A possible mechanism for high-T_c superconductivity

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A new model, which allows for the exchange interaction of electrons on the $x^2 - y^2$ and z^2-levels of copper, is suggested for explaining the mechanism that leads to unusually strong electron (hole) pairing in the conducting Cu–O layers in high-T_c superconductors (of the $YBa_2Cu_3O_7$ type). It is demonstrated that the resulting virtual bound states of conduction electrons coupled with electrons on the z^2-levels act as local two-particle states. The interaction of these bound states, whose energy is close to E_F, with conduction electrons leads to high values of T_c and arbitrary values of the ratio $2\Delta/T_c$, which depend on the energy parameters of the problem. A large body of experimental data on high-T_c superconductivity can easily be explained within the framework of the proposed theory.

1. When superconductivity with an exceptionally high transition temperature T_c was discovered in 1986 in substances of the form $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-x}$, the problem of the mechanism of such strong electron pairing emerged. Notwithstanding the fact that electron–phonon coupling in high-T_c superconductors is fairly strong, as was demonstrated subsequently in tunneling experiments, a large number of features suggest that electron-phonon coupling does not play the main role in high-T_c superconductivity. Estimates of electron–phonon coupling constants done by Friedl *et al.*[2] provide little hope of explaining the values of about 90–100 K for T_c within the framework of the tight-binding theory. At the same time, superconductivity in high-T_c superconductors in many respects resembles ordinary s-type pairing in the BCS model. However, while retaining some properties of the BCS model, the theory must, obviously, give, say, a power-law dependence of T_c on the coupling constants rather than an exponential if it is to provide a natural explanation for the high value of T_c. The same results follow from the theories proposed in Refs. 3 and 4, which consider simultaneous transitions of two electrons from the conduction band to a model two-particle center. In this paper I discuss only superconductors containing Cu–O planes and examine the properties of 2-D superconductivity in a separate layer, assuming that on the whole the interaction between layers stabilizes superconductivity on the macroscopic level. It appears that on the basis of certain physically justified assumptions one can describe the motion of electrons (or holes) in Cu–O planes via an effective Hamiltonian, which leads to results resembling those of the above-mentioned theories.[3,4] Toward the end of this paper I show how some of the experimental data can be explained within the scope of the theory proposed here.

2. In this section we will see that the appearance of a hole with a definite spin on z^2-orbitals of copper lowers the energy of a band hole with an opposite spin on the p-levels of oxygen near such a site, and repulsion of band holes with like spin occurs. This leads to an antiferromagnetic interaction similar in many respects to the kinetic exchange interaction in the Hubbard model.[5]

Let us assume that a 2-D conduction band in a Cu–O plane is formed by hybridized p-orbitals of oxygen and $d_{x^2-y^2}$-orbitals of copper. The overlap integral is denoted by t. Since it is known that in alloying the majority of holes appear on oxygen, the position of the energy levels must correspond to the one depicted in Fig. 1a. Here only one electron can be in the $d_{x^2-y^2}$-state since Coulomb repulsion is assumed strong and we are dealing with the lower Hubbard subband.

If in the antiferromagnetic phase the spins of these electrons are ordered, however, the antiferromagnetic order is disrupted in the process of alloying and the direction of the spin of each electron is not fixed. Suppose that we remove an electron with spin "down" from a deeper level of copper, z^2 (Fig. 1b). Because of strong intratomic exchange interaction (Coulomb repulsion), the spin of an electron on the x^2–y^2-orbital becomes aligned with the spin of the electron remaining on the z^2-orbital, that is, "points" up. (This is a manifestation of the Hund rule.) Now let us consider two cases: near such a copper atom there is a band hole (on oxygen) with spin (a) "up" and (b) "down." The difference in energy of these two states depicted in Figs. 1b and 1c can be estimated in the same manner as is done for the kinetic exchange term in the Hubbard model[5] or for the superexchange Kramers mechanism.[6] In the case depicted in Fig. 1b no transition of an electron from the $x^2 - y^2$-orbital of copper to oxygen is possible. But if the spins point in opposite directions (Fig. 1c), such a transition becomes possible, and in the second-order perturbation theory in the overlap integral t this leads to a lowering of energy by $\Delta E = -t^2/E_{pd}^+$, where E_{pd}^+ is the energy difference between the p-level of oxygen and the $x^2 - y^2$-level of copper with a hole on the z^2-orbital. Note that E_{pd}^+ is greater than E_{pd}, the difference in energy of the $x^2 - y^2$-orbital and the p-orbital determining the band motion proper when the z^2-orbital is completely filled. Hence, if in the tight-binding approximation the band width W is approximately $4t^2/E_{pd}$, then $|\Delta E|/W = E_{pd}/4E_{pd}^+ < 1$. The energy difference ΔE between two spin configurations (Figs. 1b and 1c) can be taken into account as is done in the superexchange theory[6] by introducing a new term into the system's Hamiltonian:

$$\hat{H}_{z^2p} = U[\hat{n}_\uparrow(z^2)\hat{n}_\downarrow(p) + \hat{n}_\downarrow(z^2)\hat{n}_\uparrow(p)], \qquad (1)$$

where $U = \Delta E = -t^2/E_{pd}^+ < 0$.

A similar expression can be written for the case of high-T_c superconductivity of the electron type in the event of interaction of an additional electron on the Δ-orbital of copper (instead of a hole on the z^2-level) with the band electrons on the $x^2 - y^2$-orbitals of the neighboring copper atoms.

