 and λ_2 correspond to points 1 and 2 of figure 6 respectively.

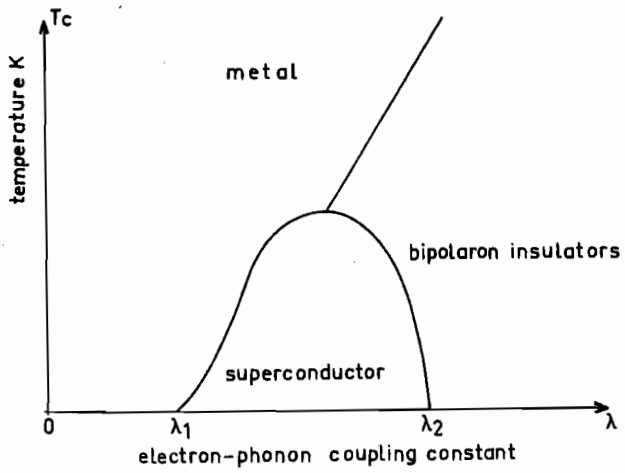

Fig. 7. — Electronic phase diagramme.

3. **Discussion.** — In reference [3], the phase diagramme figure 7 was given on intuitive grounds. In this paper, we see the reasons behind such a diagramme. The profound change from delocalized Cooper pair to localized bipolarons as the electron bandwidth is reduced reflects the inherent microscopic process of the electron-phonon interaction contributing more and more to diagonal and hence to Franck-Condon interaction. The two electron two-site model. Hamiltonian that we have proposed here and solved is amenable to rigorous discussion. The phonon part of the Hamiltonian remains to be analyzed and seen if and what is the contribution of phonon softening leading to saturation of T_c as the coupling constant is increased. We already see in the figure 2 that at $\varepsilon = \varepsilon_c$, the elastic constant (around $\varepsilon = 0$) has vanished. This means everytime a pair is formed, the deformation becomes static and real rather than a virtual process that leads to Cooper-pairing. Coupled to diminution of the non-diagonal transition, this would also lead to kill superconductivity. We may equally note in passing that transition to the insulating bipolaronic ground-state from the metal is not really a Peierls transition; there is no doubling of lattice periodicity. Like superconductivity transition no lattice symmetry change is involved. It is not unsimilar to pairing without superconductivity that Eagles [15] treated except that « Eagles pairs » are not localized and are not true bipolarons. The attractive elastic interaction leading to bipolaron-formation is of the Friedel-Eshelby kind i.e. highly anisotropic [16] and oscillating with distance. This is why bipolaron formation is not to be expected in elastically isotropic solid. In point of fact dimensionality of the system is a very key element to the problem and it is well known [17] that in one-dimensional B.C.S. pairing is incompatible with Peierls transition, or that in two-dimensions the charge-density wave formation tends to suppress superconductivity [18].

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