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Physics of High-T_c Superconductors

S. P. Kruchinin

Bogolyubov Institute for Theoretical Physics, Ukrainian National Academy of Science, Kiev 252143, Ukraine

Studies in the field of superconductivity theory is one of the most bright, fruitful, and promising trends in the theoretical physics of condensed matter, since superconductivity remains to be one of the most interesting research areas in physics. In this review consider such topics of high- T_c superconductivity as the structures of high- T_c superconductors, phase diagrams, and the problem of pseudogaps and analyze the mechanisms of superconductivity. We present general arguments as for the pairing symmetry in cuprate superconductors and investigate their thermodynamical properties within the spin-fluctuation mechanism of superconductivity, by using the method of functionals. This review deals with a wide scope of theoretical and experimental topics in superconductivity.

KEYWORDS: High- T_c Superconductors, Phase Diagram, Mechanism of Pairing, Symmetry of Pairing, Pseudogap, Antiferromagnit Spin Fluctuations, Thermodynamics, Josephson Junction.

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 8. Summary
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1. INTRODUCTION

In 1986, Müller and Bednorz discovered the phenomenon of superconductivity in Cu-oxide compounds of lanthanum and barium at the temperature $T_c = 35$ K,¹ which was marked by the Nobel's prize in 1987. This discovery gave the additional push to the intensification of the scientific activity in the field of superconductivity. For the last 23 years, the superconducting transition temperature has been increased to 140 K. Moreover, one may expect the discovery of new superconductors with higher critical temperatures. Recently, the high critical temperatures of new Mg-containing superconductors (MgBr₂) ($T_c = 39$ K) and superconducting oxypnictides LnO_(1-x)F_xFeAs ($T_c = 50$ K) were registered.

The main purpose of solid-state physics is the development and the fabrication of substances which possess the superconductivity at room temperature. At present, there proceeds the great-scale search for such high-temperature superconductors. Especially promising is the method of production of superconducting materials with the help of the laser spraying of layers.

After the discovery of HTSC, the following problems become urgent:

 Conceptual-theoretic one: the problem of the clarification of mechanisms of high-temperature superconductivity.
 Engineering and technical ones: the problem of the practical applications of HTSC.

(3) Research one: the problem of the search for materials with higher T_c .

The great interest in the phenomenon of superconductivity is caused by the basic possibility to use it in the future for the electric power transfer without losses and for the construction of quantum high-power generators. This phenomenon would be applied in superconductive electronics and computer technique (superconducting elements of memory). At the present time, a new trend in technology, namely the construction of quantum computers on the basis of high-temperature superconductors with *d*-pairing, is developed.

High-temperature superconductors have unique physical properties both in the normal state and the superconducting one.

To comprehend the physics of these complex compounds is one of the main tasks of the theory of superconductivity, whose solution will alow one to explain the mechanism ensuring the high-temperature superconductivity.

The disappearance of resistance on the cooling of superconductors down to a certain critical temperature is one of the most characteristic effects in superconductors. But, in order to understand the reason for the rising of superconductivity, it is necessary to study the other effects which accompany this phenomenon.

Consider briefly the main properties of high-temperature superconductors (HTSC):

(1) New HTSC have a great anisotropy across the axis c and possess a multilayer structure. The main block defining the metallic and superconductive properties is planes with CuO₂ which form the square lattices of Cu ions.

(2) HTSC are superconductors of the second kind $(l/\varkappa \ll 1)$, where *l*—the coherence length, and \varkappa —the penetration depth of a magnetic field).

(3) High-temperature superconductors have high critical temperatures T_c .

(4) They have antiferromagnetic ordering of spins of Cu in the CuO_2 planes and powerful spin fluctuations with a wide spectrum of excitations.

At the present time, there exists no theoretical approach which would explain the totality of thermodynamical, magnetic, and superconductive properties of hightemperature superconductors from the single viewpoint.

The electron-phonon mechanism of pairing, being principal in standard superconductors, gives a considerable contribution to the establishment of the superconducting state in high-temperature superconductors. But, in order to attain the proper description, it is necessary to consider the other mechanisms inherent to high-temperature superconductors.

One of such mechanisms is the spin-fluctuation one proposed by Pines (USA). The reason for the pairing of electrons can be the scattering of electrons on spin fluctuations. This model of pairing is one of the most actual models of high-temperature superconductivity.

The thermodynamics of superconductors at low temperatures is determined by the excitation of two quasiparticles. In the traditional superconductors with pairing of the BCS type, the energy gap is isotropic (*s*-pairing), and the temperature dependence of the heat capacity has exponential form $\sim \exp^{-\Delta/k_B T}$, where Δ is the superconductor's gap. In superconductors with anisotropic pairing, the temperature dependence of the heat capacity has power character, namely, T^n . The appearance of such temperature dependences is related to that the superconductor's gap has zeros on the Fermi surface. The development of the thermodynamics of this model is the actual problem of high-temperature superconductors.

In Section 2, we consider the history of the development of studies of the phenomenon of superconductivity. The structure of high-temperature superconductors and their



Sergei Kruchinin (1957)—is leading scientist of the Bogolyubov Institute for Theoretical Physics, NASU (Kiev, Ukraine). Head of the chair of Applied Physics at the National Aviation University. Professor of NAU. Kruchinin has published significant original works in the fields of nuclear physics and many-particle systems, solid-state physics, superconductivity, theory of nonlinear phenomena, nanophysics. He is the author and co-author of more than 100 scientific works which have been published in leading scientific journals. He has been using advanced mathematical methods to solve the posed problems. Since the time high-temperature superconductors were discovered, Kruchinin has intensively studied their physical properties. In particular, it is worth noting the work carried out jointly with Davy-dov Interlayer Effects in the Newest High-Tc Superconductors (Physica C, 1991), where the theory of the non-monotonous dependence of the critical temperature of superconduct

tivity on thenumber of cuprate layers in the elementary cell of high-temperature superconduc-tors was developed. This work has remained up to date in connection with the search for new superconductors operating at room temperature. Kruchinin's works on superconductivity were included in the monograph Modern aspects of Superconductivity: Theory of Superconductivity (World Scientific, Singapore, 2010, jointly with Nagao) which shows the contemporary status of the problems of high-temperature superconductivity. Kruchinin was the organizer of six international conferences on the current problems of high-temperature superconductivity and nanosystems whichwere held in the town of Yalta. Five books in Springer and one book in World Scientific publishing houses were published under his guidance.

physical properties are analyzed. We make survey of the mechanisms of superconductivity and discuss the problem on the symmetry of the order parameter.

We draw conclusion that, on the whole, the most probable is the "synergetic" mechanism of pairing which includes, as components, the electron–phonon and spinfluctuation interactions in cuprate planes.

Only if the interaction of all the degrees of freedom (lattice, electronic, and spin ones) is taken into account, a number of contradictory properties observed in the superconducting and normal phases can be explained. Moreover, one needs also to consider a complicated structure of hightemperature superconductors. It will be emphasized that new experiments should be executed in order to explain the available experimental data.

In this section, we also consider the thermodynamics of the spin-fluctuation mechanism of pairing, present the method of functional integration for the calculation of thermodynamical properties on the basis of the Pines spin-fluctuation Hamiltonian, and deduce the Schwinger-Dyson equations for Green's functions and equations for the thermodynamic potential. Based on the Schwinger-Dyson equation, we obtain equations for the superconductor gap, which are used in numerical calculations of the thermodynamics of high-temperature superconductors. We present analytic formulas for the thermodynamic potential and its jump. The numerical calculations of the temperature dependence of the electron heat capacity indicate that the temperature dependence of the heat capacity is proportional to the square of the temperature. We emphasize that such temperature dependence is related to the d-pairing. It is shown that the measurement of the temperature dependence of the heat capacity can be a supplementing test for the establishment of a type of the symmetry of pairing in high-temperature superconductors. The jump of the heat capacity of cuprate superconductors near the critical temperature is evaluated as well.

2. HISTORY OF THE DEVELOPMENT OF SUPERCONDUCTIVITY

The phenomenon of superconductivity was discovered by the physicist Kamerlingh-Onnes at the Leiden Laboratory (the Netherlands) in 1911, in the same year when Rutherford discovered an atom. Kamerlingh-Onnes registered the disappearance of resistance of Hg at the temperature T = 4.5 K. This state was called superconducting. Being cooled down to a temperature less than the abovementioned critical temperature, many conductors can be transferred in the superconducting state, in which the electric resistance is absent. The disappearance of resistance is the most dramatic effect in superconductors. But, in order to comprehend the reason for the origin of superconductivity, we need to study the other effects accompanying this phenomenon. The dissipationless current states in superconductors were a puzzle for a long period. The phenomenon of superconductivity is a bright example of the manifestation of quantum effects on the macroscopic scale. At present, the superconductivity occupies the place of the most enigmatic phenomenon in condensed-state physics, namely in the physics of metals.

The main purpose of solid-state physics consists in the creation of superconductors which have the superconductive property at room temperature. At the present time, the researchers continue the wide-scale search for such high-temperature superconductors by testing the variety of various substances.

A number of phenomenological models were proposed to clarify the phenomenon of superconductivity, namely the models advanced by London and Ginzburg–Landau.^{2,3}

The success of the Ginzburg–Landau theory was related to the circumstance that it is placed in the mainstream of the general theory of phase transitions.

Among the first microscopic theories devoted to the consideration of the electron–phonon interaction, the work by Fröhlich⁴ is of the greatest importance.

The following stage in the development of superconductivity started from the universal theory of BCS published in 1957⁵ which strongly promoted the subsequent study of superconductivity.⁶ The authors of this theory were awarded by the Nobel's prize.

The BCS theory gave the possibility to elucidate a lot of experiments on superconductivity of metals and alloys. However, while developing the theory, some grounded assumptions and approximations were accepted. Therefore, the BCS theory was needed in a substantiation with the help of more strict arguments. This was made by Academician Bogoliubov in Ref. [6]. He developed a microscopic theory of the phenomena of superconductivity and superfluidity. By using the Fröhlich effective Hamiltonian, Bogoliubov calculated the spectrum of excitations of a superconductor within the method of canonical transformations proposed by him in 1947.

In 1962, Josephson advanced the theory of tunnel effects in superconductors (the Josephson effect) which was marked by the Nobel's prize in 1973.⁷ This discovery strongly intensified the experimental studies of superconductivity and was applied to electronics and computer technologies.

