Model of a room-temperature superconductor.

K.V. Grigorishin∗ and B.I. Lev†
Boholyubov Institute for Theoretical Physics of the National Academy of Sciences of Ukraine, 14-b Metrolohichna str. Kiev-03680, Ukraine.
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The model of hypothetical superconductivity, where the energy gap asymptotically approaches zero as temperature increases, has been proposed. Formally the critical temperature of such a superconductor is equal to infinity. For practical realization of the hypothesis a superconducting material with such properties is predicted.

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I. INTRODUCTION

A main problem of technical application of superconductors is a low critical temperature \( T_C \) - maximum 134K at atmospheric pressure, that is considerably lower than the room temperature. The critical temperature depends on an effective coupling constant with some collective excitations \( g = \nu F \lambda \) (here \( \nu F \) is a density of states at Fermi level, \( \lambda \) is an interaction constant) and on energy of the collective excitations \( \omega \). Most often a phonon mechanism results in superconductivity, then \( g \) is an electron-phonon coupling constant (in most cases \( g \lesssim 1 \)), and \( \omega \) is a characteristic phonon frequency on the order of the Debye frequency \( \omega \sim 100 \div 400K \) (here \( \hbar = k_B = 1 \)). The larger coupling constant the larger the critical temperature. At large \( g \) (as a rule for \( g > 10 \)) we have following expressions for the critical temperature \[ 1, 2 \]:

\[ T_C \propto \omega g - BCS \text{ theory} \quad (1) \]
\[ T_C \propto \omega \sqrt{g} - \text{ Eliashberg theory} \quad (2) \]

Formally the critical temperature can be made arbitrarily large by increasing the electron-phonon coupling constant \( T_C(g \to \infty) \to \infty \). However, in order to reach room temperature such values of the coupling constant are necessary, which are not possible in real materials. Moreover we can increase the frequency \( \omega \) due nonphonon pairing mechanisms, as proposed in \[ 2 \]. However with increasing of the frequency the coupling constant decreases as \( g \propto 1/\omega \), therefore

\[ T_C(\omega \to \infty) = 1.14 \omega \exp \left( -\frac{1}{g} \right) \to 0. \quad (3) \]

Many different types of superconducting materials with a wide variety of electron pairing mechanisms exist, however all they have the critical temperature limited by values \( \lesssim 100K \), despite the fact that the highly exotic mechanisms have been proposed. In a present work we propose a fundamentally different approach to the problem of room-temperature superconductivity. This approach is not associated with increasing of the coupling constant or with change of the frequency, but it allows to circumvent the problem in the sense that, having the interaction of conventional intensity (which generates an energy gap \( \Delta \sim 10 \div 100K \)), we change ratio between the gap and the critical temperature as \( 2\Delta/T_C \to 0 \) instead of a finite value \( 3 \div 7 \) for presently known materials.

II. GENERAL IDEA.

First of all we propose a principal possibility to increase the critical temperature due to generalization of BCS model in the following sense: we consider a system of fermions with Hamiltonian:

\[ \hat{H} = \sum_{k,\sigma} \xi(k) a_{k,\sigma}^\dagger a_{k,\sigma} - \frac{\lambda}{V} \sum_{k,p} a_{k,\uparrow}^\dagger a_{p,\uparrow}^\dagger a_{-k,\downarrow} a_{k,\downarrow} + v \sum_{k} \left[ \frac{\Delta}{|\Delta|} a_{k,\uparrow}^\dagger a_{-k,\downarrow}^\dagger + \frac{\Delta^*}{|\Delta|} a_{-k,\downarrow} a_{k,\uparrow} \right] = \hat{H}_{\text{BCS}} + \hat{H}_{\text{ext}}, \quad (4) \]

*Electronic address: gkonst@ukr.net
†Electronic address: bohdan.lev@gmail.com
where \( H_{\text{BCS}} \) is BCS Hamiltonian - kinetic energy + pairing interaction (\( \lambda > 0 \)), energy \( \xi(k) \approx \nu_F |k| - k_F \) is counted from Fermi surface. The term \( H_{\text{ext}} \) is the external pair potential or “source term” \( \mathcal{E} \). Operators \( a_{k\uparrow}^+a_{k\downarrow} \) and \( a_{-k\downarrow}^+a_{k\uparrow} \) are creation and annihilation of Cooper pair operators \( \mathcal{H} \). \( \Delta \) and \( \Delta^+ \) are anomalous averages:

\[
\Delta^+ = \frac{\lambda}{\nu} \sum_p \langle a_p^+ a_{p+} \rangle, \quad \Delta = \frac{\lambda}{\nu} \sum_p \langle a_{p+}^+ a_{p-} \rangle,
\]

which are the complex order parameter \( \Delta = |\Delta| e^{i\theta} \). When we inject (remove) a Cooper pair of electrons (holes) into (from) a system then the energy of the system is changed by \( \nu \). Thus \( \nu \) is energy of a Cooper pair relative to uncoupled state of the electrons in the external field \( H_{\text{ext}} \). The multipliers \( \Delta^+ \) and \( \Delta^- \) are introduced into \( H_{\text{ext}} \) in order that the energy does not depend on the phase \( \theta \) in the absence of magnetic field \( (a \rightarrow ae^{i\theta/2}, a^+ \rightarrow a^+e^{-i\theta/2} \Rightarrow \Delta \rightarrow \Delta e^{i\theta}, \Delta^+ \rightarrow \Delta^+ e^{-i\theta}) \). In another interpretation \( H_{\text{ext}} \) is a source of Cooper pairs: if the Cooper pairs are injected into the system from the source then \( \nu < 0 \), if they are removed from the system then \( \nu > 0 \).

