Phase fluctuations and superconductivity in fullerides

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The superconductivity of fulleride is driven dominant by the electron-intramolecular-phonon interaction and, this interaction leads to a local pairing of electrons. The purpose of the present paper is to discuss the influences of the phase fluctuations of these local pairs on the superconductivity. A phenomenological model, which regards the fulleride as a superconducting network, is used. It is shown that the influences are to suppress both the magnitude of superconducting order parameter and the critical temperature, particularly to change the characteristic of the normal-superconducting transition, in which the order parameter does not continuously turn to zero but rather jumps from a finite value to zero.

I. INTRODUCTION

The superconductivity in fullerides[1–5] (alkali-doped C_{60} solids) arises some important problems about the superconductivity in low bandwidth molecular solids. The conduction bands in fullerites (undoped C_{60} solids) are derived from the lowest unoccupied molecular orbits t_{1u} (it is a triplet state) in C_{60} molecule. In fullerides, the attractive interaction between electrons leading to the superconductivity is phonon-mediated interaction.[6] The phonons playing major role relevant to this interaction are eight H_g intramolecular phonons. Their dynamic Jahn-Teller effects induce local pairing of electrons.[7–9] The superconductivity induced by such local pairing in such multi-narrow-band system arises from some interesting problems, for examples, how to modify the Migdal's theorem in this case?[10–12] The effects of the Coulomb repulsion in this pairing,[13,14] the dependence of T_c on the filling state of the conduction band,[15] etc.

The purpose of the present work is to discuss the influences of the phase fluctuations of these local pairs on the superconductivity in fullerides. If we regard a fulleride as a superconducting network composed of superconducting C_{60} molecules with local Cooper pairs and coupling between them, this system, in a sense, is similar to a granular superconductor or a Josephson junction array (JJA). In these systems the quantum and thermal fluctuations of the phase of local pairs play an important role in the normal-superconducting transition.[16,17] There are a lot of theoretical and experimental works to investigate the influences of the phase fluctuations on the superconductivity in the granular materials[18,19] or in JJAs.[20] But a greater difference between JJAs or granular superconductors and the superconducting fullerides is that, in formers the superconducting energy (exactly, the difference between the free energy of the normal state and the superconducting state) for every "granule" are greater than the superconducting coupling energy between different superconducting "granules" very much, but in fullerides, the superconducting energy for every molecule with local pairs are near to or smaller than the superconducting coupling energy for the nearest neighbor molecule. Therefore the influences of the phase fluctuations on the superconducting state are serious even critical. To clarify the influences of the phase fluctuations on the superconductivity in the ful-

lerides, or on that in the low bandwidth molecular solids is the purpose of our works.

Our discussions are kept in a phenomenological level and dealt with in the frame of Ginzburg-Landau (GL) theory. This paper is organized as follows: First a phenomenological model based on GL theory, in which the superconducting fullerides are regarded as a superconducting network composed of the local pairs, is introduced. The phase fluctuations of the local pairs are described by a dynamic model, in which the canonical variables are the phase of the local pairs and the pair number deviated from the equilibrium value in these sites. Then we deal with this model by self-consistent phonon approximation (SCPA).[21] After that, the influences of the phase fluctuations on the GL free energy of this system are discussed. Because the decrease of the magnitude of the superconducting order parameter ψ leads to intensify the phase fluctuations of the local pairs, the GL free energy of this system as the function of ψ has two extrema. The phase fluctuations of local pairs suppress the magnitude of ψ, and in general, when the normal-superconducting phase transition (NSPT) takes place, the magnitude of ψ does not continuously turn to zero but rather jumps from a finite value to zero. At absolute zero temperature the quantum NSPT may still occur if the parameters of the lattice change. In the next section, we discuss the physical meaning of this phenomenological model and the experimental links of our results, and point out that how to understand such local pairs is a very interesting problem.

II. A PHENOMENOLOGICAL MODEL FOR THE SUPERCONDUCTIVITY IN FULLERIDES

A. GL theory for the superconductivity in fullerides

If we regard a fulleride as a superconducting network composed of the local Cooper pair, the GL free energy can be approximately expressed as[22,23]

$$F = \sum_i \left(-A|\psi_i|^2 + \frac{1}{2}B|\psi_i|^4 \right) + \sum_{(i,j)} \frac{1}{2}C|\psi_i - \psi_j|^2, \quad (1)$$

where ψ_i is the superconducting order parameter on ith molecule, and (i,j) means to take summation only over all

nearest-neighbor (NN) molecules. A, B, and C are the phenomenological parameters in this model. If to express ψ_i by

$$\psi_i = |\psi_i|\exp(i\vartheta_i) \tag{2}$$

and to take an average of $|\psi_i|$ at a small macroscopic scale as

$$\langle|\psi_i|\rangle = |\psi| = \sqrt{n}, \tag{3}$$

expression (1) becomes

$$F = \sum_i \left(-An + \frac{1}{2}Bn^2\right) + \sum_{(i,j)} Cn[1 - \cos(\vartheta_i - \vartheta_j)]. \tag{4}$$

Rewrite the phase difference between site i and j as two parts,

$$\vartheta_i - \vartheta_j = \Delta\vartheta_{ij} + \theta_i - \theta_j, \tag{5}$$

where $\Delta\vartheta_{ij}$ is phase difference due to the phase fluctuations and, θ_i and θ_j are, respectively, the phases of the superconducting order parameter in macroscopic scale at site i and j. Then take an average about the phase fluctuations,

$$\langle\cos(\vartheta_i - \vartheta_j)\rangle = \langle\cos(\Delta\vartheta_{ij})\rangle\cos(\theta_i - \theta_j). \tag{6}$$

If we define

$$\langle\cos(\Delta\vartheta_{ij})\rangle = e^{-w}, \tag{7}$$

the expression (4) is rewritten as

$$F = \sum_i \left(-[A - zC(1 - e^{-w})]n + \frac{1}{2}Bn^2\right)$$
$$+ \sum_{(i,j)} Ce^{-w}n[1 - \cos(\theta_i - \theta_j)], \tag{8}$$

where z is the number of the nearest neighbors, and $z=12$ for fullerides. Therefore to take the phase fluctuations of local pairs into account of the free energy leads to modify the expression (4), and the free energy can be described by introducing some phenomenological parameters to replace the parameters in Eq. (4),

$$A \rightarrow A' = A - C\sum_{j\in n,n} (1 - e^{-w}),$$

$$C \rightarrow C' = Ce^{-w}. \tag{9}$$

Keep in mind the spatial variations of n and w in Eq. (9) is at a macroscopic scale, so that the summation can be turned to spatial integral and the corresponding free energy density is

$$f = -\alpha|\psi|^2 + \frac{1}{2}\beta|\psi|^4 + \gamma|\nabla\psi|^2. \tag{10}$$

It is easy to prove

$$\alpha = \frac{A'}{v_a}, \quad \beta = \frac{B}{v_a}, \quad \gamma = \frac{2a^2}{v_a}C', \tag{11}$$

where a is the distance between nearest-neighbor molecules, and

$$v_a = a^3/\sqrt{2}$$

which is the volume of the unit cell.