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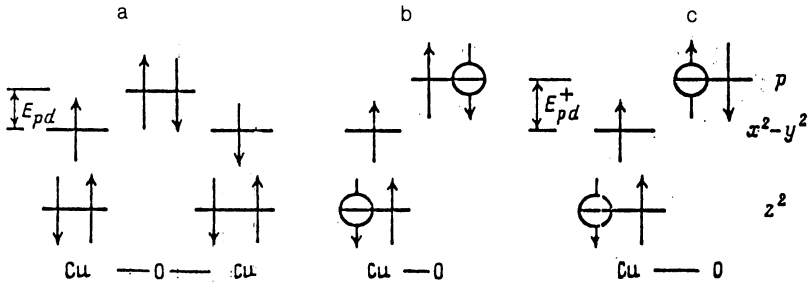

FIG. 1.

Note that naming the levels according to their classification in the atom is somewhat ambiguous since in a real crystal the eigenstates are combinations of initial states due to orbital overlap. Nevertheless, for the sake of simplicity we will use the nomenclature of initial orbitals. In what follows we will not distinguish either between alloying of the n- and p-type, and the charge carriers in a band will be called electrons for the sake of definiteness.

3. To simplify matters, let us assume that instead of moving over a real 2-D Cu–O crystal the electrons move over a simple square lattice to each site of which there corresponds a unit cell of the initial lattice. Information on the detailed structure of states in a unit cell is lost in this case, but such an approximation is quite sufficient for describing the superconducting properties as long as the coherence length ξ is much greater than the lattice constant a. Thus, we start with the following Hamiltonian:

$$\hat{H}=\sum_{i,j,\alpha} t_{ij}c_{i\alpha}^{+}c_{j\alpha}+\varepsilon_d\sum_{i,\alpha} d_{i\alpha}^{+}d_{i\alpha}$$
$$+V\sum_{i,\alpha}(c_{i\alpha}^{+}d_{i\alpha}+\text{H.c.})+U\sum_{i}(d_{i\uparrow}^{+}d_{i\uparrow}c_{i\downarrow}^{+}c_{i\downarrow}+d_{i\downarrow}^{+}d_{i\downarrow}c_{i\uparrow}^{+}c_{i\uparrow}). \tag{2}$$

Here $c_{i\alpha}^{+}$ and $d_{i\alpha}^{+}$ stand for the electron creation operators, respectively, in the conduction band and at a higher atomic level with spin α at site i. The $|c_\alpha\rangle$ states describe the conduction band formed by the hybridized p-orbitals of oxygen and the $d_{x^2-y^2}$-orbitals of copper, and the $|d_\alpha\rangle$ states describe the formation of a hole in a z^2 state for the case discussed in Sec. 2. The third term describes the weak hybridization of band and localized d states (say, the z^2 states of Cu with the p states of neighboring oxygen atoms). Finally, the fourth term, given by Eq. (1) with $U<0$, appears only when electron motion in the conduction band is strongly correlated because of strong Coulomb repulsion on the copper atom. We assume that there exists the following hierarchy of energy constants, starting with the band width $W\sim 4t$:

$$W\gg U,\quad \varepsilon_d\gg V.$$

To describe superconductivity we employ the temperature Green's function technique.[7] We introduce the following four functions:

$$\delta_{\alpha\beta}G_{ij}=-\langle Tc_{i\alpha}c_{j\beta}^{+}\rangle,\quad \delta_{\alpha\beta}D_{ij}=\langle Td_{i\alpha}c_{j\beta}^{+}\rangle,$$
$$i\sigma_{\alpha\beta}^{y}F_{ij}^{+}=\langle Tc_{i\alpha}^{+}c_{j\beta}^{+}\rangle,\quad i\sigma_{\alpha\beta}^{y}B_{ij}^{+}=\langle Td_{i\alpha}^{+}c_{j\beta}^{+}\rangle.$$

Using the equations of motion for the Matsubara operators $c(\tau)$ and $d(\tau)$, we can obtain a system of equations for the Green's functions. To make this system closed, we first represent, as usual, the contribution from the last term in the Hamiltonian (2) in the mean-field approximation in terms of pair averages. For the Fourier components of the Green's functions over space and "time" τ we arrive at the following system of equations:

$$(i\omega-\varepsilon_{\mathbf{k}})G_{\mathbf{k}\omega}-VD_{\mathbf{k}\omega}+\beta B_{\mathbf{k}\omega}^{+}=1, \tag{3a}$$
$$(i\omega-\varepsilon_d)D_{\mathbf{k}\omega}-VG_{\mathbf{k}\omega}+\beta F_{\mathbf{k}\omega}^{+}=0, \tag{3b}$$
$$(i\omega+\varepsilon_{\mathbf{k}})F_{\mathbf{k}\omega}^{+}+VB_{\mathbf{k}\omega}^{+}+\beta^{*}D_{\mathbf{k}\omega}=0, \tag{3c}$$
$$(i\omega+\varepsilon_d)B_{\mathbf{k}\omega}^{+}+VF_{\mathbf{k}\omega}^{+}+\beta^{*}G_{\mathbf{k}\omega}=0, \tag{3d}$$

where $\omega=(2n+1)\pi T$ and $\beta=|U|\ \langle d_{i\downarrow}c_{i\uparrow}\rangle = |U|B_{ii}(+0)$. Energy shifts of the $U\langle\hat{n}\rangle$ type are assumed to be included in $\varepsilon_{\mathbf{k}}$ and ε_d, which are reckoned from the chemical potential level μ. The dispersion law for $\varepsilon_{\mathbf{k}}$ is determined by the hopping integral t_{ij}, and state d is assumed to be positioned above μ, that is, $\varepsilon_d>0$.