Using the Fermi commutation relations and the anomalous averages \( \mathcal{E} \), Hamiltonian \( \mathcal{H} \) can be rewritten in a form

\[
\mathcal{H} = \sum_{k,\sigma} \xi(k) a_{k\sigma}^+ a_{k\sigma} + \left(1 - \frac{\nu}{|\Delta|}\right) \sum_k \left[ \Delta^+ a_{k\uparrow}^+ a_{-k\downarrow} + \Delta a_{k\downarrow}^+ a_{-k\uparrow}^+ \right] + \frac{1}{\lambda} |\nu| |\Delta|^2.
\]

Then normal \( G \) and anomalous \( F \) propagators have forms:

\[
G = i \frac{\xi_n + \xi}{(i\xi_n)^2 - \xi^2 - |\Delta|^2 (1 - \nu/|\Delta|)^2},
\]

\[
F = i \frac{\Delta (1 - \nu/|\Delta|)}{(i\xi_n)^2 - \xi^2 - |\Delta|^2 (1 - \nu/|\Delta|)^2},
\]

where \( \xi_n = \pi T (2n + 1) \). Then from Eq.\( 5 \) we have self-consistency condition for the order parameter

\[
\Delta = \lambda \nu_F T \sum_{n=-\infty}^{\infty} \int_{-\omega}^{\omega} d\xi F(\xi, \xi, \xi) = \frac{g}{\nu T} \frac{1 - \nu/|\Delta|}{2 \sqrt{\xi^2 + |\Delta|^2 (1 - \nu/|\Delta|)^2}} \tanh \frac{\sqrt{\xi^2 + |\Delta|^2 (1 - \nu/|\Delta|)^2}}{2T}.
\]

Solutions of Eq.\( 6 \) are shown in Fig.\( 1 \). If the external pair potential is absent \( \nu = 0 \) we have usual self-consistency equation for the gap \( \Delta \): the gap is a function of temperature such that \( \Delta(T \geq T_C) = 0 \). The larger the coupling constant \( g = \lambda \nu_F \) the larger \( T_C \). If \( \nu > 0 \) then the pairing of quasiparticles results in increase of the system’s energy that suppresses superconductivity and first order phase transition takes place. If \( \nu < 0 \) then the pairing results in decrease of the system’s energy. In this case a solution of Eq.\( 8 \) is such that the gap \( \Delta \) does not vanish at any temperature. At large temperature \( T \gg \omega, |\nu| \) the gap is

\[
|\Delta(T \rightarrow \infty)| = \frac{g|\nu|}{2T}.
\]

Then the critical temperature is \( T_C = \infty \) (in reality it limited by the melting of the substance). It should be noted that if \( \lambda = 0 \) then for any \( \nu \) a superconducting state does not exist (\( \Delta = 0 \) always). This means electron-electron coupling is the cause of the transition to superconducting state only but not the external pair potential \( \nu \).

Let us take into account the fact that electron-phonon interaction \( g D(\omega(q)) \) leads to superconductivity, where \( D \) is a phonon propagator. Eliashberg equations \( \mathcal{E} \), unlike BCS equations, can describe renormalization of quasiparticles’ mass and decrease of eﬀectiveness of the interaction at phonon energies \( \omega(q) \lesssim T - \) diﬀerence of the asymptotics \( \mathcal{E} \) and \( \mathcal{E} \). However these facts do not change the previous conclusions. In \( \mathcal{E} \), a method to consider electron-phonon interaction has been proposed, however the resulting equation is much simpler than Eliashberg equations. Phonons are dispersionless \( \omega(q) = \omega \) and the electron-phonon coupling constant does not depend on a wave vector \( \lambda(q) = \lambda \) is suggested in this method. The electron-phonon interaction generates the gap via the anomalous propagator \( \mathcal{H} \) and renormalizes a energetic parameter via the normal propagator \( G \):

\[
\Delta_n = \int \frac{d^3p}{(2\pi)^3} \frac{\lambda^2 T}{\sum_{m=-\infty}^{+\infty} iF(p, \varepsilon_m) iD(\varepsilon_n - \varepsilon_m, p)} = g \frac{\pi T \Delta_m}{\sqrt{\varepsilon_m^2 + |\Delta_m|^2}} \frac{\omega^2}{(\varepsilon_n - \varepsilon_m)^2 + \omega^2}
\]
Figure 1: Energy gaps $\Delta(T)$ as solution of Eq.(9) for three values of the external pair potential $\nu$.