B. Phase fluctuations

As a superconducting network, the phase fluctuations in fulleride can be described by a dynamic model with the Hamiltonian[21]

$$H = \frac{1}{2}\sum_{i,j} U_{ij}\Delta n_i\Delta n_j + \frac{1}{2}\sum_{(i,j)} K[1 - \cos(\vartheta_i - \vartheta_j)], \tag{12}$$

where Δn_i is the deviation from the equilibrium value of the pair number on the ith molecule, and from Eq. (4) $K=2Cn$. The first term in Eq. (12) is the Coulomb repulsion between the local pairs, and the second is the coupling between the local pairs i and j. It is emphasized that the equilibrium value of the pair number corresponds to the electrical neutralizing condition, so that $2e\Delta n_i$, in a sense, means the electrical charge on the ith molecule. The canonically conjugate variables, ϑ_i and Δn_i, have the commutation relation[25]

$$[\vartheta_i, \Delta n_j] = j\delta_{ij}. \tag{13}$$

If we introduce variables $p_i = \hbar\Delta n_i$, the commutation relation is

$$[\vartheta_i, p_i] = j\hbar\delta_{ij}. \tag{14}$$

The Hamiltonian becomes

$$H = \frac{1}{2}\sum_{i,j} \frac{1}{\hbar^2}U_{ij}p_ip_j + \frac{1}{2}\sum_{(i,j)} K[1 - \cos(\vartheta_i - \vartheta_j)]. \tag{15}$$

It is similar to a nonlinear lattice, in which the first part is the kinetic energy and the second part is the potential energy. To deal with this system, self-consistent phonon approximation (SCPA)[21] is used. We introduce a reference harmonic lattice, whose Hamiltonian is

$$H_{\text{ref}} = \frac{1}{2}\sum_{i,j} \frac{1}{\hbar^2}U_{ij}p_ip_j + \frac{1}{2}K_{\text{ref}}\sum_{(i,j)} (\vartheta_i - \vartheta_j)^2. \tag{16}$$

The parameter K_{ref} is selected to minimize the thermodynamic function

$$F_t = F_{\text{ref}} + \langle U - U_{\text{ref}}\rangle_{\text{ref}}, \tag{17}$$

where F_{ref} is the free energy of the reference lattice, U and U_{ref} are the potential energy in Eqs. (15) and (16), respectively, and $\langle\ \rangle_{\text{ref}}$ means to take statistical average on the reference lattice.

The calculation method for the thermodynamic function in the reference lattice is a standard method and can be found from the text for solid state physics.[24] In the lattice wave representation, H_{ref} is

$$H_{\text{ref}} = \frac{1}{2}\sum_{\mathbf{q}} \frac{U_{\mathbf{q}}}{\hbar^2}p_{\mathbf{q}}p_{-\mathbf{q}} + \frac{1}{2}K_{\text{ref}}\sum_{\mathbf{q}} L(\mathbf{q})\vartheta_{\mathbf{q}}\vartheta_{-\mathbf{q}}, \tag{18}$$

where $p_{\mathbf{q}}$ and $\vartheta_{\mathbf{q}}$ are, respectively, the Fourier transform of p_i and ϑ_i, $U_{\mathbf{q}}$ is the Fourier transform of U_{ij} on the variable $(i-j)$, and

$$L(\mathbf{q}) = \sum_{s \in n, n} |1 - e^{j\mathbf{q}\cdot\mathbf{R_s}}|^2, \tag{19}$$

in which $\mathbf{R_s}$ is the vector from one molecule to its sth NN molecule. If we introduce

$$M_\mathbf{q}^{-1} = \frac{U_\mathbf{q}}{\hbar^2}, \quad \omega_\mathbf{q}^2 = \frac{1}{M_\mathbf{q}}K_{\text{ref}}L(\mathbf{q}), \tag{20}$$

the quantity w defined in Eq. (7) becomes

$$w = \left\langle \frac{1}{2}(\vartheta_i - \vartheta_j)^2 \right\rangle_{\text{ref}}$$
$$= v_a\sum_\mathbf{q} \frac{\hbar}{2M_\mathbf{q}\omega_\mathbf{q}}\coth\left(\frac{\beta\hbar\omega_\mathbf{q}}{2}\right)\frac{1}{2}|1 - e^{j\mathbf{q}\cdot\mathbf{R_s}}|^2, \tag{21}$$

where $\beta = 1/k_BT$. It is easy to understand the meaning of this expression if to rewrite Eq. (21) as $w = \frac{1}{2}v_a\Sigma_\mathbf{q}(\hbar\omega_\mathbf{q}/M_\mathbf{q}\omega_\mathbf{q}^2)$ $\times(n_\mathbf{q}+\frac{1}{2})|1 - e^{j\mathbf{q}\cdot\mathbf{R_s}}|^2$, in which $n_\mathbf{q} = 1/e^{\beta\hbar\omega_\mathbf{q}}-1$ is the Bose statistical function, i.e., w is the average value of the phase difference due to the thermal and quantum fluctuations.

For the sake of convenience to calculate, we take the following approximation for function $L(\mathbf{q})$:

$$L(\mathbf{q}) \approx \frac{z}{4\pi}\int\int 2[1 - \cos(qa\cos\theta)]\sin\theta\, d\theta\, d\phi = 2zS^2(qa), \tag{22}$$

where $S^2(x) = 1 - (\sin x/x)$. Then we have

$$\omega_\mathbf{q}^2 \approx \frac{2z}{\hbar^2}U_\mathbf{q}K_{\text{ref}}S^2(qa) \tag{23}$$

and

$$w = v_a\sum_\mathbf{q} \frac{\hbar}{2M_\mathbf{q}\omega_\mathbf{q}}\coth\left(\frac{\beta\hbar\omega_\mathbf{q}}{2}\right)S^2(qa). \tag{24}$$

Now we turn to minimize the function F_t and to obtain the value of parameter K_{ref}. The minimization condition of F_t is

$$\left(\frac{\partial F_t}{\partial K_{\text{ref}}}\right)_K = \left(\frac{\partial F_t}{\partial K_{\text{ref}}}\right)_{K,w} + \left(\frac{\partial F_t}{\partial w}\right)_{K,K_{\text{ref}}} = 0. \tag{25}$$