To simplify presentation we will ignore, for the time being, the effect of hybridization V on the properties of band electrons in their normal state. Assuming that $V/\varepsilon_d\ll 1$, to within terms of the order of $(V/\varepsilon_d)^2$ we arrive at a system of equations for the functions G and F^{+} similar to the ordinary Gor'kov equations:[7]

$$(i\omega-\varepsilon_{\mathbf{k}})G_{\mathbf{k}\omega}+\left(\frac{2V\beta\varepsilon_d}{\omega^2+\varepsilon_d^2}\right)F_{\mathbf{k}\omega}^{+}=1,$$
$$(i\omega+\varepsilon_{\mathbf{k}})F_{\mathbf{k}\omega}^{+}+\left(\frac{2V\beta^{*}\varepsilon_d}{\omega^2+\varepsilon_d^2}\right)G_{\mathbf{k}\omega}=0. \tag{4}$$

This system of equations suggests that the effective order parameter Δ, which determines the gap in the band electron spectrum, is expressed in terms of the order parameter β as follows:

$$\Delta(\omega)=\frac{2V\beta\varepsilon_d}{\omega^2+\varepsilon_d^2}. \tag{5}$$

Equation (3d) makes it possible to express B_{ii}^{+}, where $B_{ii}=N^{-1}\Sigma_{\mathbf{k}}B_{\mathbf{k}}$, in terms of F^{+} and G, which leads to the following equation for β:

$$\beta=|U|\left[1+\frac{UT}{N}\sum_{\omega,\mathbf{k}}\frac{G_{\mathbf{k}\omega}}{i\omega+\varepsilon_d}\right]^{-1}\frac{T}{N}\sum_{\omega,\mathbf{k}}\frac{VF_{\mathbf{k}\omega}^{+}}{i\omega+\varepsilon_d}. \tag{6}$$

Since F^{+} and G are expressed in terms of $\Delta(\omega)$ according to (4) in the usual way (as in the BCS theory), simultaneous solution of Eqs. (5) and (6) enables one to determine both β and $\Delta(\omega)$ and find T_c. In some cases, however, simple splitting, as in system (3), is not sufficient because the important opportunity to describe the virtual bound states of the excitonic type of c- and d-electrons is then lost. This is illustrated

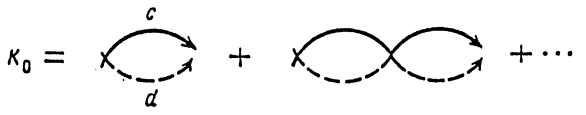

FIG. 2.

by Eq. (6). The first term in (6) allows, in the ladder approximation, for multiple scattering of a band electron on an electron in state $|d_i\rangle$ and corresponds to the sum K_0 of all diagrams depicted in Fig. 2. Using the function $G_{\mathbf{k}\omega}$ of the normal state in determining T_c, we arrive at the following expression for this sum ($N^{-1}\Sigma_{\mathbf{k}} \to W^{-1}\int d\varepsilon_{\mathbf{k}}$):

$$UK_0-1=\left[1+\frac{U}{W}\ln\frac{W}{\max\{\varepsilon_d, T\}}\right]^{-1}. \tag{7}$$

We see that for $\varepsilon_d<\varepsilon_0$, where ε_0 is determined from the equation

$$1+\frac{U}{W}\ln\frac{W}{\varepsilon_0}=0, \tag{8}$$

$K_0(T)$ becomes infinite at a certain temperature $T\sim\varepsilon_0$. The point is that if one of the electrons has transformed to state $|d_i\rangle$, the Hamiltonian (2) describes the problem of an impurity potential at site i for the band electrons. In a 2-D system such a potential always leads to the appearance of a bound state near site i separated in its energy from the continuous spectrum by a finite gap. Equation (8) determines the size of the binding energy of this state.

The singular behavior of $K_0(T)$ indicates the need to go beyond the scope of the overly simple splitting employed in deriving system (3). In determining T_c one must allow in a more precise manner for the possibility of formation of a bound state of band electrons near a site with a filled level ε_d.

To this end we consider the Green's function

$$K^i_{mm'}(\tau-\tau')=\langle Tc_{m\uparrow}(\tau)d_{i\downarrow}(\tau),\ d_{i\downarrow}^{+}(\tau')c^{+}_{m'\uparrow}(\tau')\rangle. \tag{9}$$

The idea of introducing this function is that the function provides information about the electron motion in a band on the condition that simultaneously an electron in state $|d\downarrow\rangle$ appears at the ith site. Using $K^i_{mm'}(\tau)$, we can modify Eq. (6) in the following manner.

$$\beta=|U|[1-UK_{ii}{}^{i}(\Omega=0)]\frac{T}{N}\sum_{\omega,\mathbf{k}}\frac{VF_{\mathbf{k}\omega}{}^{+}}{i\omega+\varepsilon_d}, \tag{10}$$

where $K(\Omega)=\int_0^{1/T}e^{i\Omega\tau}K(\tau)d\tau$, and $\Omega=2\pi nT$. Note that the series representing K_0 is the simplest approximation to K. Combining Eqs. (4), (5), and (10), we get a self-consistent equation for the order parameter β, which for $\beta\to 0$ determines T_c:

$$1=|U|[1-UK_{ii}{}^{i}(\Omega=0)]\frac{T_c}{N}\sum_{\omega,\mathbf{k}}\frac{2V^2\varepsilon_d{}^2}{(\omega^2+\varepsilon_d{}^2)^2(\omega^2+\varepsilon_{\mathbf{k}}{}^2)}. \tag{11}$$

