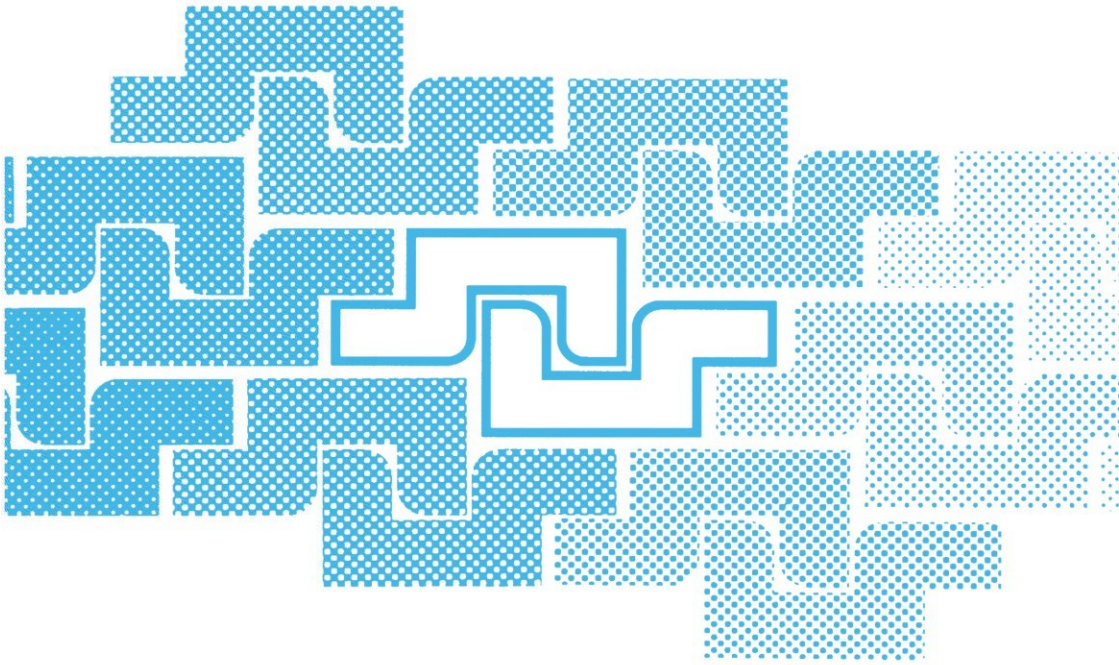

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TWO-PARTICLE GREEN FUNCTION IN THE THEORY OF SUPERCONDUCTIVITY OF HTSC AND C_{60} CRYSTALS

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1. Introduction

The explanation of high-T_c superconductivity (HTSC) in crystals is now one of important problems in the condensed matter physics. There are numerous papers and review articles [1-6] on this problem., and recent results have included the discovery of SC in molecular crystals (pentacene , T_c~2K; tetracene T_c~2.5K; antracene T_c~4K [7], and HTSC for C_{60}, T_c~52K [8, 9]) using the new field effect switching method. Also high T_c~39K was obtained for magnesium diborate, MgB_2 [10]. However the theoretical models describing this phenomena are still in development although now this one is of the most important questions. For example from see Refs. [5,7] where the special discussion about mechanisms of SC was undertaken.

The theoretical study of superconductivity (SC) is based as a rule on the physical idea [1, 3, 11-13] about paring of electrons with the opposite spins $\left(s+s^{'}=0\right)$ and momenta $\left(k+k^{'}=0\right)$. Using this postulate the possibility of appearence of the coupled states, responsible for superconductivity, in the electron (electron-phonon) system was investigated. It should be noted that coupled states can arise in the system of other type too. For example similar coupled states occur in the phonons of crystals ([14,15] and reference herein) if the anharmonic constant of fourth order, responsible for phonon-phonon interaction, is negative (V <0). For this case pairs of coupled phonons have in general arbitrary momentum $K = k + k^{'} \neq 0$. Taking into account this analogy the problem of SC from some non-traditional point of view is considered (see also works