Clearly, $(\partial F_{\text{ref}}/\partial K_{\text{ref}})_w = zw$ and $(\partial\langle U_{\text{ref}}\rangle/\partial K_{\text{ref}})_w = zw$. Therefore this condition is equivalent to $(\partial F_t/\partial w)_{K,K_{\text{ref}}} = 0$, in other words,

$$K_{\text{ref}} = \frac{1}{2}Ke^{-w} = Cne^{-w}. \tag{26}$$

C. The calculation of w

If to ignore the dependence of $U_\mathbf{q}$ on the direction of $\mathbf{q}$, and to approximate the first Brillouin zone of the fcc lattice by a sphere in q space with $|q| \leq q_m$,

$$q_m = \frac{(6\pi^2\sqrt{2})^{1/3}}{a} \approx \frac{4.375}{a}, \tag{27}$$

the summation in Eq. (24) turns to an integral in q space, and

$$w = \frac{1}{4\sqrt{2}\pi^2}a^3\int_0^{q_m}\left(\frac{U_q}{2zK_{\text{ref}}}\right)^{1/2}$$
$$\times\coth\left(\frac{\beta\sqrt{2zK_{\text{ref}}U_q}}{2}S(qa)\right)S(qa)q^2dq. \tag{28}$$

The physical meaning of U_{ij} are the interaction energy between the local pairs at sites i and j, so that the value of U_q should trend to zero when q increases. Averaging U_c for U_q in the integral (28) and taking an approximation for $S(x)$ by $S(x) \approx x/\sqrt{6}$, we receive

$$w \approx \mu_0\frac{1}{\mu_1^4}\int_0^{y_m}(\coth y)y^3dy, \tag{29}$$

where $\mu_0 = (1/8\pi^2\sqrt{6})(U_c/zK_{\text{ref}})^{1/2}$, $\mu_1 = \sqrt{zK_{\text{ref}}U_c}/2\sqrt{3}k_BT$, and $y_m = \mu_1q_ma$. In Appendix A, we take two approximations of the integral (29). One is the low temperature approximation, in which the principal term of this integral is

$$w_0 = \frac{(q_ma)^4}{32\sqrt{6}\pi^2}\left(\frac{U_c}{zK_{\text{ref}}}\right)^{1/2}, \tag{30}$$

and the subsequent expansion is near to a function of T^4. Another is the high temperature approximation, in which the principal term is

$$w_h = \frac{(q_ma)^3}{12\sqrt{2}\pi^2}\frac{k_BT}{zK_{\text{ref}}}, \tag{31}$$

and the subsequent expansion is power series of $\mu_1 \propto 1/k_BT$.

III. THE INFLUENCE ON SUPERCONDUCTING TRANSITION OF PHASE FLUCTUATIONS

A. The thermodynamic function

From the discussions on the phase fluctuations of the local pairs in Sec. II A, the expression of the GL free energy of this system is a form like Eq. (1) excepting parameters A' and C' obtained in Eq. (9) to replace A and C. We suppose the parameter A is a function of temperature,

$$A = A_0[1 - a(T)], \tag{32}$$

where $a(T)$ is a function of temperature satisfied by the following requirements: $a(T) = 0$ at $T = 0$ and $a(T) = 1$ at $T = T_{c0}$, where T_{c0} can be regarded as the critical temperature in the absence of the phase fluctuations of local pairs. Consequently,

$$A' = A_0[1 - a(T) - z\eta_0^2(1 - e^{-w})], \quad C' = Ce^{-w}, \tag{33}$$

where η_0^2 is defined as

$$\eta_0^2 = \frac{C}{A_0}. \tag{34}$$

If to ignore the spatial variations of the order parameter, the GL free energy becomes
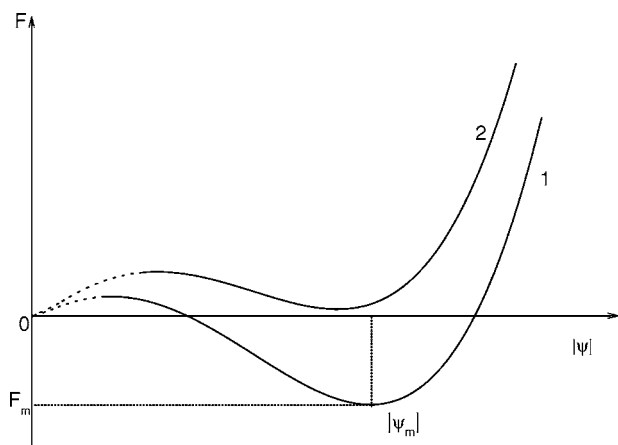
FIG. 1. Dependence of GL free energy F on the magnitude of order parameter $|\psi|$ corresponding to Eq. (35). The minimum value of curve 1 is negative and the system is superconductive, while the extremum of curve 2 is positive and the system stays at the normal state.

$$F(n) = -A_0[1 - a(T) - z\eta_0^2(1 - e^{-w})]n + \frac{B}{2}n^2. \quad (35)$$

From Eqs. (33) and (10), the zero temperature coherence length of this system can be obtained by

$$\eta_{r0}^2 = \left(\frac{\xi_0}{a}\right)^2 = \frac{2\eta_0^2 e^{-w_0}}{1 - z\eta_0^2(1 - e^{-w_0})}, \quad (36)$$

where ξ_0 and w_0 are the coherence length and the value of w at $T=0$, respectively.

In order to determine the state of this system, it is necessary to minimize the GL free energy as the function of $n = |\psi|^2$. But the problem is complicated because the parameters A' and C' both are functions of w, and w is dependent on the value of n and the temperature T. It is evident that the decrease of the magnitude of the order parameter should induce to intensify the phase fluctuation, or, to increase the value of w, which should induce to increase the GL free energy. Therefore it is easy to understand that the GL free energy as the function of $|\psi| = \sqrt{n}$ has two extremum as shown in Fig. 1. There two curves correspond to two sets of parameters of system. But of course, when the magnitude of the order parameter is too small, the model for phase fluctuations used in Sec. II B is unfeasible, so that we use the dotted line to show the region with $|\psi| \sim 0$. Such two extremum structures of function F arouse a problem—whether the minimum value of function F_m are positive or negative? If $F_m < 0$ (shown in Fig. 1 by curve 1), the superconducting state is stable; if $F_m > 0$ (shown in Fig. 1 by curve 2) the superconducting state is unstable and the system must stay at normal state; and if $F_m \approx 0$, the system, in a sense, should show fluctuation state.

