

Symmetry of superconductivity in $\text{NH}_3\text{K}_3\text{C}_{60}$ superconductors: nonadiabatic effects in multiband systems

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We have studied effects of nonadiabatic electron-intramolecular-vibration couplings on superconductivity in a multiband system of fullerenes. The self-energy of the anomalous Green function was studied. Corrections to the Migdal approximation were taken into account for both the intraband and the interband couplings. While the nonadiabatic corrections to the intraband couplings favor anisotropic superconductivity, the corrections to the interband couplings favor isotropic superconductivity. This raises the theoretical possibility of the change of superconducting pairing symmetry close to the boundary between the superconducting and the antiferromagnetic phases of $\text{NH}_3\text{K}_3\text{C}_{60}$ family of fullerenes where lifting of the degeneracy of the t_{1u} bands is expected.

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I. INTRODUCTION

The discovery and the development of mass production processes of the C_{60} molecule have opened up various opportunities for material science and nanotechnology. The molecular aggregates composed of C_{60} , sometimes called fullerenes, exhibit distinct properties such like high- T_c superconductivity and high- T_c ferromagnetism.¹ High photoconductivity may be useful for the industrial use. Some proposals have been made to use the molecule as a molecular device such as a molecular actuator, which may promote applications of the molecule in nanotechnology as well as its cousin carbon nanotube.

The superconductivity observed in doped C_{60} has attracted much attention from the first discovery because of its highest critical temperature among organic superconductors. Characteristics of this material are the narrow bandwidth owing to the large intermolecular separation and the overlapping bands crossing the Fermi level E_F , which comes from the degeneracy of the t_{1u} lowest unoccupied molecular orbitals (LUMO's) of the molecule.¹⁻³

The electron-intramolecular-vibration (e -MV) couplings have turned out to play the most important role in the mechanism of superconductivity in this family of materials. This conclusion was enforced by agreements between theoretical calculations, inelastic neutron scattering experiments, and Raman spectroscopic experiments on the mode specificity of the carrier-induced broadenings and shifts of phonon bands.^{1,4-7} The interband e -MV coupling constant originating from the kinetic energy exchange between molecular vibrations and electrons beyond the Born-Oppenheimer (BO) approximation and the standard intraband Holstein e -MV coupling constant have been estimated and were found to be relatively large.^{4,5,8} Moreover, the ratio between the phonon frequency and the bandwidth ω/W is not negligible. Vertex corrections beyond the Migdal approximation are not negligible in this system.⁹ We have to take into account all of these features.

Recently much progress has been made on the experimen-

tal research of antiferromagnetism and superconductivity observed in $\text{NH}_3\text{K}_3\text{C}_{60}$.¹⁰⁻¹² The phase transition between them may be accompanied by symmetry reduction of the crystal and subsequent lifting of the t_{1u} band degeneracy.¹³ The lifting of the degeneracy decreases the interband e -MV coupling constant.^{4,5} The ammonia-intercalated doped C_{60} is a suitable system to study details of the interband e -MV couplings.

II. THE e -MV MODEL

We start our model theory with the following molecular Hamiltonian:

$$H = \frac{p^2}{M} + V(q) + \int a^\dagger(r_1)h(r_1;q)a(r_1)dr_1 + \frac{1}{2} \int \int a^\dagger(r_1)a^\dagger(r_2)\frac{e^2}{r_{12}}a(r_2)a(r_1)dr_1dr_2, \quad (1)$$

where q , p , and M are normal coordinates of molecular vibration, nuclear momentum, and nuclear mass, respectively. The variables r_1 and r_2 denote the coordinate of electrons including the spin variables. $h(r_1;q)$ denotes the one-body term of electrons and e^2/r_{12} denotes the Coulomb repulsion between them. The annihilation operator $a(r_1)$ is defined by $a(r_1) = \sum_j \psi_j(r_1;q)c_j$, where c_j is annihilation operator of electrons defined on the orthonormalized molecular orbital ψ_j . In the BO approximation, ψ depends on q parametrically. As nuclei and electrons are independent particles, the following commutation relation should be satisfied:

$$[p, a] = 0. \quad (2)$$

On the other hand, p and c_j do not commute in the BO approximation:

$$[p, c_j] = -i \sum_i \left\langle \frac{\partial}{\partial q} \psi_j \middle| \psi_i \right\rangle c_i. \quad (3)$$

This noncommutation relation makes calculations difficult. This difficulty was removed by introducing the following function:¹⁴

$$X(r_1, r_2) \equiv \sum_k \frac{\partial}{\partial q} \psi_k(r_1) \psi_k^*(r_2), \quad (4)$$

and the recoil momentum operator

$$\pi \equiv -i \int \int a^\dagger(r_1) X(r_1, r_2) a(r_2) dr_1 dr_2. \quad (5)$$

With the help of relations

$$\int X(r_1, r_2) \psi_k(r_2) dr_2 = \frac{\partial}{\partial q} \psi_k(r_1), \quad (6a)$$

$$\int \psi_k^*(r_1) X(r_1, r_2) dr_1 = -\frac{\partial}{\partial q} \psi_k^*(r_2), \quad (6b)$$

we found the following relation is satisfied:

$$[\pi, c_j] = [p, c_j]. \quad (7)$$

If we define new nuclear momentum P by

$$P \equiv p - \pi, \quad (8)$$

then we observe that

$$[P, c_j] = 0. \quad (9)$$

The commutation relation between P and q is satisfied too. Now we have a set of canonical variables that has desirable commutation relations. If we use the new nuclear momentum P , the molecular Hamiltonian given by Eq. (1) is reformulated as follows:^{5,14}