[16-18]). As a first step the density of electron states in crystals was studied. In the framework of our approach we do not suppose *a priori* any special mechanism of pairing of electrons (with opposite spins and momenta as it is traditionally supposed for example in BCS method) takes place. However electrons in the crystal satisfy the following natural conditions: i) they are moving in the periodic crystal field generated by the lattice ions; ii) the electrons interact with each other and the ions of lattice by the Coulomb law: it means that at colliding electrons may possess the arbitrary momenta (k) and spins (s) allowed for them by the corresponding electron zone (band) they belong to; iii) the structure and symmetry of electron bands are given by the crystal structure.

From these calculations it follows that in the electron-phonon system studied, there can exist coupled states which give rise to lowering of system energy and to appearence of new features in the density of the electron states. The arising of these states depends on the constants of electron-electron and electron-phonon interactions, on the structure of electron bands and on the temperature of crystal. Similar types of excitations are well known in phonon and polariton spectra of crystals as was already mentioned (see [14,15] and references herein). The essential difference is that the electrons have their own magnetic moment (spin) therefore the coupled states in the electron system also depend on the spins of the crystal electron bands which take part in the generation of these coupled states. It will be seen that the energy of some of these coupled states (at k=0) precisely coincides with the value of energy which is obtained for superconducting gap using the traditional BCS pairing approach. However our results show that many other states (with nonzero momenta (K=k+k'≠0) and spins (S=s+s'≠0) of interacting electrons) also give contributions to SC of the crystal (see also [16-18]). It should be also noted that the presence of several electron bands crossing the Fermi level (or located close to it) gives rise to qualitatively new features in the density of states of the electron system (for example, coupled states with finite, S≠0, spin located below the Fermi level can arise [18]).

2. Short theory

2.1. DENSITY OF CURRENT AND HAMILTONIAN

The general idea of our approach was presented in [16-18].The density of current can be written [19]

$$\langle j'(x,t)\rangle = \langle j(x)\rangle_0 - \frac{e^2}{mc}\langle n(x)\rangle_0 A(x,t) + (h.ord.). \qquad (1)$$

As an example the density of electron states (DES) $\langle n(x)\rangle_0$ was investigated. It can be expressed by Green function (GF)

$$\langle n(x)\rangle_0 = \langle \Psi^+(x)\Psi(x)\rangle_0 =$$

$$= \lim_{x'\to x, t'\to t-0}\left\{\delta(x-x') - i\langle -iT\Psi(x,t)\Psi^+(x',t')\rangle\right\} = , \qquad (2)$$

$$= \frac{1}{V_0}\{\sum_k 1 - i\sum_{k,\omega} G(k,\omega)\}$$

The DES is expressed (2) by the Fourier components of Green function $G(k,\omega)$; V_0 is the volume of crystal; the operators $\Psi(x)$ satisfy to Fermi commutation relations and are given by the expressions

$$\Psi(x) = \sum_{k,\sigma,\nu} a^{\nu}_{k,\sigma}\varphi^{\nu}_{k,\sigma}(x), \qquad (3)$$

$$\varphi^{\nu}_{k,\sigma}(x) = \varphi^{\nu}_{k}(x)\chi_{\sigma}(s),$$

$$\left[a^{\nu}_{k,\sigma}, a^{+\nu'}_{k',\sigma'}\right]_+ = \delta_{k,k'}\delta_{\sigma,\sigma'}\delta_{\nu,\nu'}, \qquad (4)$$

where $\varphi^{\nu}_{k}(x)$ is the Bloch function of an electron in the ν-th energy band of the crystal and $\chi_{\sigma}(s)$ describes the spin of this electron. The density of electron states (DES) $\langle n(x)\rangle_0$ is expressed (2) by the Fourier components of Green function $G(k,\omega)$; V_0 is the volume of the crystal.