The equation to determine the minimum is

$$\frac{\partial F(n)}{\partial n} = 0. \quad (37)$$

From $K_{\text{ref}} = \frac{1}{2}Ke^{-w} = Cne^{-w}$ it is easy to obtain

$$\frac{\partial K_{\text{ref}}}{\partial n} = \frac{1}{n} \frac{k_{\text{ref}}}{1 + K_{\text{ref}} \dfrac{\partial w}{\partial K_{\text{ref}}}}. \quad (38)$$

If to introduce

$$\mu = \frac{1}{1 + K_{\text{ref}} \dfrac{\partial w}{\partial K_{\text{ref}}}}, \quad (39)$$

Eq. (37) becomes

$$n = n_0[1 - a(T) - z\eta_0^2(1 - \mu e^{-w})], \quad (40)$$

in which we define

$$n_0 = \frac{A_0}{B}, \quad (41)$$

the value of $|\psi|^2$ in absence of the phase fluctuations of local pairs. But because of $n = (K_{\text{ref}}/C)e^w$ and the dependence of w on K_{ref}, Eq. (40) also determines the value of $K_{\text{ref},m}$ [the subscript m denotes the value corresponding to the minimum of $F(n)$ without additional declarations]. To solve Eq. (40) obtains the minima $K_{\text{ref},m}$, w_m, and n_m, and then

$$F_m = -F_0[1 - a - z\eta_0^2(1 - \mu_m e^{-w_m})]$$
$$\times \{1 - a - z\eta_0^2[1 - (2 - \mu_m)e^{-w_m}]\}. \quad (42)$$

In this expression, $F_0 = A_0^2/2B$, which can be understood as the GL free energy of one unit cell in superconducting state in the absence of the phase fluctuations of local pairs.

For the sake of simplicity and convenience, we introduce the following reduced quantities:

$$n_d = \frac{n}{n_0}, \quad f_d = \frac{F}{F_0}, \quad t_d = \frac{k_B T}{Cn_0},$$

$$u_c = \frac{U_c}{Cn_0}, \quad M_z = z\eta_0^2, \quad k = \frac{K_{\text{ref}}}{Cn_0} = n_d e^{-w}. \quad (43)$$

It should be emphasized that all these quantities are dimensionless, and all equations can be simplified by these dimensionless quantities. For example, the quantities μ_0 and μ_1 in Eq. (29) can be written as

$$\mu_0 = \frac{1}{8\pi^2\sqrt{6z}} \sqrt{\frac{u_c}{k}}, \quad \mu_1 = \frac{\sqrt{z}}{2\sqrt{3}} \frac{\sqrt{u_c k}}{t_d} = \frac{\sqrt{u_c k}}{t_d}. \quad (44)$$

B. The case at $T=0$ K

When $T=0$ K, only quantum fluctuations occur. From Eq. (29) we get

$$w = w_0 = \Omega_0 \sqrt{\frac{u_c}{k}}, \quad \Omega_0 = \frac{(q_m a)^4}{32\pi^2\sqrt{6z}} \approx 0.1367. \quad (45)$$

And from Eq. (39),

$$\mu = \frac{1}{1 - \frac{w_0}{2}}. \tag{46}$$

The equation to determine k_m is obtained from Eq. (40),

$$k = e^{-w_0}\left[1 - M_z\left(1 - \frac{e^{-w_0}}{1 - \frac{w_0}{2}}\right)\right]. \tag{47}$$

For given parameters of system (M_z, u_c), k_m is obtained from Eq. (47) (an approximation expression for k_m has been given in Appendix B), and then w_{0m} from Eq. (44), further n_{dm} and f_{dm} are obtained,

$$n_{dm} = 1 - M_z\left(1 - \frac{e^{-w_{0m}}}{1 - \frac{w_{0m}}{2}}\right),$$

$$f_{dm} = -n_{dm}\left(n_{dm} - \frac{w_{0m}}{1 - \frac{w_{0m}}{2}}M_z e^{-w_{0m}}\right). \tag{48}$$

From Eq. (48), it is evident that $n_{dm} < 1$, in other words, the quantum fluctuations of the phase of the local pairs suppress the magnitude of superconducting order parameter. It also is easy to prove that the increase of the value of the parameter u_c or M_z should lead to decrease of n_{dm}, and at a critical value, $f_{dm} = 0$ and the system transforms into normal state, which is schematically shown in Fig. 2.

From Eq. (48), the f_{dm}, the difference between free energies of normal state and superconducting state, is also suppressed due to the phase fluctuations of local pairs. The condition for $f_{dm} \geqslant 0$ is

$$n_{dm} - \frac{w_{0m}}{1 - \frac{w_{0m}}{2}}M_z e^{-w_{0m}} \leqslant 0. \tag{49}$$

Because the root of Eq. (49) is determined by two parameters of the system u_c and M_z, function

$$n_{dm} - \frac{w_{0m}}{1 - \frac{w_{0m}}{2}}M_z e^{-w_{0m}} = 0 \tag{50}$$

corresponds to the dividing line (separatrix) in (u_c, M_z) plane. In the upper region $f_{dm} > 0$, the superconducting states are instable and the system stays at normal state. In the under region $f_{dm} < 0$, the superconducting states are stable. An approximation expression for this separatrix has been given in Appendix B,

$$u_c = \frac{8}{27\Omega_0^2}\left(M_z + \frac{1}{2}\right)^{-2}, \tag{51}$$

which is shown in Fig. 3.

Now, if to increase the lattice constant of this system, it should lead to increase of A_0 and decrease of C, and then lead to decrease of M_z. Also the increase of lattice constant
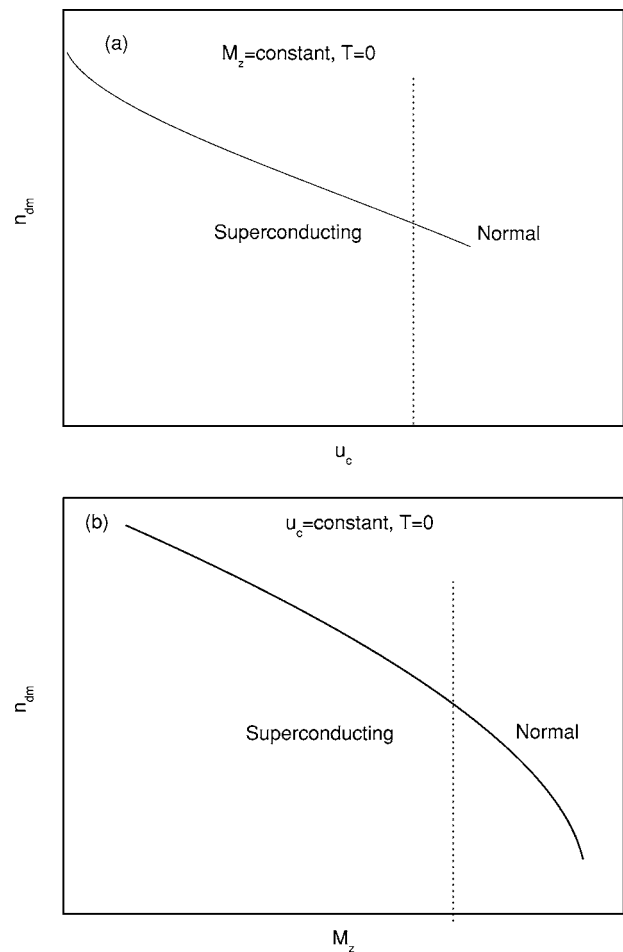