$$\begin{aligned} H = & \frac{P^2}{M} + V(q) + \sum_{ij} \langle \psi_i | h | \psi_j \rangle c_i^\dagger c_j \\ & + \frac{1}{2} \sum_{ijkl} ([il|jk] - \{il|jk\}) c_i^\dagger c_j^\dagger c_k c_l \\ & + \frac{1}{2} \sum_{ij} i \left\langle \psi_i \left| \frac{\partial}{\partial Q} \psi_j \right. \right\rangle c_i^\dagger c_j \cdot i\sqrt{\omega/2}(b - b^\dagger) \\ & - \frac{1}{2} \sum_{ij} \left(\left\langle \frac{\partial}{\partial Q} \psi_i \left| \frac{\partial}{\partial Q} \psi_j \right. \right\rangle + \left\langle \psi_i \left| \frac{\partial^2}{\partial Q^2} \psi_j \right. \right\rangle \right) c_i^\dagger c_j, \end{aligned} \quad (10a)$$

$$[ij|kl] = \int \int \psi_i^*(r_1) \psi_j(r_1) \frac{e^2}{r_{12}} \psi_k^*(r_2) \psi_l(r_2) dr_1 dr_2, \quad (10b)$$

$$\{ij|kl\} = \left\langle \psi_i \left| \frac{\partial}{\partial Q} \psi_l \right. \right\rangle \left\langle \frac{\partial}{\partial Q} \psi_k \left| \psi_j \right. \right\rangle, \quad (10c)$$

where Q is the mass-weighted normal coordinate defined by $Q = \sqrt{M}q$ and ω is the molecular vibrational frequency. Equation (10) is the most convenient Hamiltonian to start

with the e -MV problem in multiband systems. On the basis of the previous arguments, doped C_{60} may be best described by the following model Hamiltonian proposed before:^{4,5}

$$H = H_0 + H_1, \quad (11a)$$

$$H_1 = H_{11} + H_{12}, \quad (11b)$$

$$\begin{aligned} H_0 = & \sum_{i=1}^n \epsilon_i^n n_i + \sum_i \sum_{l \neq m, \sigma} t_{lm}^i c_{i\sigma}^\dagger c_{im\sigma} + \sum_l \omega_l \left(b_l^\dagger b_l + \frac{1}{2} \right) \\ & + U_{11} + U_{12}, \end{aligned} \quad (11c)$$

$$H_{11} = \sum_i \sum_l g_l^n n_l (b_l + b_l^\dagger), \quad (11d)$$

$$H_{12} = \sum_{(ij)} \sum_{l\sigma} \{i \kappa_l^{ij} c_{i\sigma}^\dagger c_{j\sigma} (b_l - b_l^\dagger) + \text{H.c.}\}, \quad (11e)$$

$$U_{11} = \sum_i \sum_l u_l^{ii} n_l^\uparrow n_l^\downarrow, \quad (11f)$$

$$U_{12} = \sum_{i \neq j} \sum_l u_l^{ij} n_l^i n_l^j, \quad (11g)$$

where $c_{i\sigma}^\dagger$ and b_l^\dagger are creation operators of electrons with σ spin on the l th site of the i th band and of molecular vibrational bosons on the l th site, respectively. ϵ_i , t_{lm}^i , g_l^i , and κ_l^{ij} are the site energy of the i th band, the transfer integral of the i th band, the intraband e -MV coupling constant of the i th band and the interband e -MV coupling constant between the i th and the j th bands, respectively. H_{11} and H_{12} are the intraband and the interband e -MV couplings.⁵ U_{11} and U_{12} are the intraband and the interband Coulomb repulsions, respectively. H_1 is the perturbation in our e -MV model.

III. CORRECTIONS TO THE MIGDAL APPROXIMATION FOR THE INTRABAND AND INTERBAND e -MV COUPLINGS

We start our perturbation calculations with the Dyson equation for the normal and the anomalous Green functions:¹⁵

$$\begin{aligned} G(p) = & G^{(0)}(p) + G^{(0)}(p) \tilde{\Sigma}_N(p) G(p) \\ & - G^{(0)}(p) \tilde{\Sigma}_S(p) F^\dagger(p), \end{aligned} \quad (12)$$

$$F(p) = G^{(0)}(p) \tilde{\Sigma}_S(p) G(-p) + G^{(0)}(p) \tilde{\Sigma}_N(p) F(p). \quad (13)$$

G and $G^{(0)}$ are full and the noninteracting single-particle normal Green functions and $\tilde{\Sigma}_N$ is its self-energy. F is the anomalous Green function and $\tilde{\Sigma}_S$ is its self-energy. p is the four-dimensional momentum $p = (i\omega_p, \vec{p})$, where $i\omega_p$ is the

Matsubara frequency for fermions. We neglect $|\tilde{\Sigma}_S(p)|^2$ closely below the superconducting critical temperature T_c such that¹⁶

$$F(p) \simeq G(-p)\tilde{\Sigma}_S(p)G(p). \quad (14)$$

The self-energy for the anomalous Green function is then given by

$$\tilde{\Sigma}_S(p) = \sum_k V_S(p,k)G_1(k)G_1(-k)\tilde{\Sigma}_S(k), \quad (15)$$

where the potential for the Cooper pair V_S may be given as follows:

$$V_S(p,k) = V_{S,a}(p,k) + V_{S,n}(p,k). \quad (16)$$

$V_{S,a}$ and $V_{S,n}$ are the intraband and the interband contributions to the potential. We also assume for simplicity that the number of overlapping bands close to the Fermi level is two. To simplify our argument further, only the potential for the Cooper pair in the band 1 will be discussed hereafter. G_1 denotes the normal Green function for band 1. The intraband contribution to the potential may be given as a sum of the polarization and the cross diagrams:¹⁶

$$V_{S,a}(p,k) = V_a(p-k)\{1 + 2P_a(p,k)\} + C_a(p,k). \quad (17)$$

$P_a(p,k)$ is the intraband contribution from the polarization diagram,

$$P_a(p,k) = \sum_q V_a(p-q)G_1(q-p+k)G_1(q), \quad (18)$$

and $C_a(p,k)$ is that from the cross diagram,

$$C_a(p,k) = \sum_q V_a(p-q)V_a(q-k)G_1(q)G_1(q-p-k). \quad (19)$$

The interband contribution to the potential may be given as a sum of the polarization and the two cross diagrams:

