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Density of states of the superconducting fullerides $\mathbf{Na_2Cs_xC_{60}}$ and $\boldsymbol{M}_{\mathbf{3-y}}\mathbf{Ba_yC_{60}}$

Hai Huang
Department of Physics, Peking University, Beijing 100871, China

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From experiment it was found that the superconducting transition temperature of the fulleride compounds $Na_2Cs_xC_{60}$ $(0<x<1)$ and $M_{3-y}Ba_yC_{60}$ $(0.2<y<2, M=\text{K, Rb, or Cs})$ drops quickly when the carrier concentration is deviated from the half filling of the t_{1u} band. We propose an impurity model to study the density of states (DOS) of these alkali-doped C_{60} compounds. Based on the phase shift analysis of Friedel, we find the density of states at the Fermi level decreases sharply due to the strong *s*-wave scattering. This gives a reasonable explanation to the strange behavior of the superconducting transition temperature of these two families of fulleride systems.

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The fulleride superconductors A_3C_{60} are face-centered cubic (fcc) crystals, and contain three alkali ions per molecule which occupy two tetrahedral sites and one octahedral site. Due to the high electron affinity of the C_{60} molecule and the low ionization potentials of alkali metals,[1] the electrons of the alkali metals are completely transferred to the neutral C_{60} molecules according to the frequency measurement of $A_g(2)$ Raman mode.[2] As to the superconducting fullerides deviated from the half filling $n=3$, Yildirim *et al.* studied two families of fulleride compounds: $Na_2Cs_xC_{60}$ $(0<x<1)$ and $M_{3-y}Ba_yC_{60}$ $(0.2<y<2, M=\text{K, Rb, or Cs})$.[3] They found that the superconducting transition temperature for these compounds drops quickly as the valence $n=2+x$ or $3+y$ is deviated from 3, and the superconductivity is lost when $|n-3|>0.5$. They then suggest that a correct theory of fulleride superconductivity should predict the density of states at the Fermi level decreasing rapidly as the molecular valence is deviated from the half filling in either direction. But on the theoretical side, the calculations on the density of states show a steady reduction with energy around half filling $n=3$.[4,5] When we increase the filling n, the density of states at the Fermi level drops, which can explain the drop in T_c on $n>3$ side; but there is no such an explanation for $n<3$. The situation can be slightly changed if the potential of the vacancies from the alkali atoms is taken into account.[6,7] But based on a self-consistent Hartree calculation for a model of $A_{3-x}C_{60}$ $(A=\text{K,Rb})$, it was found that the density of states is only weakly influenced by the presence of vacancies. We propose an impurity model for the alkali-doped C_{60} fullerides away from the half filling. We treat A_3C_{60} as a perfect crystal which consists of A^+ and C_{60}^{3-} ions. Ignoring the difference of alkali ions, $Na_2Cs_xC_{60}$ can be looked as putting vacancies with the concentration $1-x$ in the Na_3C_{60} crystal. Similarly, for $M_{3-y}Ba_yC_{60}$ some M^+ sites of M_3C_{60} are occupied by Ba^{2+} ions. So from the physical point of view, we can understand the former (or later) case as imposing the acceptors (or donors) with the concentration $1-x$ (or y) on the background of A_3C_{60} crystal. The acceptors (or donors) possess charge $-e$ (or $+e$) at the corresponding alkali ion sites. It is assumed here that all C_{60} molecules and alkali ions are at their ideal positions, and that there are no distortions due to the impurities. Based on this impurity model, we will argue that the density of states at the Fermi level can be changed very rapidly because of the impurity scattering when the valence is deviated from $n=3$. We use the Green's function methods to deal with this impurity problem.

We start by formulating the problem of scattering a single electron from an impurity potential. The total Hamiltonian is given by

$$H=H_0+H_1, \tag{1}$$

where H_0 is the electron Hamiltonian without the impurity and H_1 is the impurity potential. H_0 can include both the tight-binding and the electron-electron correlation terms. The retarded Green's functions with and without the impurity potential can be defined, respectively, as[8,9]

$$G(E)=\frac{1}{E-H+i\eta} \tag{2}$$

and

$$G_0(E)=\frac{1}{E-H_0+i\eta}(\eta\to 0^+). \tag{3}$$

The scattering matrix T can therefore be written as[8,9]

$$T(E)=\frac{H_1}{1-G_0H_1}. \tag{4}$$

Due to the strong screening effect of the conducting electrons,[7] we suppose the potential produced by the charged impurity is pointlike

