Pis'ma v ZhETF, vol.65, iss.5, pp.419 - 424

SUPERCONDUCTIVITY IN IMPURITY BANDS

A.I.Agafonov, E.A.Manykin

Russian Research Center "Kurchatov Institute"

Moscow 123182, Russia

Submitted 15 January 1997

We present a theory of superconductivity in doped insulators. In the magnetic metal state of the compound we obtain the self-consistency equations for the superconducting state in the spin-dependent impurity bands of both extended and localized states in the initial insulator gap. A BCS-type triplet pairing field is considered. We show that the superconducting gap in which single-electron extended states do not exist is overlapped by the distribution of the localized states. The formation of a latent superconducting gap is discussed in connection with the unusual properties of high-T_c compounds.

PACS: 71.27.+a, 71.30.+h, 74.20.Mn, 74.72.-h

A surprising feature of high-T_c materials is the strong doping dependence of the density of electronic states (DOS). It has been established from experimental studies of the optical properties of these materials is that doping diminishes the DOS above the initial insulator gap and gives rise to new features deep in the gap [1-5].

The formation of the substitution-induced gap states is inherent to the doped compounds [6]. The parent compounds have an antiferromagnetic insulating state. The magnetic phase disappears with small doping, and the material goes to a poor-metallic phase with a large T_c.

An adequate model for describing high-T_c superconductors must be consistent with the position of the Fermi level with doping. The most commonly used approach is to relate the superconductivity to processes occurring in structure elements of the parent compound, e.g., in the CuO_2 planes of the cuprates [6-11]. Then one would expect the Fermi level to lie outside the initial insulator gap in both the metal and superconducting states [6,12]. However, there are reliable experimental data which indicate that the Fermi level lies inside the gap, among the doping-induced gap states (see [6] and references therein). Moreover, the Fermi level appears to depend weakly on impurity concentrations.

From our point of view, the combined effect of disorder caused by impurity atoms and electron correlations in the doped system is a central issue in high-T_c superconductivity.

Upon substitutional doping, in $La_{2-x}Sr_xCuO_4$, for example, La^{3+} is randomly replaced by Sr^{2+}. Both valence electrons of Sr go to satisfy the bonding requirements, and a singly occupied acceptor level arises in the initial gap. Doping with nominal Ce^{4+} for Nd^{3+} in $Nd_{2-x}Ce_xCuO_4$ gives a singly occupied donor level in the gap. Hybridization between the impurity levels and the initial band states of the insulator can significantly change the DOS.

The DOS modification caused by the hybridization and potential scattering of band electrons by impurity atoms randomly distributed in the host lattice has been studied in [13]. With the use of multiple-scattering theory, the configuration-averaged Green's functions over the impurity ensemble were calculated by the

Matsubara method. It was shown that doping sharply decreases the DOS above the gap near the band edge and gives rise to impurity bands of both extended and localized states in the gap region. The formation of the narrow, high-density band of extended states is caused by hybridization, which induces virtual electronic transitions over the impurity ensemble: an initial impurity site → a band state → another site → a band state, etc. It is important that the main high-concentration peak of the localized states lies within this band.

The Anderson model with strong on-site electron correlations for the impurity levels and the hybridization has been used to study magnetic ordering and insulator → metal phase transitions in the impurity bands in the self-consistent Hartree–Fock approximation [14]. The narrow, high-density bands of extended states (which are spin-degenerate only in the case of a paramagnetic metal) within the insulator gap have the same origin as in [13]. Although the impurity band structure depends strongly on the impurity concentration (as a matter of fact, it causes the transitions in the system), the Fermi level depends only weakly on the doping. For the singly occupied donor levels a magnetic insulator state with a finite magnetic moment per impurity atom is realized in the system at low impurity concentrations. With increasing concentration, two metallization stages of the system have been found [14], which correspond to the transitions: magnetic insulator → magnetic metal → paramagnetic metal. In these metallic states the Fermi level lies within the main peak of the localized states, but this peak lies within the impurity band of extended states.

In this letter we present a model of high-T_c superconductivity in the impurity bands. In the magnetic metal state the problem reduces to searching for superconductivity in a subsystem with low concentrations and kinetic energies of the electrons but with a high density of extended states at the Fermi level. Because of the spin dependence of the DOS in this state, only triplet pairing can be realized. Here we restrict ourselves to the BCS-type triplet pairing field caused by electron–phonon coupling. The hopping mechanism of superconductivity, which is also predicted by the model, will not be calculated numerically. We shall show that the superconducting gap in which single-electron extended states do not exist is overlapped by the distribution of the localized states. The latent superconducting gap must result in unusual properties of these superconductors.