In 1986, Müller and Bednorz discovered hightemperature superconductors,¹ which initiated the huge "boom" manifested in the publication of plenty of works. The principal thought of Müller was the following: by selecting the suitable chemical composition, one can enhance the electron-phonon interaction and, thus, increase the critical temperature T_c . Müller and Bednorz found a new class of high-temperature superconductors, the so-called cuprate superconductors.

High-temperature superconductors are studied already 26 years by making significant efforts, but the while pattern is not else clear completely. This is related to a complicated structure of cuprates, difficulties in the

Physics of High- T_c Superconductors



Fig. 1. The evolution of critical temperatures since the discovery of superconductivity.

production of perfect single crystals, and a hard control over the degree of doping. The comprehension of HTSC will be attained if our knowledge about HTSC will approach some critical level which will be sufficient for the understanding of a great amount of experimental data from the single viewpoint.

In Figure 1, we present the plot of the critical temperatures of superconductivity over years.^{8,9}

3. STRUCTURAL PROPERTIES OF HIGH-TEMPERATURE SUPERCONDUCTORS

The properties of new high-temperature superconductors differ essentially from the properties of traditional superconductors which are described by the BCS theory. Let us briefly consider the main properties of high-temperature superconductors. As known, the atomic structure defines the character of chemical bonds in solids and a number of relevant physical properties. Even small changes of the structure lead frequently to significant changes of their electron properties; for example, at the phase transitions metal-dielectric. Therefore, the study of a crystal structure with long-range atomic order and its dependence on the temperature, pressure, and composition is of great importance for high-temperature superconductors. These investigations are significant for the comprehension of mechanisms of high-temperature superconductivity.

At the present time, we have several families of HTSC: thermodynamically stable Cu oxides containing lanthanum, yttrium, bismuth, thallium, and mercury.⁹

We note that the structure of all Cu-oxide superconductors has a block character. The main block defining

4



Fig. 2. Elementary cell of yttrium ceramics YBa_2CuO_7 : (1)—yttrium, (2)—barium, (3)—oxygen, (4)—copper.

metallic and superconductive properties of a compound is the plane with CuO₂ which form the square lattices of Cu ions coupled with one another through oxygen ions. Depending on the composition, the elementary cell of a high-temperature compound can have one, two, and more cuprate layers. In this case, the critical temperature of the superconducting transition increases with the number of cuprate layers. In Figure 2, we present an elementary cell of the orthorhombic structure of yttrium ceramics YBa₂Cu₃O_{7- δ}, $\delta \approx 0.1$ –0.3. The maximum $T_c \approx 90$ K. The size of the cell is characterized by the following parameters: a = 3.81 Å, b = 3.89 Å, c = 11.7 Å.

Thus, the high-temperature superconductors are characterized by both large volumes of elementary cells and a clearly manifested anisotropy of layers.

Of significant interest is the discovery of the compounds $Bi_2CaSr_2Cu_2O_8$ (Bi/2-1-2-2) and $Tl_2CaBa_2Cu_2O_8$ (Tl/2-1-2-2) with the temperature of the superconducting transition $T_c > 100$ K. These compounds can have different numbers of cuprate layers and are described by the general formula $A_2Ca_nY_2Cu_nO_{2n4}$, where A = Bi(Tl), Y = Sr(Ba). Their temperature T_c depends on the number of cuprate layers and take values of 10, 85, and 110 K for the compounds with Bi and 85, 105, and 125 K for the compounds with Tl for n = 1, 2, 3, respectively. We mention also the compounds with Tl with the single layer Tl–O with the general formula TlCa_{n-1}Ba₂Cu_nO_{2n+3}(Tl/1...), where the number of cuprate layers reaches n = 5.

Below, we present the structures of the family of Tlbased superconductors in Figures 3 and 4.





Fig. 3. Schematic distribution of ions in the unit cell of superconductors $Tl_1Ba_2Ca_{N-1}Cu_NO_{2N+4}$ or, in the brief notation, Tl(1:2:N-1:N) at N = 1, 2, ..., 5.

In Table I, we show the dependences of T_c and the interplane distance (Å) on the number of layers in the unit cell *N*. The explanation of the dependence of the critical temperature on the number of cuprate layers is an urgent problem.^{10,11}

All high-temperature superconductors have a complicated multiband structure ¹² shown in Figure 5.

We note the importance of the structure of zones near the Fermi level. For example, the structures of the bands



Fig. 4. Schematic distribution of ions in the unit cell of superconductors $Tl_1Ba_2Ca_{N-1}Cu_NO_{2N+4}$ or, in the brief notation, Tl(1:2:N-1:N) at N = 1, 2, ..., 5.

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Table I. Tl-based systems $Tl_1Ba_2Ca_{N-1}Cu_NO_{2N+3}$.									
Ν	1	2	3	4	5	6			
a (Å) T _c (K)	_ 13–15	3.8500 78–91	3.8493 116–120	3.8153 122	3.8469 106				

of two superconductors (high-temperature $Bi_2Sr_2CaCu_2O_8$ and low-temperature $Bi_2Sr_2CaCuO_6$) are significantly different at point *K*. The energy interval from the band bottom to the Fermi surface is equal to 0.7 eV at point *K* for the high-temperature superconductor and 0.1 eV for the low-temperature one. The explanation of the influence of the multiband structure on T_c is given in paper.¹²

It is worth noting that all copper-oxide superconductors have block character of their structure. The main block defining the metallic and superconductive properties of a compound of a plane with CuO_2 which contains the square lattice of Cu ions coupled with one another through oxygen ions. Depending on the composition, the elementary cell of a high-temperature compound can have one, two, three, and more cuprate layers. Moreover, the critical temperature of the superconducting transition has a nonmonotonous dependence on the number of cuprate layers.¹⁰

3.1. Phase Diagram of Cuprate Superconductors

All electron properties of high-temperature superconductors depend strongly on the doping. High-temperature superconductors without doping are dielectrics and antiferromagnetics. As the concentration x increases, these materials become metals. Superconductivity arises at large



Fig. 5. Structure of energy bands near the Fermi energy for: (a) high-temperature superconductor $Bi_2Sr_2CaCu_2O_8$ and (b) low-temperature superconductor $Bi_2Sr_2CaCuO_6$.



Fig. 6. Phase diagram of cuprate superconductors in the temperaturedoping variables, T_N —the Néel temperature, T_c —the critical temperature of the superconducting transition, T^* —the characteristic temperature of a pseudogap, T^0 —upper crossover temperature.

x, behind the limits of the magnetically ordered phase. The experiments showed that the charge carriers have the hole character for all classes of high-temperature superconductors.

It becomes clear recently that the high-temperature superconductivity is related to peculiarities of the behavior of these compounds in the normal phase. As seen from the phase diagram (Fig. 6), the superconducting states arise near the antiferromagnetic phase. In yttriumcontaining systems, the antiferromagnetic and superconducting regions adjoin one another.

The experiments on the inelastic magnetic scattering of neutrons indicate the existence of strong magnetic fluctuations in the doped region, even beyond the limits of the antiferromagnetic phase. This points out the important role of antiferromagnetic fluctuations in the compounds with high-temperature superconductivity.

In high-temperature superconductors, the gap is present in the absence of the phase coherence, i.e., in nonsuperconducting specimens. This gap is called a pseudogap. A pseudogap is shown in Figure 6. It appears at temperatures less than some characteristic temperature T^* which depends on the doping. Its nature is not completely explained else.

The study of a pseudogap in the electron spectrum of high-temperature superconductors was carried out in many works.¹³

Metals become superconductors, if their free electrons are bound in Cooper's pairs. Moreover, the pairs are formed in such a way that their wave functions have the same phase. The phase coherence is responsible for the change of the resistance on the cooling below the critical temperature T_c . The presence of coupled pairs in a superconductor causes the appearance of a gap in the spectrum of excitations. In the standard superconductors, the phase coherence of pairs appears simultaneously with the appearance of pairs. From one viewpoint, a pseudogap is related to the appearance of coupled pairs, which is not related to the phase coherence. Another viewpoint consists in the following. The pseudogap arises in HTSC in connection with the formation of magnetic states which compete with superconducting states. The efforts of experimenters aimed at the solution of this dilemma are complicated by a strong anisotropy of the superconductor gap. Some physicists believe that the most probable situation is related to the creation of the superconducting state with paired electrons at a certain doping which coexists with antiferromagnetism. It is possible that just it is the "new state of matter" which has been widely discussed for the last years in connection with HTSC.

3.1.1. Antiferromagnetism of HTSC

An interesting peculiarity of copper-oxide compounds which has universal character consists in the presence of the antiferromagnetic ordering of spins of Cu in the CuO₂ planes. The sufficiently strong indirect exchange interaction of spins of Cu induces the 3D long-range antiferromagnetic order with the relatively high Néel temperatures $T_N = 300-500$ K.¹⁴ Though the long-range order disappears in the metallic (and superconducting) phase, strong fluctuations with a wide spectrum of excitations are conserved. This allows one to advance a number of hypotheses on the possibility of electron pairing in copper-oxide compounds through the magnetic degrees of freedom.

Therefore, the study of the antiferromagnetic properties of high-temperature superconductors is of importance for the verification of the hypotheses on the magnetic mechanism of superconductivity. The interaction of spins of Cu in a plane has 2D character, and their small values, S = 1/2, lead to significant quantum fluctuations.

The first indications to the existence of antiferromagnetism in the copper-oxide compounds were obtained on the basis of macroscopic measurements of susceptibility. The detailed investigation of both the magnetic structure and spin correlations in the metallic phase became possible only with the help of the neutron scattering.

4. MECHANISMS OF PAIRING OF HIGH-TEMPERATURE SUPERCONDUCTORS

To explain the high-temperature superconductivity, a lot of models and mechanisms of this unique phenomenon were proposed. The key question is the nature of the mechanism of pairing of carriers. There are available many different models of superconductivity, among which we mention the following ones: the magnon model, exciton model, model of resonant valence bonds, bipolaronic model, bisoliton model, anharmonic model, model of local pairs, plasmon model, etc. We give some classification of mechanisms of pairing for high-temperature superconductors which is shown in Figure 7, according to Ref. [15].

This classification demonstrates the diverse physical pattern of high-temperature superconductors.



Fig. 7. Classification of mechanisms of pairing in HTSC.