To find K^i_{ii} ($\Omega=0$), we write the equation that $K^i_{mm'}(\tau)$ satisfies:

$$\begin{aligned}\frac{\partial}{\partial\tau}K^i_{mm'}=&\delta(\tau)[\delta_{mm'}(1-\langle\hat{n}_d\rangle)-\langle c_{m'}{}^{+}c_m\rangle]\\&+\delta_{mi}UK^i_{mm'}-\varepsilon_dK^i_{mm'}-t_{ml}K^i_{lm'}\\&+U\langle Tc_i{}^{+}c_ic_md_i, d_i{}^{+}c_{m'}{}^{+}\rangle+U\langle Tc_md_m{}^{+}d_md_i, d_i{}^{+}c_{m'}{}^{+}\rangle.\end{aligned} \tag{12}$$

Since we are speaking of free charge carriers appearing in a zone during alloying, we assume that both the electron concentration in the band and the probability of state $|d_i\rangle$ being filled are low. In this case the last two terms in Eq. (12) contribute little because they contain only one extra annihilation operator, which requires that an additional electron be present near the given site. Later we will return to an explanation of this approximation. If the last two terms are dropped, Eq. (12) becomes closed. Its solution can be expressed in terms of the eigenfunctions $\psi_\lambda(m)$ of the problem of an impurity defect positioned at a fixed point i:

$$\hat{H}_i\psi_\lambda=\sum_j(t_{jm}+\delta_{jm}\delta_{im}U)\psi_\lambda(j)=\varepsilon_\lambda\psi_\lambda(m). \tag{13}$$

Employing the functions $\psi_\lambda(m)$ and allowing for the fact that

$$\langle c_{m'}{}^{+}c_m\rangle=\sum_\lambda\psi_\lambda{}^{*}(m')\psi_\lambda(m)\langle\hat{n}_\lambda\rangle,$$

we arrive at the following expression for the Fourier components $K^i_{mm'}$:

$$K^i_{mm'}(\Omega)=-\sum_\lambda\frac{\psi_\lambda{}^{*}(m)\psi_\lambda(m')}{i\Omega-(\varepsilon_\lambda+\varepsilon_d)}(1-n_d-n_\lambda), \tag{14}$$

where $\Omega=2\pi nT$, $n_d=\langle\hat{n}_d\rangle$, and $n_\lambda=\langle\hat{n}_\lambda\rangle$.

It is essential that for a 2-D band the lowest energy value ε_{λ_0} must always correspond to a state localized near the ith site and separated by a finite gap from the bottom of the conduction band. From Eq. (9) it is easily established that the binding energy ε_0 is determined from Eq. (6):

$$\varepsilon_0=W\exp(-W/U).$$

For greater clarity, the energy level diagram is depicted in Fig. 3. In what follows we will also use the amplitude value of the wave function of the bound state at the impurity point (site i with a filled $|d\rangle$ state):

$$\psi_0{}^2=W\varepsilon_0/U^2. \tag{15}$$

For states in the continuous spectrum, however, we have $|\psi_\lambda(i)|^2\sim N^{-1}$. For $|\varepsilon_{\lambda_0}+\varepsilon_d|<\varepsilon_0$ this bound state will provide the main contribution to $K^i_{ii}(0)$, as shown by formula (14). The occupation numbers n_λ and n_d entering into the expressions for K remain indeterminate and must be found self-consistently, allowing for the fact that the possible existence of a bound state greatly influences the effective one-electron energies. Combining (14) with (9) yields

$$K^i_{\lambda_0\lambda_0}(\tau=-0)=\langle\hat{n}_d\hat{n}_{\lambda_0}\rangle=\frac{1-n_d-n_{\lambda_0}}{\exp[(\varepsilon_{\lambda_0}+\varepsilon_d)/T]-1}. \tag{16}$$

Since n_d is assumed small, sites with filled states $|d\rangle$ are far from each other, and in the vicinity of a given site i we can introduce a model Hamiltonian that allows for spectrum transformation for $n_d\neq 0$:

$$\hat{H}_\lambda=\sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}c_{\mathbf{k}}{}^{+}c_{\mathbf{k}}(1-d_i{}^{+}d_i)+\left(\sum_\lambda\varepsilon_\lambda c_\lambda{}^{+}c_\lambda+\varepsilon_d\right)d_i{}^{+}d_i. \tag{17}$$

Using $\hat{H}_\lambda$, we can easily show that

$$\langle\hat{n}_d\hat{n}_{\lambda_0}\rangle\approx f(\varepsilon_{\lambda_0})\langle\hat{n}_d\rangle, \tag{18}$$

where $f(\varepsilon_{\lambda_0})$ is the Fermi distribution function. In other

words, if there is an electron in state $|d\rangle$, the filling of state $|\lambda\rangle$ is determined by the one-electron energy levels defined by Eq. (13). Moreover, we have the following expression for n_{λ_0}:

$$n_{\lambda_0}=(1-n_d)\sum_{\mathbf{k}} f(\varepsilon_{\mathbf{k}})|\psi_0(\mathbf{k})|^2+n_d f(\varepsilon_{\lambda_0}), \tag{19}$$

where $\psi_0(\mathbf{k})$ is a Fourier component of the wave function of the bound state $|\lambda_0\rangle$. The same formula can be obtained by solving the equation for the Green's function of band electrons that allows for multiple scattering on a point-like potential Un_d at site i. Employing the properties of $\psi_0(m)$ that follow from the solution to Eq. (13), we obtain

$$\sum_{\mathbf{k}} f(\varepsilon_{\mathbf{k}})|\psi_0(\mathbf{k})|^2=1-\frac{\varepsilon_0}{\mu}. \tag{20}$$