FIG. 2. Dependences of n_{dm} on u_c [schematically shown in curve (a)] and on M_z [in curve (b)] corresponding to Eq. (48). At a critical value, the system transforms into normal state.

should lead to increase of u_c. This process illustrated in the (u_c, M_z) plane is shown in Fig. 4, the point (u_c, M_z) (label "1") moves towards the separatrix with decreasing the lattice constant; when it crosses the separatrix and enters into the
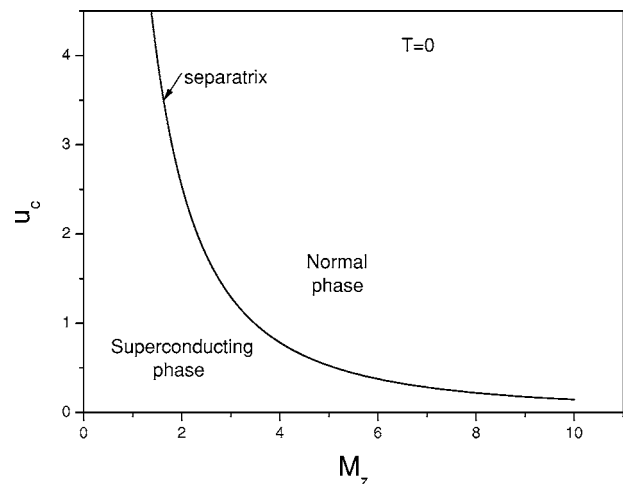

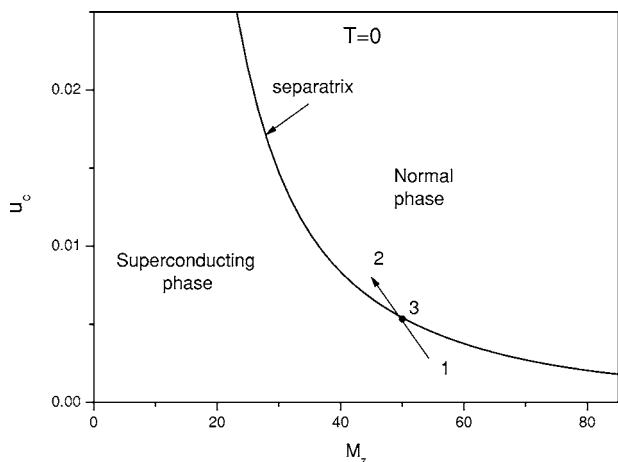FIG. 3. Separatrix between superconducting and normal phases at $T = 0$.

FIG. 4. With the increase of lattice constant, point "1" (it represents the system in superconducting state) moves towards point "2" (in normal state). When it crosses the separatrix at point "3," a quantum phase transition takes place. This process is discussed in detail in the text.

region with $f_{dm} > 0$, a quantum phase transition occurs, in which the free energy of superconducting state f_{dm} becomes higher than normal state, and then the superconducting state transforms into normal state. But it is emphasized that, although $f_{dm} = 0$ at the separatrix, $n_{dm} > 0$ at this point also, i.e., this phase transition is not a second order phase transition, but a transition that the order parameter jumps from a finite value to zero. This observation is a probable reason of the similar phenomenology observed in the ammonia intercalated compounds, though structural and magnetic instabilities of the normal state are also probably present in the normal state.[26]

C. The case at $T > 0$ K

When $T \geq 0$, the equation to determine the minimum of GL free energy becomes

$$k = e^{-w}[1 - a(T) - M_z(1 - \mu e^{-w})]. \tag{52}$$

In this equation, w is the function of μ_0 and μ_1, whose expressions had been shown in Eq. (44). If to introduce the following quantities:

$$k' = \frac{k}{1 - a(T)}, \quad M'_z = \frac{M_z}{1 - a(T)}, \quad u'_c = \frac{u_c}{1 - a(T)},$$

and

$$t'_d = \frac{t_d}{1 - a(T)}, \tag{53}$$

and to remember the expressions of μ_0 and μ_1 are unchanged after to replace u_c, k, and t_d by u'_c, k'_d, and t'_d, respectively, Eq. (52) can be rewritten as

$$k' = e^{-w'}[1 - M'_z(1 - \mu' e^{-w'})], \tag{54}$$

where the functions w' and μ' are understood as to substitute the quantities k', u'_c, t'_d to replace the quantities k, u_c, t_d into (29) and

$$\mu' = \frac{1}{1 + k' \dfrac{\partial w'}{\partial k'}}. \tag{55}$$

If we regard Eq. (54) as the equation for k' with the parameters u'_c, M'_z, and t'_d, the problem is similar to solve Eq. (47), and the only difference is the expression of w' [see Eq. (29)] is different from that of w_0 [see Eq. (45)]. If the root of Eq. (55) has been obtained, we obtain the values of n_{dm} and f_{dm} by $k = (1-a)k'$. From Eq. (42), if to introduce $n'_d = n_d/(1-a)$ and $f'_d = f_d/(1-a)$, it is easy to prove

$$f'_d = -n'_d[n'_d - 2M'_z(\mu' - 1)e^{-w'}]. \tag{56}$$

Therefore analogous to the discussions in Sec. III B, the equation

$$n'_{dm} - 2M'_z(\mu'_m - 1)e^{-w'} = 0 \tag{57}$$

determines the separatrix in (u'_c, M'_z) plane at a fixed temperature, which is the dividing line for regions $f_{dm} \geq 0$ and region $f_{dm} < 0$. But from the approximation expressions for w in Appendix A, at lower temperatures

$$w = w_0 \left\{ 1 + \frac{3}{y_m^4} \sum_1^\infty \frac{1}{n^4} \left[1 - e^{-2ny_m}\left(1 + 2ny_m + 2n^2 y_m^2 \right. \right. \right.$$
$$\left. \left. \left. + \frac{4}{3} n^3 y_m^3 \right) \right] \right\}, \tag{58}$$

where $y_m = q_m a \mu_1 \propto T^{-1}$. Therefore at lower temperature, it is a better approximation that $w \approx g w_0$, where g is a function of T and greater than 1 a little. So in order to discuss the properties of this separatrix, a better approximation is a equation like Eq. (51),

$$u'_c = \frac{8}{27\Omega_0'^2}\left(M'_z + \frac{1}{2}\right)^{-2}, \tag{59}$$

in which $\Omega_0' > \Omega_0$ and it is an increasing function of T.