Together with the ordinary BCS mechanism based on the electron-phonon interaction, there exist many other mechanisms, as was mentioned above. All these models used the conception of pairing with the subsequent formation of the Bose-condensate at temperatures T_c irrespective of the nature of the resulting attraction.

4.1. Specific Mechanisms of Pairing in Superconductivity

Consider the models most popular at the present time. Along with the ordinary BCS mechanism based on the electron-phonon interaction, we turn to the magnetic, exciton, plasmon, and bipolaronic mechanisms of pairing. All these models applied the conception of pairing with the subsequent formation of a Bose-condensate (at certain temperatures T_c) regardless of the reasons for the attraction.

The BCS theory presents the formula for the critical temperature T_c in the case of the weak electron–phonon interaction:

$$T_c = 1.14\Theta \exp(-1/N_0 V) \tag{1}$$

where $\Theta = \hbar \Omega_D / k_{\rm B}$, $\hbar \Omega_D$ is the Debye energy, N_0 is the density of states of the Fermi level, and V is the attractive pairing potential acting between electrons.

The maximum value of the critical temperature given by the BCS theory is 40 K. Therefore, there arises the question about the other mechanisms of pairing. The interaction of electrons is repulsive, i.e., one needs to seek a "transfer system" in metals which is distinct from the phonon system. The general scheme of the interaction of electrons via a transfer system X can be schematically presented as

$$\begin{vmatrix}
 e_1 + X \to e_1^1 + X^* \\
 e_2 + X^* \to e_2^1 + X
 \end{cases}
 (2)$$

where e_i corresponds to an electron with momentum p_i , X is the ground state, and X^* is the excited state of the transfer system.

As a result of this reaction, the system returns to the initial state, and the electrons make exchange by momenta.

It can be shown that such an interaction leads to the attraction, and the critical temperature is given by the formula

$$T_c \sim \Delta E \exp(-1/\lambda)$$

where ΔE is the difference of energies of the states *X* and *X*^{*}, and λ depends on the interaction of electrons with the system *X*.¹⁶

4.2. Magnetic Mechanism of Pairing

The magnetic mechanism of pairing in high-temperature superconductors was studied by many researchers. These studies used the assumption that the pairing is realized due the exchange by spin excitations-magnons, i.e., the transfer system is the system of spins in a magnetic metal. Magnon is a quasiparticle which is the quantum synonym of a spin wave of excitation in a magnetically ordered system. A great attention was attracted by the pioneer work by Akhiezer and Pomeranchuk (see Refs. [17, 18]). They considered the interaction between conduction electrons caused by both the exchange by acoustic phonons and an additional interaction related to the exchange by spin waves (magnons). It was shown that superconductivity and ferromagnetism can coexist in the same spatial regions. At sufficiently low concentrations of the ferromagnetic component, an increase of its concentration leads to an increase of T_c in the case of the triplet pairing. Within the phonon mechanism, the pairing occurs in a singlet state, then an increase of the concentration of the ferromagnetic component induces a decrease of T_c . It is known that ferromagnetism competes with superconductivity. The different situation is characteristic of antiferromagnetism. High-temperature superconductors are antiferromagnetic dielectrics. As was mentioned above, high-temperature superconductors reveal strong magnetic fluctuations in the region of doping which can be responsible for the pairing. In this chapter, we will consider the spin-fluctuation model of pairing.

After the discovery of HTSC, a lot of relevant works dealt with namely the problem of the evolution of a system

of Cu ions under the transition from the dielectric antiferromagnetic state to the metallic one.

It is worth also noting the model of resonance valence bonds (RVB) which was advanced by Nobel's Prize winner Anderson in 1987¹⁹ who made attempt to explain the Cooper pairing in HTSC by the participation of magnetic excitations. The Anderson model is based on the conception of magnetic ordering which was named the model of resonance valence bonds. The RVB mechanism ensures the joining of carriers in pairs with compensated spin, the socalled spinons. At the doping of HTSC compounds, there arise holes which can form the complexes with spinonsholons. Superconductivity is explained by the pairing of holons, i.e., by the creation of spinless bosons with double charge. That is, the pairing of carriers in the RVB model is realized due to the exchange by magnons. At low temperatures, the paired holons form a superconducting condensate. The RVB model has played a positive role, by attracting the attention of researchers to the study of antiferromagnetism in HTSC though spinons and holons have not been experimentally identified.

4.3. Exciton Mechanisms of Pairing

According to the general principle concerning the "transfer system" in superconductors, the electron-phonon interaction should not be obligatorily realized. Some other interaction ensuring the pairing of electrons can be suitable. In principle, the mechanism of superconductivity can be switched on by bound electrons which interact with conduction electrons. The first exciton model, in which the pairing is realized due to electron excitations, was proposed by Little²⁰ for organic superconductors and Ginzburg and Kirzhnitz² for layered systems. In the construction of this model, it was necessary to assume the existence of two groups of electrons: one of them is related to the conduction band, where the superconducting pairing occurs due to the exchange by excitons which are excitations in the second group of almost localized electrons. In view of the many-band character of the electron spectrum, layered structure, and other peculiarities of the electron subsystem in high-temperature superconductors, such a distribution of electron states is quite possible. This underlies the development of a lot of exciton models. The searches for superconductivity in organic materials were stimulated to a significant degree by the idea of Little about a possibility of high-temperature superconductivity due to the excitonic mechanism of the Cooper pairing of electrons in long conducting polymeric chains containing lateral molecular branches-polarizers. Since the mass M of such excitonic excitations is small, it would be expected to observe a high value of the temperature $T_c \sim M^{-1/2}$. But this model was not practically realized, since highenergy intramolecular excitonic excitations cannot ensure the binding of electrons in pairs.

At the present time, a number of quasi-one-dimensional organic superconductors with metallic conductance have been synthesized. They pass to the superconducting state at T = 10 K. Crystals of similar organic superconductors consist of, as a rule, planar molecules packed in zigzag-like stacks which form chains. The good overlapping of electron wave functions of neighboring molecules in a stack ensures the metallic conductance along a chain. The overlapping of electron wave functions of neighboring chains is small, which leads to the quasi-one-dimensional character of the electron spectrum and to a strong anisotropy of electronic properties of a crystal. Up to now, no experimental proofs of a manifestation of the excitonic mechanism is such systems are available.

As the example of a laminar system, we mention a quasi-two-dimensional structure of the "sandwich" type (dielectric-metal-dielectric). In such structures, the Cooper pairing of electrons in a metal film occurs due to the attraction caused by their interaction with excitons in the dielectric plates.

4.4. The Anharmonic Model and Superconductivity

It is known that the appearance of superconductivity is often preceded by structural transformations in a crystal. They are usually explained within the anharmonic model. In the opinion of some researchers,⁹ such structural transformations foregoing the start of superconductivity decrease significantly the frequencies of phonons and, due to this, increase the parameter of electron-phonon interaction. The softening of the phonon spectrum is caused by the great amplitudes of displacements of ions in the two-well potential which models the structural transformations. In some works,¹⁴ the effect of a structural transformation on superconductivity in the limiting case of a weak pairing interaction and the isotropic gap was studied. The properties of high-temperature superconductivity were studied also within the model, where the superconductivity is enhanced due to the singularity of the density of electron states which appears at structural or antiferromagnetic phase transitions. The weak point of the models relating the superconductivity to structural phase transitions owes to a significant temperature interval between the known structural transitions and the temperature T_c . The works, where non-phonon pairing mechanisms are introduced, include the studies14 which use the Hubbard Hamiltonian in systems, where only the interaction of repulsive type is present. It is considered that the effect of pairing is caused by the kinematic interaction at a non-complete occupation of Hubbard subbands. Unfortunately, no clear comprehension of the nature of the arising attraction is attained in this case. It is possible that the bound state of quasiparticles is virtual, i.e., it decays. The search for new mechanisms of superconductivity caused by a strong correlation of electrons in cuprate superconductors with quasi-twodimensional electron structure is reduced to the search for new non-standard ground states. We briefly mention the polaron mechanism of pairing which is related to the Jahn–Teller effect well-known in the quantum chemistry of complex compounds. The essence of the Jahn–Teller effect consists in that a non-linear system in the presence of the electron degeneration deforms spontaneously its structure so that this degeneration disappears or decreases. The Jahn–Teller effect leads to the rearrangement of the atomic orbitals of copper under conditions of the octahedral oxygen surrounding. A displacement of oxygen ions inside of an elementary cell which is caused by the appearance of a quasiparticle induces the displacement of equilibrium positions in the neighboring cells. In such a way, there arises the strong electron–phonon interaction of a quasiparticle with a local deformation.

4.5. Van Hove Singularities (vHs)

A van Hove singularity (vHs) in the density of states (DOS) N(E) has been proposed as a T_c -enhancement mechanism for intermetallic superconductors two decades ago. All cuprate superconductors possess two-dimensional elements of their structures. In the construction of the microscopic theory of high-temperature superconductivity, it is important to clarify the specific features of the dispersion E(k) and the behavior of the density of states N(E). For a two-dimensional problem (n = 2, 2D), the density of states is independent of the energy, N(E) = constant, and the band is dispersionless. The photoemission experiments indicate the existence of an almost flat band near the Fermi surface for cuprate superconductors. The presence of a flat band and an isoenergetic surface in the form of the elongated saddle leads to the existence of van Hove singularities in the density of states near the Fermi surface. In this model in the calculations of T_c by the BCS formula, N(E) is replaced by $N(E_{\rm F})$. The formula for T_c looks like

$$T_c = 1.14\Theta \exp(-1/\lambda) \tag{3}$$

where $\lambda = VN(E)$.

If the function N(E) has the corresponding singularity at $E = E_F$, it will be related to the van Hove singularity. In the two-dimensional case, the presence of a logarithmic singularity of the density of states on the Brillouin zone boundary is possible:

$$N(E) \sim \ln \left| \frac{D}{E - E_{\rm F}} \right| \tag{4}$$

where D is the characteristic energy cutoff. Then T_c has the form:

$$T_c \sim D \exp(-1/\sqrt{\lambda}) \tag{5}$$

We note that, in connection with the quasi-twodimensionality of lattices of HTSC, the hypothesis of anyonic superconductivity is of a certain interest (Fig. 7). Anyons are quasiparticles with intermediate statistics (between the Bose- and Fermi-statistics) which can exist just in two-dimensional structures. The term "anyon" was introduced by Wilczek in the framework of the conception of supersymmetry.