Now if we combine Eqs. (16) and (18)–(20), we arrive at the following system of equations for determining n_d and n_{λ_0}:

$$\begin{aligned} &n_{\lambda_0}=(1-n_d)(1-\varepsilon_0/\mu)+n_d f(\varepsilon_{\lambda_0}),\\ &f(\varepsilon_{\lambda_0})n_d\left[\exp\left(\frac{\varepsilon_{\lambda_0}+\varepsilon_d}{T}\right)-1\right]=1-n_d-n_{\lambda_0}. \end{aligned} \tag{21}$$

For $f(\varepsilon_{\lambda_0})\simeq 1$ this yields

$$n_d=\left[1+\frac{\mu}{\varepsilon_0}\exp\left(\frac{\varepsilon_{\lambda_0}+\varepsilon_d}{T}\right)\right]^{-1}. \tag{22}$$

Retaining in Eq. (14) only the state $|\lambda_0\rangle$ and expressing n_{λ_0} in terms of n_d via Eqs. (16) and (21), we get

$$K_{ii}^{i}(\Omega=0)=\psi_0^2 n_d\frac{\exp[(\varepsilon_{\lambda_0}+\varepsilon_d)/T]-1}{\varepsilon_{\lambda_0}+\varepsilon_d}. \tag{23}$$

The most interesting case is when $T_c\gtrsim|\varepsilon_{\lambda_0}+\varepsilon_d|$ and $K_{ii}^{i}(0)=\psi_0^2 n_d/T$. The transition temperature is determined by Eq. (11), which after summing over ω and k yields (only the term with UK_{ii}^{i} is retained)

$$T_c=2\psi_0^2 n_d\left(\frac{VU}{\varepsilon_d}\right)^2\frac{1}{W}\ln\frac{\varepsilon_d}{T_c}. \tag{24}$$

This assumption is justified if

$$2\psi_0^2 n_d\left(\frac{VU}{\varepsilon_d}\right)^2\frac{1}{W}\geqslant|\varepsilon_{\lambda_0}+\varepsilon_d|. \tag{25}$$

Equation (24) demonstrates that to within insignificant logarithmic correction terms T_c is a power function of the coupling constants.

Let us return to the approximations that made it possible to arrive at the above result. First, the average occupation numbers n_d are assumed small. Hence, the bound states that form at each moment of time at different sites are assumed to be independent of each other. This requires

$$(n_d R_{\lambda_0}^2)<1, \tag{26}$$

where $R_{\lambda 0}^2\sim a^2/W/\varepsilon_0$ is the radius of the bound state ψ_{λ_0}, with a the lattice constant. This condition makes it possible to ignore the last term in Eq. (12) and justifies the use of Eqs. (18)–(21). In addition, (26) shows that in accordance with (22) the Fermi level cannot lie above a certain quantity (see Fig. 3).

The second constraint stems from the fact that the concentration n of electrons in a band must be so low that the

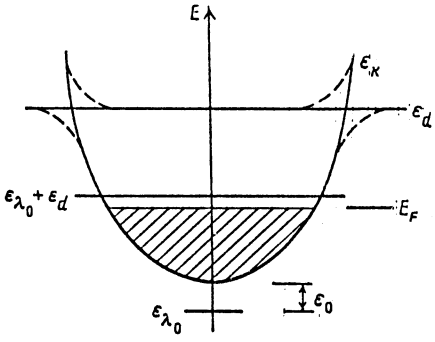

FIG. 3.

formation of the bound state ψ_0 at site i leads to a considerable change in the effective one-particle energy for state $|d_i\rangle$. This is determined by the condition

$$Un<U\psi_0^2. \tag{27}$$

In this case the average occupation numbers $|n_d\rangle$ are determined in a nontrivial manner: by the energy of the bound pair $|d_i\lambda_0\rangle$ rather than by the one-particle energy ε_d. If the correlation between these states that leads to the formation of a bound state with U were not sufficiently strong, then although Eqs. (14) and (16) remain valid for any two states, for $T\to 0$ we would have $n_d\propto\exp(-\varepsilon_d/T)\to 0$, and the singularity in K_{ii}^{i} ($\Omega=0$) given by (23) would vanish. In other words, in the calculation of the average energy of the band state described by the wave packet coinciding with $\psi_0(m)$, $E_{\lambda_0}=\Sigma_{\mathbf{k}}|\psi_0(\mathbf{k})|^2\varepsilon_{\mathbf{k}}$, pair correlations due to U are important when ε_d and E_{λ_0} lie considerably higher than E_F and the energy of the bound state is close to E_F. When the density of states in the band is constant, this condition is equivalent to (27). If this condition is met, the penultimate term in (12) can also be ignored, since qualitatively it describes the change in properties of the bound state when there is an electron in the continuous spectrum and the corrections introduced by the electron are small. This also supports the fact that when the splitting

$$\langle Tc_i^+c_i c_m d_i, d_i^+c_{m'}^+\rangle\to\langle c_i^+c_m\rangle K_{im'}^{i},$$

is used, allowing for this term has no effect on ε_{λ_0} and ψ_0 in the present theory.

