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Theory of Superconducting T_c of doped fullerenes

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Abstract

We develop the nonadiabatic polaron theory of superconductivity of M_xC_{60} taking into account the polaron band narrowing and realistic electron-phonon and Coulomb interactions. We argue that the crossover from the BCS weak-coupling superconductivity to the strong-coupling polaronic and bipolaronic superconductivity occurs at the BCS coupling constant $\lambda \sim 1$ independent of the adiabatic ratio, and there is nothing "beyond" Migdal's theorem except small polarons for any realistic electron-phonon interaction. By the use of the polaronic-type function and the "exact" diagonalization in the truncated Hilbert space of vibrons ("phonons") we calculate the ground state energy and the electron spectral density of the C_{60}^- molecule. This allows us to describe the photoemission spectrum of C_{60}^- in a wide energy region and determine the electron-phonon interaction. The strongest coupling is found with the high-frequency pinch A_{g2} mode and with the Frenkel exciton. We clarify the crucial role of high-frequency bosonic excitations in doped fullerenes which reduce the bare bandwidth and the Coulomb repulsion allowing the intermediate and low-frequency phonons to couple two small polarons in a Cooper pair. The Eliashberg-type equations are solved for low-frequency phonons. The value of the superconducting T_c, its pressure dependence and the isotope effect are found to be in a remarkable agreement with the available experimental data.

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1 Introduction

Any phonon mediated superconductivity is a nonadiabatic phenomenon. Nonadiabaticity of electrons in metals measured by the ratio of the characteristic phonon frequency to the Fermi energy is normally small ($\leq 10^{-2}$), so is their superconducting T_c. High temperature superconductivity of doped fullerenes [1, 2] seems to be due to large nonadiabaticity. The phonon frequencies are high, $\omega \leq 0.2eV$ while the bare Fermi energy is very low $E_F \leq 0.2eV$ [3]. Tolmachev *logarithm* in the definition of the Coulomb pseudopotential μ^* does not apply in this nonadiabatic case and the electron-phonon coupling should be strong ($\lambda \geq 1$) to overcome the Coulomb repulsion. The strong electron-phonon interaction implies the nonadiabatic polaron or bipolaron superconductivity as discussed in detail by Alexandrov and Mott[4]. However, the final answer on the origin of high T_c depends not only on the adiabatic ratio ω/E_F but also on the coupling constants with different phonons . If a relatively weak coupling ($\lambda \leq 0.5$) with low-frequency phonons dominates and the Coulomb repulsion is not very large, then the Migdal-Eliashberg theory is applied with the BCS ground state. On the other hand, if the coupling is strong and (or) high-frequency phonons are involved, the nonadiabatic polaron theory is more appropriate.

In the past years several different calculations of the electron-phonon coupling constants have been reported for fullerenes[5, 6, 7, 8, 9]. Some of them yield the strongest coupling with the high frequency H_g modes with a moderate electron-phonon coupling, $\lambda \leq 0.5$. On the other hand Picket *et al*[5] predicted the strongest coupling with the high frequency $A_g(2)$ mode and $\lambda \sim 3$. The difference in calculated coupling constants is quite remarkable, and may result in a qualitatively different understanding of the nature of superconductivity of doped fullerenes. Therefore, the experimental determination of λ and more extensive theoretical work are required.

Recent photoemission spectroscopy (PES) of the molecule C_{60}^- [10] allows us to estimate the relative contribution of different phonons. While the variations analysis by Gunnarsson *et al* in the truncated space up to five phonons showed the strongest coupling with a *low*-frequency H_g mode, we found by applying the polaron theory of PES that the coupling with the high-frequency A_{g2} mode dominates [11]. The coupling constant with this mode appears

at least by factor ~ 1.5 larger than with any other mode in a qualitative agreement with the tight-binding analysis by Picket *et al*[5]. This demonstrate that an estimate of the electron-phonon coupling constants from PES, the Raman and neutron scattering using the canonical theory of metals may be inconclusive, since doped fullerenes are not conventional metals to which Migdal's "theorem" can be applied.

There is some confusion in the literature concerning the violation of Migdal's theorem. As was realized long time ago [12] the Migdal [13] theory of electron-phonon effects in the normal state and the Eliashberg theory [14], which generalizes BCS theory to incorporate Migdal theory in the normal limit, provide a rigorous basis for understanding T_c in the weak and intermediate coupling regime. By the use of the $1/\lambda$ expansion technique[15] one can readily show that small polarons appear at $\lambda \sim 1$ and thus Migdal's theorem fails. The breakdown of the Migdal-Eliashberg theory at $\lambda \sim 1$ has nothing to do with the nonadibatic corrections due to the so-called "crossing" diagrams (vertex corrections). Small polarons are formed at $\lambda \geq 1$ both in the initially adiabatic $\omega \ll E_F$ or nonadiabatic $\omega \geq E_F$ system irrespectively of the ratio ω/E_F[16]. Their formation is the result of the broken translation symmetry as discussed in ref.[17, 18]. Of course, in special cases Migdal's theorem will not hold even for small $\lambda < 1$: first, if either characteristic phonon has small momentum $q \ll q_D$ (q_D is the Debye momentum), and second, if the Fermi surface has a nested topology. In these textbook examples [12, 19] the "crossing" diagrams are no longer small. Several authors [20, 21, 22, 23] suggested a theoretical treatment of the vertex corrections with quite opposite conclusions about their role for T_c. While many authors generated the opinion that vertex corrections should, in general, be negative, Grimaldi *et al* [23] obtain a strong enhancement of T_c from non-adiabatic terms.