\[ \bar{\varepsilon}_n = i\varepsilon_n + \int \frac{d^3p}{(2\pi)^3} \lambda^2 T \sum_{m=\infty}^{+\infty} iG(p, \bar{\varepsilon}_m) iD(\varepsilon_n - \varepsilon_m, k) \]

\[ = i\varepsilon_n + g \sum_{m=\infty}^{+\infty} \frac{\pi T i\varepsilon_m}{\sqrt{\varepsilon_m^2 + |\Delta_m|^2}} \frac{\omega^2}{(\varepsilon_n - \varepsilon_m)^2 + \omega^2}, \]  

(12)

where $g \equiv \lambda^2 \nu F^2 \frac{2}{\omega_0}$ is the coupling constant. The phonon propagator can be represented in a form:

\[ \frac{\omega^2}{(\varepsilon_n - \varepsilon_m)^2 + \omega^2} \rightarrow \frac{\omega}{\sqrt{\varepsilon_n^2 + \omega^2}} \frac{\omega}{\sqrt{\varepsilon_m^2 + \omega^2}} \equiv w_n w_m, \]

(13)

and the gap depends on the energetic parameter as $\Delta_n = \Delta w_n$. Then the energetic parameter is not renormalized: $\bar{\varepsilon}_n = i\varepsilon_n$, because there is an odd function under the sign of sum in (12) taking into account (13). Equation for the gap has a form:

\[ 1 = g \sum_{n=-\infty}^{+\infty} \frac{\pi T w_n^2}{\sqrt{\varepsilon_n^2 + |\Delta_n|^2} w_n^2} \]  

(14)

When $T_C \ll \omega$ (small $g$) Eq.(14) has the asymptotic [3], when $T_C \gg \omega$ (large $g$) one has the asymptotic [2]. Eq.(14) is easier than Eliashberg equations, however one is more correct than BCS equation.

Substituting the propagators (7,8) in Eqs.(11,12) we have an analog of Eq.(9):

\[ 1 = g \sum_{n=-\infty}^{+\infty} \frac{\pi T (w_n - \nu/|\Delta|) w_n}{\sqrt{\varepsilon_n^2 + |\Delta|^2 (w_n - \nu/|\Delta|)^2}} \]  

(15)

If to suppose $\nu = 0$ then Eq.(15) is transformed into Eq.(14). The function $\Delta(T)$ for the cases $\nu > 0, \nu = 0, \nu < 0$ is the same as in Fig.(1). If $\nu < 0$ then in a limit $T \gg \omega, T \gg |\nu|$ we have

\[ |\Delta(T \rightarrow \infty)| = \frac{2g\omega|\nu|}{\pi T}. \]  

(16)

III. MODEL OF A SUPERCONDUCTOR.

In the previous section we demonstrated a principal possibility to increase the critical temperature due to the external pairing potential $\nu$. In this section we propose a model of the system where such a situation can be realized.
Let us consider superconductors alkali-doped fullerenes $A_2C_{60}$ ($A = K, Rb, Cs$). The threefold degenerate $t_{1u}$ level is partly occupied and electrons couple strongly to eight $H_g$ intramolecular Jahn-Teller phonons (electron-vibron interaction). Hamiltonian of the system has a form [9]:

$$
\hat{H} = - \sum_{ij} t_{ij} a_{i\sigma}^+ a_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + \omega \sum_{\nu} b_{\nu}^+ b_{\nu} + \lambda \sum_{i} v^{(\nu)}_{i\uparrow} a_{i\uparrow}^+ a_{i\downarrow} \left(b_{\nu}^+ + b_{\nu}\right).
$$

(17)

$a_{i\sigma}^+(a_{j\sigma})$ is the electron creation (annihilation) operator acting on site $i$, orbital $m = 1, 2, 3$ and spin $\sigma$. $b_{\nu}^+(b_{\nu})$ is the phonon creation (annihilation) operator with the vibration mode $\nu = 1, 2, 3$. $t_{ij}$ is the hopping integral, $U$ is the on-site Coulomb interaction, $\omega$ is the phonon frequency, and $\lambda$ is the electron-phonon coupling constant. The coupling matrices $v^{(\nu)}$ are determined by icosahedral symmetry. The dimensionless electron-phonon coupling constant is $g = \frac{2}{3} \lambda^2 R / \omega$. Typical parameters are $g \sim 0.5 \div 1$, $\omega / W \sim 0.1 \div 0.25$ and $U / W \sim 1.5 \div 2.5$, where $W \sim 0.5eV$ is an electron bandwidth. Basic mechanisms resulting in superconductivity are:

1. The dynamical Jahn-Teller effect (interaction with $H_g$ intramolecular oscillations) favors the formation of a local singlet [10][12]:

$$
|\Phi_{\uparrow\downarrow}\rangle = \frac{1}{\sqrt{3}} \sum_m C_{m\uparrow}^+ C_{m\downarrow}^+ |0\rangle,
$$

(18)

where the spin-up and spin-down electrons have the same $m$ quantum number, i.e., a local pairing takes place. Here $|0\rangle$ is the neutral $C_{60}$ molecule for the alkali-metal-doped materials, the quantum number $m$ labels the three orthogonal states of $t_{1u}$ symmetry (LUMO state). Thus coupling with $H_g$ phonons, which leads to low spin state of $C_{60}$ molecule [18], overpowers Hund’s rule coupling, which leads to high spin state of the molecule:

$$
|\Phi_{\uparrow\uparrow}\rangle = C_{m\uparrow}^+ C_{m\uparrow}^+ |0\rangle.
$$

(19)

Experimental confirmation of this fact is that $A_2C_{60}$ must be anti-ferromagnetic insulator (Hubbard-like model predicts), while it is known experimentally there are no moments in $A_2C_{60}$.

2. In a work [9] the following result has been obtained. For noninteracting electrons the hopping tends to distribute the electrons randomly over the molecular levels. This makes more difficult to add or remove an electron pair with the same $m$ quantum numbers. However as $U$ is large $U > W$ the electron hopping is suppressed and the local pair formation becomes more important. The Coulomb interaction actually helps local pairing. For $A_g$ phonons, the phonon-induced attractive interaction $U_{ph}$ is of the order of $U_{ph}/W \sim -0.47$. However $T_C$ is vanished when $U + U_{ph} \geq 0$. For the Jahn-Teller $H_g$ phonons the attractive interaction is smaller $U_{ph}/W \sim -0.2$. This attractive interaction is therefore quickly overwhelmed by the Coulomb repulsion. Superconductivity remains, however, even for $U + U_{ph} \gg 0$, and $T_C$ drops surprisingly slowly as $U$ is increased. The reason is that local pairing arises from correlation of spin and orbital structures within each site, and therefore is not suppressed by the charge interaction. Superconductivity is expected to exist in the metal right up to the Mott transition.

This situation is very different from Eliashberg theory. We can see, because of the local pairing, the Coulomb repulsion enters very differently for Jahn-Teller and non-Jahn-Teller models, and it cannot be easily described by a Coulomb pseudopotential: $g = \mu^*$. Thus in an alkali-doped fullerene the Cooper pairs are formed on one molecule size of $R = 3.55\AA$ as result of a of electron-vibron interaction and suppression of hopping between molecules with one-site Coulomb interaction $U$. This situation is fundamentally different from superconductivity in metals, where the size of a Cooper pair - macroscopic quantity $\sim 10^3 \div 10^4 \AA$. Let us consider some features of the molecular structure $C_{60}$. Van der Waals radius of a carbon atom is $R_U(C) = 1.70\AA$. Thus a fullerene has inner cavity in its center the size of $\Delta R = R(C_{60}) - R_U(C) = 1.85\AA$. An atom $X$ can be placed into the inner cavity if $R_U(X) \leq \Delta R$ (Fig.2). Large variety of endohedral complexes - atoms, ions or molecules inside the $C_{60}$ cage is known now [13]. For our aim the endohedral complexes $X@C_{60}$, where $X$ is a noble gas atom ($He, Ne, Ar, Kr, Xe$) trapped in a carbon cage [14][15][20], are suitable. A noble gas atom interact with the carbon cage by van der Waals interaction but it does not make a covalent bond with the cage. Van der Waals radii of noble gas atoms are $R_U(He) = 1.40\AA$, $R_U(Ne) = 1.54\AA$, $R_U(Ar) = 1.88\AA$, $R_U(Kr) = 2.02\AA$, $R_U(Xe) = 2.16\AA$. Thus $He, Ne, Ar$ can be placed into a fullerene [14][15][20] with an energy gain. If a noble gas atom is placed into each fullerene molecule in alkali-doped fullerenes then we have hypothetical material $A_2X@C_{60}$. The noble gas atom $X$ has not intrinsic magnetic moment, does not violate the original symmetry of the molecule $C_{60}$, does not causes
Waals radius of \( R \) redistribution of charge on its surface. If \( R(x) \) does not change due to an infinitely small overlap of wave functions of a noble gas atom and wave functions of electrons on the carbon cage, chemical properties of the molecule does not change, solid state behavior of \( X@C_{60} \) must be similar to that of \( C_{60} \), electronic spectrum of \( A_{3}C_{60} \) must coincide with electronic spectrum of \( A_{3}C_{60} \), change in oscillation spectrum of a fullerene can be neglected.