Direct solution of system (3) yields the following expression for T_c:

$$T_c=\varepsilon_d\exp\left[-\frac{W\varepsilon_d^2}{2|U|V^2}\right], \tag{28}$$

which corresponds to the BCS expression with an effective constant $\tilde{V}=VU/\varepsilon_d$ in the conduction band, a constant that appeared because of hybridization of the d and c states. The transition from Eq. (6), which follows from (3d), to Eq. (10) and, respectively, from (28) to (24) follows from the fact that instead of the simplest vertex representing the interaction of band electrons and depicted in Fig. 4a we use the vertex of Fig. 4b with a virtual intermediate bound state. This modification must be allowed for only for certain degrees of occupation of the band (see Fig. 3). Since for low n condition (25) breaks down, n_d is much lower than unity for $\varepsilon_{\lambda_0}+\varepsilon_d\gg T$, and the term with $K_{ii}^{i}(0)$ in Eq. (11) becomes negligible. However, as the concentration increases, n_d

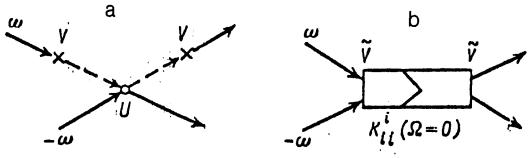

FIG. 4.

grows fairly rapidly according to Eq. (22) after the point $\varepsilon_{\lambda_0}+\varepsilon_d=0$ is passed, condition (26) breaks down, and the bound states begin to interact strongly with each other, which leads to a broadening in the pair-level energy and disappearance of the auxiliary effect.

4. Solving Eqs. (5) and (6) for any temperature below T_c enables one to find $\beta(T)$ and $\Delta(T)$. This, however, requires a correct definition of the Green's function $K(\Omega)$ when anomalous averages appear. In this case Eq. (12) changes. Because of the appearance of anomalous averages $F^+_{ij}=\langle c^+_{i\downarrow}c^+_{j\uparrow}\rangle$, with allowance for transition V, one must bear in mind in calculating the function $K^i_{mm'}(\omega)$ that a closed loop may be inserted into a diagram at any point,

$$\sigma^*=UVT\sum_\omega G_d^0(-\omega)F_{ii}^+(\omega)=UVT\sum_\omega\frac{F_{ii}^+(\omega)}{i\omega+\varepsilon_d}, \quad (29)$$

just as in Eq. (6) this fact is taken into account for the simplest series K_0. Accordingly, into the effective Hamiltonian used to write the equation of motion for $K^i_{mm'}$ we must introduce an additional term,

$$\hat{H}_\sigma=\sigma^*\sum_i(c_{i\uparrow}d_{i\downarrow}+d_{i\uparrow}c_{i\downarrow})+\text{H.c.} \quad (30)$$

Using the same approximations as before, we assume that virtual bound states appear at different sites independently of each other. Then we find that by expanding the operator c_i in the operators c_λ corresponding to the states ψ_λ,

$$c_{i\uparrow}d_{i\downarrow}=\sum_\lambda\psi_\lambda(i)c_{\lambda\uparrow}d_{i\downarrow}, \quad (31)$$

to a first approximation, we can leave in (30) only the state with $\lambda=\lambda_0$ if, as earlier, we have $|\varepsilon_{\lambda_0}+\varepsilon_d|\ll\varepsilon_0$. Let us demonstrate the validity of this fact by employing an important relation linking the order parameter $B_\lambda=\langle c_{\lambda\uparrow}d_{i\downarrow}\rangle$ with the occupation numbers n_λ and n_d. The equation of motion for the quantity $\langle c_{m\uparrow}(\tau)d_{i\downarrow}(\tau)\rangle$, which is actually a constant independent of τ, implies, if we allow for (30), the following:

$$\frac{\partial}{\partial\tau}\langle c_md_i\rangle=\sum_\lambda\psi_\lambda(m)[B_\lambda(\varepsilon_\lambda+\varepsilon_d)+\sigma\psi_\lambda(i)(1-n_d-n_\lambda)]=0. \quad (32)$$

Since this is true for every m, we get

$$B_\lambda=-\frac{\sigma}{\varepsilon_\lambda+\varepsilon_d}\psi_\lambda(i)(1-n_d-n_\lambda). \quad (33)$$

This leads us to the following estimate:

$$\sum_{\lambda\neq\lambda_0}\psi_\lambda(i)\langle c_{\lambda\uparrow}d_{i\downarrow}\rangle\approx\frac{\sigma}{W}\int_{\varepsilon_0}^{W}\frac{d\varepsilon}{\varepsilon}=\frac{\sigma}{W}\ln\frac{W}{\varepsilon_0}. \quad (34)$$

In proceeding from (33) to (34) we have allowed for the fact that $\varepsilon_{\lambda_0+\varepsilon_d}\ll\varepsilon_0$, $\psi_{\lambda\neq\lambda_0}(i)\sim N^{-1/2}$, and $1-n_\lambda-n_d\lesssim 1$.

We can express σ in terms of β via (5), which yields

$$\frac{\sigma}{W}\ln\frac{W}{\varepsilon_0}=\frac{V^2U}{\varepsilon_d^2W}\frac{\beta}{U}=\left(\frac{U}{W}\right)\left(\frac{V}{\varepsilon_d}\right)^2\langle c_{i\uparrow}d_{i\downarrow}\rangle\ll\langle c_{i\uparrow}d_{i\downarrow}\rangle.$$

We see that $\langle c_{i\uparrow}d_{i\downarrow}\rangle$ is indeed determined mainly by the term with $\lambda=\lambda_0$ in (31) and that the states of the continuous spectrum provide a contribution that is small, of order $(U/W)(V/\varepsilon_d)^2$. If we substitute (31) into the Hamiltonian (30) and keep only the term with λ_0, instead of Eq. (12) we arrive at a system of equations for the $K^i_{mm'}$ in the λ-representation:

$$\left[\frac{\partial}{\partial\tau}+(\varepsilon_{\lambda_0}+\varepsilon_d)\right]K_{\lambda_0}{}^i-\psi_0\sigma J=(1-n_d-n_{\lambda_0})\delta(\tau),$$
$$\frac{\partial}{\partial\tau}J+2\psi_0\sigma S^+-2\psi_0\sigma^*K_{\lambda_0}{}^i=2B_{\lambda_0}{}^+\delta(\tau),$$
$$\left[-\frac{\partial}{\partial\tau}+(\varepsilon_{\lambda_0}+\varepsilon_d)\right]S^+-\psi_0\sigma^*J=0, \quad (35)$$

where $J=\langle T[d_{i\downarrow}^+c^+_{\lambda_0\uparrow},c_{\lambda_0\uparrow}d_{i\downarrow}]\rangle$, $d_{i\downarrow}^+c^+_{\lambda_0\uparrow}\rangle$, $B_{\lambda_0}^+=\langle d_{i\downarrow}^+c^+_{\lambda_0\uparrow}\rangle$, and $S^+=\langle Td_{i\downarrow}^+c^+_{\lambda_0\uparrow},d_{i\downarrow}^+c^+_{\lambda_0\uparrow}\rangle$.