4.6. Plasmon Mechanism of Pairing

Many works are devoted to attempts to explain the hightemperature superconductivity on the basis of the idea of the pairing as a result of the exchange by quanta of longitudinal plasma waves-plasmons.

Longitudinal plasma waves are formed in solids in the region of frequencies, at which the dielectric permeability of the medium becomes zero. The characteristic frequency of plasma waves in 3D crystals is defined by the formula

$$\tilde{\omega}_p = 4\pi e^2 N/m \tag{6}$$

where N is the concentration of electrons, and e and m are their charge and mass, respectively. At the electron density $N \sim (1-3) \times 10^{22}$ cm⁻³, the plasma frequency $\tilde{\omega}_p \sim 10^{15}$ – 10^{16} . We might assume that the exchange by plasmons, rather than by phonons, would induce an increase of the pre-exponential factor in the formula deduced in the BCS theory,

$$T_c = \Theta \exp\left(\frac{1}{\lambda - \mu^*}\right) \tag{7}$$

by two-three orders, if $\Theta = \hbar \tilde{\omega}_p / k_{\rm B}$. However, such an increase does not cause a significant growth of T_c , because the plasmons at the frequency $\tilde{\omega}_p$ which is close to the frequency of electrons, $E_{\rm F}/\hbar$, cannot cause the superconducting pairing and their role is important only for the dielectric properties of crystals.⁸

4.7. Bipolaronic Mechanism of Superconductivity

One of the attempts to explain the phenomenon of hightemperature superconductivity was named the bipolaronic theory. Bipolarons are Bose-particles like the ordinary Cooper's pairs.

In the theory of bipolarons, the superconductivity is caused by the superfluidity of the Bose-condensate of bipolarons.

The ideas of polarons and bipolarons were used by Aleksandrov and Ranninger²¹ to clarify the hightemperature superconductivity.

The idea of a polaron is based on the assumption about the autolocalization of an electron in the ion crystal due to its interaction with longitudinal optical vibrations under the local polarization which is caused by the electron itself. The electron is confined in the local polarization-induced potential well and conserves it by the own field. The idea of the autolocalization of electrons in ion crystals was intensively developed by Pekar.²²

The efficiency of the interaction of an electron with mass m and charge e with long-wave longitudinal optical vibrations with frequency Ω in the medium is characterized by the dimensionless parameter

$$g = \frac{e^2}{\tilde{\varepsilon}} \sqrt{m/2\Omega\hbar^2} \tag{8}$$

introduced by Fröhlich. Here, $\tilde{\varepsilon}$ —the dielectric permeability of the inertial polarization. The interaction is assumed to be small if g < 1. Due to a high frequency Ω , the deformation field is a faster subsystem. Therefore, it has time to follow the movement of an electron. This field accompanies the movement of the electron in the form of a weak cloud of phonons. The energy of interaction of the field and the electron is proportional to the first degree of g.

In the BCS theory, the pairing of conduction electrons is realized due to the interaction with acoustic phonons and is characterized by the dimensionless constant of interaction

$$\lambda = VN(E_{\rm F}) \tag{9}$$

where N(Ef)—the density of energy states of electrons on the Fermi surface, and the quantity V is inversely proportional to the coefficient of elasticity of a crystal.

In the bipolaronic model, we have the parameter

$$\lambda * = (2\lambda^2 \hbar \Omega z - V_c)/D \tag{10}$$

where λ is defined by relation 9, *z*—the number of the nearest neighbors, *D*—the width of the conduction band of free quasiparticles.

A bipolaron, like a Cooper's pair, has charge 2e, and its effective mass is determined by the formula

$$\tilde{m} \approx m \frac{\Delta}{D} \exp(\lambda^2)$$
 (11)

The effective mass \tilde{m} can be very high and can excess the mass of a free quasiparticle in the conduction band by several orders.

To calculate the superconducting transition temperature T_c which corresponds to the Bose-condensation, the authors applied the formula for the ideal Bose-gas

$$k_{\rm B}T_c = 3.31\hbar^2 N^{2/3}/\tilde{m} \tag{12}$$

At $\tilde{m} = 100$ and $N = 10^{21}$ cm⁻³, the last formula yields $T_c \sim 28$ K.

Analogously to the bipolaronic model, the bisoliton mechanism of high-temperature superconductivity was proposed in Refs. [9, 10].

5. THE SYMMETRY OF PAIRING IN CUPRATE SUPERCONDUCTORS

Of great importance for high-temperature superconductors is the pairing symmetry or the symmetry of the order parameter. This question was considered at many conferences and seminars over the world. Several NATOseminars and conferences on this trend which hold in Ukraine in the town of Yalta were organized by one of the authors of this review.^{23–26}

The development of the microscopic theory of superconductivity was followed by the interest in the question about the nontrivial superconductivity corresponding to the Cooper's pairing with nonzero orbital moment.

The system, in which the nontrivial pairing was first discovered, is He³. To explain this phenomenon, it was

necessary to introduce a supplementing mechanism of pairing due to spin fluctuations.

5.1. Superconductor's Order Parameter

Most physical properties depend on the properties of the symmetry of a superconductor's order parameter which is defined by the formula

$$\Delta_{\alpha\beta}(\mathbf{k}) = \langle a_{\alpha\mathbf{k}} a_{\beta-\mathbf{k}\alpha} \rangle \tag{13}$$

The problem of pairing symmetry is the problem of the pairing of charged fermions into states with the final orbital moment.

As usual, both the standard pairing called the *s*-pairing and the nonstandard *d*-pairing are considered. They differ by the orbital moment of the pair: in the first and second cases, the moments are L = 0 and L = 2, respectively.

We note also that the continuous symmetry group in crystals is broken, and it is necessary to speak not about the orbital moment, but about the irreducible representations, by which the order parameter is classified. We will consider this question in the following subsection.

Usually, the standard pairing frequently called the *s*-pairing and the nonstandard pairing are distinguished. At the nonstandard pairing, the symmetry of the order parameter is lower than the symmetry of a crystal.

For a two-dimensional tetragonal crystal (square lattices), the possible symmetries of the superconductor's order parameter were enumerated by Sigrist and Rice²⁷ on the basis of the theory of group representations. The basis functions of relevant irreducible representations define the possible dependence of the order parameter on the wave vector.

It is worth noting that the anisotropic pairing with the orbital moment L = 2, i.e., $d_{x^2-y^2}$, has the following functional form in the *k* space:

$$\Delta(\mathbf{k}) = \Delta_o[\cos(k_x a) - \cos(k_y a)] \tag{14}$$

where Δ_o is the maximum value of the gap, and *a* is the lattice constant. The gap is strongly anisotropic along direction (110) in the *k* space. In this case, the order parameter sign is changed in the directions along k_x and k_y .

Together with the d-symmetry, it is worth to consider also the s-symmetry, for which we can choose two collections of basis functions:

$$\Delta(\mathbf{k}) = \Delta_o \tag{15}$$

The anisotropic *s*-pairing is considered as well. This form of the pairing is analyzed in works by Anderson¹⁹ with co-workers who have studied the mechanism of pairing on the basis of the tunneling of electrons between layers. In these states, the order parameter sign is invariable, and its amplitude is varied along direction (110):

[anisotropic s]
$$\Delta(k) = \Delta_o [\cos(k_x a) - \cos(k_y a)]^4 + \Delta_1$$
 (16)

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where Δ_1 corresponds to the minimum along direction (110).

It follows from the symmetry-based reasoning that the mixed states with various symmetries can be realized. We mention the states which are mostly in use. The "extended" s-coupled states were considered in works by Scalapino.²⁸ A possible functional form of these states is as follows:

[extended s wave] $\Delta(k)$

$$= \Delta_o \{ (1 + \gamma^2) [\cos(k_x a) - \cos(k_y a)]^2 - \gamma^2 \}$$
(17)

They have eight parts with alternating signs and eight nodes which are split by $\pm \gamma \pi/2$ along direction (110). Kotliar with co-workers used mixed s + id states:²⁸

$$[s+id]\Delta(k) = \Delta_o[\varepsilon + i(1-\varepsilon)[\cos(k_x a) - \cos(k_y a)]]$$
(18)

Laughlin²⁹ analyzed the mixed states $d_{x^2+y^2} + id_{xy}$ on the basis of the anyonic mechanism of pairing:

$$[d+id]\Delta(k) = \Delta_o[(1-\varepsilon)[\cos(k_x a) - \cos(k_y a)] + i\varepsilon[2\sin(k_x a)\sin(k_y a)]]$$
(19)

where ε is the share of s or d_{xy} states mixed with the $d_{x^2+y^2}$ states, and $\varepsilon \Delta_o$ is the minimum value of the energy gap. These mixed states are of interest because they are not invariant with respect to the inversion in the time. The value and phase of the superconductor's order parameter, as functions of the direction in cuprate planes CuO₂ are given in Figure 8 for various kinds of the pairing symmetry.

5.2. Classification of the Superconductor's **Order Parameter by the Representations** of Symmetry Groups

It should be noted that there is no classification of states by the orbital moment for crystals.

The general theory of nonstandard pairing has been developed on the basis of the analysis of point symmetry groups.

Annett was one of the first who classified superconducting states by the irreducible representations of groups for high-temperature superconductors.³⁰ As for superconductors with heavy fermions, the group analysis was carried out in Ref. [31].

Of importance is the question whether the symmetry of the order parameter in HTSC is lower than the symmetry of the crystal lattice.

The order parameter can be represented as a linear combination

$$\Delta_k = \sum \eta_{\Gamma_i} f_{\Gamma_i}(k) \tag{20}$$

where η_{Γ_i} —the irreducible representation of groups, by which the order parameter is transformed, $f_{\Gamma}(k)$ basis functions of the irreducible representation, A_{1e}



Fig. 8. Kinds of pairing symmetries which are considered for hightemperature superconductors.

corresponds to the anisotropic symmetry, and B_{1g} corresponds to the *d* pairing.

An analogous decomposition of the superconducting order parameter was performed for a superconductor with heavy fermions

 UPt_3

The symmetric states of the system can be presented by the indication of all possible subgroups of the full group, relative to which the order parameter is invariant.³² The full symmetry group of a crystal includes a point symmetry group G, operations of inversion of the time R, and the group of calibration transformations U(1). That is, we have the following partition into subgroups:

$$G \times R \times U(1) \tag{21}$$

The La- and Y-based superconductors which have the tetragonal symmetry of crystal lattices, i.e., $G = D_{4h} = D_4 \times I$,²⁴ are most studied. In the Y-based compounds, one observes small orthorhombic distortions of a crystal lattice.