After this discussion, the rise of temperature can be manifested as the moving in (u'_c, M'_z) plane—on the one hand is the increase of u'_c and M'_z, which leads to decrease of the values of n'_{dm} and $-f'_{dm}$; on the other hand is the shift downwards to the separatrix due to the increase of Ω_0'. From $n_{dm} = [1 - a(t)]n'_{dm}$ and $f_{dm} = [1 - a(t)]^2 f'_{dm}$, it is evident that the rise of temperature suppresses both the magnitude of superconducting order parameter ψ and the value of $-f_{dm}$. If the point (u'_c, M'_z) crossing the separatrix, the transition from superconducting state to normal state occurs, which is similar to that shown in Sec. III B—generally, the magnitude of superconducting order parameter jumps from a finite value to zero. This process is schematically illustrated in Fig. 5. For example, if we assume the parameters $\eta_0^2 = 1.2$ and $u_c = 0.04$ at $T = 0$, we can obtain $f_{dm} \approx 0$ and $n_{dm} \approx 0.8 \times 0.623 \approx 0.506$ when temperature rises to $a(T) \approx 0.2$; that is to say, if $a(T) = T/T_{C0}$, at $T = 0.2T_{C0}$ the GL free energy for superconducting state tends to zero and the transition from superconducting state to normal state occurs, while the superconducting order parameter jumps from about 0.5 to zero.
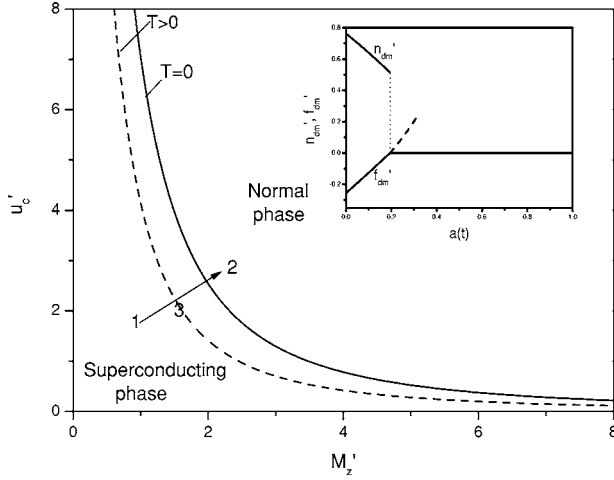
FIG. 5. With temperature increasing, the point "1" (it represents the system in superconducting state) moves towards "2" (in normal state) and the separatrix moves downwards. At T_C, (u'_c, M'_z) meets the separatrix of temperature T_C at point "3." The inset illustrates n_{dm} and f_{dm} functions of temperature, in which n_{dm} jumps to zero at T_C.

IV. DISCUSSIONS

In order to clarify the physical meaning of the results obtained in the preceding discussions, we first make some numerical estimates for the physical parameters. In Sec. III, when we introduce the dimensionless parameters in Eq. (43), an energy scale $\varepsilon_0 = C n_0$ is used. From Eqs. (34) and (41),

$$\varepsilon_0 = C \frac{A_0}{B} = \frac{C}{A_0} \frac{A_0^2}{B} = \eta_0^2 \frac{H_{C0}^2}{4\pi} v_a, \tag{60}$$

where H_{C0} is the thermodynamic critical field for the system in absence of the phase fluctuations at $T=0$ K. As we known, the experimental thermodynamic critical field H_c at $T=0$ K for fullerides is about $3-5 \times 10^3$ G. But, from Eqs. (42) and (48) the experimental value of the thermodynamic critical field is smaller than H_{C0}, so that it is reasonable to take the value of ε_0 to be about $1-4 \times 10^{-3}$ eV (or $10-30$ K).

In fact, many problems in fullerides are still open. For example, although it was claimed that the weak coupling limit of BCS theory was observed,[27] it is still questionable whether Migdal's theorem is valid because the bandwidth is not much larger than the phonon frequencies. A distribution of superconducting energy gap was also suggested.[28] If we notice that an orientation transition of C_{60} molecules takes place at about 250 K (Ref. 29) and the orientation of the molecules is freezed at about 90 K[30] in C_{60} solids, a probable explanation is that the disordered orientation of C_{60} molecules leads to a distribution of M_z, and then leads to the gap distribution. Moreover, the temperature dependence of the superconducting gap, particularly close to T_C, is beyond the precision of the BCS prediction[31]) which indicates a jump of energy gap at T_C. This jump can be naturally explained in our model with the phase fluctuations of the local pairs. Many other problems, such as the properties near the superconducting transition, will be discussed in further work.

Now we turn to investigate the value of U_q, the Fourier transform of U_{ij}. The expression of the mean value of U_q in the integral (28) in Sec. III C is for the sake of convenience. In fact, it is equivalent to assume

$$U_{ij} = U_c \delta_{ij}. \tag{61}$$

As a result of this assumption, the quantum fluctuations of all vibration modes in the reference lattice are involved into the calculation for w. It is easy to understand that may be over-estimated too much. If we take another form

$$U_{ij} \approx U_0 \exp\left(-\frac{R_{ij}^2}{\lambda_0^2}\right), \tag{62}$$

the approximation expression of U_q is

$$U_q \approx U_{q0} \exp\left(-\frac{\lambda_0^2 q^2}{4}\right), \tag{63}$$

where

$$U_{q0} = \sqrt{2}\pi^{3/2}\left(\frac{\lambda_0}{a}\right)^3 U_0. \tag{64}$$

To substitute this expression into Eq. (28). If $\lambda_0/a \gg \sqrt{8}/q_m a$, the expression of w_0 can be approximated by

$$w_0 = \frac{4}{\sqrt{6}\pi^2}\left(\frac{a}{\lambda_0}\right)^4 \sqrt{\frac{U_{q0}}{z K_{\mathrm{ref}}}}. \tag{65}$$

So, for same value of w_0, the parameter u_c in the preceding section is corresponded to the value of $u_0 = U_0/\varepsilon_0$, and the corresponding relation between u_c and u_0 is

$$u_0 = u_c\left(\frac{1}{128}\right)^2\left(\frac{1}{\pi^{3/2}\sqrt{2}}\right)(q_m a)^8\left(\frac{\lambda_0}{a}\right)^5. \tag{66}$$

If to substitute the value of $q_m a$ [see Eq. (27)] into this equation,

$$u_0 \approx 1.02 \times \left(\frac{\lambda_0}{a}\right)^5 u_c. \tag{67}$$

For example, if $\lambda_0/a = 2$, $u_0 \approx 32.6 u_c$, is greater than u_c. This result implicated that due to the value of U_q is trending toward zero as $|q|$ increases, the phase fluctuations for short wavelength are restrained.