As noted above, in an endohedral fullerene the noble gas atom interacts with a carbon cage by van der Waals force. As is well known van der Waals interaction depends on electronic configuration of interacting subsystems. In alkali-doped fullerenes alkali metal atoms give valent electrons to fullerene molecules. Then energy of the van der Waals interaction has to depend on a state of the excess electrons on surface of a molecule \( C_{60} \). Any two electrons can be in the paired state \([18]\) or in the normal state \([19]\). Let this energy for the paired state is \( \nu_{\uparrow \downarrow} \) and the energy for the normal state is \( \nu_{\uparrow \uparrow} \). If \( \nu_{\uparrow \downarrow} < \nu_{\uparrow \uparrow} \) then the paired state is more energetically favorable than the normal state: a molecule \( X@C_{60} \) has lower energy if the excess electrons are in the paired state than the energy if the electrons are in the normal state. Hence a function

\[
\nu = \nu_{\uparrow \downarrow} - \nu_{\uparrow \uparrow}
\]

plays the role of the external pair potential. For our purpose we have to consider the case \( X = \text{He} \). Van der Waals interaction in this case is interaction due to virtual transitions of the Cooper pair from a level \( t_{1u} \) \((l = 5)\) to levels \([21]\) \( t_{1g} \) \((l = 5)\), \( h_{g}, t_{2u}, h_{u} \) \((l = 6)\), \( g_{g}, g_{u}, t_{1g} \) \((l = 7)\), where \( l \) is an orbital index for \( \pi \)-electrons:

\[
\Phi_{0\uparrow \downarrow} \equiv \Omega_{l=5,\gamma}(R_{1})\Omega_{l=5,\gamma}(R_{2}) \leftrightarrow \frac{1}{\sqrt{2}} \left[ \Omega_{l,\gamma}(R_{1})\Omega_{l=5,\gamma}(R_{2}) + \Omega_{l=5,\gamma}(R_{1})\Omega_{l,\gamma'}(R_{2}) \right] \equiv \Phi_{k\uparrow \downarrow},
\]

and of the helium atom from a level \( 1s \) to levels \( 2s, 2p, 3s, 3p, 3d \ldots \):

\[
\Psi_{0} \equiv f_{0,0}(r_{1})Y_{0,0}(r_{1})f_{0,0}(r_{2})Y_{0,0}(r_{2})
\]

\[
\leftrightarrow \frac{1}{\sqrt{2}} \left[ f_{n,l}(r_{1})Y_{l,m}(r_{1})f_{0,0}(r_{2})Y_{0,0}(r_{2}) + f_{0,0}(r_{1})Y_{0,0}(r_{1})f_{n,l}(r_{2})Y_{l,m}(r_{2}) \right] \equiv \Psi_{p},
\]

where the index \( \gamma \) labels irreducible representation of icosahedral symmetry group: \( n, l, m \) are principal quantum number, orbital quantum number and magnetic quantum number accordingly; \( f_{n,l}(r) \) is a radial wave function, \( Y_{l,m} \) is a spherical wave functions. \( \Phi_{0} \) and \( \Psi_{0} \) are ground-states of a Cooper pair and a helium atom accordingly. \( \Phi_{k} \) and \( \Psi_{p} \) are the excited states of the Cooper pair and the helium atom accordingly, \( k \) and \( p \) are sets of quantum indices of the corresponding exited states. \( R_{1} \) and \( R_{2} \) are radius-vectors of electrons of the Cooper pair, and \( |R_{1}| \approx |R_{2}| \approx R \) since the Cooper pair is on surface of the molecule. \( r_{1} \) and \( r_{2} \) are radius-vectors of electrons of the helium atom, and \( \langle r \rangle = 0.31 \text{Å} \ll R = 3.55 \text{Å} \) - the atom is much less than the fullerene molecule. Signs ”+” in the sums are caused by the fact that the ground states of both the Cooper pair and the helium atom are singlet, and transitions between singlet
and triplet states are allowed only when there is the spin-orbit interaction, but this interaction can be neglected. Energy of the van der Waals interaction is defined with the second order correction:

\[ v_{\uparrow\downarrow} = \sum_{k,p} \frac{|\langle \Phi_{k\uparrow\downarrow}, \Psi_p | \hat{V}| \Psi_0, \Phi_{0\uparrow\downarrow} \rangle|^2}{E_0 + E_0 - E_k - E_p}, \quad (23) \]

where the summation is made over the indexes of all possible excited states of the Cooper pair \( k \) and of the helium atom \( p \); \( E_0 \) and \( \tilde{E}_0 \) are ground state energies of the Cooper pair and the helium atom accordingly, \( E_k \) and \( \tilde{E}_p \) are energies of the corresponding excited states. Since \( E_0 < E_k, \tilde{E}_0 < \tilde{E}_p \) then \( v_{\uparrow\downarrow} < 0 \). An operator of the interaction is (within a single molecule the effects of screening can be neglected)

\[ \hat{V}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}_1, \mathbf{r}_2) = \frac{e^2}{|\mathbf{R}_1 - \mathbf{r}_1|} + \frac{e^2}{|\mathbf{R}_1 - \mathbf{r}_2|} + \frac{e^2}{|\mathbf{R}_2 - \mathbf{r}_1|} + \frac{e^2}{|\mathbf{R}_2 - \mathbf{r}_2|} - \frac{2e^2}{|\mathbf{R}_1|} - \frac{2e^2}{|\mathbf{R}_2|} \quad (24) \]