$$V_{S,n}(p,k) = 2V_b(p-k)P_n(p,k) + C_{1n}(p,k) + C_{2n}(p,k). \quad (20)$$

$P_n(p,k)$ is the interband contribution from the polarization diagram,

$$P_n(p,k) = \sum_q V_n(p-q)G_2(q-p+k)G_2(q), \quad (21)$$

and $C_{1n}(p,k)$ and $C_{2n}(p,k)$ are the two distinct interband contributions from the cross diagrams,

$$C_{1n}(p,k) = \sum_q V_n(p-q)V_n(q-k)G_2(q)G_2(-q), \quad (22)$$

$$C_{2n}(p,k) = \sum_q V_n(p-q)V_n(q-k)G_2(q)G_2(q-p-k). \quad (23)$$

To derive working formulas, we substitute the noninteracting electron Green function; $G_i^{(0)}(k) = 1/[i\omega_k - \epsilon_i(\vec{k})]$, where $\epsilon_i(\vec{k})$ denotes the band dispersion of the i th band in place of the full Green function G_i . The bare potentials are given by $V_a(k-k') = g_1(\vec{k}-\vec{k}')^2\tilde{D}(k-k')$, $V_b(k-k') = g_1(\vec{k}-\vec{k}') \times g_2(\vec{k}-\vec{k}')\tilde{D}(k-k')$, $V_n(k-k') = \kappa(\vec{k}-\vec{k}')^2(-1)\tilde{D}(k-k')$, where $\tilde{D}(q)$ is the phonon Green function; $\tilde{D}(q) = -\omega_0^2/(\omega_0^2 + \omega_q^2)$ and $g_i(\vec{q})$ and $\kappa(\vec{q})$ are the intraband e -MV coupling constant of the i th band and the interband e -MV coupling constant, respectively. The summation over the four-dimensional momentum should be read as $\sum_k = -(1/\beta)\sum_{\omega_k}\sum_{\vec{k}}$. The intraband contributions $P_a(p,k)$ and $C_a(p,k)$ are now given as follows:

$$P_a(p,k) = \frac{\omega_0}{2} \frac{1}{N} \sum_{\vec{q}} \frac{g_1(\vec{p}-\vec{q})^2}{\epsilon_1(\vec{q}) - \epsilon_1(\vec{q}-\vec{p}+\vec{k}) - i(\omega_p - \omega_k)} \left\{ \frac{n_F(\epsilon_1(\vec{q})) + n_B(-\omega_0)}{\epsilon_1(\vec{q}) - i\omega_p + \omega_0} - \frac{n_F(\epsilon_1(\vec{q})) + n_B(\omega_0)}{\epsilon_1(\vec{q}) - i\omega_p - \omega_0} \right. \\ \left. - \frac{n_F(\epsilon_1(\vec{q}-\vec{p}+\vec{k})) + n_B(-\omega_0)}{\epsilon_1(\vec{q}-\vec{p}+\vec{k}) - i\omega_k + \omega_0} + \frac{n_F(\epsilon_1(\vec{q}-\vec{p}+\vec{k})) + n_B(\omega_0)}{\epsilon_1(\vec{q}-\vec{p}+\vec{k}) - i\omega_k - \omega_0} \right\}, \quad (24)$$

and

$$C_a(p,k) = \frac{\omega_0^3}{2} \frac{2\omega_0 + i\omega_p + i\omega_k}{(\omega_p - \omega_k)^2 + 4\omega_0^2} \frac{1}{N} \sum_{\vec{q}} \frac{g_1(\vec{p}-\vec{q})^2 g_1(\vec{q}-\vec{k})^2}{\epsilon_1(\vec{q}) - \epsilon_1(\vec{q}-\vec{p}-\vec{k}) - i(\omega_p + \omega_k)} \left\{ \frac{\lambda_1 n_F(\epsilon_1(\vec{q})) + \alpha_1 n_B(\omega_0)}{[\epsilon_1(\vec{q}) - i\omega_p - \omega_0][\epsilon_1(\vec{q}) - i\omega_k - \omega_0]} \right. \\ \left. - \frac{\lambda_1 n_F(\epsilon_1(\vec{q})) + \beta_1 n_B(-\omega_0)}{[\epsilon_1(\vec{q}) - i\omega_p + \omega_0][\epsilon_1(\vec{q}) - i\omega_k + \omega_0]} - \frac{\lambda_2 n_F(\epsilon_1(\vec{q}-\vec{p}-\vec{k})) + \alpha_2 n_B(\omega_0)}{[\epsilon_1(\vec{q}-\vec{p}-\vec{k}) + i\omega_p - \omega_0][\epsilon_1(\vec{q}-\vec{p}-\vec{k}) + i\omega_k - \omega_0]} \right. \\ \left. + \frac{\lambda_2 n_F(\epsilon_1(\vec{q}-\vec{p}-\vec{k})) + \beta_2 n_B(-\omega_0)}{[\epsilon_1(\vec{q}-\vec{p}-\vec{k}) + i\omega_p + \omega_0][\epsilon_1(\vec{q}-\vec{p}-\vec{k}) + i\omega_k + \omega_0]} \right\}, \quad (25)$$

where

$$\begin{aligned}
\lambda_1 &= -\frac{4\omega_0^2 + (\omega_p - \omega_k)^2}{4\epsilon_1(\vec{q})^2 + (\omega_p + \omega_k)^2} \frac{2\epsilon_1(\vec{q}) + i\omega_p + i\omega_k}{2\omega_0 + i\omega_p + i\omega_k}, \\
\lambda_2 &= -\frac{4\omega_0^2 + (\omega_p - \omega_k)^2}{4\epsilon_1(\vec{q} - \vec{p} - \vec{k})^2 + (\omega_p + \omega_k)^2} \frac{2\epsilon_1(\vec{q} - \vec{p} - \vec{k}) - i\omega_p - i\omega_k}{2\omega_0 + i\omega_p + i\omega_k}, \\
\alpha_1 &= \frac{-2\epsilon_1(\vec{q}) + i\omega_p + i\omega_k}{2\omega_0 + i\omega_p + i\omega_k}, \quad \alpha_2 = \frac{-2\epsilon_1(\vec{q} - \vec{p} - \vec{k}) - i\omega_p - i\omega_k}{2\omega_0 + i\omega_p + i\omega_k}, \\
\beta_1 &= \frac{2\epsilon_1(\vec{q}) + 4\omega_0 - i\omega_p - i\omega_k}{2\omega_0 + i\omega_p + i\omega_k}, \quad \beta_2 = \frac{2\epsilon_1(\vec{q} - \vec{p} - \vec{k}) + 4\omega_0 + i\omega_p + i\omega_k}{2\omega_0 + i\omega_p + i\omega_k}.
\end{aligned} \tag{26}$$