The Hamiltonian of the system is

$$H = H_A + H_{el-ph}, \tag{1}$$

where H_{el-ph} describes the electron–phonon interaction, and H_A is the Anderson Hamiltonian describing the insulator in the single-band approximation (for definiteness, the valence band) with an ensemble of impurity atoms randomly distributed in the host lattice:

$$H_A = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} a^+_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} + \sum_{j\sigma} \varepsilon_0 d^+_{j\sigma} d_{j\sigma} + \sum_j U n_{j\sigma} n_{j,-\sigma} + \sum_{j,\mathbf{k},\sigma} \{V_{\mathbf{k}j} a^+_{\mathbf{k}\sigma} d_{j\sigma} + \text{h.c.}\}, \tag{2}$$

where $a_{\mathbf{k}\sigma}$ and $d_{j\sigma}$ are the usual annihilation operators; σ is the spin index; $\mathbf{k}$ is the wave vector of an electron in the band state with the energy $\varepsilon_{\mathbf{k}}$; j is the number of the impurity atom; ε_0 is the bare impurity level located in the gap above the band top; $V_{\mathbf{k}j}$ is the matrix element of the hybridization; U is the

on-site electron correlation for the impurity levels. Here $\sum_{\mathbf{k}\sigma} = N_t$ is the total number of band states; $\sum_j = N_{im}$ is the impurity concentration.

The Hamiltonian (2) has been solved in the Hartree–Fock approximation with self-consistent determination of the Fermi level (see [14] for details). To model the DOS modification, we chose the "semi-elliptical" model of a symmetrical, narrow valence band with a width of $2D_b$. At a certain impurity concentration the system goes to a metallic phase with a finite magnetic moment per impurity atom. The fraction of the σ-spin DOS per impurity atom near the Fermi level in the initial insulator gap at $N_{im} = 0.15N_t$ is shown in Fig.1. Here $\sigma = \pm$ denotes the spins. The δ-function peak of the localized states D_m^σ corresponds to a simple pole ξ_d^σ of the Green's function $G_{jj}^{(1)\sigma}$. This peak lies within the high-density band of extended states E_g^σ. That the position of this pole lies within the band E_g^σ is a common feature for the various parameter sets. The Fermi energy $E_F^0 = \xi_d^+$ and, accordingly, the D_m^+ and E_g^+ bands are partially occupied. The total number of localized states per impurity atom (or, in other words, the pole amplitude) is $N_m^+ = 0.597$, and the occupation per impurity atom is $\eta_m^+ = 0.394$. The total number of extended states per impurity atom is $N_g^+ = 0.128$, and their occupation per impurity atom is $\eta_g^+ = 0.063$. The magnetic moment is $0.466\mu_B$; the bands with $\sigma = -$ are unoccupied.

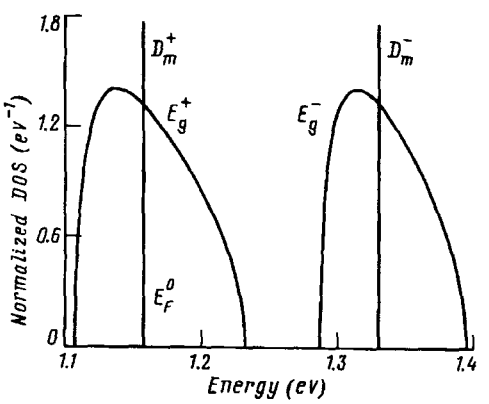

Fig. 1. The DOS per impurity atom for the magnetic metal state near the Fermi level $E_F^0 = 1.158$ eV. The energy is reckoned from the unperturbed valence band top. Parameter set: $N_t = 0.2\,\text{Å}^{-3}$, $D_b = 1.5$ eV, $\epsilon_0 = D_b + 0.5$ eV, $N_{im} = 0.15N_t$, $V_{\mathbf{k}j}N_t^{1/2} = 1.3$ eV, $U = 0.5$ eV