The van der Waals interaction is a high-frequency process because the interaction is result of virtual transitions between atomic (molecular) levels. This means that screening of the interaction must be determined by a high-frequency dielectric function \( \varepsilon_{\infty} \), that is by a plasmon mechanism. However transition between molecular levels of \( \varepsilon_{\infty} \), hence between energy bands of \( k_0 \), takes place. This means that plasmons can not exist with such energies. The frequency of the transitions between the levels of a helium atom is even larger: \( \sim 20\text{eV} \). Hence screening of the van der Waals interaction by condition electrons is very inefficient and it can be neglected.

To calculate the energy of van der Waals interaction if electrons are in the normal state \[ (19) \] we can use an antisymmetric wave function:

\[ \Phi_{0\uparrow\downarrow} = \frac{1}{\sqrt{2}} \left[ \Omega_{l=5, \gamma_1}(\mathbf{R}_1) \Omega_{l=5, \gamma_2}(\mathbf{R}_2) - \Omega_{l=5, \gamma_1}(\mathbf{R}_2) \Omega_{l=5, \gamma_2}(\mathbf{R}_1) \right] \]

\[ \leftarrow \frac{1}{\sqrt{2}} \left[ \Omega_{l, \gamma}(\mathbf{R}_1) \Omega_{l=5, \gamma_2}(\mathbf{R}_2) - \Omega_{l, \gamma}(\mathbf{R}_2) \Omega_{l=5, \gamma_2}(\mathbf{R}_1) \right] = \Phi_{k\uparrow\downarrow}. \quad (25) \]

Energy of the van der Waals interaction is

\[ v_{\uparrow\downarrow} = \sum_{k,p} \frac{|\langle \Phi_{k\uparrow\downarrow}, \Psi_p | \hat{V}| \Psi_0, \Phi_{0\uparrow\downarrow} \rangle|^2}{E_0 + E_0 - E_k - E_p}. \quad (26) \]

It should be noted that due to electroneutrality of a helium atom and small size of the atom compared to radius of the molecule \( \langle r \rangle = 0.31 \text{Å} \ll R = 3.55 \text{Å} \) we have that \( \langle 00|V|00 \rangle = 0 \) - the first order process can be neglected. Moreover we can neglect the exchange processes between the helium atom and electrons on the molecule’s surface, that can not be done, for example, for an atom Ar due to a not small overlap of the atom’s wave functions with the wave functions of electrons on the fullerene cage \[ (23) (24) \]. In this work we neglect the higher order processes, i.e. non-additivity of van der Waals interaction between the helium atom, the pair of excess electrons and the carbon cage of a fullerene molecule.

To estimate \( \nu \) a fullerene molecule can be considered as a sphere, that simplifies the calculation of the matrix elements \( \langle kp | V | 00 \rangle \). Then wave functions on the fullerene’s surface \( \Omega_{l, \gamma} \) are spherical wave functions \( Y_{l,m} \), where \( l \) and \( m \) is orbital quantum number and magnetic quantum number accordingly, \( |\mathbf{R}_1| = |\mathbf{R}_2| = R \). Energy of each level is

\[ E_l = \frac{\hbar^2 l(l+1)}{2m_e R^2}. \quad (27) \]

In a ground state \( l = 5 \), each state is degenerated in \( m = -l \ldots l \). Let wave function of a Cooper pair in the ground state is

\[ Y_{5,m}(\mathbf{R}_1)Y_{5,m}(\mathbf{R}_2), \quad (28) \]

and the wave function of some a excited state is:

\[ \frac{1}{\sqrt{2}} \left[ Y_{l',m'}(\mathbf{R}_1)Y_{5,m}(\mathbf{R}_2) + Y_{5,m}(\mathbf{R}_1)Y_{l',m'}(\mathbf{R}_2) \right], \quad (29) \]

where \( l' > 5 \), \( m' = -l' \ldots l' \). The antisymmetric wave functions are

\[ \frac{1}{\sqrt{2}} \left[ Y_{5,m_1}(\mathbf{R}_1)Y_{5,m_2}(\mathbf{R}_2) - Y_{5,m_1}(\mathbf{R}_2)Y_{5,m_2}(\mathbf{R}_1) \right] \leftarrow \left[ Y_{l',m'}(\mathbf{R}_1)Y_{5,m_2}(\mathbf{R}_2) - Y_{l',m'}(\mathbf{R}_2)Y_{5,m_2}(\mathbf{R}_1) \right]. \quad (30) \]
It should be noted that in this case the energies of van der Waals interaction \[^{[23]}\] and \[^{[26]}\] are functions of the magnetic quantum number: \(v_{\perp}(m), v_{\perp}(m)\). Below we will calculate \(v\) for each \(m\). The Coulomb potential is convenient to be expanded in spherical harmonics:

\[
\frac{1}{|R - r|} = \begin{cases} 
\frac{4\pi}{R} \sum_{L,M} \frac{1}{2L+1} \left( \frac{r}{R} \right)^L Y_{L,M}^+(\theta, \varphi) Y_{L,M}(\Theta, \Phi), & r < R \\
\frac{4\pi}{R} \sum_{L,M} \left( \frac{r}{R} \right)^L Y_{L,M}^+(\theta, \varphi) Y_{L,M}(\Theta, \Phi), & r > R 
\end{cases}
\]