In this paper we develop the theory of the superconducting T_c which takes into account the nonadiabatic effects, strong coupling with some phonons, and the realistic Coulomb interaction. First, we discuss in more details the origin of the breakdown of Migdal's theorem due to the broken translation symmetry. We argue that while a strong enhancement of T_c due to vertex corrections [23] is an artifact of an unrealistic electron-phonon interaction, the polaronic band-narrowing provides such enhancement quite naturally. It means that the multiphonon

dressing is important for high-T_c superconductivity as was predicted by one of us [24]. Then we analyze the PES data [10] for C_{60}^- using the polaronic displacement transformation for A_{g2} mode and the truncated Hilbert space for other phonons. Our fit to the experimental PES is just as good as the variations approach [10] for the low binding energies and better than that for the high-energy region. We obtain the strongest coupling with the high-lying $A_g(2)$ pinch mode and with the Frenkel-type excitons. As a result, we determine the *bare* coupling constants to formulate and solve the Eliashberg-type equations fully taking into account multiphonon dressing and nonadiabatic motion of carriers. These provide us with the value of T_c, its pressure dependence and with the isotope effect which are in excellent agreement with experiment. In conclusion we analyze a possibility for the bipolaron formation and $2e$ Bose-liquid ground state of doped fullerenes.

2 Broken translational symmetry and breakdown of Migdal's theorem.

In doped semiconductors the carriers become small polarons or bipolarons at the intermediate value of the coupling constant $\lambda \geq 1$ or $\lambda \geq 0.5$, respectively [25]. However, within the adiabatic Migdal description of electrons and phonons coupled by the linear electron-phonon interaction there is no instability at any value of λ if the bare ionic plasmon mode is replaced by the acoustic phonon mode[12]. The corrections to the normal state spectrum due to the coupling are adiabatically small ($\sim \omega/E_F$). In particular, the critical temperature of the BCS superconductor is adiabatically small, $T_c/E_F < \omega/E_F \ll 1$ for all relevant values of λ. Therefore, the self-consistent Migdal-Eliashberg approach does not allow for the possibility to study the small-(bi)polaron formation in the intermediate and strong-coupling regime. This drawback is due to the basic assumption of the canonical theory that the Green's functions (GFs) are translationally invariant, thus $G(\mathbf{r}, \mathbf{r}', t) = G(\mathbf{r}-\mathbf{r}', t)$. This assumption excludes the possibility of the local violation of the translational symmetry due to the lattice deformation followed by the self-trapping. To enable the electron to relax into the lowest polaron state, one can introduce an infinitesimal translationally noninvariant potential, which should be set equal zero only in the final solution for GFs [17]. As in the case of the off-diagonal

superconducting order parameter, a small potential violating a translational symmetry drives the system into a new ground state at sufficiently large λ. Setting it equal to zero in the solution to the equation of motion restore the translational symmetry but in a new polaronic band rather than in the electron one, which turns out to be an excited state.

In the Holstein model, in which electrons interact with the local (molecular) phonons one can notice the polaronic instability of the Fermi liquid at $\lambda \sim 1$ already with Migdal's diagrams for the electron self-energy. The interaction is described by the Hamiltonian

$$H_{e-ph} = \frac{1}{\sqrt{2N}} \sum_{\mathbf{q},\mathbf{k}} \gamma(\mathbf{q})\omega(\mathbf{q}) c^{\dagger}_{\mathbf{k}+\mathbf{q}} c_{\mathbf{k}} d_{\mathbf{q}} + H.c., \tag{1}$$

where the coupling constant $\gamma(\mathbf{q})$ and the phonon frequency $\omega(\mathbf{q})$ are momentum independent. The electron self-energy Σ in the Migdal approximation contains two contributions, Σ_M, Fig.1a and Σ_μ, Fig.1b. $\Sigma_M \simeq \lambda\omega$ and therefore remains adiabatically small compared with the bandwidth $2D \simeq N(0)^{-1}$ in the relevant region of the coupling ($\lambda < D/\omega$), which guarantees the self-consistency of the approach. On the other hand for the molecular phonons $\Sigma_\mu \simeq D\lambda n$ is not small and it turns out to be comparable or larger than the Fermi energy already at $\lambda \sim 1$ for any filling of the band (n is the electron density per cell). As a rule this diagram, which is momentum and frequency independent, is included in the definition of the chemical potential E_F. While this is justified for a weak-coupling regime, Σ_μ leads to an instability for a strong coupling. To show this let us consider a one-dimensional chain in the tight-binding approximation with the nearest-neighbor hopping integral $D/2$. The renormalized chemical potential is given by

$$E_F = Dsin\left(\frac{\pi(n-1)}{2}\right) - 2D\lambda n, \tag{2}$$

with $\lambda = \gamma^2\omega/2D$. The system is stable if the derivative dE_F/dn is positive, which yields the following region for the stability of the Migdal solution:

$$\lambda < \frac{\pi}{2} cos\left(\frac{\pi(n-1)}{2}\right). \tag{3}$$

For two and three-dimensional lattices the numerical coefficient is different, but the critical value of λ remains of the order of unity.