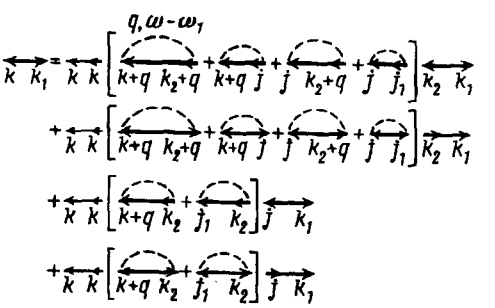

Fig. 2. The diagram equation for the anomalous Green's function $F^+_{-\mathbf{k}\mathbf{k}_1}(\omega)$. The line $\longleftrightarrow$ shows the anomalous Green's function F^+, the line $\rightarrow\!\!\rightarrow$ shows the single-electron Green's function G, and the dashed line shows the unperturbed phonon Green's function $D(\mathbf{q}, \omega - \omega_1)$

Thus the problem reduces to one of searching for superconductivity in a subsystem with low concentrations and kinetic energies of the electrons but a high density of extended states at the Fermi level. From Fig.1 one can estimate that the average DOS in the narrow band E_g^+, which has a width of $\Delta = 0.124$ eV, is equal to $N_g^+ N_{im}/\Delta \simeq 0.3 \cdot 10^{23}$ cm^{-3}eV^{-1}.

When the D_m^+ and E_g^+ bands are taken into account. the Hamiltonian (1) can be reduced to the form (the spin index is omitted):

$$H = \sum_{\mathbf{k}} \xi_{\mathbf{k}} c^+_{\mathbf{k}} c_{\mathbf{k}} + \sum_{l} \xi_d f^+_l f_l + H^0_{ph} +$$

$$+ \sum_{l,\mathbf{k},\mathbf{q}} \left(\kappa_{l\mathbf{k}\mathbf{q}} f^+_l c_{\mathbf{k}} + \text{h.c.}\right)\phi_{\mathbf{q}} + \sum_{\mathbf{k},\mathbf{q}} \lambda_{\mathbf{q}} c^+_{\mathbf{k}} c_{\mathbf{k}-\mathbf{q}} \phi_{\mathbf{q}}, \tag{3}$$

where $c_{\mathbf{k}}$ is the annihilation operator of an electron in the E^+_g band state with energy $\xi_{\mathbf{k}}$; f_l is the annihilation operator of an electron in the D^+_m band state; $\kappa_{l\mathbf{k}\mathbf{q}}$ and $\lambda_{\mathbf{q}}$ are the matrix elements for electron–phonon scattering; $\phi_{\mathbf{q}} = b_{\mathbf{q}} + b^+_{-\mathbf{q}}$; $b_{\mathbf{q}}$ is the annihilation operator of a phonon with wave vector $\mathbf{q}$; H^0_{ph} describes the unperturbed phonons. Here $\sum_{\mathbf{k}} = N^+_g N_{im}$ and $\sum_l = N^+_m N_{im}$.

From (3) one can easily obtain a system of eight equations for the Green's functions in the superconducting state. In Fig. 2 we only show the diagram equation for the anomalous Green's function $F^+_{-\mathbf{k}\mathbf{k}_1}(\omega)$. These diagrams use the conventional notation. It is interesting to note here that for the mechanism of hopping superconductivity the diagrams including the anomalous Green's functions $F^+_{l_1 l_2}(\omega)$ and $F^+_{l\mathbf{k}}(\omega)$ are important. For this reason the most commonly used approximation in terms of the diagonal Green's functions cannot be applied. Here, since we are restricting ourselves to this approximation, hopping superconductivity will not be considered. Using the representation of a given number of electrons, the system of equations is reduced to the form (at least at zero temperature):

$$G_{ll}(\omega) = \left(\omega - \xi_d - \Sigma_{ll}(\omega)\right)^{-1}, \tag{4}$$

where the self-energy

$$\Sigma_{ll}(\omega) = i \sum_{\mathbf{k}\mathbf{q}} \int \frac{d\omega_1}{2\pi} |\kappa_{\mathbf{k}l\mathbf{q}}|^2 D(\mathbf{q}, \omega - \omega_1) G_{\mathbf{k}\mathbf{k}}(\omega_1), \tag{5}$$

$$\left(\omega - \xi_{\mathbf{k}} - \Sigma^{loc}_{\mathbf{k}\mathbf{k}}(\omega) - \Sigma^{ext}_{\mathbf{k}\mathbf{k}}(\omega)\right) G_{\mathbf{k}\mathbf{k}}(\omega) = 1 + \Delta(\mathbf{k}, \omega) F^+_{-\mathbf{k}\mathbf{k}}(\omega), \tag{6}$$

where the self-energies

$$\Sigma^{loc}_{\mathbf{k}\mathbf{k}}(\omega) = i \sum_{l,\mathbf{q}} \int \frac{d\omega_1}{2\pi} |\kappa_{\mathbf{k}l\mathbf{q}}|^2 D(\mathbf{q}, \omega - \omega_1) G_{ll}(\omega_1), \tag{7}$$