The Hamiltonian describing the system of interacting the electrons and phonons of the crystal after transformation by unitary operator is written in the following form (in more details it will be described elsewhere, see also [16, 17])

$$H = \sum_{k,\nu}(\varepsilon^{\nu}_k - \frac{1}{N}\sum_{s,q}\frac{\left|\chi^s_q\right|^2}{\Omega_{s,q}})A^+_{k,\nu}A_{k,\nu} +$$

$$+\frac{1}{2N}\sum_{q,k,\nu,k',\nu'}(V_q - 2\sum_s\frac{\left|\chi^s_q\right|^2}{\Omega_{s,q}})A^+_{k,\nu}A^+_{k',\nu'}A_{k'+q,\nu'}A_{k-q,\nu} + , \qquad (5)$$

$$+\sum_{s,q}\Omega_{s,q}\beta^+_{s,q}\beta_{s,q} - \frac{1}{\sqrt{N}}\sum_{k,q,\nu}(\varepsilon^{\nu}_k - \varepsilon^{\nu}_{k-q})A^+_{k,\nu}A_{k-q,\nu}\sigma_q$$

where $V_q = V_{-q}$, $\chi^{*s}_q = \chi^s_{-q}$ are the Fourier components of the Coulomb interaction of electrons between each other and their coupling constant with the lattice phonons respectively; and ε^{ν}_k is the energy of electron. The both the V_q and χ^s_q constants are independent of the band and spin indices of electrons.

$$a^{\nu}_k = [\exp S]A_{k,\nu}[\exp(-S)];$$

$$b^s_q = [\exp S]\beta_{s,q}[\exp(-S)]; \qquad (6)$$

where S is the anti-hermitian operator (S^+= -S) which (and also σ_q in (5)) are both linear in the phonon $\beta_{s,q}, \beta^+_{s,q}$ operators. In (5) we combined the two indices so that $\nu = (\nu, \sigma), \mu = (\mu, \sigma')$ are the complex indices which characterize the number of crystal band and spin of electron.
The unitary transformation gives rise to a renormalization of the electron energy (first term) and renormalization of the Fourier component of the Coulomb electron-electron interaction. In the later case we can conclude that if the crystal unit cell contains many atoms the effective Coulomb potential can became negative and large in value .

2.2. TWO-PARTICLE GREEN FUNCTION, COUPLED STATES AND GAP.

It is well known that superconductivity (SC) of electron systems is due to the attractive interaction arising between the electrons in electron-phonon system at special conditions (though some other mechanisms are actively discussed too). The description of SC properties in the theory -field approach is, as usual, based on the Green function (GF) method where side by side the normal GF a special type of "anomalalous"-Gorkov [11] GF are used. According to the Gorkov approach (this idea was then used in many following theoretical works [12, 13] etc.) the two-particle (TP) GF can be approximately presented as a product of two "anomalalous" GF

$$\begin{aligned} &\left\langle T\Psi^+(x,t)\Psi(x,t)\Psi(x,t)\Psi^+(x',t')\right\rangle \approx \\ &\approx \left\{\left\langle T\Psi(x,t)\Psi(x,t)\right\rangle\left\langle T\Psi^+(x,t)\Psi^+(x',t')\right\rangle\right\}, \end{aligned} \tag{7}$$

As a result it gives the possibility of obtaining two equations for the normal and anomalalous GF and the equation for the superconductive (SC) gap first described in the work of BCS. However so far as the two-particle GF (left hand side in (7)) more fully (in more detail) describes the properties of the interacting electron system we use a different approach and obtained an equation for the full two-electron GF. With some simplifying assumptions (see [16, 17]) it can be solved and the Fourier components of such a GF can be written as follows.