In doped semiconductors and metals phonons are screened and the diagram Σ_μ containing only zero momentum phonons vanishes. Therefore, one can erroneously conclude that there

is nothing to worry about as far as the applicability of the Migdal approach. However, it is sufficient to violate the translation symmetry and then restore it to observe the instability of the bare band. The polaronic instability is essentially an adiabatic effect [16, 18]. Therefore, to see how the same self-energy Σ_μ leads to the polaronic collapse independent of the type of phonons we consider the extreme adiabatic limit of the classical deformation field $\phi(\mathbf{r})$ coupled with the electron field $\psi(\mathbf{r})$ as

$$H = H_e + \int d\mathbf{r}d\mathbf{r}' \left[g(\mathbf{r}-\mathbf{r}')\phi(\mathbf{r}')\{\psi^\dagger(\mathbf{r})\psi(\mathbf{r}) - n^0(\mathbf{r})\} + h.c.\right] + s^2|\nabla\phi(\mathbf{r})|^2. \tag{4}$$

Here H_e is the electron kinetic energy, s is the sound velocity, $g(\mathbf{r})$ is the coupling constant with the Fourier component $g_\mathbf{q} = \omega_\mathbf{q}^{3/2}\gamma(\mathbf{q})/\sqrt{2N}$, $n^0(\mathbf{r})$ is the periodic density of carriers respecting the translational symmetry, and $\omega_\mathbf{q} = sq$. Minimizing Eq.(4) with respect to the classical field $\phi^*(\mathbf{r})$ we obtain

$$s^2\nabla^2\phi(\mathbf{r}) = \int d\mathbf{r}' g^*(\mathbf{r}-\mathbf{r}')\{n(\mathbf{r}') - n^0(\mathbf{r}')\}. \tag{5}$$

The solution is

$$\phi(\mathbf{r}) = -\sum_\mathbf{q} \frac{g^*_\mathbf{q}}{s^2q^2} e^{i\mathbf{q}\cdot\mathbf{r}}\{n_\mathbf{q} - n^0_\mathbf{q}\}, \tag{6}$$

where $n_\mathbf{q}$ is the Fourier component of the electron density $n(\mathbf{r}) \equiv \langle\psi^\dagger(\mathbf{r})\psi(\mathbf{r})\rangle$. Substituting Eq.(6) into the Hamiltonian Eq.(4) we find that the adiabatic lattice deformation leads to the lowering of the electron energy by the value

$$\delta\mu(\mathbf{r}) = -2\sum_\mathbf{q} \frac{|g_\mathbf{q}|^2}{\omega^2_\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}\{n_\mathbf{q} - n^0_\mathbf{q}\}. \tag{7}$$

If the electron density is periodic, $n_\mathbf{q} = n^0_\mathbf{q}$ the shift of the energy is zero. Otherwise, it is not. For example, one can consider a random statistically uncorrelated distribution with the *ansamble* average $\langle n_\mathbf{q} n_{\mathbf{q}'}\rangle = Nn^2\delta_{\mathbf{q},-\mathbf{q}'}$. In that example the chemical potential is shifted by the value

$$\langle|\delta\mu|\rangle = n\left[\frac{1}{N}\sum_\mathbf{q}|\gamma(\mathbf{q})|^4\omega^2_\mathbf{q}\right]^{1/2} \simeq 2n\lambda D, \tag{8}$$

which is practically the same as in Eq.(2). However, now

$$\lambda D \equiv E_p = \frac{1}{2N}\sum_\mathbf{q}|\gamma(\mathbf{q})|^2\omega_\mathbf{q} \tag{9}$$

depends on the phonon spectrum, integrated over *all* Brillouin zone rather than on zero momentum phonons. The broken translational symmetry lowers the energy by the value $2E_p \simeq 2\lambda D$ per particle. The corresponding increase of the deformation energy is E_p. Therefore, the system prefers to relax into the self-trapped state if $E_p > D$. The nonadiabatic vertex corrections neglected within the Migdal approach are also completely irrelevant for the small polaron formation and, therefore for the breakdown of this approach. The extension of the Migdal approximation to the strong-coupling limit is unacceptable because of the broken translation symmetry.