If we regard the superconducting order parameters ψ_i as the Wannier representation for the wave function of the mass center of the copper pairs, the mode (62), in which the interactions between local pairs are not limited in the same molecule, is more reasonable than the mode (61), which is used in the last two sections only due to the briefness in the calculations. For this reason, the problem, which arises from the smallness of value for u_c, may be not a serious problem.

An important question is the characters of this system in the neighbor of the NSC transition, or, in the neighbor of the "separatrix." In this region, the difference of GL free energies of unit volume for the superconducting state and for normal state, in which the superconducting order parameter is finite and the normal one is zero, is a smaller value. As a result, a "mixed state," or in other words, the fluctuation state

emerges. How to describe such mixed state is the key for the investigation of the NSC transition. We will discuss this problem in further works.

Another interesting question is the characters of the local pairs due to the intramolecular attractive interactions. As it had been discussed by some authors, in a sense, these pairs can be regarded as pairs by polarons, which are results from electron-intramolecular phonons. Therefore such local pair is not limited in the same molecule, though it can be marked by this molecule. We will discuss the characters of such pairs in further works.

V. CONCLUSIONS

The superconductivity in fullerides is phonon mediated, and the intramolecular vibration modes play the major role. As a result the pairing of electrons, in a sense, is the local pairing. In preceding discussions, it is evident that the influences of the phase fluctuations of this local pairs on the superconducting normal transition are critical. The phase fluctuations increase the free energy of superconducting state, suppress the magnitude of superconducting order parameter, and lower the critical temperature. In particular, because of the intensification of the phase fluctuations induced by the decrease of magnitude of superconducting order parameter, the character of the superconducting normal transition changes, i.e., the superconducting order parameter does not continuously decrease to zero but rather jumps from a finite value to zero. These results comparing with experiments are discussed in the text. The physical model for the dynamic of phase fluctuations and its parameters play important roles in the discussion. An important problem, which must be discussed in further works, is to describe the physical properties in the neighborhood of the superconducting normal transition in this system, and to compare with the experimental measurements. The theoretical basics of the model for dynamic of phase fluctuations also is an interesting problem, especially, the interactions between the deviations from equilibrium value of the pair number in various molecules, which links to the question about the effect of Coulomb interactions in the pairing of electrons of fullerides, and requires detailed future study.

APPENDIX A: CALCULATION OF w

1. Low temperature approximation $(y \to \infty)$

We find

$$\coth y = 1 + 2\sum_{n=1}^{\infty} e^{-2ny}, \tag{A1}$$

$$\int_0^{y_m} (\coth y) y^3 dy = \frac{1}{4} y_m^4 + 2\sum_{n=1}^{\infty} \left[\frac{3}{8n^4} - e^{-2ny_m} \left(\frac{3}{8n^4} + \frac{3}{4n^3} y_m \right. \right.$$
$$\left. \left. + \frac{3}{4n^2} y_m^2 + \frac{1}{2n} y_m^3 \right) \right]. \tag{A2}$$

Thus,

$$w = w_0 \left[1 + \left(\frac{1}{\mu_1} \right)^4 \frac{3}{(q_m a)^4} \sum_{n=1}^{\infty} \frac{1}{n^4} - \left(\frac{1}{\mu_1} \right)^4 \frac{3}{(q_m a)^4} \sum_{n=1}^{\infty} \frac{e^{-2ny_m}}{n^4} \right.$$
$$- \left(\frac{1}{\mu_1} \right)^3 \frac{6}{(q_m a)^3} \sum_{n=1}^{\infty} \frac{e^{-2ny_m}}{n^3} - \left(\frac{1}{\mu_1} \right)^2 \frac{6}{(q_m a)^2} \sum_{n=1}^{\infty} \frac{e^{2ny_m}}{n^2}$$
$$\left. - \frac{1}{\mu_1} \frac{4}{q_m a} \sum_{n=1}^{\infty} \frac{e^{-2ny_m}}{n} \right], \tag{A3}$$

whose principle term is

$$w_0 = \frac{(q_m a)^4}{32\sqrt{6}\pi^2} \frac{\sqrt{u_c}}{\sqrt{zK_{\text{ref}}}} \approx 0.474 \sqrt{\frac{u_c}{zK_{\text{ref}}}}, \tag{A4}$$

and the subsequent expansion is $[\sum_{n=1}^{\infty}(1/n^4) = \pi^4/90]$

$$w_0 \frac{144\pi^4}{30(q_m a)^4} \frac{(k_B T)^4}{(zK_{\text{ref}} U_c)^2}. \tag{A5}$$

2. High temperature approximation $(y \to 0)$

We find

$$\coth y = \frac{1}{y} + \sum_{n=1}^{\infty} \frac{2y}{y^2 + (\pi n)^2}, \tag{A6}$$

$$\int_0^{y_m} (\coth y) y^3 dy$$
$$= \frac{1}{3} y_m^3 + \frac{2}{3} \sum_{n=1}^{\infty} \left[y_m^3 + 3(\pi n)^3 \left(\tan^{-1} \frac{y_m}{\pi n} \right. \right.$$
$$\left. \left. - \frac{y_m}{\pi n} \right) \right]. \tag{A7}$$

When $y_m/\pi n \ll 1$, $\tan^{-1}(y_m/\pi n)$ could be expanded as

$$\tan^{-1} x = x - \frac{1}{3} x^3 + \frac{1}{5} x^5 - \frac{1}{7} x^7 + \cdots, \tag{A8}$$

then

$$w = \frac{1}{3} \mu_0 (q_m a)^3 \frac{1}{\mu_1} \left\{ 1 + 6\sum_{n=1}^{\infty} \left[\frac{1}{5} \left(\frac{y_m}{\pi n} \right)^2 - \frac{1}{7} \left(\frac{y_m}{\pi n} \right)^4 \right] \right.$$
$$\left. + \frac{1}{9} \left(\frac{y_m}{\pi n} \right)^6 - \cdots \right\}. \tag{A9}$$

The principle term of w is

$$\frac{(q_M a)^3}{12\sqrt{2}\pi^2} \frac{k_B T}{zK_{\text{ref}}} \tag{A10}$$

and the subsequent expansion is power series of $\mu_1 \propto 1/T$.

It should be emphasized that the dimensionless variables μ_0, μ_1, and y_m are used in the upper expressions.