In solving this system we wish to employ relations of the form (16), which link the occupation numbers and the order parameter with the values of the functions K and J at $\tau=\pm 0$. It must be borne in mind, however, that Eqs. (35) determine only the part of these functions that is τ-dependent. In addition, when anomalous averages appear, the total Green's function defined in (9) contains a contribution from the decomposition into unconnected anomalous parts (of the form $\langle cdd^+c^+\rangle\to\langle cd\rangle\langle d^+c^+\rangle$), which are independent of τ. If we denote such a constant contribution for the functions K and J, respectively, by $\varkappa$ and ζ, the first equation in (35) yields

$$(\varepsilon_{\lambda_0}+\varepsilon_d)\varkappa+\sigma\zeta=0. \quad (36)$$

From system (35) an expression for the complete function J then follows:

$$J(\Omega)=\frac{2B_{\lambda_0}{}^+(i\Omega+\varepsilon_{\lambda_0}+\varepsilon_d)}{\Omega^2+(\varepsilon_{\lambda_0}+\varepsilon_d)^2+4\psi_0^2|\sigma|^2}+\zeta\delta(\Omega). \quad (37)$$

Using the definition of function J, we arrive at the relation

$$J(\tau=+0)=\lim_{\tau\to+0}T\sum_\Omega e^{i\tau\Omega}J(\Omega)=B_{\lambda_0}{}^+, \quad (38)$$

from which we get

$$\zeta(T)=\frac{2(\varepsilon_{\lambda_0}+\varepsilon_d)B_{\lambda_0}{}^+}{\tilde{\varepsilon}}\operatorname{cth}\frac{\tilde{\varepsilon}}{2T}, \quad (39)$$

where $\tilde{\varepsilon}=[(\varepsilon_{\lambda_0}+\varepsilon_d)^2+4\psi_0^2|\sigma|^2]^{1/2}$. Now, using (36), we can determine $\varkappa$ and, using (35) to calculate the value of the complete function $K(\tau=+0)$, we obtain a formula for the occupation numbers:

$$\langle\hat{n}_{\lambda_0}\hat{n}_d\rangle=\frac{1}{2}(1-n_d-n_{\lambda_0})\left[\frac{\tilde{\varepsilon}}{\varepsilon_{\lambda_0}+\varepsilon_d}\operatorname{cth}\frac{\tilde{\varepsilon}}{2T}-1\right]. \quad (40)$$

Since the transition to the superconducting state affects the occupation numbers only near the Fermi surface, Eqs. (18) and (19) remain valid when we determine n_{λ_0} to within $(\Delta/E_F)^2$. Combining this with (39) yields

$$n_d=\frac{\varepsilon_0}{\mu}\left[1+\frac{\varepsilon_0}{\mu}+2\left(\frac{\tilde{\varepsilon}}{\varepsilon_{\lambda_0}+\varepsilon_d}\operatorname{cth}\frac{\tilde{\varepsilon}}{2T}-1\right)^{-1}\right]^{-1} \quad (41)$$

At $\varepsilon_{\lambda_0}+\varepsilon_d=0$ the occupation numbers n_d are temperature independent. Now we can find the temperature dependence of the order parameter $B_{\lambda_0}^+$ [see Eqs. (33), (40), and (41)]:

$$B_{\lambda_0}^+=-\frac{2\sigma^*\psi_0}{\varepsilon_{\lambda_0}+\varepsilon_d}n_d\left(\frac{\tilde{\varepsilon}}{\varepsilon_{\lambda_0}+\varepsilon_d}\operatorname{cth}\frac{\tilde{\varepsilon}}{2T}-1\right)^{-1}. \tag{42}$$

Thus, we have the following hierarchy of order parameters at $T=0$, which is especially simple when $\varepsilon_{\lambda_0}+\varepsilon_d\simeq 0$:

$$\begin{aligned}\beta(0)&=|U|\langle d_{i\downarrow}c_{i\uparrow}\rangle=|U|\psi_0(-B_{\lambda_0})=|U|\psi_0 n_d,\\ \sigma(0)&=\left[\frac{U}{W}\left(\frac{V}{\varepsilon_d}\right)^2\ln\frac{\varepsilon_d}{\Delta(0)}\right]\beta(0),\\ \Delta(0)&=\frac{2V}{\varepsilon_d}\beta(0)=\frac{2V|U|}{\varepsilon_d}\psi_0 n_d.\end{aligned} \tag{43}$$

Since $\Delta(0)$ is the gap in the spectrum of band electrons [see Eq. (4)], it determines the ratio $2\Delta/T_c$ measured in experiments, which is found to be given by the following formula:

$$\frac{2\Delta(0)}{T_c}\approx\frac{2}{\psi_0\ln(\varepsilon_d/T_c)}\left(\frac{W\varepsilon_d}{VU}\right). \tag{44}$$

Hence, in contrast to the BCS model, this ratio can assume any value depending on the energy parameters of our model.