3 Exact nonadiabatic solution and polaron band restoring translational symmetry

In the small polaron regime, $\lambda \geq 1$ the kinetic energy remains smaller than the interaction energy and a selfconsistent treatment of a many polaron system is possible with a $'1/\lambda'$ expansion technique in the nonadiabatic regime[15]. This possibility results from the fact, known for a long time, that there is an exact solution for a single electron without hopping term. Following Lang and Firsov [30] one can apply the canonical transformation to diagonalise the Hamiltonian in the site representation

$$H = \sum_{<ij>} T(\mathbf{m}-\mathbf{n}) c_i^\dagger c_j + \sum_{\mathbf{q}} \omega(\mathbf{q})(d_{\mathbf{q}}^\dagger d_{\mathbf{q}} + 1/2) + \sum_{\mathbf{q},i} \omega(\mathbf{q}) n_i [u_i(\mathbf{q}) d_{\mathbf{q}} + H.c.] + H_c, \qquad (10)$$

where $T(\mathbf{m})$ is the bare hopping integral, $i = (\mathbf{m}, s)$, $j = (\mathbf{n}, s)$ (s stands for spin), $u_i(\mathbf{q}) = \gamma(\mathbf{q}) exp(i\mathbf{q}\cdot\mathbf{m})/\sqrt{2N}$, and H_c is the *direct* Coulomb repulsion. The diagonalisation is exact if $T(\mathbf{m}) = 0$ (or $\lambda = \infty$):

$$\tilde{H} = e^S H e^{-S}, \qquad (11)$$

where

$$S = \sum_{\mathbf{q},i} \hat{n}_i \left(u_i(\mathbf{q}) d_{\mathbf{q}} - h.c. \right). \qquad (12)$$

The electron operator transforms as

$$\tilde{c}_i = c_i exp\left(\sum_{\mathbf{q}} u_i(\mathbf{q}) d_{\mathbf{q}} - h.c. \right) \qquad (13)$$

and the phonon one as

$$\tilde{d_{\mathbf{q}}} = d_{\mathbf{q}} - \sum_i \hat{n}_i u_i^*(\mathbf{q}) \tag{14}$$

From Eq.(14) it follows that the Lang-Firsov canonical transformation is the displacement transformation for the multi-polaron system shifting ions to the new equilibrium positions. In a more general sense it changes the boson vacuum. As a result:

$$\tilde{H} = \sum_{i,j} (\hat{\sigma}_{ij} - \mu\delta_{i,j}) c_i^\dagger c_j - E_p \sum_i \hat{n}_i + \frac{1}{2}\sum_{i,j} v_{ij} c_i^\dagger c_j^\dagger c_j c_i + \sum_{\mathbf{q}} \omega_{\mathbf{q}} (d_{\mathbf{q}}^\dagger d_{\mathbf{q}} + 1/2) \tag{15}$$

where

$$\hat{\sigma}_{ij} = T(\mathbf{m}-\mathbf{n})\delta_{s.s'} exp\left(\sum_{\mathbf{q}} [u_i(\mathbf{q}) - u_j(\mathbf{q})] d_{\mathbf{q}} - h.c.\right) \tag{16}$$

is the new hopping integral depending on the phonon variables,

$$v_{ij} = V_c(\mathbf{m}-\mathbf{n}) - 2\sum_{\mathbf{q}} \omega_{\mathbf{q}} \left(u_i(\mathbf{q}) u_j^*(\mathbf{q})\right) \tag{17}$$

is the polaron-polaron interaction comprising the direct Coulomb repulsion V_c and the attraction via a *nonretarded* lattice deformation (second term in Eq.(17)). In the extreme strong-coupling limit $\lambda \to \infty$ one can neglect the hopping term of the transformed Hamiltonian. The rest has analytically determined eigenstates and eigenvalues. The eigenstates $|\tilde{N}\rangle = |n_i, n_{\mathbf{q}}\rangle$ are classified with the polaron $n_{\mathbf{m},s}$ and phonon $n_{\mathbf{q}}$ occupation numbers and the energy levels are:

$$E = (T(0) - E_p - \mu)\sum_i n_i + \frac{1}{2}\sum_{i,j} v_{ij} n_i n_j + \sum_{\mathbf{q}} \omega_{\mathbf{q}} (n_{\mathbf{q}} + 1/2) \tag{18}$$

where $n_i = 0, 1$ and $n_{\mathbf{q}} = 0, 1, 2, 3, ...\infty$. The interaction term does not include the on-site interaction $i = j$ for parallel spins because of the Pauli principle. The polaronic (Franck-Condon) level shift is expressed in a general form independent on the type of phonons in Eq.(9).

Thus we conclude that the Hamiltonian Eq.(10) in zero order of the hopping describes localized polarons and independent phonons which are vibrations of ions relative to new equilibrium positions depending on the polaron occupation numbers. The phonon frequencies remain unchanged in this limit[27, 18]. The middle of the electronic band $T(0)$ falls down by E_p as a result of a potential well produced by the lattice deformation due to the self-trapping.