$$H_1(\vec{x})=U\delta(\vec{x}) \tag{5}$$

and we have its Fourier transformation

$$H_1(\vec{q})=U/\Omega, \tag{6}$$

where Ω is the volume of the system. This simplified potential allows us to derive exact expressions for the physical quantities of interest and it has been proved very successful in the discussions of the semiquantitative effects of the short-ranged potentials due to impurities in systems such as real metals. In this particular model, the scattering matrix can be calculated as

$$T = \frac{U/\Omega}{1 - \overline{G_0(E)}U}, \tag{7}$$

where

$$\overline{G_0(E)} = \frac{1}{\Omega}\sum_{\vec{p}} G_0(\vec{p},E) = F(E) - i\pi\rho^0(E). \tag{8}$$

Here $\rho^0(E)$ is the density of states of the electron in the crystal without the impurity and $F(E)$ is defined as its Hilbert transformation. We see that the T matrix is isotropic, showing that this potential corresponds to neglecting the higher angular momentum components in the scattering amplitude. Following Ref. 9, the s-wave phase shift δ_0 is given by

$$\tan \delta_0 = \frac{\pi\rho^0(E)}{F(E) - \frac{1}{U}}. \tag{9}$$

At the same time, the s-wave phase shift at the Fermi level is also confined by the Friedel sum rule[10,11]

$$\frac{1}{\pi}\delta_0(E_f) = \frac{1}{2}Z, \tag{10}$$

where Z is the charge of the impurity. This sum rule can be evaluated explicitly using Green's function techniques.[9] Here we give an intuitive argument due to Friedel. Let us consider an impurity to be put at the center of a large sphere of radius R. From the scattering theory of quantum mechanics,[12] the eigenvalues are given by the condition

$$pR + \delta_0(p) = m\pi \quad (m\text{:integer}), \tag{11}$$

where p is the momentum of incoming particle. Thus the change in the number of states per unit change of p is given by $\frac{1}{\pi}\frac{d\delta_0}{dp}$. Then the total change up to some particular momentum p (or energy E) is just $\pi^{-1}\delta_0(E)$. Now if the perturbation H_1 is produced by a point charge e, we need $\frac{1}{2}Z$ new levels to appear below the Fermi level E_f to neutralize the system, which gives us the Friedel sum rule. Since $\delta_0(E_f)$ is related to U through Eq. (9), Eq. (10) is the condition for self-consistency of the perturbation.

Now we can calculate the change in the density of states at the Fermi level per added impurity

$$\begin{aligned}\delta\rho(E_f) &= \left.\frac{1}{\pi}\frac{d\delta_0(E)}{dE}\right|_{E_f}\\ &= \frac{1}{2\pi}\left(\frac{1}{\rho^0}\frac{d\rho^0}{dE}\right)_{E_f}\sin(\pi Z) - \frac{1}{\pi^2}\left(\frac{1}{\rho^0}\frac{dF}{dE}\right)_{E_f}\sin^2\left(\frac{1}{2}\pi Z\right).\end{aligned} \tag{12}$$

This result can be compared with the rigid-band model, which postulates that an energy increment ΔE is induced by the perturbation in the band, such that the number of states displaced is $\rho^0(E_f)\Delta E = \frac{1}{2}Z$. The change in the density of states at Fermi level is then

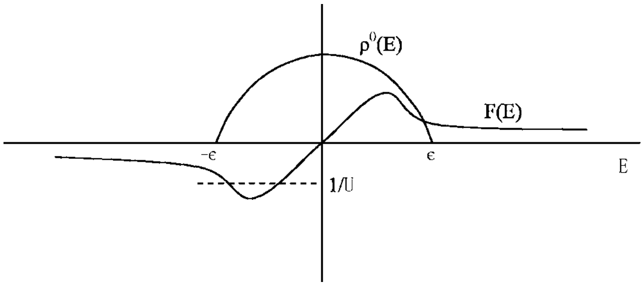

FIG. 1. The density of states $\rho^0(E)$ and its Hilbert transformation $F(E)$ for the parabolic model.

$$\delta\rho(E_f) = \Delta E\left(\frac{d\rho^0}{dE}\right)_{E_f} = \frac{1}{2}Z\left(\frac{1}{\rho^0}\frac{d\rho^0}{dE}\right)_{E_f}. \tag{13}$$

So the rigid-band result represents a good approximation to the first term of Eq. (12) in the limit of small Z.