Group D_{4h} includes the operations of rotations C_n , around the z axis by angles of $\pi n/2$ and rotations U_n by angles of π :

$$x\cos(\pi n/2) + y\cos(\pi n/2) \tag{22}$$

where n = 0, 1, 2, 3 have 5 reducible representations: four one-dimensional $(A_{1g}, A_{2g}, B_{1g}, B_{2g})$ and one twodimensional (E).

6. EXPERIMENTAL STUDIES OF A SYMMETRY OF THE SUPERCONDUCTING ORDER PARAMETER

At the present time, the results of three groups of experiments, in which the symmetry of the order parameter is revealed, are available.

The first group joins different low-temperature characteristics of superconductors such as the Knight shift, the rate of relaxation in NMR, the temperature dependence of the heat capacity, the penetration depth, etc.

If the superconductor's order parameter has zeros on different areas of the Fermi surface (as in the case of the $d_{x^2-y^2}$ -symmetry), the mentioned quantities will have the power temperature dependence, rather than the exponential one.

The second group of experiments is based on the direct measurement of the phase of the order parameter with the help of interference phenomena on Josephson junctions in a magnetic field.

The third group deals with the direct measurements of a value of the gap by means of spectroscopic experiments. Here, the most interesting results are presented by photoemission spectroscopy with angle resolution, and Raman and neutron spectroscopies.

6.1. Measurements of the Josephson Tunnel Current

The most definite information about a symmetry of the superconducting order parameter can be obtained from the studies of the phase of the order parameter, in which the critical current in Josephson junctions positioned in a magnetic field is measured. The critical current for a rectangular Josephson junction oscillates with the field by the Fraunhofer diffraction law:

$$I_c(\Phi) = J_0 A \frac{\sin(\pi \Phi/\Phi_0)}{\pi \Phi/\Phi_0}$$
(23)

where Φ —the magnetic flux through the junction, Φ_0 —the quantum flux, J_0 —the density of the critical current in the zero field, and A—the junction area. A diffraction pattern is shown in Figure 9(a). Let us consider the superconductor



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Fig. 9. Critical current in a Josephson junction versus the applied magnetic field: (a) standard tunnel contact, (b) corner tunnel junction for a superconductor with the *s*-symmetry of the order parameter, (c) corner tunnel junction for a superconductor with the *d*-symmetry of the order parameter.³³

YBCO which possesses the tetragonal symmetry. Let its axis be oriented normally to the plane of the figure, and let its edges be perpendicular to the axes \mathcal{A} and \mathcal{B} of the base plane. In the tunnel junction with corner geometry, another superconductor is applied to both edges which are perpendicular to \mathcal{A} and \mathcal{B} and, moreover, are joined with each other (Figs. 9(b) and (c)).

This experiment can be compared with that involving a two-junction SQUID, in which there occurs a superposition of tunnel currents produced by electrons with wave vectors k_x and k_y , so that the resulting diffraction pattern depends on the symmetry of the order parameter of a superconductor under study. At the *s*-symmetry, the order parameter on both edges of the corner junction is the same, and the resulting diffraction pattern will be such as that in the case of the standard junction. But, in the case of the *d*-symmetry, the order parameter on the corner junction



Fig. 10. Critical current as a function of the magnetic field in a Josephson junction YBCO–Au–Pb in two geometries: (a) standard and (b) corner ones.³³

edges has different signs, and this fact changes basically the diffraction pattern.

The total current is illustrated in Figure 10(c). In the zero field, the critical current turns out to be zero due to the mutual compensation of its two components.

In the symmetric contact, the dependence on the field is determined by the formula³³

$$I_{c}(\Phi) = J_{0}A \frac{\sin^{2}(\pi \Phi/2\Phi_{0})}{\pi \Phi/2\Phi_{0}}$$
(24)

corresponding to the pattern in Figure 10(c).

Thus, by the difference of a diffraction pattern from both the standard one and that corresponding to the corner Josephson junction, we can judge about a symmetry of the order parameter. In work,³³ a similar experiment was carried out on the tunnel junction YBCO–Au–Pb. The results presented in Figure 10 testify to the *d*-symmetry of the order parameter in superconducting YBCO.

All the above-mentioned experiments with Josephson junctions were performed with a single crystal $YBa_2Cu_3O_6$.

6.2. Measurements of the Quantization of a Flow by the Technique of Three-Crystal Unit

Another type of experiments on the determination of a symmetry of the order parameter is based on the



Fig. 11. Scheme of the experiment on the measurement of a half-integer number of quanta of the flow captured by a superconducting ring with three Josephson junctions with the *d*-symmetry of the order parameter.³⁴

measurement of a flow quantum in a superconducting ring fabricated from three superconducting single crystals of yttrium with different orientations.

The idea of such an experiment is based on the theoretical result obtained by Sigrist and Rice:²⁷ for superconductors with the *d*-symmetry, the tunnel current between two superconducting crystals separated by a thin boundary depends on the orientation of the order parameter with respect to the interface. The current between the superconductors with numbers ij is given by the formula

$$I_s^{ij} = (A^{ij}\cos 2\theta_i \cos 2\theta_j)\sin \Delta\Phi_{ij}$$
(25)

Here, A^{ij} —the constant which characterizes the junction of ij, θ_i , θ_j —the angles of the crystallographic axes with the boundary plane, and Φ_{ij} —the difference of phases of the order parameters on both sides of the boundary. It was shown that a spontaneous magnetization, which corresponds to the flow equal to a half of Φ_0 , appears in a superconducting ring with a single Josephson junction with the phase difference π . If the ring has odd number of π -junctions, the result is the same. The direct measurement of a half-quantum of the flow through such a ring would testify to the *d*-symmetry of the order parameter. The direct measurement of a half-quantum of the flow was realized in work.³⁴ The scheme of the experiment is shown in Figure 11.

7. THERMODYNAMICS OF THE *d*-PAIRING IN CUPRATE SUPERCONDUCTORS

7.1. Introduction

The basic question of the theory of superconductivity concerns the mechanism ensuring the pairing of electrons. In the BCS theory, it is the electron–phonon interaction. Some recent theoretical models postulate the mechanism of antiferromagnetic spin fluctuations,^{35–41} so that the electron scattering on them can be the reason for the pairing of electrons. Spin fluctuations play an important role in superconductors with heavy fermions.^{38,39} The authors of works^{30,31} performed the calculations of a value of the superconductor gap, the critical temperature, the temperature dependence of the resistance, and many other quantities, but the thermodynamics was not considered. For this reason, it is of interest to calculate the thermodynamics of antiferromagnetic spin fluctuations, namely the temperature dependence of the heat capacity, its jump near T_c , and the parameter $R = \Delta C / (\gamma T_c)$ equal to 1.42 by the BCS theory.

The purpose of this section is the calculation of the thermodynamics of antiferromagnetic spin fluctuations, namely the electron heat capacity and the jump of the heat capacity.

The thermodynamics of superconductors at low temperatures is determined by the excitation of two quasiparticles. In the traditional superconductors with pairing of the BCS-type, the energy gap is isotropic (*s*-pairing), and the temperature dependence of the heat capacity has the exponential form $\sim \exp^{-\Delta/k_{\rm B}T}$, where Δ is the superconductor's gap. In the superconductors with the anisotropic pairing, the temperature dependence of the heat capacity has a power character, namely, T^n . The appearance of such temperature dependences is related to the fact that the superconductor's gap has zeros on the Fermi surface.

As was noted above, the anisotropic pairing with the orbital moment L = 2, i.e., with the $d_{x^2-y^2}$ -symmetry, has the following functional form in the *k* space:

$$\Delta(\mathbf{k}) = \Delta_o[\cos(k_x a) - \cos(k_y a)]$$
(26)

where Δ_o is the maximum value of the gap, and *a* is the lattice constant.

The gap is strongly anisotropic in direction (110) in the k space, and the sign of the order parameter is changed along the directions k_x and k_y .

The main results of this section are published in works Refs. [42, 43, 44, 45].

7.2. Antiferromagnetic Spin Fluctuations in High-Temperature Superconductors

For the first time, the idea of the possibility for the electron pairing through spin fluctuations was advanced by Akhiezer and Pomeranchuk.⁴⁵ They showed that the indirect interaction of electrons through spin waves in a ferromagnetic metal has the character of attraction in the triplet state and, hence, can lead to the triplet pairing. Consider some experiments and facts on antiferromagnetic spin fluctuations.

The basis for the hypothesis on the spin-fluctuation mechanism of pairing consists in the fact that the stoichiometric compounds La_2CuO_4 and $YBa_2Cu_3O_6$ are antiferromagnetic dielectrics. The doping of superconductors leads to the appearance of the metallic state and superconductivity. The closeness of high-temperature superconductors to the antiferromagnetic transition with the wave vector $Q = (\pi/a, \pi/a)$ defines the important role of spin fluctuations, the interaction with which forms the quasiparticle spectrum of electrons and can simultaneously cause the Cooper's pairing.

High-temperature superconductors are referred to the class of strongly correlated systems which are theoretically studied in the frame of the Hubbard model. This model describes the hops of electrons in the lattice with the matrix element t for the nearest neighbors with regard for the Coulomb repulsion U, when the electrons are positioned at the same site. The model is set by the Hamiltonian

$$H = -t \sum_{i,j,\sigma} C_{i\sigma}^{\dagger} C_{j\sigma} + U \sum_{i,} n_{i\uparrow} n_{i\downarrow}$$
(27)

where $C_{i\sigma}^{\dagger}(C_{j\sigma})$ —the operator of creation (annihilation) of an electron at the site *i* with spin σ , and $n_{i\uparrow} = C_{i\sigma}^{\dagger}C_{j\sigma}$ the number of electrons at the site. In the given region of the parameters *t*, *U*, and *n* (the electron concentration), the appearance of magnetically ordered phases is possible. Near the boundary of the existence of such a phase from the side of the paramagnetic region, strong fluctuations of the magnetic order parameter, paramagnons, must be manifested.