n_F and n_B denote fermionic and bosonic distribution functions, respectively. The interband contributions $P_n(p, k)$ and $C_{2n}(p, k)$ are given simply by replacing g_1 and ϵ_1 by κ and ϵ_2 in Eqs. (24), (25), and (26), respectively. The interband contribution to the cross diagram $C_{1n}(p, k)$ is given as follows:

$$\begin{aligned}
C_{1n}(p, k) &= \frac{\omega_0^3}{4} \frac{2\omega_0 + i\omega_p + i\omega_k}{(\omega_p - \omega_k)^2 + 4\omega_0^2} \frac{1}{N} \sum_{\vec{q}} \frac{\kappa(\vec{p} - \vec{q})^2 \kappa(\vec{q} - \vec{k})^2}{\epsilon_2(\vec{q})} \left\{ \frac{\eta_1 n_F(\epsilon_2(\vec{q})) + \zeta_1 n_B(\omega_0)}{[\epsilon_2(\vec{q}) - i\omega_p - \omega_0][\epsilon_2(\vec{q}) - i\omega_k - \omega_0]} \right. \\
&\quad - \frac{\eta_2 n_F[-\epsilon_2(\vec{q})] + \zeta_2 n_B(\omega_0)}{[\epsilon_2(\vec{q}) + i\omega_p + \omega_0][\epsilon_2(\vec{q}) + i\omega_k + \omega_0]} + \frac{\eta_2 n_F(-\epsilon_2(\vec{q})) + \nu_1 n_B(-\omega_0)}{[\epsilon_2(\vec{q}) + i\omega_p - \omega_0][\epsilon_2(\vec{q}) + i\omega_k - \omega_0]} \\
&\quad \left. - \frac{\eta_1 n_F(\epsilon_2(\vec{q})) + \nu_2 n_B(-\omega_0)}{[\epsilon_2(\vec{q}) - i\omega_p + \omega_0][\epsilon_2(\vec{q}) - i\omega_k + \omega_0]} \right\},
\end{aligned} \tag{27}$$

where

$$\begin{aligned}
\eta_1 &= \frac{4\omega_0^2 + (\omega_p - \omega_k)^2}{4\epsilon_2(\vec{q})^2 + (\omega_p + \omega_k)^2} \frac{2\epsilon_2(\vec{q}) + i\omega_p + i\omega_k}{2\omega_0 + i\omega_p + i\omega_k}, \quad \eta_2 = \frac{4\omega_0^2 + (\omega_p - \omega_k)^2}{4\epsilon_2(\vec{q})^2 + (\omega_p + \omega_k)^2} \frac{-2\epsilon_1(\vec{q}) + i\omega_p + i\omega_k}{2\omega_0 + i\omega_p + i\omega_k}, \quad \zeta_1 = \frac{2\epsilon_2(\vec{q}) - i\omega_p - i\omega_k}{2\omega_0 + i\omega_p + i\omega_k}, \\
\zeta_2 &= \frac{-2\epsilon_1(\vec{q}) - i\omega_p - i\omega_k}{2\omega_0 + i\omega_p + i\omega_k}, \quad \nu_1 = \frac{2\epsilon_2(\vec{q}) - 4\omega_0 + i\omega_p + i\omega_k}{2\omega_0 + i\omega_p + i\omega_k}, \quad \nu_2 = \frac{-2\epsilon_1(\vec{q}) - 4\omega_0 + i\omega_p + i\omega_k}{2\omega_0 + i\omega_p + i\omega_k}.
\end{aligned} \tag{28}$$

The self-energy of the normal Green function for the band 1 is given by

$$\tilde{\Sigma}_N(p) = \sum_k V_N(p, k) G_1(k). \tag{29}$$

Within the same approximation used in the previous arguments, only the intraband e -MV coupling has contributions to the potential $V_N(p, k)$:

$$V_N(p, k) = V_a(p - k) \{1 + P_a(p, k)\}. \tag{30}$$

The momentum integration in Eq. (29) may be simplified as follows:

$$\begin{aligned}
\tilde{\Sigma}_N(i\omega_p) &= -T \sum_k \int \frac{d^3k}{(2\pi)^3} \frac{V_N(p, k)}{i\omega_k - \epsilon_k - \tilde{\Sigma}_N(i\omega_k)} \\
&\simeq -TN_0 \sum_k \int_{-W/2}^{W/2} d\epsilon \frac{\langle V_N(p, k) \rangle}{i\omega_k Z(i\omega_k) - \epsilon},
\end{aligned} \tag{31}$$

where we have assumed that the real part of $\tilde{\Sigma}_N$ is negligible,

$$\tilde{\Sigma}_N(i\omega_n) = \chi(i\omega_n) + i\omega_n [1 - Z(i\omega_n)] \simeq i\omega_n [1 - Z(i\omega_n)], \tag{32}$$

and that the band structure is approximated by a box-shaped density of states. W is the bandwidth and the density of state takes a constant nonzero value N_0 only within the energy interval $-W/2 \leq \epsilon \leq W/2$. $\langle V_N(p, k) \rangle$ is the potential averaged over the Fermi surface:

$$\langle V_N(p, k) \rangle = \frac{\int \frac{d^3p}{(2\pi)^3} \frac{d^3k}{(2\pi)^3} \delta(\epsilon_p) \delta(\epsilon_k) V_N(p, k)}{\int \frac{d^3p}{(2\pi)^3} \frac{d^3k}{(2\pi)^3} \delta(\epsilon_p) \delta(\epsilon_k)}. \tag{33}$$