$$G_2\left(\begin{matrix}k_2,\nu;k_1,\mu\\ k_1+q,\mu;k_2-q,\nu\end{matrix}\middle|\omega\right) \sim \frac{f(k_1,\mu;k_2,\nu;\omega)\sum_{\sigma,\sigma'}\varphi(\mu,\nu;\sigma,\sigma')}{1-VK(k_1,\mu;k_2,\nu;\omega)}, \tag{8}$$

$$K(k_1,\mu;k_2,\nu;\omega) = \frac{1}{N}\sum_q \frac{1-n^{\mu}_{k_1+q}-n^{\nu}_{k_2-q}}{\omega-\varepsilon_{k_1+q,\mu}-\varepsilon_{k_2-q,\nu}}, \tag{9}$$

$$V = \tilde{V}_q = V_q - 2\sum_s \frac{\left|\chi^s_q\right|^2}{\Omega_{s,q}} \approx const., \tag{10}$$

where n_k^v is the filling number of electrons; V is the effective Fourier component of electron-electron (e-e) interaction.

It is obvious that in the proposed approach the special equation for the SC gap will not be obtained. All new properties are only described by poles of the function (3). If the constant of e-e interaction renormalized by e-ph interaction and becomes negative (V <0) the new type of states (coupled states) can arise in the electron system. The Eqs. (8), (9) describe these spectral features. It is seen from Eqs.(8), (9) that if the wave vectors of the interacting electrons obey $k_1=k_2=0$ or $k_2=-k_1$ the denominator (3) is reduced to the well known expression describing the SC gap of crystal, but for other arbitrary meanings of wave vectors k_1 and k_2 of electrons the situation are significantly different. From Eqs.(8), (9) it follows also that besides states corresponding to the traditional BCS pairing case, k=0, there are many new states with k≠0, Eq.(8), and which give contributions into SC gap too.

In Eq.(8) $f(k_1,\mu;k_2,\nu;\omega)$ is a function depending on the frequency (ω) and wave vectors k_1 and k_2 of the interacting electrons; the second function $\varphi(\mu,\nu;\sigma,\sigma')$ is expressed by some numbers of delta-functions $\delta_{i,j}$ and defines the spin forbidden rules for the coupled states (responsible for superconductivity effects)

$$\varphi(\mu,\nu;\sigma,\sigma') = \delta_{\sigma\sigma}\delta_{\sigma'\sigma'} - \delta_{\mu\nu}\delta_{\sigma\sigma'}\delta_{\sigma\sigma'} , \qquad (11)$$

where σ,σ' are the spins of the first (σ) and second (σ') electron respectively; and μ, ν show the number of the electron band.

The Eqs.(8)-(10) show that there is not a rigid restriction on wave vectors and spins of interacting electrons in the creation of coupled states responsible for SC of crystals. Moreover all the electrons of the Brillouin zone may take part in this processes, but there are a special conditions for the existence of the coupled states resulting in SC of crystals.

3.Numerical calculations

In this communication, a series of numerical calculations were made to analyse the conditions of under which the coupled states arise, and changes the T-dependence of the SC gap as a function of the structure of the electron bands, here taken in the form

$$\varepsilon_{k\pm q,\mu} = \varepsilon_\mu + \frac{(k\pm q)^2}{2m_\mu} = \varepsilon_f + \Delta_\mu + \frac{(k\pm q)^2}{2m_\mu}, \qquad (12)$$

with k the wave vector of the electrons (for simplicity we suppose $k_1=k_2=k$).

In (12) m_μ is the effective mass of electron in the μ-th ($\mu = 1,2$) energy band of the crystal; and Δ_μ is a parameter which points out the position of the μ-band extremum

relative to the Fermi level. It may be negative or positive and the effective mass will be the same.