In the two-dimensional system of CuO layers in cuprate superconductors, the electron spectrum is presented by the formula

$$\varepsilon(t) = -2t\cos k_x a + \cos k_y a \tag{28}$$

and the chemical potential μ is determined by the given electron concentration *n*. On the half-filling (n = 1), this spectrum has the nesting at the wave vector q = Q, which induces a sharp peak in the spin susceptibility near this point. This means an instability of the system relative to the formation of the antiferromagnetic state with the wave vector Q and the intensification of spin fluctuations near the point of the magnetic phase transition.

Near the half-filling, when the system is really antiferromagnetically unstable, the numerical calculations indicate that the superconducting order parameter has *d*-symmetry, i.e., the gap depends on the wave vector by relation 26.

Gap 26 is an alternating function of the wave vector (Fig. 12) and has zero values on the diagonals.

Figure 12 shows that the wave function of a Cooper's pair is equal to zero just on the diagonals of the square. Therefore, the repulsive interaction on these diagonals does not act on the pair, and a Cooper's pair with the d-symmetry survives even at large values of U. The superconductors with the d-pairing should have a number of particular properties which can be observed in experiments. Many of these peculiarities are related to the zeros of the order parameter. The quasiparticle spectrum at low temperatures must give the power contribution to the thermodynamic properties, such as the heat capacity,



Fig. 12. Distribution of signs of the gap function in the limits of the Brillouin first band.

parameters of NMR, and the penetration depth of a magnetic field, rather than the exponential one as in ordinary isotropic superconductors.

The observation of such power contributions will indicate the presence of a nontrivial order parameter with zeros on the Fermi surface. The totality of experimental data for various high-temperature superconductors indicates the certain realization of the anisotropic order parameter in them and, with a high probability, with the *d*-symmetry. The last circumstances present the important argument in favor of the spin-fluctuation mechanisms of hightemperature superconductors. One of them is intensely developed by Pines and his co-workers^{35,37} who used a phenomenological form of the magnetic susceptibility with the parameters determined from the experiments on cuprates.

Let us consider this model in more details.

We introduce a Hamiltonian which involves antiferromagnetic spin fluctuations, as it was made in works by Pines:^{35,36}

$$H = H_0 + H_{\rm int} \tag{29}$$

where H_0 —Hamiltonian of free electrons. The interaction is described by the Hamiltonian

$$H_{\rm int} = \frac{1}{\Omega} \sum_{q} g(q) s(q) S(-q) \tag{30}$$

where Ω —the cell volume, g(q)—the interaction constant;

$$s(q) = \frac{1}{2} \sum_{\alpha,\beta,k} \Psi_{k+q}^{+} \sigma_{\alpha\beta} \Psi_{k\beta}$$
(31)

—operator of spin density; $\sigma_{\alpha\beta}$ —Pauli matrix; $\Psi_{k+q,\alpha}^+$ operator of creation of an electron with the momentum k+q and the spin projection α ; $\Psi_{k\beta}$ — operator of creation of a hole with the momentum k and the spin projection β ; S(-q)—operator of spin fluctuations, whose properties are set by the correlator $\chi(q, \omega)$,^{35,36} $\chi_{ij}(\mathbf{n}, \mathbf{m})$ is the spin

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susceptibility which is modeled by

$$\chi(q,\omega) = \frac{\chi_Q}{1 + \xi^2 (q - Q)^2 - i\omega/\omega_{\rm SF}}$$
(32)
$$q_{\rm x} > 0, \ q_{\rm y} > 0$$

where χ_Q is the static spin susceptibility with the wave vector $Q = (\pi/a, \pi/a)$, ξ is the temperature-dependent antiferromagnetic correlation length, and ω_{SF} is the characteristic frequency of spin fluctuations of the paramagnon energy. All parameters are taken from experiments, including the data from NMR studies.³⁵ In this case, the interaction constant is a free parameter of the theory. It can be determined, by calculating some quantity with the help of the Hamiltonian and by comparing the result with experiments.

We now define the quantities χ_Q and $\omega_{\rm SF}$ as

$$\chi_Q = \chi_0 (\xi/a)^2 \beta^{1/2}$$
(33)

$$\omega_{\rm SF} = \Gamma / (\pi (\xi/a)^2 \beta^{1/2}) \tag{34}$$

where χ_0 —the experimentally measured long-wave limit of the spin susceptibility, $\beta = \pi^2$, and Γ —the energy constant. The NMR data for the compounds yield $\xi(T_c) =$ $2.3a, \omega_{\rm SF} = 8$ meV, $\Gamma = 0.4$ meV.

It is foreseen that the phenomenological Hamiltonian will give a self-consistent description of the spin dynamics of the system in the sense that the spin susceptibility calculated with its help (through the characteristics of a quasiparticle spectrum which themselves depend on the susceptibility) will agree with values determined by formula (32).

7.3. Continual Model of Antiferromagnetic Spin Fluctuations

The authors of works^{42–45} proposed a continual model for the spin-fluctuation mechanism of pairing which allows one to efficiently solve the problem of thermodynamics for this mechanism.

Let us consider this model in more details.

We now calculate the thermodynamics which is set by the Pines spin-fluctuation Hamiltonian. We write the Hamiltonian in the lattice representation

$$H = H_0 + H_{\rm int} \tag{35}$$

$$H = -t \sum_{\mathbf{n},\mathbf{p}} \psi_{\alpha}^{+}(\mathbf{n}) \psi_{\alpha}(\mathbf{n}+\mathbf{p}) + \frac{1}{2} \sum_{\mathbf{n},\mathbf{m}} S_{i}(\mathbf{n}) \chi_{ij}^{-1}(\mathbf{n},\mathbf{m}) S_{j}(\mathbf{m})$$

$$+g\sum_{\mathbf{n}}\psi_{\alpha}^{+}(\mathbf{n})\left(\frac{\sigma_{i}}{2}\right)_{\alpha\beta}\psi_{\beta}(\mathbf{n})S_{i}(\mathbf{n})$$

$$H_{0} = -t\sum_{\alpha}\psi_{\alpha}^{+}(\mathbf{n})\psi_{\alpha}(\mathbf{n}+\mathbf{p})$$
(36)

$$+\frac{1}{2}\sum_{\mathbf{n},\mathbf{m}} S_i(\mathbf{n})\chi_{ij}^{-1}(\mathbf{n},\mathbf{m})S_j(\mathbf{m})$$
(37)

$$H_{\rm int} = g \sum_{\mathbf{n}} \psi_{\alpha}^{+}(\mathbf{n}) \left(\frac{\sigma_i}{2}\right)_{\alpha\beta} \psi_{\beta}(\mathbf{n}) S_i(\mathbf{n})$$
(38)

where the sum is taken over all the sites of the infinite lattice (the lattice constant is equal to *a*), ρ —the unit vector joining the neighboring sites, S_i —the spin operator, $N = \sum_{\mathbf{n}} \psi_{\alpha}^+(\mathbf{n})\psi_{\alpha}(\mathbf{n})$ —the operator of the number of particles, *t*—the half-width of the conduction band,^{35,36} and $\chi_{ij}(\mathbf{n}, \mathbf{m})$ —the spin correlation function.

It is necessary to calculate the grand partition function

$$\exp\{-\beta\Omega(\mu,\beta,g)\} \equiv \operatorname{Tr}\exp\{-\beta(H-\mu N)\}$$
(39)
$$\beta = 1/kT$$

where μ —the chemical potential; *g*—the coupling constant; and $\Omega(\mu, \beta, q)$ —the thermodynamic potential.

It is convenient to use the formalism of continual integration for a system of Fermi-particles. The method of functional integration, i.e., the integration in the space of functions, was proposed by Wiener in 1925, but the physicist-theorists paid no attention to this method. Continual integrals were introduced in physics by Feynman⁴⁶ in the 1940s and were used for the reformulation of quantum mechanics. The continual integration is one of the most powerful methods of the contemporary theoretical physics which allows one to simplify, accelerate, and clarify the process of analytic calculations. The application of the method of continual integration to a system with infinite number of degrees of freedom allows one to develop, in such a way, the diagram theory of perturbations.

The grand partition function can be written in the form of a continual integral:⁴⁷

$$\exp -\beta\Omega = N \int \prod_{\mathbf{n}} dS_i(n) d\psi_{\alpha}^+(n,\tau) d\psi_{\alpha}(n,\tau)$$
$$\times \exp\left\{-\int_0^\beta d\tau L(\tau)\right\}$$
(40)

where

$$L(\tau) = \sum_{\mathbf{n}} \psi_{\alpha}^{+}(\mathbf{n}, \tau) \left(\frac{\partial}{\partial \tau} - \mu\right) \psi_{\alpha}(\mathbf{n}, \tau)$$
$$- t \sum_{\mathbf{n}, \mathbf{p}} \psi_{\alpha}^{+}(\mathbf{n}, \tau) \psi_{\alpha}(\mathbf{n} + \mathbf{p}, \tau)$$
$$+ g \sum_{\mathbf{n}} \psi_{\alpha}^{+}(\mathbf{n}, \tau) \left(\frac{\sigma_{i}}{2}\right)_{\alpha, \beta} \psi_{\beta}(\mathbf{n}, \tau) S_{i}(\mathbf{n}, \tau)$$
$$+ \frac{1}{2} \sum_{\mathbf{n}, \mathbf{m}} S_{i}(\mathbf{n}, \tau) \chi_{ij}^{-1}(\mathbf{n}, \mathbf{m}, \tau) S_{j}(m, \tau) \quad (41)$$

where $L(\tau)$ —the Lagrangian of the system, and N—the normalizing factor,

$$N^{-1} = \int \prod_{\mathbf{n}} dS_i(n) d\psi_{\alpha}^+(n,\tau) d\psi_{\alpha}(n,\tau)$$
$$\times \exp\left\{-\int_0^\beta d\tau L(\tau,\mu=g=0)\right\}$$
(42)

We will use the matrix formalism to construct the theory of perturbations for the Green functions. It is convenient Kruchinin

to introduce a four-component bispinor (Majorana)

$$\Psi = \begin{pmatrix} \psi \\ -\sigma_2 \psi^* \end{pmatrix}, \quad \psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$
(43)

where σ_1 —Pauli spin matrices. The Majorana spinor is a Weyl spinor written in the four-component form.