Justifications to these simplifications were discussed in Ref. 16. Using these simplifications, we have the following expression of the renormalization factor;

$$Z(i\omega_p) \simeq 1 - \frac{2N_0T}{\omega_p} \sum_{\omega_k} \langle V_N(i\omega_p, i\omega_k) \rangle \frac{\omega_k}{|\omega_k|} \\ \times \arctan \left\{ \frac{W}{2|\omega_k Z(i\omega_k)|} \right\}. \quad (34)$$

The momentum integration in Eq. (15) may also be approximated as follows;

$$\tilde{\Sigma}_S(i\omega_p) = -T_c \sum_k \int \frac{d^3k}{(2\pi)^3} \frac{V_S(p, k)}{i\omega_k - \epsilon_k - \tilde{\Sigma}_N(i\omega_k)} \\ \times \frac{\tilde{\Sigma}_S(i\omega_k)}{-i\omega_k - \epsilon_k - \tilde{\Sigma}_N(-i\omega_k)}, \\ \simeq -2N_0T_c \sum_{\omega_k} \langle V_S(i\omega_p, i\omega_k) \rangle \frac{\Delta(i\omega_k)}{|\omega_k|} \\ \times \arctan \left\{ \frac{W}{2|\omega_k Z(i\omega_k)|} \right\}, \quad (35)$$

where $\Delta(i\omega_n) = \tilde{\Sigma}(i\omega_n)/Z(i\omega_n)$ is the superconducting order parameter. Equations (34) and (35) form the coupled gap equations, which correspond to the Eliashberg equation if we neglect our corrections to the Migdal approximation. In the theory of superconductivity, most of the Coulomb repulsion effects are supposed to be renormalized into the band structure and the residual Coulomb repulsion effect is taken into account in the gap equation.¹⁷ We simplify our argument by setting $u_i^j = U\delta_{ij}$, where U is the intraband residual Coulomb repulsion that should result from static screening processes. The retardation effect is taken into account by introducing the following pseudo-Coulomb potential,

$$U^*(i\omega_p, i\omega_k) = U^* \frac{\omega_0^2}{(\omega_p - \omega_k)^2 + \omega_0^2}, \quad (36)$$

in the gap equation

$$\Delta(i\omega_p)Z(i\omega_p) \simeq -2N_0T_c \sum_{\omega_k} \langle V_S(i\omega_p, i\omega_k) \\ + U^*(i\omega_p, i\omega_k) \rangle \frac{\Delta(i\omega_k)}{|\omega_k|} \\ \times \arctan \left\{ \frac{W}{2|\omega_k Z(i\omega_k)|} \right\}. \quad (37)$$

The pseudo-Coulomb potential U^* is derived by introducing two different frequency cutoffs into an equation to obtain the Coulomb self-energy. The cutoffs have the energy scales of valence electrons and phonons, W and ω_0 , respectively. U^* is derived such that¹⁷

$$N_0U^* = \frac{N_0U}{1 + N_0U \ln\{W/\omega_0\}}. \quad (38)$$

Appreciable renormalization of Coulomb potential is expected if $W \gg \omega_0$. Rigorous estimation of the Coulomb effect is difficult, because the derivation used to obtain Eq. (38) adopts lot of working hypotheses that neglect possibilities of Coulomb enhancement of the superconducting temperature. While $\mu^* = N_0U^*$ of K₃C₆₀ is estimated to be fairly small ($\mu^* \sim 0.4$) within the random phase approximation (RPA),³ it may be enhanced close to the antiferromagnetic phase of NH₃K₃C₆₀. Equations (34), (36), and (37) form the self-consistent gap equations for the s-wave Cooper pair ($l=0$). For the d -wave channel, we replace the average $\langle V_S(i\omega_p, i\omega_k) + U^*(i\omega_p, i\omega_k) \rangle$ by

$$\langle V_S(i\omega_p, i\omega_k) + U^*(i\omega_p, i\omega_k) \rangle_l = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{-il\theta} d\theta \frac{\int \frac{d^3p}{(2\pi)^3} \frac{d^3k}{(2\pi)^3} \delta(\epsilon_p) \delta(\epsilon_k) \{V_S(p, k) + U^*(i\omega_p, i\omega_k)\}}{\int \frac{d^3p}{(2\pi)^3} \frac{d^3k}{(2\pi)^3} \delta(\epsilon_p) \delta(\epsilon_k)}, \quad (39)$$

where $\theta = \arccos(\vec{p} \cdot \vec{k}/pk)$, $l=2$, and $\langle U^*(i\omega_p, i\omega_k) \rangle_{l=2} = 0$ because of the momentum independence of U^* .

IV. CORRECTIONS IN TWO AND THREE DIMENSIONS

The corrections to the Migdal approximations for the intraband and interband e -MV couplings derived in the preceding section were studied in the two and three dimensions. The summations over \vec{q} were made numerically on discretized momentum space points of 128×128 or $128 \times 128 \times 128$ size. The two bands were supposed to have the same dispersion, but one of them is lifted by a constant

energy; $\epsilon_1(\vec{k}) = -2t[\cos(k_x) + \cos(k_y)] - \mu$ and $\epsilon_2(\vec{k}) = -0.2t[\cos(k_x) + \cos(k_y)] - \mu - \Delta\epsilon$ in two dimensions or $\epsilon_1(\vec{k}) = -2t[\cos(k_x) + \cos(k_y) + \cos(k_z)] - \mu$ and $\epsilon_2(\vec{k}) = -0.2t[\cos(k_x) + \cos(k_y) + \cos(k_z)] - \mu - \Delta\epsilon$ in three dimensions. We take t as a unit of energy and hence $t=1$ throughout this article. We fixed the chemical potential $\mu=0.4$. The band splitting energy $\Delta\epsilon$ is a variable that simulates the effect of lifting of the band degeneracy. The interband e -MV coupling constant $\kappa(\vec{k} - \vec{k}')$ is proportional to the inverse of the band splitting energy $\Delta\epsilon$ except the region where $\Delta\epsilon \ll \omega$.^{4,5,18} We assume that $\kappa(\vec{k} - \vec{k}') = 0.09/\Delta\epsilon$. The coupling constants of the intraband e -MV coupling for bands 1 and 2, $g_1(\vec{k} - \vec{k}')$, $g_2(\vec{k} - \vec{k}')$, were supposed to be constant with