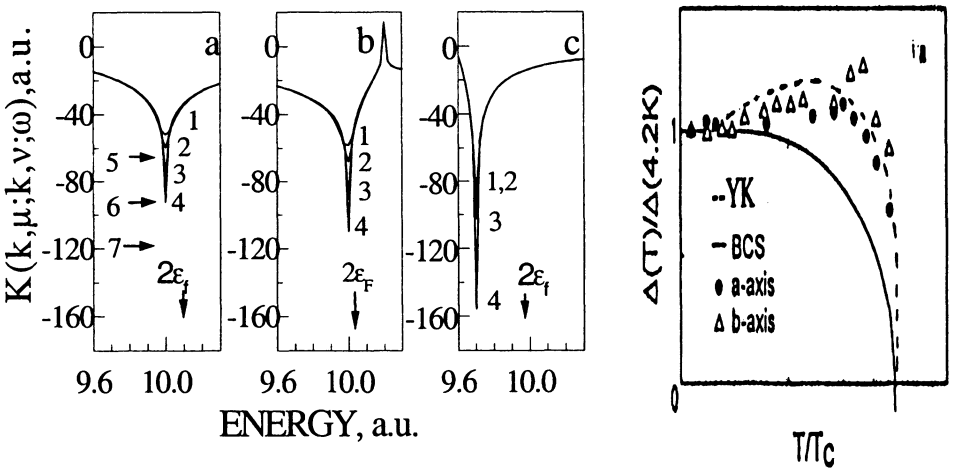

Figure 1. The effect of temperature on the $K(k,\mu;k,\nu;\omega)$ function ($E=k^2/2m=0$) for different structures of energy bands: :a) Δ_1=-1, $m_1^* = 1$; b) $\Delta_2 = 0.2, m_2^* = -2$; and c) Δ_1=-1, $m_1^* = 1$, $\Delta_2 = 0.2, m_2^* = -2$; curve 4, T=2K; curve 3, T=10K; curve 2, T=50K; curve 1, T=100K; arrows 5-7 corresponds to different of values 1/V, their intersection with curves 1-4 gives SC gap. (All energetic values are taken as arbitrary units: V=V/M, ets., M is scale factor, for convenience M=1ev; $m_i^* = m_i / m$, m is free electron mass).

Figure 2 (right), Experimental data for T-dependence of superconducting gap (from work [21], Tc=95K) of $Bi_2Sr_2CaCu_2O_8$ crystal (•,Δ) and theoretical dependences (solid is BCS and dashed is our calculation [17, 18]).

Some calculations are presented in Figures 1-5. The temperature dependences are shown in Figs.1, 2. The following conclusions were obtained. For crystals having several electron bands crossing the Fermi level (ε_f) (see for example [20] where the band structure of $Bi_2Sr_2CaCu_2O_8$ crystals is presented) there are two type of states: located near ε_f in Fig.1a,b and other one, located deeply inside of electron band Fig.1c, can be responsible for SC of crystal. The singularity of the two-electron density of states gives rise to such a result. These new states, Fig.1c, have as usual singlet and triplet properties and may be dominant in the SC even at very low temperatures.

The numerical calculations also show, Fig.3, that the wave-vector k of the interacting electrons has a strong influence on the arising of the coupled states (SC gap).

The SC gap disappears with increasing k, depending on the parameters of the bands (effective mass, Δ_μ etc.) this occurs at either small k or at sufficiently big k, Fig.4.

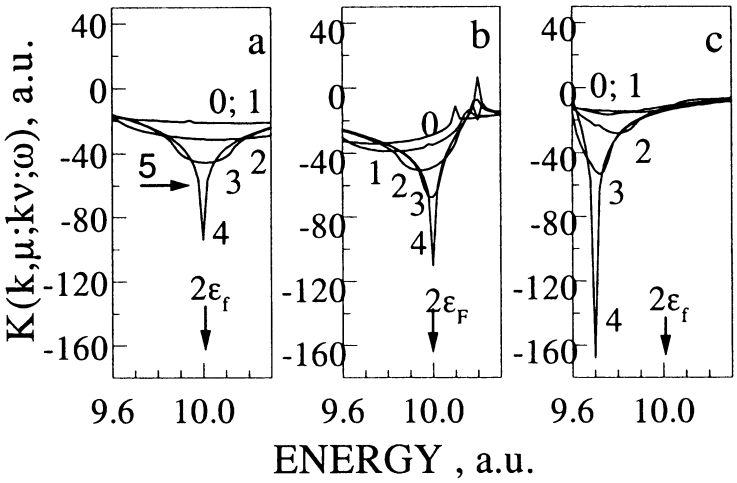

Figure 3. The dependence of the $K(k,\mu;k,\nu;\omega)$ function on momenta k of the interacting electrons (in the calculations we used the value $E = k^2/2m$, therefore, talking about momentum k we keep in mind E as an equivalent but more convenient parameter), T=5K;. In curve 4, E=0; curve 3 E=0.0001; curve 2 E=0.001; curve 1 E=0.01; curve 0, E=0.05. Figs.3a-c correspond, respectively, to the structure of bands used in Figs.1a-c.