Before we compare the conclusions of the model with the experimental data on high-T_c superconductivity, one remark is in order. The hybridization parameter V is assumed small in our model. However, an alternative approach to the Hamiltonian (2) is possible if first diagonalization in the interaction V is carried out and then new operators a and b are introduced:

$$\begin{aligned}&c_k=\alpha_k a_k+\beta_k b_k,\quad d_k=\alpha_k b_k-\beta_k a_k,\\ &\alpha_k^2=\frac{1}{2}\left[1-\frac{\varepsilon_k-\varepsilon_d}{[(\varepsilon_k-\varepsilon_d)^2+4V^2]^{1/2}}\right],\\ &\beta_k^2=\frac{1}{2}\left[1+\frac{\varepsilon_k-\varepsilon_d}{[(\varepsilon_k-\varepsilon_d)^2+4V^2]^{1/2}}\right].\end{aligned} \tag{45}$$

The respective change in the band structure is depicted by the dashed curves in Fig. 3. the operators a_k correspond to the lower (light) branch of the spectrum and the b_k to the upper (heavy) branch, and different terms appear in the pair interaction:

$$\begin{aligned}Uc^+cd^+d\to&U\alpha^4a^+ab^+b+U\alpha^3\beta a^+a(a^+b+b^+a)\\&+\ldots+U\alpha^2\beta^2a^+aa^+a+\ldots\end{aligned} \tag{46}$$

The first term leads to the formation of a bound state of the excitonic type. In the previous discussion we assumed the mass of one of the particles, d, infinite; now we allow for the finiteness of the mass and a small variation in the attraction potential. The second term describes the transition of two electrons from the light band to the excitonic state with an effective transition constant $U\alpha_k^3\beta_k\sim UV/\varepsilon_d$ when $V/\varepsilon_d\ll 1$. The third term corresponds to induced effective attraction in the light subband. If we ignore the double filling of d-states due to Hubbard repulsion, the other terms in (46) are actually corrections to the above three. On the whole, the idea of the role of intermediate exciton-like states with a zero total momentum remains valid, the states themselves being constructed more accurately. When ε_d lies considerably higher than the Fermi level, that is, $V/\varepsilon_d\ll 1$, all the above formulas remain valid to within terms of order $(V/\varepsilon_d)^2$. For instance, in the calculation of T_c $(\beta\to 0)$, the exact expression for F^+ that allows for hybridization is

$$F_{\mathbf{k}\omega}^+=\frac{2\varepsilon_d V\beta}{(\omega^2+E_1^2)(\omega^2+E_2^2)}, \tag{47}$$

where $E_{1,2}(\mathbf{k})=\frac{1}{2}\{(\varepsilon_{\mathbf{k}}+\varepsilon_d)\pm[(\varepsilon_{\mathbf{k}}-\varepsilon_d)^2+4V^2]^{1/2}\}$. It can easily be verified that to within terms of order $(V/\varepsilon_d)^2$ Eq. (47) corresponds to (4) and (5).

5. In conclusion we will briefly discuss the agreement between the given model and some experimental data. Let us first see whether a reasonable choice of W, V, and ε_d can ensure that $T_c\sim 100$ K. It is known that the band width W in a high-T_c superconductor is about 4 eV. The estimates of Sec. 2 yield a value of about $0.25W$ for the antiferromagnetic interaction energy U. The common value of the hybridization constant V lies within the range of several tenths of an electron volt, that is, $V\simeq 0.1W$. Finally, knowing that T_c attains its maximum value at alloying levels of roughly 0.15 (i.e., $\mu=0.15W$), from the condition that $\varepsilon_{\lambda_0}+\varepsilon_d=0$ we obtain $\varepsilon_d=\mu=0.15W$. Such a choice of the parameter scales yields, via (24), the value $T_c=100$ K for a concentration $n_d\sim 0.05$ (per cell). In order of magnitude this value of n_d agrees with both formula (22) and constraint (26). For the same choice of parameters, the ratio $2\Delta/T_c$ varies between 5 and 10, which agrees with the experimental data.[2,8] These estimates, naturally, cannot serve as proof that the theory is correct; they only show that there are no contradications in principal with the experimental data. The model contains a simple explanation of the dependence of T_c on the alloying degree (the filling of the conduction band) characteristic of all high-T_c superconductors.[9] For low alloying degrees, when $\varepsilon_{\lambda_0}+\varepsilon_d\gg T_c$ holds, the bound state plays a very small role owing to (23) and the exponentially small T_c is defined by formula (28). Then T_c grows, attaining its maximum value (24) at $\varepsilon_{\lambda_0}+\varepsilon_d\simeq 0$. A further increase in the alloying degree drives up n_d (22) and condition (26) breaks down, which leads to a drop in T_c. An important corollary of Eq. (24) is the proportionality of T_c to the occupation number n_d. This pattern was observed in photoemission experiments involving different families of high-T_c superconductors.[10] The model also explains on the qualitative level the similar behavior of the rate of spin relaxation of the copper and oxygen nuclei below T_c (see Ref. 11), since the appearance of the averages $\langle c_{i\uparrow}d_{i\downarrow}\rangle$ in the initial picture in Sec. 2 means the emergence of rigid coupling between electron spins on copper and oxygen.

On the whole, notwithstanding the above-noted features, the properties of the superconducting state in the proposed model resemble the properties in the ordinary BCS model. It is this that distinguishes the present theory from the theories with local pairs,[12] where local pairs exist at temperatures above T_c. Superconductivity sets in not as a result of Bose condensation of pairs but owing to strong renormalization of the effective interelectronic interaction, with allowance for processes where virtual bound states act as intermediate states.

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