With the finite hopping term polarons tunnel in a narrow band because of the degeneracy of the zero order Hamiltonian relative the site position of a single polaron in a regular lattice. To show this self-consistently one can apply perturbation theory using $1/\lambda$ as a small parameter. Because of the degeneracy terms of the first order in $T(\mathbf{m})$ should be included in a zero order Hamiltonian H_0:

$$H_0 = \sum_{i,j}(\sigma(\mathbf{m}-\mathbf{n}) - \mu\delta_{i,j})c_i^\dagger c_j + \sum_{\mathbf{q}} \omega_{\mathbf{q}}(d_{\mathbf{q}}^\dagger d_{\mathbf{q}} + 1/2) \tag{19}$$

where

$$\sigma(\mathbf{m}-\mathbf{n}) = \langle\langle \hat{\sigma}_{ij} \rangle\rangle = T(\mathbf{m}-\mathbf{n})\delta_{s,s'} exp[-g^2(\mathbf{m}-\mathbf{n})] \tag{20}$$

is the hopping integral averaged with the phonon equilibrium distribution. It is calculated by the use of the relation

$$e^{A+B} = e^A e^B e^{-[AB]/2}, \tag{21}$$

For zero temperature one obtains

$$\begin{aligned} \sigma(\mathbf{m}-\mathbf{n}) &= T(\mathbf{m}-\mathbf{n}) e^{-g^2(\mathbf{m}-\mathbf{n})} \\ &\times \langle 0| exp\left[-\sum_{\mathbf{q}} [u_i^*(\mathbf{q}) - u_j^*(\mathbf{q})] d_{\mathbf{q}}^\dagger \right] exp\left[\sum_{\mathbf{q}} [u_i(\mathbf{q}) - u_j(\mathbf{q})] d_{\mathbf{q}} \right] |0\rangle, \end{aligned} \tag{22}$$

where

$$g^2(\mathbf{m}-\mathbf{n}) = \frac{1}{2}\sum_{\mathbf{q}} \left(|u_i(\mathbf{q})|^2 + |u_j(\mathbf{q})|^2 - 2u_i^*(\mathbf{q})u_j(\mathbf{q}) \right). \tag{23}$$

The bracket is equalto unity for $T = 0$. The straightforward generalization for finite temperatures [16, 30] yields

$$g^2(\mathbf{m}) = \frac{1}{2N}\sum_{\mathbf{q}} |\gamma(\mathbf{q})|^2 coth\left(\frac{\omega_{\mathbf{q}}}{2T}\right)[1 - cos(\mathbf{q}\cdot\mathbf{m})]. \tag{24}$$

Earlier we have shown [28] by the numerical diagonalization of a finite site Holstein model that the expression for the polaron bandwidth, Eq.(20) is valid for the nonadiabatic and intermediate regime $\omega \geq D$ for *all* coupling strength. In the adiabatic case important corrections appear. However, the main exponential term remains almost the same in the strong coupling regime, $\lambda >> 1$. As a result of this brief recourse to the multi-polaron theory, one can conclude that the major effect of high-frequency phonons is the reduction of the bandwidth and of the Coulomb repulsion. While optical phonons cannot overscreen the repulsion they reduce

its value significantly. Then the acoustical and and low-frequency molecular modes provide a net attraction.

It was argued by one of us [24] that the polaron band narrowing can provide a high value of T_c because of the enhancement of the density of states. This enhancement does not depend on the particular choice of the electron-phonon interaction contrary to the enhancement of T_c due to the vertex corrections [23]. The latter can be obtained only if the electron-phonon scattering is dominated by small momentum transfer $q \ll q_D$. A simple estimate of the screening radius in doped fullerenes and cuprates yields a value of the order or even less than the lattice constant. Therefore, a long-range electron-phonon interaction is ruled out by screening, which makes the positive effect of the vertex corrections quite unrealistic [29].

4 PES and bare electron-phonon interaction

Because of the diversity in the theoretical results for electron-phonon interaction the coupling strength can be unambiguously determined only from the experiment. Allowing a small shift of the phonon frequencies due to screening the coupling with the intraball modes are expected to be the same in doped fullerenes as in the C_{60}^{-n} molecule. The recent photoemission spectroscopy of a molecule C_{60}^{-} [10] allows us to estimate the relative contribution of different phonon modes and other bosonic excitations to the interaction.

In this section we analyze the PES data [10] using the exact polaronic diagonalization with respect to the $A_g(2)$ mode and introducing the $polaron-exciton$ coupling. We obtain the strongest coupling with the high-lying $A_g(2)$ pinch mode and with a Frenkel-type exciton. As a result we provide a strong evidence for the nonadiabatic coupling with high-energy bosonic excitations in M_xC_{60}.