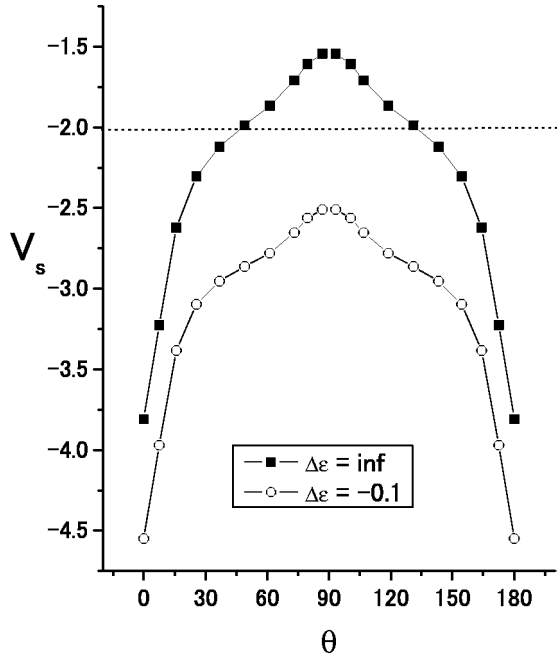


FIG. 1. The potential for the Cooper pair V_S as a function of $\theta = \arccos(\vec{p} \cdot \vec{k}/pk)$ of the two-dimensional square lattice model. The unit of energy is the transfer integral $t=1$. The dotted line denotes the bare potential $V_a(p,k) \approx -2$. The input and output Matsubara frequencies are fixed to be $\omega_p = 0.02512$ and $\omega_k = 0.8$, respectively. We take the molecular vibrational frequency $\omega_0 = 0.8$. The temperature and the chemical potential are $T = 0.008$ and $\mu = 0.4$. $\Delta\epsilon = \text{inf}$ denotes $\Delta\epsilon = \infty$.

the value 2.0. We took the frequency of the molecular vibration as $\omega_0 = 0.8$. All these parameter values were used throughout this article. We plot the potential $V_S(p,k)$ as a function of $\theta = \arccos(\vec{p} \cdot \vec{k}/pk)$. The input and output momenta \vec{p} and \vec{k} were then taken as variables. The results of the two-dimensional square lattice and the three-dimensional cubic lattice were plotted in Figs. 1 and 2, respectively. The temperature T was chosen to be 0.008. The Matsubara frequencies ω_p and ω_k of the input and the output four dimensional momentum used to obtain the data to draw Figs. 1 and 2 were supposed to be 0.025 12 and 0.8, respectively.¹⁶ The dotted line in Figs. 1 and 2 denotes the bare potential $V_a(\vec{p}, \vec{k}) \approx -2$ without the correction. Therefore, V_S approximately below -2 denotes the attractive correction and that approximately above -2 denotes the repulsive correction. The both are due to the corrections to the Migdal approximations for the intraband and interband e -MV couplings. In general, the potential $V_S(p,k)$ may be expanded as follows:

$$\begin{aligned} V_S(p,k) + U^*(i\omega_p, i\omega_k) \\ \approx V_0 + U^*(i\omega_p, i\omega_k) + V_1[\cos(p_x)\cos(k_x) \\ + \cos(p_y)\cos(k_y) + \gamma\cos(p_z)\cos(k_z)], \end{aligned} \quad (40)$$

where $\gamma = 0$ in two dimensions and $\gamma = 1$ in the three dimensions. Here we assume $U^*(i\omega_p, i\omega_k) = 2$ to simplify our argument. This corresponds to $\mu^* = 0.6$ if the density of states at the Fermi level is 5 states/eV spin. A large attraction in

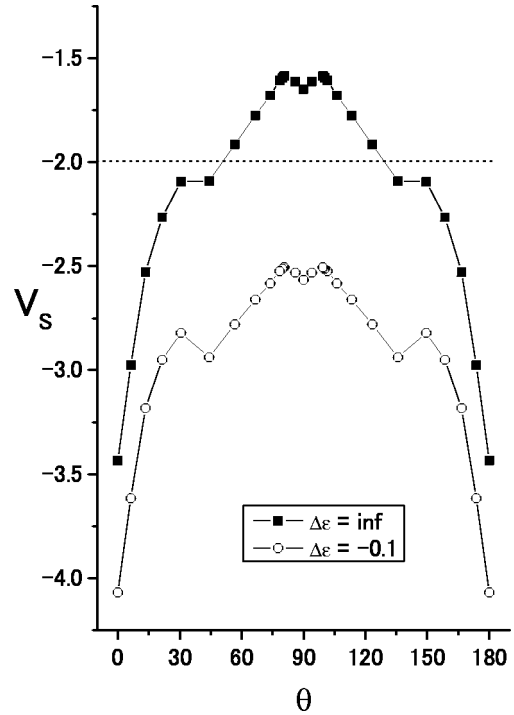


FIG. 2. The potential for the Cooper pair V_S as a function of $\theta = \arccos(\vec{p} \cdot \vec{k}/pk)$ of the three-dimensional cubic lattice model. Notations and parameters are same as those in Fig. 1.