Usualy the SC gap has a maximum between 0 and T_c for k=0, Fig.2. However this maximum disappears with the increasing of k and the T-dependence of the SC gap becoms monotonic and is close to that described by BCS theory (see Fig.4).

In experiments some k averaged SC gap ismeasured, therefore the T-dependence of the SC gap must be a function of the crystal parameters and need not obey the BCS universal relation between T_c and the value of SC gap. That becomes especially clear if one takes into account the singularities (to some degree similar to Van Hove singularities) in the two electron density of states which give rise to coupled states located deep inside of bands (Figs.1c,3c SC gap ~ -0.3ev) and are also responsible for the SC of the crystal. A SC gap with a maximum was clearly observed in experiments by H. Enomoto (see Ref. in [21]).

In Fig.5 several functions , $K(k,\mu;k,\nu;\omega)$ calculated for different values of the Δ_μ parameters, are shown. It is seen that for any given value of the V parameter (the

arrow 4 in Fig.5) only curve 1, corresponding to Δ_μ=-1, may be crossed by the continuation of arrow 4. For two other curves 2, 3 the intersection impossible, and hence coupled states do not arise and SC should not occur. This conclusion clearly explains the difference in the presence and absence of the superconductivity for two Bi-based crystals ($Bi_2Sr_2CaCu_2O_8$ and $Bi_2Sr_2CuO_6$ respectively).

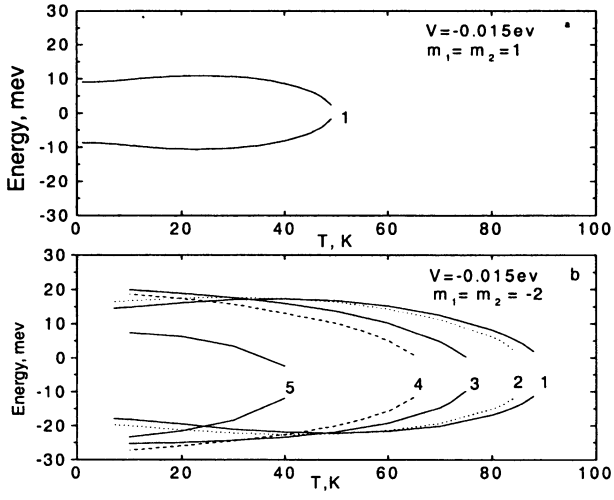

Figure 4. The dependence of SC gap on wave vector k of interacting pair of electrons (in calculations we use the value $E = (k^2/2m)/M$, which depends on wave vector k but is the more convenient parameter); a) curve 1, E=0; b) curve 1, E=0; curve 2, E=0.0001; curve 3, E=0.0004; curve 4, E=0.0006; curve 5, E=0.001;.(in case a) for used values E≠0 SC gap was absent).

4. Experimental results on SC in C_{60} and discussion.

We would like to discuss shortly the experimental results obtained in works [8, 9] using the new method of field-effect swithing the conductivity of crystal from isolating to electron or hole type. Authors observed the SC effects for both type of carriers but in case of electron conductivity T_c = 11K was obtained and for hole conductivity T_c = 52K was registrated. The last temperature is the highest for fullerides crystal. In work [8] such difference is explained by fact that valence-band density of states (DOS) is higher as it derived from a fivefold degenerate (h_{1u}) HOMO (highest occupated molecular orbital) state compared to threefold degenerate (t_{1u}) LUMO (lowest unoccupied molecular orbital) state, asuming similar electron-phonon coupling for valence and electron bands.