The Hamiltonian at hand, describing three degenerate t_{1u} states coupled with phonons, is diagonalized with respect to the A_{g2} coupling using the canonical Lang-Firsov displacement transformation as described above. The result is

$$\tilde{H} = e^S H e^{-S} = -E_p^{A_{g2}} \sum_{m=1}^{3} \psi_m^\dagger \psi_m + \sum_{\nu=1}^{8} g^\nu \omega_\nu \sum_{n,m=1}^{3} \psi_n^\dagger M_{nm}^\nu \psi_m + \sum_{\nu}^{8} \sum_{\mu=1}^{5} \omega_\nu n_{\nu,\mu}, \qquad (25)$$

where $E_p^{A_{g2}} = g^2 \omega_{A_{g2}}$ is the polaron shift due to the A_{g2} mode, 3×3 dimensionless matrix $\hat{M}$

is taken from ref.[30]

$$\hat{M} = \begin{pmatrix} \sqrt{3}Q_4 + Q_5 & \sqrt{3}Q_1 & \sqrt{3}Q_2 \\ \sqrt{3}Q_1 & -\sqrt{3}Q_4 + Q_5 & \sqrt{3}Q_3 \\ \sqrt{3}Q_2 & \sqrt{3}Q_3 & -2Q_5 \end{pmatrix},$$

and $n_{\nu,\mu}$ are the phonon occupation numbers of eight five-degenerate H_g modes with the phonon operators $Q^{\nu}_{\mu} = d^{\dagger}_{\nu,\mu} + d_{\nu,\mu}$. The interaction with H_g modes is responsible for the dynamic Jahn-Teller effect in C_{60}. According to calculations [31] singly ionised C^{-}_{60} is in the intermediate coupling regime, while the doubly and triple ionised molecules are in the strong coupling limit with respect to the coupling with H_g modes. Therefore a reasonable estimate of the ground state energy is obtained by taking into account only diagonal part of $\hat{M}$. Nevertheless, to avoid any ambiguity we calculated the spectral function $I_{pol}(\omega)$ of the Hamiltonian, Eq.(25) by the exact numerical diagonalisation in truncated Hilbert space (up to 4 phonons) for the H_g modes as described in ref.[28]. A self-trapped exciton in neutral C_{60} was observed and discussed by several authors [32, 33, 34]. Because of the polaron-exciton coupling we add the same spectral function to the total spectral density shifted by the exciton energy ω_{ex}, and multiplied by the polaron-exciton coupling constant g^2_{ex} as

$$I(\omega) = I_{pol}(\omega) + g^2_{ex} I_{pol}(\omega + \omega_{ex}). \tag{26}$$

This is an exact procedure if the interaction with excitons is linear as with phonons. Then we integrate $I(\omega)$ with the Gaussian instrumental resolution function of width $\sim 41meV$ [10] taking into account the damping γ_{ex} of the exciton in the second (excitonic) contribution with the substitution $\omega_{ex} \rightarrow \omega_{ex} + i\gamma_{ex}$. We thus can fit the PES in a wide energy region as shown in Fig.2 with g^{ν} being the fitting parameters (inset). The polaron-exciton coupling constant is found to be $g^2_{ex} = 0.5$, the exciton energy $\omega_{ex} \simeq 0.5eV$ in agreement with the luminescent data [32]. The inverse exciton lifetime is estimated to be $\gamma_{ex} \simeq 580cm^{-1}$. The coupling to the $A_g(2)$ mode turns out most important in agreement with the tight-binding calculations [3] and with the doping dependence of the phonon frequencies and the Raman linewidths. The $A_g(2)$ mode shows a clear shift with doping from $1467cm^{-1}$ in undoped C_{60} to $1446cm^{-1}$ in K_3C_{60} and to $1431cm^{-1}$ in K_6C_{60}. The linewidth increases by $\sim 3cm^{-1}$ in the metallic state (K_3C_{60}) and comes back to the value of C_{60} with further doping in an insulator K_6C_{60}. At

the same time high frequency $H_g(7,8)$ modes also show large broadening in the metallic state. However, Na_xC_{60}, which does not exhibit metallic state with doping, shows the same strong line broadening and the bleaching of the $H_g(7,8)$ modes [35]. Consequently, the broadening of phonon lines does not provide information about the electron-phonon coupling. Moreover, as has been pointed by Gelfand [36] $A_g(2)$ mode cannot decay into electron-hole pair, no mater how strong the electron-phonon coupling is. This decay is prohibited by the conservation of the energy because the estimated half-bandwidth is below the $A_g(2)$ frequency. We believe that an increase of the linewidth of H_g modes in the metallic phase is associated with the crystal field splitting of the five-fold degenerate mode. If this splitting is not very large it may result in an increase of the Raman linewidth. Therefore, the large broadening of H_g modes does not contradict to our conclusion that their coupling with the electron is weak.

In general, an estimate of the electron-phonon coupling constants from the Raman and neutron scattering using the canonical theory of metals may be inconclusive since doped fullerides are not conventional metals. In particular, the Migdal "theorem" can not be applied.