$V_S + U^*$ close to $\theta = 0$ and $\theta = \pi$ and a repulsion close to $\theta = \pi/2$ were observed when $\Delta\epsilon = \infty$ in the both dimensions. This means that the potential $V_S + U^*$ is repulsive when the input and the output momenta \vec{p} and \vec{k} are orthogonal but is attractive when \vec{p} and \vec{k} are parallel or antiparallel. In the single-band case, $\Delta\epsilon = \infty$, the symmetry of superconductivity should be anisotropic.¹⁹ On the other hand, it is isotropic when the two bands overlap each other closely; $\Delta\epsilon = -0.1$. The potential $V_S + U^*$ in this case is attractive everywhere. The results may indicate that the symmetry of the superconductivity changes as the degeneracy of the bands is lifted. The change is solely due to the interband e -MV coupling, because only the interband e -MV coupling constant is dependent on the degeneracy in our model. While the intraband e -MV coupling brings about the anisotropic pairing potential, the interband e -MV coupling brings about the momentum-independent attractive interaction that reduces the effect of Coulomb repulsion. Our theory provides a good reason why the symmetry of the superconductivity in alkali-metal-doped C_{60} such as K_3C_{60} is s -wave in spite of the non-negligible ω/W ratio and large on-site Coulomb repulsion. This is because the large interband e -MV coupling due to the strong degeneracy of the t_{1u} bands reduces the pseudo-Coulomb-repulsion U^* and also the anisotropy of the potential $V_{S,a}$.

To make it sure the previous arguments, we have solved the gap equation numerically. We have mapped the gap equation onto the following linear equation:

$$\Gamma(T)\Delta(i\omega_p) = \sum_{\omega_k} K(i\omega_p, i\omega_k)\Delta(i\omega_k), \quad (41)$$

where

$$K(i\omega_p, i\omega_k) = -\frac{2N_0T_c}{Z(i\omega_p)|\omega_k|} \langle V_S(i\omega_p, i\omega_k) + U^*(i\omega_p, i\omega_k) \rangle \arctan \left\{ \frac{W}{2|\omega_k Z(i\omega_k)|} \right\}. \quad (42)$$

$\Gamma(T)$ is a monotonically decreasing function of T and $\Gamma(T_c)=1$, where T_c is the superconducting transition temperature. Hence $\Gamma(T)<1$ when $T>T_c$ and $\Gamma(T)>1$ when $T<T_c$. $\Gamma(T)$ is proportional to a magnitude of the superconducting correlation. The linear equation was solved iteratively:¹⁶

$$\Gamma^{(n)}(T) = \frac{\sum_{\omega_p, \omega_k} \Delta^{(n)}(i\omega_p)^* K(i\omega_p, i\omega_k) \Delta^{(n)}(i\omega_k)}{\sum_{\omega_k} |\Delta^{(n)}(i\omega_k)|^2}, \quad (43)$$

$$\Delta^{(n+1)}(i\omega_p) = \frac{1}{\Gamma^{(n)}(T)} \sum_{\omega_k} K(i\omega_p, i\omega_k) \Delta^{(n)}(i\omega_k). \quad (44)$$

Usually, after several iterations, $\Gamma^{(n)}(T)$ converges to the largest eigenvalue of K , which should be equal to $\Gamma(T)$. The numerical code to obtain the solution of the gap equation includes quadruple do loops for the momentum and the frequency variables. Using a large number of momentum space pointing down to low temperature $T/\omega_0 \sim 0.001$ is not so easy. We have studied the two-dimensional square lattice model. We used the equally spaced 10×10 grid points for the numerical integration in the momentum space. The three-dimensional momentum integrals in Eqs. (31), (33), (35), and (39) should be considered as those in two dimensions. We had made sure that the potentials V_S obtained by using this smaller system size is comparable to that obtained by using the larger (128×128) size. We found a small deviation close to $\theta = \pi/2$. The $\Delta\epsilon$ dependence of $\Gamma(T)$ was calculated and summarized in Fig. 3. We set $T=0.01$, $N_0=10$, and $E=0.5$. We found that there is a critical value of $|\Delta\epsilon| = |\Delta\epsilon_c|$ beyond which the d -wave superconducting correlation $\Gamma_{d\text{-wave}}$ is larger than the s -wave correlation $\Gamma_{s\text{-wave}}$. If $|\Delta\epsilon|$ is smaller than the critical value, the s -wave pairing is more dominant. This transition is observed only when U^* is larger than a critical value $U_c^* \simeq 4$. The physical parameters we used satisfy the relation $U_c^* \simeq 5\omega_0$. If we take the phonon energy $\omega_0 = 200 \text{ cm}^{-1}$ and adopt the standard value of the density of states $N_0 = 5 \text{ states/eV spin}$, $\mu^* = N_0 U^* = 0.6$. This is somewhat larger than that expected in K_3C_{60} , but it may not be impossible that the value is realized in the family of $NH_3K_3C_{60}$ fullerides. When $|\Delta\epsilon| > |\Delta\epsilon_c|$, we get a finite value of T_c for the s -wave pairing even though μ^* is large. This is shown in Fig. 4. Here we set $\Delta\epsilon = -0.08$ and $\mu^* = 0.6$. It was argued that strong electron correlation effects suppress large momentum transfer scatterings of electron-phonon coupling origin.^{16,20} In the presence of strong elec-

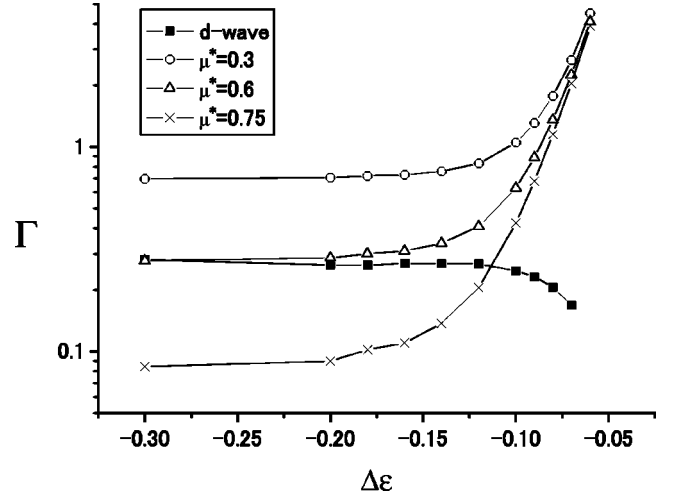


FIG. 3. The $\Delta\epsilon$ dependence of the s -wave and the d -wave superconducting correlations $\Gamma(T)$. Closed squares, open circles, open triangles, and crosses denote the d -wave correlation, the s -wave correlation when we put the pseudo-Coulomb potential $\mu^* = 0.3$, the s -wave correlation when $\mu^* = 0.6$, and the s -wave correlation when $\mu^* = 0.75$, respectively. The temperature was set as $T = 0.01$.