and

$$\Sigma^{ext}_{\mathbf{k}\mathbf{k}}(\omega) = i \sum_{\mathbf{q}} \int \frac{d\omega_1}{2\pi} |\lambda_{\mathbf{q}}|^2 D(\mathbf{q}, \omega - \omega_1) G_{\mathbf{k}-\mathbf{q},\mathbf{k}-\mathbf{q}}(\omega_1), \tag{8}$$

$$\left(\omega + \xi_{\mathbf{k}} - 2E_F + \Sigma^{loc}_{\mathbf{k}\mathbf{k}}(-\omega) + \Sigma^{ext}_{\mathbf{k}\mathbf{k}}(-\omega)\right) F^+_{-\mathbf{k}\mathbf{k}}(\omega) = 1 + \Delta^+(\mathbf{k}, \omega) G_{\mathbf{k}\mathbf{k}}(\omega). \tag{9}$$

Here the superconducting gap function is given by

$$\Delta^+(\mathbf{k}, \omega) = -i \sum_{\mathbf{q}} \int \frac{d\omega_1}{2\pi} |\lambda_{\mathbf{q}}|^2 D(\mathbf{q}, \omega - \omega_1) F^+_{-\mathbf{k}+\mathbf{q},\mathbf{k}-\mathbf{q}}(\omega_1). \tag{10}$$

The system (4)–(10) should be supplemented by the equation for determination of the Fermi level, which can be written in the form:

$$\eta_g^+ + \eta_m^+ = -\frac{1}{\pi N_{im}} \int_{-\infty}^{E_F} d\omega Im\Big(\sum_l G_{ll}(\omega) + \sum_{\mathbf{k}} G_{\mathbf{kk}}(\omega)\Big). \tag{11}$$

The self-energy (8) has the same form as in the Eliashberg equations obtained for pure metals. This term is important in the strong-coupling case and its role is understood. A distinction of the present model is that both localized and extended states exist at E_F. Moreover the total number of the localized states and their occupation are much greater than those for the extended states, as was shown above. In order to determine how the localized states influence the pair condensate, we henceforth take into account the self-energy (7) only.

In the calculations $\kappa_{\mathbf{k}l\mathbf{q}}$ is taken to be independent of k and q. Using the unperturbed Green's function for phonons, one obtains:

$$(2\pi)^{-1} \sum_{\mathbf{q}} |\kappa_{\mathbf{k}l\mathbf{q}}|^2 D(\mathbf{q}, \omega - \omega_1) = -\frac{2\kappa_{\mathbf{k}l\mathbf{q}}^2}{(\theta_D a_0)^3} T(\omega - \omega_1), \tag{12}$$

where

$$T(\omega) = \theta_D^2 + \omega^2 \log \frac{|\theta_D^2 - \omega^2|}{\omega^2} + i\pi\omega^2 \Theta\Big(\theta_D - |\omega|\Big). \tag{13}$$

Here θ_D is the Debye temperature and a_0 is the crystal lattice parameter. On introducing the effective constant λ_{eff}, Eq.(10) can be reduced to a BCS-type equation for the superconducting gap Δ_0:

$$\Delta^+ = -i\lambda_{\text{eff}} \sum_{\mathbf{k}} \int \frac{d\omega}{2\pi} F^+_{-\mathbf{k},\mathbf{k}}(\omega) \Theta\Big(\theta_D - |\xi_{\mathbf{k}} - E_F|\Big). \tag{14}$$

The self-consistency equations (4)–(7), (9), (11), and (14) for the superconducting state were solved by an iteration procedure.

The single-electron DOS per impurity atom for the superconducting state is shown in Fig.3. Here $\Delta_0 = 10$ meV. In the superconducting gap region the density of single-electron extended states is equal to zero. The lower edge of the region is sharp, whereas the upper edge is smeared. The width of the region is about 14 meV, which is less than the $2\Delta_0$ corresponding to the "big" gap in the BCS model. Near the edges the DOS increases sharply, as expected.