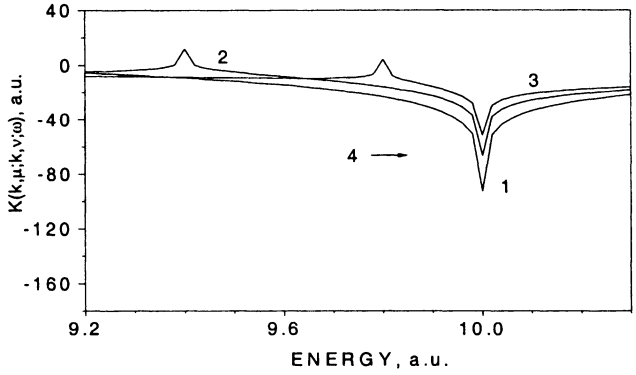

Figure 5. The dependence of the $K(k,\mu;k,\nu;\omega)$ function on the Δ_μ value (the band parameters correspond to case (a) in Fig.1), E=0, T=5K; curve 1 Δ_μ=-1; curve 2 Δ_μ=-0.5; curve 3 Δ_μ=-0.3; arrow 4 corresponds to the value of 1/V, (V=-0.015ev).

The electron band structures of both compounds are significantly different near Fermi level [20].

It should emphasized that in a crystal a fivefold degeneracy cannot be realised and any such state is split into two states ($H_u \rightarrow F_{2u}+E_u$). For such a splitting of levels the situation can be realized in which some states of both bands F_{2u} and E_u will be located below the Fermi energy. This gives rise to a new result. Indeed it was shown in [22] that for doped C_{60} crystals (A_xC_{60}) the fraction of superconducting material was maximized using a starting composition near x=3. One of the reasons for this is that the electrons donated by the alkali atoms populate the t_{1u} level which is three-fold degenerate. Therefore x=3 corresponds to half-filling of this level and should correspond to a maximum in conduction electron density.

In this case the Fermi level can be located so that the full density of electrons (or holes) in both actual bands $F_{2u}+E_u$ can be higher that may take place for half-filled band alone. As a result, the effective charge filling per moleculeof C_{60} may became higher, x>3. For the valence band filling of x=3.2 per C_{60} a maximum T_c = 52K was obtained in Ref.[8].

The reason for the significant difference in T_c between the electron and hole conductivity cases can be understood from Figure 4a,b (curves 1), where is shown that T_c strongly depends on the effective mass for the same value of coupling constant, V. Additionally, Figure 1c shows that the participation of different bands can also increase the T_c. Moreover, according to our results the effect on SC depends on not only the density of electron states at the Ferni level, E_F, but on the all the states located under the Fermi level. The parameter detemining the position of the band maximum relative to E_F is Δ_μ(μ is a number of band). Figure 5 shows the change of the sharp minimum (curves

1-3) as a function of Δ_μ relative to the level of arrow 4 (the value of coupling constant). Therefore a variation of the carrier concentration, i.e. $E_{F,}$, in some range will conserve the SC of the crystal, as was also noted by the authors of Ref. [10]. A more detailed analysis of experiments will be made elsewhere.

Conclusion

The theoretical study of crystal SC from our analysis of the two-particle Green function spectral properties shows that the following conclusions can be drawn:
i) In our proposed approach the usual "forbidden rules" concerning the spins and momenta of interacting by Coulomb electrons arise authomatically and there is no need to introduce them as additional postulates in the explanation of SC, unlike in other theories; ii) all electrons of the band (not only those located on the Fermi level) are responsible for SC effects and for the T_c value; iii) the features of electron band structure and electron phonon-coupling constant define both the spins and the range of wave vector (k) of the electrons which are responsible for the SC of crystals; iy) the T-dependence of the SC-gap can be non-monotonic and for complex structures of the crystal electron bands mixed singlet and triplet coupled states can be responsible for SC.

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