APPENDIX B: APPROXIMATION OF k_m AND f_{dm}

When w_0 is much smaller or $w_0 \ll 1$, Eqs. (47) and (50) could be approximately expanded as a series of a simple term of w_0, then

$$k = e^{-w_0}\left[1 - M_z\left(1 - \frac{1}{1 - \frac{w_0}{2}}e^{-w_0}\right)\right] \approx 1 - \left(\frac{M_z}{2} + 1\right)w_0.$$

$$(B1)$$

But $w_0 = \Omega_0\sqrt{u_c/k}$. If let $\sqrt{k} \equiv x$, (B1) becomes

$$x^3 - x + q = 0, \qquad (B2)$$

where $q = [(M_z/2) + 1]\Omega_0\sqrt{u_c}$. According to the normal solution of the cubic function, the discriminant is $\Delta = (q/2)^2 + (-1/3)^3 = -\frac{1}{27} + (q^2/4)$,

(1) $\Delta > 0$, there are a couple of conjugating complex roots and a negative root, which is unphysical in our discussions;

(2) $\Delta < 0$, there are three roots, two positive and one negative. The larger one of the positive roots corresponds to minimum;

(3) $\Delta = 0$, the two real roots are equal to each other.

Thus the criterion from $\Delta < 0$ is

$$u_c < \frac{4}{27}\left(\frac{1}{2}M_z + 1\right)^{-2}\frac{1}{\Omega_0^2}, \qquad (B3)$$

and the three roots could be expressed as triangle functions

$$x_1 = \frac{2}{\sqrt{3}}\cos\theta, \quad x_2 = \frac{2}{\sqrt{3}}\cos(\theta + 120\,^\circ),$$

$$x_3 = \frac{2}{\sqrt{3}}\cos(\theta + 240\,^\circ), \qquad (B4)$$

where $\theta = 60^\circ - \frac{1}{3}\cos^{-1}[(3\sqrt{3}/2)q]$. It is obvious that $x_1, x_3 > 0$ and x_1 is the root corresponding to the minimum.

Now, look at Eq. (42) with the approximation of simple function of w_0. With combinations of equation $n_{dm} - \{w_{0m}/[1 - (w_{0m}/2)]\}M_z e^{-w_{0m}} = 0$ and equation $n_{dm} = 1 - \frac{1}{2}M_z w_0$ deduced from Eq. (B1), the separatrix could be expressed as

$$w_{0m} \approx \frac{2}{3M_z}. \qquad (B5)$$

Using this in the expression of k_m, the separatrix becomes

$$u_c = \frac{1}{\Omega_0^2}\frac{8}{27}\frac{1}{M_z^2}\left(1 - \frac{1}{M_z}\right) \qquad (B6)$$

or

$$u_c = \frac{8}{27}\frac{1}{\Omega_0^2}\frac{1}{\left(M_z + \frac{1}{2}\right)^2}. \qquad (B7)$$

[1] C. H. Pennington and V. A. Stenger, Rev. Mod. Phys. **68**, 855 (1996).

[2] M. S. Dresselhaus, G. Dresselhaus, and P. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, New York, 1996).

[3] O. Gunnarsson, Rev. Mod. Phys. **69**, 575 (1997).

[4] L. Degiorgi, Adv. Phys. **49**, 207 (1998).

[5] Y. Iwasa and T. Takenolu, J. Phys.: Condens. Matter **15**, R495 (2003).

[6] M. Schluter, M. Lannoo, M. Needels, G. A. Baraff, and D. Tománek, Phys. Rev. Lett. **68**, 526 (1992).

[7] J. E. Han, O. Gunnarsson, and V. H. Crespi, Phys. Rev. Lett. **90**, 167006 (2003).

[8] V. M. Loktev, A. Pashitski, É. R. Shekhter, and M. Jonson, Low Temp. Phys. **28**, 821 (2002).

[9] S. Suzuki, S. Okada, and K. Nakao, J. Phys. Soc. Jpn. **69**, 2615 (2000).

[10] P. Paci, E. Cappelluti, C. Grimaldi, L. Pietronero, and S. Strassler, Phys. Rev. B **69**, 024507 (2004).

[11] Y. Asai, Phys. Rev. B **68**, 014513 (2003).

[12] E. Cappelluti, C. Grimaldi, L. Pietronero, S. Strassler, and G. A. Ummarino, Eur. Phys. J. B **21**, 383 (2001).

[13] A. S. Alexandrov and V. V. Kabanov, Phys. Rev. B **54**, 3655 (1996).

[14] J. W. Yoo, T. H. Park, and H. Y. Choi, Physica C **364**, 64 (2001).

[15] Y. Takada and T. Hotta, Int. J. Mod. Phys. B **12**, 3042 (1998).

[16] T. K. Kopec and J. V. Jose, Phys. Rev. Lett. **84**, 749 (2000).

[17] S. Sachdev and O. A. Starykh, Nature (London) **405**, 322 (2000).

[18] S. Doniach, in *Proceedings of the NATO ASI on Percolation, Localization, and Superconductivity 1983*, edited by A. M. Goldman and S. A. Wolf (Plenum, New York, 1984).

[19] D. Das and S. Doniach, Phys. Rev. B **60**, 1261 (1999).

[20] R. Fazia and H. van der Zart, Phys. Rep. **355**, 235 (2001).

[21] D. M. Wood and D. Stroud, Phys. Rev. B **25**, 1600 (1982).

[22] G. Deutscher, Y. Imry, and L. Gunther, Phys. Rev. B **10**, 4598 (1974).

[23] B. K. Chakraverty, A. Taraphder, and M. Avignon, Physica C **235-240**, 2323 (1994).

[24] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, Suppl. 3, edited by F. Seitz, D. Turnbull, and H. Ehrenrech (Academic, New York, 1963).

[25] M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975).

[26] H. Shimoda, Y. Iwasa, Y. Miyamoto, Y. Maniwa, and T. Mitani, Phys. Rev. B **54**, R15653 (1996).

[27] L. D. Rotter, Z. Schlesinger, J. P. Cauley, N. Coustel, J. E. Fischer, and A. B. Smith, Nature (London) **355**, 532 (1992).

[28] S. A. FitzGerald, S. G. Kaplan, A. Rosenberg, A. J. Sievers, and R. A. S. McMordie, Phys. Rev. B **45**, 10165 (1992).

[29] P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. M. Denenstien, J. P. McCauley, Jr., Amos B. Smith III, and D. E. Cox, Phys. Rev. Lett. **66**, 2911 (1991).

[30] W. I. F. David, R. M. Ibberson, T. J. S. Dennis, J. P. Hare, and K. Prassides, Europhys. Lett. **18**, 225 (1992).

[31] L. Degiorgi, G. Briceno, M. S. Fuhrer, A. Zettl, and P. Wachter, Nature (London) **359**, 541 (1994).