The important result is that although single-electron extended states do not exist in the superconducting gap region, the peak of the localized states overlaps this region, as can be seen from Fig.3. Thus the distribution of the localized states can obscure the superconducting gap in experimental observations. This can explain the observed qualitative distinction between the optical conductivity of $La_{1.85}Sr_{0.15}CuO_4$ and the conductivity of the classical BCS superconductor NbN [15]. A clear superconducting gap opens up in the conductivity of NbN at a photon energy ≤ 6 mev. For $La_{1.85}Sr_{0.15}CuO_4$ the gap did not manifest itself up to a photon energy ≤ 3 mev. In the present model, because the band D_m^+ of localized states is partially occupied and overlaps the superconducting gap, the optical conductivity at such low photon energies can be due to both hopping conductivity in the D_m^+ band and optical transitions From the localized states to the extended states above the upper edge of the E_g^+ band.

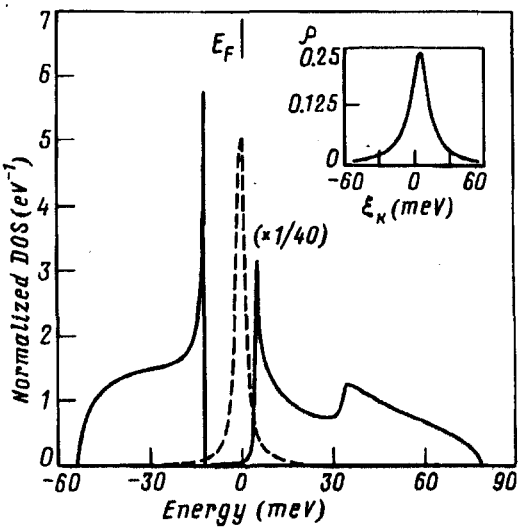

Fig.3. The single-electron DOS for the superconducting state. The energy is reckoned from the E_F^0. The Fermi level E_F = 0.672 meV. The solid curve is the impurity band E_g^+. The dashed curve is the impurity band D_m^+. The superconducting gap Δ_0 =10 meV. Inset: The energy distribution of the electron pairs. Parameter set: θ_D =33 meV, λ_{eff} =16.9 eVÅ^3 $\kappa^2_{kiq} N_t/(\Theta_D^2 a_0^3)$=0.47

In conclusion we present data on the electron concentration in the superconducting state. The energy distribution of the electron pairs $\rho(\xi_k)$ is shown in the inset of Fig.3. One can see that the distribution tends to 1/4 near E_F. We calculated the pair concentration $N_p = 2.3\times10^{20}$ cm^{-3}. From E_F and Eq.(11) we obtained the occupation number $\eta_m^+ = 0.396$ for the localized states $\eta_g^+ = 0.061$ for the extended states. The concentration of localized electrons $N_l = \eta_m^+ N_{im} = 1.188\cdot10^{22}$ cm^{-3}, and the electron concentration in the single-particle extended states $N_s = \eta_g^+ N_{im} - 2N_p = 1.38\cdot10^{21}$ cm^{-3}. Thus the relation $N_p \ll N_s \ll N_l$ shows the unusual character of the superconducting state.

1. S.Uchida, T.Ido, H.Takagi et al., Phys. Rev. B **43**, 7942 (1991).
2. J.Orenstein, G.A.Thomas, A.J.Millis et al., Phys. Rev. B **42**, 6342 (1990).
3. G.A.Thomas, D.H.Rapkine, S.L.Cooper et al., Phys. Rev. B **45**, 2474 (1992).
4. S.L.Cooper, D.Reznik, A.Kotz et al., Phys. Rev. B **47**, 8233 (1993).
5. R.O.Anderson, R.Claessen, J.W.Allen et al., Phys. Rev. Lett. **70**, 3163 (1993).
6. E.Dagotto, Rev. Modern Phys. **66**, 673 (1994).
7. Y.Fukuzumi, K.Mizuhashi, K.Takenaka et al., Phys. Rev. Lett. **76**, 684 (1996).
8. P.Monthoux and D.Pines, Phys. Rev. Lett. **69**, 961 (1992).
9. C.H.Pao and N.E.Bickers, Phys. Rev. Lett. **72**, 1870 (1994);
10. P.Fulde and P.Horsch, Europhys. News **24**, 73 (1993).
11. J.Hirsch, Physica B **199-200**, 366 (1994).
12. D.Dessau, Z.-X.Shen, D.M.King et al., Phys. Rev. Lett. **71**, 2781 (1993).
13. A.I.Agafonov and E.A.Manykin, Phys. Rev. B **52**, 14571 (1995).
14. A.I.Agafonov and E.A.Manykin, JETP **109**, 1405 (1996).
15. H.S.Somal, B.J.Feenstra, J.Schützmann et al., Phys. Rev. Lett. **76**, 1525 (1996).

Edited by Steve Torstveit