For $Z = \pm 1$, which is the case in our problem, we have a simple form

$$\delta\rho(E_f) = -\frac{1}{\pi^2}\left(\frac{1}{\rho^0}\frac{dF}{dE}\right)_{E_f} \tag{14}$$

from Eq. (12).

It is proper to suppose $\left(\frac{dF}{dE}\right)_{E_f}$ is positive around the middle of the band, which can qualitatively be seen by using a simple model with the density of states

$$\rho^0(E) = \rho^0\left(1 - \frac{E^2}{\epsilon^2}\right) \tag{15}$$

extending from $E = -\epsilon$ to $E = +\epsilon$. Then $F(E)$ can be found by Kramers-Kronig relation

$$F(E) = \rho^0\left[2\left(\frac{E}{\epsilon}\right) - \left(1 - \frac{E^2}{\epsilon^2}\right)\ln\left|\frac{E-\epsilon}{E+\epsilon}\right|\right]. \tag{16}$$

Based on the consensus on the alkali-metal-doped fullerides so far: $n=2$ or 4 is a nonmagnetic Jahn-Teller-Mott (JTM) insulator[13] and $n=3$ is a conductor, we use this particular Green's function to simulate the narrow band between $n=2$ and $=4$.[14] We plot the density of states $\rho^0(E)$ and its Hilbert transformation $F(E)$ for this parabolic model in Fig. 1. Now let us include the effect of the impurity. Suppose that the impurity potential is attractive, i.e., U is negative, and is large enough to intersect $F(E)$ in two points as shown in Fig. 1. The s-wave phase shift δ_0 rises from zero at the left band edge until it reaches $\pi/2$ at the first intersection, then approaches close to π, falls to the value of $\pi/2$ again at the second intersection, and then goes to zero as the energy continues to increase. We can interpret the behavior of the phase shift as following. Close to the first intersection, a virtual state has been created. If $\rho_0(E)$ is small, we will get a very sharp peak which is called a "resonance." Since the total number of states is conserved, the phase shift has to drop to zero at the right edge of the band. It tells us that the virtual state has been removed from the vicinity of the second intersection. So the change in the density of states at the Fermi level depends on the location of the Fermi energy. If the

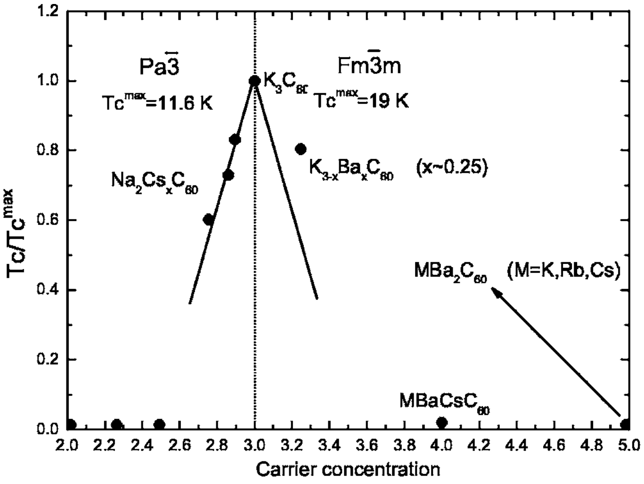

FIG. 2. $T_c/T_c^{\max}$ vs carrier concentration n in two families of fulleride superconducting compounds. Here we scale T_c by the end members Na_2CsC_{60} and K_3C_{60}.

Fermi energy is near the band edge, a large increase of the density of states will be predicted because of the presence of the virtual state at the Fermi level. If the Fermi energy is close to the middle of the band, the density of states is expected to decrease.

The width of the virtual state is also of interest. This is controlled by the value of $\rho^0(E)$ at the point of intersection. When $\rho^0(E)$ is small, the state is very narrow. If the intersection is below the edge of the band, $\rho^0(E)$ will be zero, and we get a bound state which is infinitely sharp. So the distinction between virtual states and bound states is largely one of degree.

For the parabolic model, we have the change of the density of states in the middle of the band from Eqs. (14)–(16)

$$\delta\rho(E_f) = -\frac{8}{\pi^2 w} \tag{17}$$

if the charge of the impurity is $\pm e$. Here $w=2\epsilon$ is the band width. We see that the impurity will cause a large decrease in the density of states if the band width is narrow. It is also interesting to note that it is independent of the sign of the impurity charge.