tron correlation effects, we may have to introduce a momentum cutoff q_c for the e -MV coupling constant $g_1(\vec{k} - \vec{k}') = g_1 \theta(q_c - |\vec{k} - \vec{k}'|)$. q_c is parameter other than $\Delta\epsilon$ that may control the symmetry of the superconductivity. Small q_c may incorporate such strong electron correlation effects phenomenologically and have not been discussed here explicitly. Our theory predicts that the anisotropic superconductivity should be observed in the case where the degeneracy of the bands is lifted. The predicted change of the pairing symmetry may be observed close to the phase boundary between antiferromagnetism and superconductivity in the $NH_3K_3C_{60}$ family of fullerides, where the symmetry reduction of the crystal is expected to lift the band degeneracy and U^* is expected to

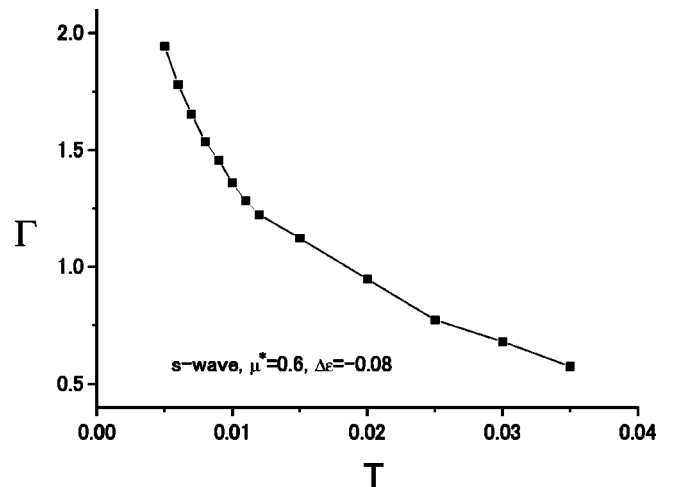


FIG. 4. The temperature dependence of the s -wave correlation $\Gamma(T)$ when the pseudo-Coulomb-potential is given by $\mu^* = 0.6$. We set the energy difference as $\Delta\epsilon = -0.08$.

have a favorable value. To test our theory such experiments should be conducted to search the possible change of the superconducting symmetry.

To summarize, we have studied symmetry of the pairing potential of the superconductivity in the multiband electron-phonon model. Corrections to the Migdal approximations for both the intraband and interband e -MV couplings were studied. In the degenerate limit where $\Delta\epsilon\approx 0$, the potential is attractive everywhere such that isotropic pairing is expected. In the single-band limit of $\Delta\epsilon=\infty$, the potential is attractive for parallel or antiparallel alignment of electron momentum, but it is repulsive when the momentum is orthogonal. In this case, we expect anisotropic pairing. The change of pairing

symmetry may be observed close to the boundary between the antiferromagnetic phase and the superconducting phase of the $\text{NH}_3\text{K}_3\text{C}_{60}$ family of fullerenes where lifting of band degeneracy due to the symmetry reduction of the crystal may be expected.

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- ¹M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, New York, 1996).
- ²W.E. Pickett, in *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen (Academic Press, New York, 1994), Vol. 48.
- ³O. Gunnarsson, *Rev. Mod. Phys.* **69**, 575 (1997).
- ⁴Y. Asai and Y. Kawaguchi, *Phys. Rev. B* **46**, 1265 (1992).
- ⁵Y. Asai, *Phys. Rev. B* **49**, 4289 (1994).
- ⁶K. Prassides, C. Christides, M.J. Rosseinsky, J. Tomkinson, D.W. Murphy, and R.C. Haddon, *Europhys. Lett.* **19**, 629 (1992).
- ⁷M.G. Mitch, S.J. Chase, and J.S. Lannin, *Phys. Rev. Lett.* **68**, 883 (1992).
- ⁸S. Suzuki, S. Okada, and K. Nakano, *J. Phys. Soc. Jpn.* **69**, 2615 (2000).
- ⁹L. Pietronero, S. Strässler, and C. Grimaldi, *Phys. Rev. B* **52**, 10516 (1995).
- ¹⁰T. Takenobu, T. Muro, Y. Iwasa, and T. Mitani, *Phys. Rev. Lett.* **85**, 381 (2000).
- ¹¹H. Tou, Y. Maniwa, Y. Iwasa, H. Shimoda, and T. Mitani, *Phys. Rev. B* **62**, R775 (2000).
- ¹²S. Margadonna, K. Prassides, H. Shimoda, T. Takenobu, and Y. Iwasa, *Phys. Rev. B* **64**, 132414 (2001).
- ¹³N. Manini, G.E. Santoro, A.D. Corso, and E. Tosatti, *Phys. Rev. B* **66**, 115107 (2002).
- ¹⁴H. Fukutome, *Prog. Theor. Phys.* **64**, 1931 (1980).
- ¹⁵A.A. Abrikosov, L.P. Gorkov, and I.E. Dzyalosinski, *Methods of Quantum Field Theory in Statistical Physics* (Dover, New York, 1975).
- ¹⁶C. Grimaldi, L. Pietronero, and S. Strässler, *Phys. Rev. B* **52**, 10 530 (1995).
- ¹⁷P.B. Allen and B. Mitrović, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic Press, New York, 1982), Vol. 37.
- ¹⁸Y. Asai, *Chem. Phys. Lett.* **195**, 551 (1992).
- ¹⁹A. Perali, C. Grimaldi, and L. Pietronero, *Phys. Rev. B* **58**, 5736 (1998).
- ²⁰M. Kulić and R. Zeyher, *Phys. Rev. B* **49**, 4395 (1994).