5 Polaron theory of T_c

It follows from the PES analyses that the frequencies of essential bosonic excitations (phonons and excitons) strongly coupled with electrons ($g \sim 0.6$) are above or of the same order as the electron half-bandwidth in doped fullerenes. This fact as well as the observation of the phonon and exciton-sided bands in PES by itself favor the nonadiabatic small polaron theory [4] rather than the adiabatic Migdal-Eliashberg approach to M_xC_{60}. On the other hand the total contribution of intermediate and low-frequency modes is not negligible, while their individual coupling is relatively weak ($g \leq 0.3$). This allows us to treat these modes within the Migdal-Eliashberg approximation by the use of the Eliashberg function

$$\alpha^2 F(\Omega) = \frac{1}{2} \sum_{\nu=1}^{8} \lambda_\nu \omega_\nu \delta(\Omega - \omega_\nu) \tag{27}$$

where $\nu = 1, ...8$ is the sum over 8 H_g modes with

$$\lambda_\nu = \frac{20}{3} \cdot g_\nu^2 \omega_\nu N(0), \tag{28}$$

and g_ν, ω_ν from the inset in Fig.2. The additional coefficient 10 in the partial λ_ν appears due to the five-fold degeneracy and the nondiagonal terms in the matrix $\hat{M}$ as explained in ref. [8]. At the same time the strong nonadiabatic interaction with the pinch mode is fully taken into account by the renormalization of the halfbandwidth D as

$$W = De^{-g^2} \tag{29}$$

and by the reduction of the bare Coulomb repulsion as

$$\tilde{V}_c = V_c - 2g^2\omega_{A_{g2}}. \tag{30}$$

The excitonic contribution is taken into account via the high-frequency dielectric constant ϵ. Because of the covalent nature of C_{60} molecules we do not expect any significant dispersion of ϵ, which is estimated as $\epsilon \simeq 4.4$ [37]. In a solid the exciton frequency ω_{ex} appears to be rather close to the fundamental gap $\sim 2eV$. Therefore, we assume that the excitonic effect on the bandwidth is included in the LDA density of states (DOS) $N(0) = 1/2D$. In the following we take into account the polaron band narrowing due to the coupling with the pinch mode only. A possibility remains that we overestimate this coupling at the expense of the coupling with the two high-frequency H_g modes as discussed by Gunnarsson *et al* [10]. If so, one should also include the contribution of these two modes in the polaron band narrowing and in the reduction of the Coulomb repulsion by a simple redifinition of the high-frequency coupling constant g.

With $g^2\omega_{A_{g2}} \simeq 0.06eV$ (inset Fig.2) we obtain the lowering of the Coulomb repulsion by about $0.12eV$. By the use of the Coulomb law, the dielectric constant $\epsilon \simeq 4.4$ and the lattice constant $a \simeq 14\mathring{A}$ we estimate *intracell* bare repulsion as $V_c \simeq 0.25eV$. This value is in agreement with the binding exciton energy in solid C_{60} [35]. As a result, the residual repulsion is estimated as $0.13eV$. The polaron density of states determined as

$$N_p(0) = N(0)e^{g^2} \tag{31}$$

appears to be about $N_p(0) \simeq 9 states/eV spin$ if the bare density $N(0) \simeq 6.6 states/eV spin$ according to some LDA calculations for K_3C_{60} [3]. Because different LDA calculations yield rather different values of the bare $N(0)$ from 6.6 up to $12.5 states/eV spin$ [36] the

polaronic density can be in the range from $9 states/eV spin$ up to about $17 states/eV spin$. These values of the polaron density of states are compared with those measured with NMR ($17 states/eV spin$), thermopower ($14 states/eV spin$), and magnetic susceptibility ($14 states/eV spin$)[2], and estimated from the heat capacity jump and ESR ($\sim 10 states/eV spin$) for K_3C_{60}. We note that different from the ordinary metals the polaron heat capacity and the Pauli susceptibility are renormalized by the same amount in the polaronic system[4]. By taking $6.6 states/eV spin$ as the bare total DOS of three degenerate bands we estimate the bare intraband Coulomb pseudopotential as

$$\mu = \frac{1}{3} N(0) V_c = 0.55, \tag{32}$$

and the renormalized one as

$$\mu^* = \frac{1}{3} N_p(0) \tilde{V}_c = 0.4. \tag{33}$$

Now we are prepared to solve the Eliashberg equations for T_c:

$$\begin{aligned} Z(\omega_n) &= 1 + 8T \frac{N_p(0)}{N(0)} \sum_{\omega_{n'}>0} \omega_{n'} tan^{-1} \left(\frac{W}{2\omega_{n'} Z(\omega_{n'})} \right) \\ &\times \int_0^\infty d\Omega \alpha^2 F(\Omega) \frac{2\Omega}{((\omega_{n'} - \omega_n)^2 + \Omega^2)\,((\omega_{n'} + \omega_n)^2 + \Omega^2)}, \end{aligned}$$

$$\begin{aligned} \Delta(\omega_n) &= \frac{T}{Z(\omega_n)} \sum_{\omega_{n'}} \frac{2\Delta(\omega_{n'})}{\omega'_n} tan^{-1} \left(\frac{W}{2\omega_{n'} Z(\omega_{n'})} \right) \\ &\times \left[\frac{N_p(0)}{N(0)} \int_0^\infty d\Omega \alpha^2 F(\Omega) \frac{2\Omega}{(\omega_{n'} - \omega_n)^2 + \Omega^2} - \mu^* \right] \end{aligned} \tag{34}$$

First we show the normal DOS $\tilde{N}(E)$ in Fig.3 calculated with the analytical continuation of the normal state self-energy ($\sim Z - 1$) to real frequencies. $\tilde{N}(E)$ takes into account the finite bandwidth,the band narrowing effect and scattering by low-frequency phonons. these results in drastic changes of the renormalized DOS compared with the initial DOS. The latter is taken energy independent for simplicity.