Now, we can write L in the form

$$L = \frac{1}{2} \sum_{\mathbf{n},\mathbf{p}} \Psi(\mathbf{n},\tau) \left[\left(\Gamma^0 \frac{\partial}{\partial \tau} - \Gamma^0 \Gamma_5 \mu \right) \hat{\delta} - t(\tau - \hat{\delta}) \Gamma^0 \Gamma_5 \right] (44) \\ \times \psi(\mathbf{n} + \mathbf{p},\tau) + \frac{g}{4} \sum_{\mathbf{n}} \Psi(\mathbf{n},\tau) \Gamma^i \Gamma_5 \Psi(\mathbf{n},\tau) S^i(\mathbf{n},\tau) \\ + \frac{1}{2} \sum_{\mathbf{n},\mathbf{m}} S_i(\mathbf{n},\tau) \chi_{ij}^{-1}(\mathbf{n},\mathbf{m},\tau) S_j(\mathbf{m},\tau)$$
(45)

where

$$\Gamma^{0} = \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix}, \quad \Gamma^{i} = \begin{pmatrix} 0 & -\sigma_{i} \\ \sigma_{i} & 0 \end{pmatrix}, \quad I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (46)$$

where Γ^i are the Dirac gamma matrices, $\bar{\Psi} \equiv \Psi^+ \Gamma^0$, $\hat{\delta} = \delta_{\mathbf{n},\mathbf{n}+\mathbf{p}}$, and Γ^i are given in the chiral representation.

There exists the connection between Ψ and $\bar{\Psi}$: $\Psi = C\bar{\Psi}^T$, where *C* is the matrix of charge conjugation, $C = \Gamma^0 \Gamma^2$, $C^T = -C$. In terms of Ψ , the partition function takes the form

$$e^{-\beta\Omega} = N \int \prod n dS_i(n,\tau) d\Psi(n,\tau) e^{-\int_0^\beta d\tau L(\tau)}$$
(47)

We now use the method of bilocal operators⁴⁸ to calculate the grand partition function. In this way, we obtain the Schwinger–Dyson equation and the equation of free energy. The details of calculations can be found in Refs. [42-45].

In order to calculate Ω , we introduce a source of the bilocal operator⁴⁸

$$e^{-\beta\Omega(J)} = N \int dS d\Psi e - \int_0^\beta d\tau \left[L(\tau) + \frac{1}{2} \sum_{\mathbf{n},\mathbf{m}} \int_0^\beta \bar{\Psi}(\mathbf{n},\tau) \times J(\mathbf{m},\mathbf{n},\tau,\tau') \Psi(\mathbf{m},\tau') \right]$$
(48)

The full Green fermion function is determined by the formula

$$G_{nm}(J) = e^{\beta\Omega(J)} \int dS \, d\Psi \, \Psi(n,\tau) \bar{\Psi}(m,\tau') \exp\{\dots\}$$
$$= \langle 0|T\Psi(n,\tau) \bar{\Psi}(m,\tau')|0\rangle$$
(49)

Let us write the Schwinger–Dyson equation for the Green function G, by using the method of bilocal operator:⁴⁵

$$\frac{\delta F}{\delta G} = 0 \tag{50}$$

$$F(G) = \beta \Omega(J = 0) \tag{51}$$

First, we consider the case of a free system. By integrating over the fermion fields in the functional integral, we obtain

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$$F_{0} = \beta \Omega(J)$$

= $-\frac{1}{2} \operatorname{Tr} \operatorname{Ln}(G_{0}^{-1} - \Gamma^{0} \Gamma_{5} \mu + J) + \frac{1}{2} \operatorname{Tr} \operatorname{Ln} G_{0}^{-1}$ (52)

$$G_0 = \left[\Gamma^0 \frac{\partial}{\partial \tau} - t(1-\widehat{\delta})\Gamma^0 \Gamma_5\right]^{-1}$$
(53)

For the interacting system, the free energy takes the form

$$F = F_0 + F_{\text{int}} \tag{54}$$

We represent F_{int} as a series in g: $F_{\text{int}} = \sum_{n=1}^{\infty} (g^2) F_n$. In the lowest order in g, we get the relation

$$F_1 = -\frac{g^2}{32} \operatorname{Tr}\{\Gamma^i G \operatorname{Tr}\Gamma^j G - 2G\Gamma^i G\Gamma^j\}\chi_{ij}$$
 (55)

where the Green function for fermions and spins is as follows:

$$\langle \Psi(x,\tau)\Psi(y,\tau')\rangle = G(x,\tau;y,\tau') \langle S_i(x,\tau)S_j(y,\tau')\rangle = \chi_{ij}(x,\tau;y,\tau')$$
(56)

Taking the condition $\delta F/\delta G = 0$ into account, we obtain the Schwinger-Dyson equation

$$G^{-1} = G_0^{-1} - \Gamma^0 \Gamma_5 \mu + \frac{g^2}{12} \{ \Gamma^i \text{Tr} \Gamma^j G \chi_{ij} - 2\Gamma^i G \Gamma^j \chi_{ij} \}$$
(57)

where Γ_0 and Γ^i —Dirac matrices (Fig. 13).

Here, the continuous line corresponds to the Green function for fermions G, and the wavy line does to the Green function for spins $\chi_{i,i} (= \delta_{ii} \chi)$. The equation for free energy

$$F_1 = -\frac{g^2}{32} \operatorname{Tr} \{ \Gamma^i G \operatorname{Tr} \Gamma^j G - 2G \Gamma^i G \Gamma^j \} \chi_{ij}$$
 (58)

where G and χ_{ii} are, respectively, the Green fermion and spin functions, corresponds to the contribution of two vacuum diagrams (Fig. 14).

7.4. Equation for Superconducting Gap

From Eq. (57), it is easy to deduce the equation for a gap which can be found in Ref. [36]. By executing the Fourier transformation



Fig. 13. Graphical form of Eq. (57).

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we rewrite Eq. (57) in the momentum space as

$$G^{-1}(\mathbf{k}, i\omega_n) = \widetilde{G_0^{-1}}(\mathbf{k}, i\omega_n) + \frac{g^2}{4\beta} \sum_{m=-\infty}^{\infty} \int_{-\pi/a}^{\pi/a} \frac{d^2 p}{(2\pi)^2} \\ \times [\Gamma^i \Gamma_5 \operatorname{Tr} \Gamma^i \Gamma_5 G(\mathbf{p}, i\omega_m) \\ - 2\Gamma^i \Gamma_5 G(\mathbf{p}, i\omega_m) \Gamma^i \Gamma_5] \\ \times \chi(\mathbf{k} - \mathbf{p}, i\omega_n - i\omega_m)$$
(59)

where we set $\chi_{ij} = \delta_{ij} \chi$,

$$G_0^{-1}(\mathbf{k}, i\omega_n) = \begin{pmatrix} 0 & \{i\omega_n - (\varepsilon(\mathbf{k}) - \mu)\}I\\ \{i\omega_n + \varepsilon(\mathbf{k}) - \mu\}I & 0 \end{pmatrix}$$
$$= \Gamma^0 i\omega_n - \Gamma^0 \Gamma_5(\varepsilon(\mathbf{k}) - \mu)$$
(60)

$$\varepsilon(\mathbf{k}) = -2t[\cos k_x a + \cos k_y a] \tag{61}$$

According to the standard relation of the diagram technique, we denote the free energy by $\Sigma(\mathbf{k}, i\omega_n)$. Then we have

$$G^{-1}(\mathbf{k}, i\omega_n) = \widetilde{G_0^{-1}}(\mathbf{k}, i\omega_n) - \Sigma(\mathbf{k}, i\omega_n)$$
(62)

and Eq. (57) is the equation for Σ . We write the solution for Σ in the form

$$\Sigma = \Gamma^0 A + \Gamma^0 \Gamma_5 B + \Delta + \Gamma^0 \Gamma_5 \Gamma^i \Delta_i \tag{63}$$

(A, B, Δ , and Δ_i are functions of **k** and $i\omega_n$).

By determining the matrix which is inverse to (62), we get

$$G(\mathbf{k},i\omega_n)$$

$$=\frac{\Gamma^{0}(\omega_{n}-A)-\Gamma^{0}\Gamma_{5}(\varepsilon(\mathbf{k})-\mu+B)+\Delta+\Gamma^{0}\Gamma_{5}}{(\omega_{n}-A)^{2}-(\varepsilon(\mathbf{k})-\mu+B)^{2}-\Delta^{2}-\Delta_{i}^{2}} \quad (64)$$

Substituting (64) and (63) in (63), we obtain the system of equations for the functions A, B, Δ , and Δ_i :

$$A(\mathbf{k}, i\omega_n) = \frac{3g^2}{4\beta} \sum_m \int \frac{d^2p}{(2\pi)^2} \frac{i\omega_n - A(\mathbf{p}, i\omega_m)}{D(i\omega_m, \mathbf{p})} \times \chi(\mathbf{k} - \mathbf{p}, i\omega_n - i\omega_m)$$
(65)

$$B(\mathbf{k}, i\omega_n) = \frac{3g^2}{4\beta} \sum_m \int \frac{d^2p}{(2\pi)^2} \frac{\varepsilon(\mathbf{p}) - \mu + B(\mathbf{p}, i\omega_m)}{D(i\omega_m, \mathbf{p})} \times \chi(\mathbf{k} - \mathbf{p}, i\omega_n - i\omega_m)$$
(66)

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Fig. 14. Graphical form of the right-hand side of Eq. (58).

$$\Delta(\mathbf{k}, i\omega_n) = \frac{3g^2}{4\beta} \sum_m \int \frac{d^2p}{(2\pi)^2} \frac{\Delta(\mathbf{p}, i\omega_m)}{D(i\omega_m, \mathbf{p})} \times \chi(\mathbf{k} - \mathbf{p}, i\omega_n - i\omega_m) \quad (67)$$
$$\Delta_i(\mathbf{k}, i\omega_n) = -\frac{g^2}{4\beta} \sum_m \int \frac{d^2p}{(2\pi)^2} \frac{\Delta_i(\mathbf{p}, i\omega_m)}{D(i\omega_m, \mathbf{p})} \times \chi(\mathbf{k} - \mathbf{p}, i\omega_n - i\omega_m) \quad (68)$$

where

$$D(i\omega_m, \mathbf{p}) = (\omega_n - A)^2 - (\varepsilon(\mathbf{k}) - \mu + B)^2$$
(69)

Equations (67) and (68) correspond, respectively, to the singlet and triplet pairings. Moreover, the singlet channel is characterized by the repulsion, whereas the triplet one by the attraction. Therefore, it is necessary to take the trivial solution, $\Delta = 0$, of Eq. (67). In the following calculations, we will neglect the contributions from the functions A and B, which leads only to the renormalization of the wave function and the chemical potential, and will study only Eq. (67). By neglecting Δ^2 in the denominator, we get the linearized equations for Δ_0 which determine the critical temperature T_c .