(31)

where \(M = -L, -L + 1 \ldots L\). Since \(\langle r \rangle = 0.31 \text{Å} \ll R = 3.55 \text{Å}\) then the expansion at \(r > R\) can be omitted. The matrix element of the interaction can be represented as

\[
\langle \Phi_{k\perp\perp}, \Psi_p \mid \hat{V} \mid \Psi_0, \Phi_{0\perp\perp} \rangle = 2e^2 \sum_{L,M} ABC,
\]

where

\[
A = \frac{4\pi}{R} \frac{1}{2L+1} \int_0^\infty f_{n,\ell} f_{0,0} r^2 \left( \frac{r}{R} \right)^L dr \\
B = \int Y_{l,m}^+ Y_{0,0}^+ Y_{L,M}^+ \sin \theta d\theta d\varphi \\
C = \int Y_{l',m'}^+ Y_{5,m}^+ Y_{L,M} \sin \Theta d\Theta d\Phi
\]

Transitions to states \(l' = 6\) for a Cooper pair and to states \(2p, 3p, 4d\) for a helium atom when the magnetic quantum numbers change as \(m' - m = \tilde{m} = 0, \pm 1\) give the largest contribution to Eq.32. \(E_{5,m} - E_{6,m'} \approx 3.6 \text{eV}, E_{0,0,0} - E_{n,\tilde{m},m} \approx 21 \text{eV}\). Calculation shows that \(v\) is almost independent of \(m\):

\[
v_{\perp}(m = 0 \ldots 5) \approx -80 \text{K},
\]

(33)

that indicates the correctness and usability of the spherical wave functions instead of the functions \[^{[21]}\] to estimate the potential \(v\). It is easy to show that

\[
\langle \Phi_{k\perp\perp}, \Psi_p \mid \hat{V} \mid \Psi_0, \Phi_{0\perp\perp} \rangle = \sqrt{2} \langle \Phi_{k\perp\perp}, \Psi_p \mid \hat{V} \mid \Psi_0, \Phi_{0\perp\perp} \rangle,
\]

(34)

hence

\[
v_{\perp} = 2v_{\perp}
\]

(35)

Thus a fullerene molecule with excess electrons has a lower energy if the electrons are in the paired state \[^{[18]}\] than energy if the electrons are in the state according to Hund’s rule \[^{[19]}\]. For each pair the energy gain is \(v = -40 \text{K} - \text{Eq.}29\). The reason of the relation \[^{[31]}\] consists in the fact that in the singlet state \[^{[28,29]}\], when the wave functions are symmetric \(\Phi_{\perp\perp}(R_1, R_2) = \Phi_{\perp\perp}(R_2, R_1)\), the electrons are close to each other, the charge density is concentrated at one location. On the contrary, in the triplet state \[^{[30]}\], when the wave functions are antisymmetric \(\Phi_{\perp\perp}(R_1, R_2) = -\Phi_{\perp\perp}(R_2, R_1)\), the electrons avoid to be located next to each other, the charge density is smeared on surface of the molecule. Hence the electrons in the singlet state stronger polarizes the noble gas atom than the electrons in the triplet state.

To estimate the energy gap \(\Delta\) we can use the continuum approximation \[^{[15]}\] instead the Hubbard hamiltonian \[^{[18]}\]. The characteristic frequency of intramolecular \(H_g\) oscillations can be taken as the effective frequency \(\omega\). Let the frequency is \(\omega/W = 0.1\) where \(W = 0.5 \text{eV}\) is the electron bandwidth. The effective coupling parameter \(g\) must be such that the critical temperature calculated with Eq.14 is equal to critical temperature \(T_C = 19.3 \text{K}\) of \(K_S\), then we have \(g = 0.283\). The functions \(\Delta(T)\) calculated with Eqs.14,15 are shown in Fig.3. We can see for \(v < 0\) the gap tends to zero asymptotically with increasing temperature. Thus the critical temperature is equal to infinity, in practice it is limited by the melting point of the substance.