With the experimental data now in hand, the superconductivity in the alkali-metal-doped fullerenes can be understood by the conventional electron-phonon (BCS) mechanism, although the parameters of the theory have been pushed to the limit of applicability. A simple estimate of the transition temperature T_c can be obtained from the McMillan formula[15]

$$T_c = \frac{\omega_{\ln}}{1.2}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right], \tag{18}$$

where $\omega_{\ln}$ is a typical phonon frequency (logarithmic average), the parameter λ represents the electron-phonon coupling which is the product of the density of states at the Fermi level $\rho(E_f)$ and a coupling matrix V, and μ^* is the Coulomb pseudopotential which describes the effects of the repulsive Coulomb interaction. C_{60} has intramolecular vibrations with energies up to around 0.2 eV. All the theoretical calculations find that the strongest electron-phonon coupling is from one of the uppermost phonons,[16–19] we then set $\omega_{\ln} \sim 0.2$ eV. It was very early pointed out that the Coulomb repulsion can be reduced by the retardation effects.[20–23] Summing over the ladder diagrams in simple models, we can get the Coulomb pseudopotential $\mu^* \sim 0.2$ which is only slightly larger than the conventional superconductor case. As to the density of states at the Fermi level, there have been several theoretical calculations on K_3C_{60}, which gives about 8 states/eV spin.[4,5,24–28] This result has been verified by the measurement of NMR relaxation rate,[29] the experiment on the specific-heat jump at the superconducting transition,[16] and the susceptibility measurement from SQUID and EPR experiments.[30]

If the deviation of the carrier concentration from $n=3$ is small, to a first approximation, the transition temperature in Eq. (18) can be rewritten as

$$T_c \approx T_c^{\max}\left[1 + \frac{1.1V\,\delta\rho(E_f)}{(0.9\lambda-0.2)^2}|n-3|\right], \tag{19}$$

where $T_c^{\max}$ is the transition temperature at the half filling. (For the family of $Na_2Cs_xC_{60}$ or $K_{3-y}Ba_yC_{60}$, $T_c^{\max}$ is for Na_2CsC_{60} or K_3C_{60}.) Here we assume that V is unchanged in the presence of the impurities. Some measurements have been made of the superconducting transition temperature in two families of the fulleride compounds $Na_2Cs_xC_{60}$ $(0<x<1)$ and $M_{3-y}Ba_yC_{60}$ $(0.2<y<2)$. The results are shown as the experimental points in Fig. 2. We note first that the decrease of the transition temperature deviated from the half filling is in agreement with Eq. (19). We also show in Fig. 2 a straight-line fitting to the experimental data for $n<3$, since continuous tuning of $n>3$ in experiment proved to be more difficult than $n<3$ due to the limited solubility of Ba in M_3C_{60}, and has yielded only partial success.[3] Plugging in

$$T_c^{\max} = 19 \text{ K} \tag{20}$$

and

$$\rho^0(E_f) \approx 8 \text{ states/eV spin} \tag{21}$$

for K_3C_{60}, we get the bandwidth

$$w \approx 0.2 \text{ eV} \tag{22}$$

from Eqs. (19) and (17). From Ref. 14, the total t_{1u} bandwidth is roughly $3w \approx 0.6$ eV, which is very close to the value of 0.61 eV from the first-principles calculations.[24]

The similar magnitudes of the typical phonon energy and the bandwidth of the fullerides raise doubt about the validity of Migdal's theorem,[31] which is assumed to be valid in the derivation of the McMillan formula.[15,32] But it is reasonable to imagine that the DOS at Fermi level is strongly related to the number of the Cooper pairs produced or the superconducting gap. So even if the McMillan formula may not work in our problem, we can still get the following qualitative picture: With the drop of the DOS at Fermi level away from half filling, there is a peak of the superconducting transition temperature exactly at $n=3$ due to the impurity effect.

This result seems also inconsistent with the Anderson's theorem, which says the nonmagnetic impurities do not have spectacular effects on the transition temperature in the metallic systems.[33,34] But Anderson's theorem is based on the gradual change of the density of states on the Fermi surface. In our problem, due to the strong impurity scattering the density of states at Fermi level can be sharply changed. So it can produce the rapid drop of the superconducting transition temperature.