The result for T_c is

$$T_c = 20K, \tag{35}$$

for K_3C_{60}, and

$$T_c = 35K, \tag{36}$$

for Rb_3C_{60}. These values are obtained with the Eliashberg function, Eq.(27) and with the bare (LDA) DOS $N(0) = 6.6 states/eV spin$ and $N(0) = 7.5 states/eV spin$ for K_3C_{60} and Rb_3C_{60}, respectively.

Assuming the inverse square root dependence of all intraball frequencies on the carbon mass and the square root dependence of g_ν^2 we calculate the isotope effect. Normally, in the polaronic superconductor the isotope exponent $\alpha = -d\ln(T_c)/d\ln(M)$ is negative because of the increase of the polaronic density of states with the increase of the ion mass M ($g^2 \sim \sqrt{M}$ in Eq.(31)) [38]. However, the usual positive contribution to α from low-frequency modes can change its sign, which is indeed the case here. By the use of the Eliashberg equations with the *isotope mass dependent* polaronic DOS, Eq.(31) we obtain

$$\alpha = 0.27 \tag{37}$$

for K_3C_{60}, and

$$\alpha = 0.31 \tag{38}$$

for Rb_3C_{60}. These values are rather close to those reported in the literature [3].

Finally, we calculate the dependence of T_c on pressure P assuming that only hopping integrals depend on pressure. In that case the polaronic halfbandwidth W has the same pressure dependence as the bare one, which according to ref. [39] is described by

$$W(P) = W(0) exp\left(\frac{5P}{K}\right), \tag{39}$$

with the elastic modulus $K \simeq 24.5 GPa$ [40]. Solving the Eliashberg equations with the pressure dependent bare and polaronic bandwidth we arrive with the curve of Fig.4, which agrees well with the available experimental data.

6 Conclusion

A simple estimate of the characteristic energy scale of phonons and electrons in M_xC_{60} clearly shows that the canonical Migdal-Eliashberg theory should be modified to include the polaronic nonadiabatic effects. As discussed in the beginning of the paper the polaron collapse of the band is the consequence of the broken translation symmetry and has nothing to do with

the vertex corrections. The polaron band narrowing represents a universal origin of the high T_c value. We argue that the high-temperature superconductivity of doped fullerenes is an example of the nonadibatic polaronic superconductivity discussed by one of us earlier [24]. In that regime the polaron halfbandwidth is below the characteristic phonon frequency but still above the effective attraction between polarons. Therefore, the canonical BCS-Migdal-Eliashberg theory can be applied with the finite polaronic bandwidth and reduced Coulomb repulsion. The high frequency bosonic excitations play an important role reducing the bandwidth and the repulsion. They can be integrated out with the canonical displacement transformation, while the interaction with the low-frequency modes is still described by the Eliashberg equations. As a result our theory gives the experimentally observed values of T_c, the isotope and pressure effects in M_xC_{60} with the realistic coupling constants based on the PES data, the Coulomb law and common sense.

Our calculated polaron halfbandwidth is about $W \simeq 150meV$, or less, Fig.3. The total contribution of all vibration modes to the attraction is $2E_p^{total} \simeq 330meV$ (insert in Fig.2). As a result the attractive interaction between two small polarons is estimated as $\Delta = 2E_p - V_c \simeq 80meV$. The condition $W \geq \Delta$, necessary for the Fermi-liquid approach seems to be satisfied. However, the system is very close to the bipolaronic instability $\Delta > W$ with the 2e Bose-liquid ground state. The final answer on the nature of the ground state remains with the experiment. The hallmarks of small bipolarons are those of small polarons, plus

- superfluid phase transition similar to that of He^4,

- spin gap in the magnetic susceptibility, that is $\chi_s \to 0$ at $T \to 0$ if a singlet is the ground state, and the absence of the Hebel-Slichter peak in the NMR,

- electrodynamics of the charged Coulomb Bose gas with the divergent $H_{c2}(T)$,

- double elementary charge $2e$ in the normal state.

The first three features are clearly observed in doped cuprates [4]. The upward $H_{c2}(T)$ curvature near T_c is measured also in M_xC_{60} as discussed in Ref.[42, 3].

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Figures

Fig. 1 Self-energy in Migdal's approximation.

Fig. 2 Polaron theory fit (full line) to the experimental PES (dashed line). Frequencies $\omega = \omega_\nu$, coupling constants $g = g^\nu$, and the contribution to the ground state energy $E = E_p^\nu$ for different modes are shown in the inset. For comparison we also show the coupling constants (g(Gun), inset) and the calculated variations PES (dotted line) of ref.[10].

Fig. 3 Polaron density of states in K_3C_{60}. The bare DOS is shown with the dashed line.

Fig. 4 Pressure dependence of T_c for K_3C_{60} and Rb_3C_{60} [41] compared with the theory.