**IV. CONCLUSION.**

In this work a model of a hypothetical room-temperature superconductor has been proposed. Our idea is based on the fact that the phase independent external pair potential can be added in BCS Hamiltonian - Eqs.40. This field
acts on a Cooper pair changing its energy relative to uncoupled state of the electrons. In a case of increasing of Cooper pair’s energy by the external pair field a suppression of superconductivity takes place. In a case of decreasing of Cooper pair’s energy by the field we have a fundamental difference between the temperature dependence of the energy gap and ordinary behavior of an order parameter - it tends to zero asymptotically with increasing temperature - Fig.1. Thus the ratio between the gap and the critical temperature is $2\Delta/T_C = 0$ instead of a finite value in BCS theory. For practical realization of this model we propose a hypothetical superconductor on the basis of alkali-doped fullerenes $K_3C_{60}$ or $Rb_3C_{60}$ with the use of endohedral structures $He@C_{60}$, where a helium atom is in the center of each fullerene molecule. According to [9][12] in alkali-doped fullerene Cooper pairs are formed on surface of the fullerene molecules due electron-vibron interaction and suppression of hopping between molecules by one-cite Coulomb interaction. In an endohedral fullerene the noble gas atom interacts with a carbon cage by van der Waals force. The van der Waals interaction depends on a state of excess electrons on surface of the molecule. We have shown that energy of the molecule if the excess electrons on its surface are in the paired state is lower than the energy if the electrons are in the normal state. Then difference of the energies of the van der Waals interaction plays a role of the external pair potential, moreover $\nu < 0$ that means the paired state of electrons is more energetically favorable than the normal state. We have calculated the temperature dependence of the energy gap for a hypothetical material $K_3He@C_{60}$ neglecting the non-additivity of the van der Waals interaction - Fig.3. In this material the superconducting phase exists at any temperature unlike the pure system $K_3C_{60}$ where the phase is limited by the finite critical temperature.

In connection with the obtained results it should be noted that in works [25] it had been reported about the synthesis of the first endohedral fullerene superconductors $A_3Ar@C_{60}$ having critical temperatures on 2 – 3 kelvins less than critical temperatures of the pure materials $A_3C_{60}$. As noted above van der Waals radius of Ar is slightly more than radius of the inner cavity in center of a fullerene molecule. In this case an overlap of the argon atom’s wave functions with the wave functions of electrons on the fullerene cage takes place, hence the exchange interaction plays a role. The radii of Kr and Xe are much larger hence role of the exchange interaction is more significant. Thus the influence of Ar, Kr, Xe requires special consideration that goes beyond the present work.

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[1] Gerald D. Mahan, Many-particle physics (Physics of Solids and Liquids), 3rd edition, Plenum Publ. Corp. 2000
[2] V.L. Ginzburg, D.A. Kirzhnits, High-temperature superconductivity, Consultants Bureau, New York 1982
[3] R. D. Mattuk, B.Johansson, Advances in Physics 17, 509 (1968).
[4] John R. Schrieffer, Theory of Superconductivity, benjamin, 1964.
[5] Richard D. Mattuk, A guide to Feynman diagrams in the many-body problem (H. C. Oersted Institute University of Copenhagen, Denmark, 1967).
[6] Levitov L.S., Shitov A.V. Green’s Functions. Problems and Solutions, Fizmatlit, Moscow, 2003 (in Russian)
[7] K.V. Grigorishin, B.I. Lev, Physica C 495, 174 (2013)
[8] K.V. Grigorishin, arXiv:1308.6459v3 [cond-mat.supr-con] (2013); K.V. Grigorishin, Phys. Scr., in print
[9] J. E. Han, O. Gunnarsson and V. H. Crespi, Phys.Rev.Lett. 90, 167006 (2003)
[10] Paul E. Lammert and Daniel S. Rokhsar, Phys.Rev.B 48, 4103 (1993) 4103
[11] D. M. Deaven, P. E. Lammert, D. S. Rokhsar, Phys.Rev.B 52, 16377 (1995)
[12] J. E. Han, O. Gunnarsson, Physica B 292, 196 (2000)
[13] A.V. Eletskii, Physics-Uspekhi 43, 111 (2000)
[14] J. Breton, J. Gonzalez-Platas and C. Girardet, J. Chem. Phys. 99, 4036 (1993)
[15] Jerzy Cioslowski and Eugene D. Fleischmann, J. Chem. Phys. 94, 3730 (1991)
[16] Martin Saunders et al., J. Am. Chem. Soc. 116, 2193 (1994)
[17] Yves Rubin et al., Angew. Chem. Int. Ed. 40, 1321 (2001)
[18] Dennis P. Clougherty, Can. J. Chem. 74, 965 (1996)
[19] H. A. Jimenez-Vazquez and R. J. Cross, J. Chem. Phys. 104, 5589 (1996)
[20] S. Patchkovskii and W. Thiel, J. Chem. Phys. 106, 1796 (1997)
[21] F. Allonoso-Marroquin and other, Rev. Mex. Fis. 44 S3, 18 (1998)
[22] R. C. Haddon, Acc. Chem. Res. 25, 127 (1992)
[23] M. Morscher et al., Phys.Rev.B 82, 051201(R) (2010)
[24] Alexey V. Verkhovtsev and other, arXiv:1108.0918 [physics.atm-clus] (2011)
[25] Kenichi Yakigaya et al., New J. Chem. 31, 973 (2007)