In summary, from the experimental results of both families $Na_2Cs_xC_{60}$ and $M_{3-y}Ba_yC_{60}$, it was shown that the superconducting transition temperature T_c peaks at $n=3$. This result cannot be explained by one-electron band theory or strong correlated models. We propose an impurity model to study this problem. With the help of the phase shift analysis, we predict that the density of states at the Fermi level decreases very rapidly due to the s-wave impurity scattering when the carrier concentration is deviated from the half filling. This gives a reasonable explanation to the strange behavior of the superconducting transition temperature of these two families of fulleride compounds. How to include this impurity effect into the quantitative theories of the alkali-metal-doped fullerides is the work we reserve for the near future.

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[1] For a review, see R. C. Haddon, Acc. Chem. Res. **25**, 127 (1992).

[2] H. Kuzmany *et al.*, Adv. Mater. (Weinheim, Ger.) **6**, 731 (1994).

[3] T. Yildirim, L. Barbedette, J. E. Fischer, C. L. Lin, J. Robert, P. Petit, and T. T. M. Palstra, Phys. Rev. Lett. **77**, 167 (1996).

[4] M. P. Gelfand and J. P. Lu, Phys. Rev. Lett. **68**, 1050 (1992).

[5] M. P. Gelfand and J. P. Lu, Phys. Rev. B **46**, 4367 (1992).

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

[7] O. Gunnarsson, Proc.-Electrochem. Soc. **97-42**, 488 (1997).

[8] E. N. Economou, *Green's Functions in Quantum Physics* (Springer-Verlag, Berlin, 1990).

[9] S. Doniach and E. H. Sondheimer, *Green's Functions for Solid State Physicists* (Addison-Wesley, New York, 1982).

[10] J. Friedel, Nuovo Cimento, Suppl. **7**, 287 (1958).

[11] A. M. Clogston, Phys. Rev. **125**, 439 (1962).

[12] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1955).

[13] M. Fabrizio and E. Tosatti, Phys. Rev. B **55**, 13465 (1997).

[14] M. Granath and S. Östlund, Phys. Rev. B **68**, 205107 (2003).

[15] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[16] V. P. Antropov, O. Gunnarsson, and A. I. Liechtenstein, Phys. Rev. B **48**, 7651 (1993).

[17] C. M. Varma, J. Zaanen, and K. Raghavachari, Science **254**, 989 (1991).

[18] M. Schluter, M. Lannoo, M. Needels, G. A. Baraff, and D. Tomanek, J. Phys. Chem. Solids **53**, 1473 (1992).

[19] J. C. R. Faulhaber, D. Y. K. Ko, and P. R. Briddon, Phys. Rev. B **48**, 661 (1993).

[20] N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, *A New Method in Superconductivity* (Consultants Bureau, New York, 1958).

[21] P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

[22] J. R. Schrieffer, *Theory of Superconductivity* (Benjamin, New York, 1964).

[23] V. L. Ginzburg and D. A. Kirzhnits, *High-temperature Superconductivity* (Consultants Bureau, New York, 1982).

[24] S. C. Erwin and W. E. Pickett, Science **254**, 842 (1991).

[25] S. C. Erwin and W. E. Pickett, Phys. Rev. B **46**, 14257 (1992).

[26] S. Satpathy, V. P. Antropov, O. K. Andersen, O. Jepsen, O. Gunnarsson, and A. I. Liechtenstein, Phys. Rev. B **46**, 1773 (1992).

[27] V. P. Antropov, O. Gunnarsson, and O. Jepsen, Phys. Rev. B **46**, 13647 (1992).

[28] Martin P. Gelfand and J. P. Lu, Phys. Rev. B **47**, 4149(E) (1993).

[29] V. P. Antropov, I. I. Mazin, O. K. Andersen, A. I. Liechtenstein, and O. Jepsen, Phys. Rev. B **47**, 12373 (1993).

[30] A. P. Ramirez, M. J. Rosseinsky, D. W. Murphy, and R. C. Haddon, Phys. Rev. Lett. **69**, 1687 (1992); W. H. Wong, M. E. Hanson, W. G. Clark, G. Grüner, J. D. Thompson, R. L. Whetten, S.-M. Huang, R. B. Kaner, F. Diederich, P. Petit, J.-J. Andre, and K. Holczer, Europhys. Lett. **18**, 79 (1992).

[31] A. B. Migdal, Sov. Phys. JETP **7**, 996 (1958).

[32] G. M. Eliashberg, Sov. Phys. JETP **11**, 696 (1960).

[33] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).

[34] P. G. de Gennes, *Superconductivity of Metals and Alloys* (Addison-Wesley, New York, 1966).