For the correlation function $\chi(q, i\omega_n)$, we will use the dispersion relations

$$\chi(q, i\omega_n) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{d\omega' \operatorname{Im} \chi(q, \omega')}{i\omega_n - \omega'} = -\frac{1}{\pi} \left[\int_{0}^{\infty} \frac{d\omega' \operatorname{Im} \chi(q, \omega')}{i\omega_n - \omega'} + \int_{0}^{\infty} \frac{d\omega' \operatorname{Im} \chi(q, -\omega')}{i\omega_n + \omega'} \right]$$
(70)

In order to sum over m in (70), we consider the contour $C = C_1 + C_2$ (Fig. 15).

The following formula for $\omega_n = ((2n+1)\pi)/\beta$ is valid:

$$\sum_{n=-\infty}^{\infty} F(i\omega_n) = -\frac{\beta}{2\pi i} \int_C \frac{F(\omega)d\omega}{\exp\beta\omega + 1}$$
$$= -\frac{\beta}{2\pi i} \int_C \frac{F(\omega)d\omega}{\exp-\beta\omega + 1}$$
(71)

or

$$\sum_{n=-\infty}^{\infty} F(i\omega_n) = -\frac{\beta}{2\pi i} \frac{1}{2} \int_C F(\omega) \operatorname{th} \frac{\beta\omega}{2} d\omega \qquad (72)$$

Taking into account that $\operatorname{Im} \chi(q, -\omega) = -\operatorname{Im} \chi(q, \omega)$, Eq. (70) can be reduced to

$$\chi(q, i\omega_n) = -\frac{1}{\pi} \int_0^\infty d\omega' \operatorname{Im} \chi(q, \omega') \left[\frac{1}{i\omega_n - \omega'} - \frac{1}{i\omega_n + \omega'} \right] (73)$$



Fig. 15. Integration contour $C = C_1 + C_2$.

With the help of formula (72), we can rewrite (67) in the form

 $\Delta(\mathbf{k}, i\omega_n)$

$$=\frac{g^2}{8\pi(2\pi i)}\int\frac{d^2p}{(2\pi)^2}\int_C d\omega F(\mathbf{p},\omega)\int_0^\infty d\omega' \mathrm{Im}\,\chi(\mathbf{k}-\mathbf{p},\omega')$$
$$\times \left[\frac{1}{i\omega_n-\omega-\omega'}-\frac{1}{i\omega_n-\omega+\omega'}\right]\mathrm{th}\frac{\beta\omega}{2}$$
(74)

where

$$F(\mathbf{p}, \omega) = \frac{\Delta(\mathbf{k}, i\omega_n)}{\omega^2 - (\varepsilon(\mathbf{p}) - \mu)^2}$$

After some calculations and transformations, we get the general formula for the superconducting parameter:⁴³⁻⁴⁵

$$\operatorname{Re}(\mathbf{k},\omega)$$

$$= \frac{g^2}{8} \int_{-\pi/a}^{\pi/a} \frac{d^2 p}{(2\pi)^2} \left\{ \frac{\operatorname{th}(\beta(\varepsilon(\mathbf{p}) - \mu))/2}{2(\varepsilon(\mathbf{p}) - \mu)} \times [\operatorname{Re} \chi(\mathbf{k} - \mathbf{p}, \omega - (\varepsilon(\mathbf{p}) - \mu))] + \operatorname{Re} \chi(\mathbf{k} - \mathbf{p}, \omega - (\varepsilon(\mathbf{p}) - \mu))] \operatorname{Re}\Delta(\mathbf{p}, \nu) \right. \\ \left. + \operatorname{Re} \chi(\mathbf{k} - \mathbf{p}, \omega + (\varepsilon(\mathbf{p}) - \mu))] \operatorname{Re}\Delta(\mathbf{p}, \nu) \right. \\ \left. - 2 \int_0^\infty \frac{d\nu}{\pi} \operatorname{cth} \frac{\beta\nu}{2} \operatorname{Im} \chi(\mathbf{k} - \mathbf{p}, \nu) \right. \\ \left. \times \left[\frac{(\omega - \nu)^2 - (\varepsilon(\mathbf{p}) - \mu)^2 - \delta^2}{((\omega - \nu)^2 - (\varepsilon(\mathbf{p}) - \mu)^2 - \delta^2)^2 + 4(\omega - \nu)^2 \delta^2} \right. \\ \left. \times \operatorname{Re}\Delta(\mathbf{p}, \omega - \nu) \right. \\ \left. + \frac{(\omega + \nu)^2 - (\varepsilon(\mathbf{p}) - \mu)^2 - \delta^2}{((\omega + \nu)^2 - (\varepsilon(\mathbf{p}) - \mu)^2 - \delta^2)^2 + 4(\omega - \nu)^2 \delta^2} \right. \\ \left. \times \operatorname{Re}\Delta(\mathbf{p}, \omega + \nu) \right] \right\}$$
(75)

$$\operatorname{Re} F(\mathbf{p}, \omega + i\delta) = \operatorname{Re} \Delta(\mathbf{p}, \omega) \frac{\omega^2 - (\varepsilon(\mathbf{p}) - \mu)^2 - \delta^2}{[\omega^2 - (\varepsilon(\mathbf{p}) - \mu)^2 - \delta^2]^2 + \omega^2 \delta^2}$$
(76)

If the superconducting gap depends weakly on the frequency, then $\Delta(\mathbf{k}, \omega) \simeq \Delta(\mathbf{k}, 0)$. In this case, we set

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 $\omega = 0$ in Eq. (75). Considering the relation $\operatorname{Re} \chi(q, \omega) = \operatorname{Re} \chi(q, -\omega)$ and making the simple transformations, we obtain the equation similar to that in Ref. [36]:

$$\Delta(\mathbf{k}) = \frac{g^2}{8} \int_{-\pi/a}^{\pi/a} \frac{d^2 p}{(2\pi)^2} \left\{ \operatorname{Re} \chi(\mathbf{k} - \mathbf{p}, \varepsilon(\mathbf{p}) - \mu) \right. \\ \left. \times \frac{\operatorname{th}(\beta(\varepsilon(\mathbf{p}) - \mu))/2)}{(\varepsilon(\mathbf{p}) - \mu)} \right. \\ \left. + 2 \int_0^\infty \frac{d\nu}{\pi} \operatorname{cth} \frac{\beta\nu}{2} \operatorname{Im} \chi(\mathbf{k} - \mathbf{p}, \nu) \right. \\ \left. \times \frac{(\varepsilon(\mathbf{p}) - \mu)^2 - \nu^2 + \delta^2}{[(\varepsilon(\mathbf{p}) - \mu)^2 - \nu^2 + \delta^2]^2 + 4\nu^2 \delta^2} \right\} \Delta(\mathbf{p}) \quad (77)$$

It is important that our method of calculations yields a more general equation for the superconducting gap than that obtained by Pines. Our equation coincides with the Pines equations after some simplification, which is the test for our calculations.

7.5. Thermodynamic Potential of Antiferromagnetic Spin Fluctuations

For the free energy, we have the equation

$$F(G) = \beta \Omega = -\frac{1}{2} \operatorname{Tr} [\ln G_o G^{-1} + (G_o^{-1} + \Gamma^o \Gamma_5 \mu) G^{-1}] - \frac{g^2}{32} \operatorname{Tr} \{ \Gamma^i G \operatorname{Tr} \Gamma^j G \chi_{ij} - 2G \Gamma^i G \Gamma^j \chi_{ij} \}$$
(78)

where G satisfies Eq. (57). We now multiply Eq. (58) by G and take the trace, Tr. This allow us to obtain

$$\frac{g^2}{8} \operatorname{Tr} \{ \Gamma^i G \operatorname{Tr} \Gamma^j G \chi_{ij} - 2G \Gamma^i G \Gamma^j \chi_{ij} \}$$
$$= -\operatorname{Tr} \{ (G_o^{-1} + \Gamma^o \Gamma_5 \mu) G - 1 \}$$
(79)

Using (57), we can rewrite relation (79) for the functional of free energy calculated with the use of solutions of the Schwinger–Dyson equation in the form

$$\beta \Omega = -\frac{1}{2} \operatorname{Tr} \left[\ln G_o \Gamma^{-1} + \frac{1}{2} (G_o^{-1} + \Gamma^o \Gamma_5 \mu) G - \frac{1}{2} \right]$$
(80)

By implementing the Fourier transformation, we get

$$\Omega = \frac{1}{2\beta} V \sum_{n=-\infty}^{\infty} \int_{-\pi/a}^{\pi/a} \frac{d^2k}{(2\pi)^2} \operatorname{Tr} \left[\ln G_o(\mathbf{k}, iw_n) G^{-1}(\mathbf{k}, iw_n) + \frac{1}{2} (G_o^{-1}(\mathbf{k}, iw_n) + \Gamma^o \Gamma_5 \mu) G(\mathbf{k}, iw_n) - \frac{1}{2} \right]$$
(81)

where V is the two-dimensional volume (the area of the cuprate plane), and Tr stands for the trace of a matrix.

For the free energy functional $\Omega(\Delta)$, we have the formula

$$\Omega = -\frac{V}{2\beta} \sum_{n=-\infty}^{\infty} \int \frac{d^2k}{(2*\pi)^2} \operatorname{Tr} \left[\ln G_o(\mathbf{k}, i\omega_n)^{-1}(\mathbf{k}, i\omega_n) + \frac{1}{2} (G_o^{-1}(\mathbf{k}, i\omega_n) + r^o r_5 \mu) G(\mathbf{k}, i\omega_n) - \frac{1}{2} \right]$$
(82)

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where $G_o^{-1}(\mathbf{k}, i\omega_n) = r^o i\omega_n - r^o r_5 \varepsilon(\mathbf{k})$, and $G(\mathbf{k}, i\omega_n)$ is given by formula (57). We note that the functional $\Omega(\Delta, \mu)$ is normalized so that $\Omega(\Delta = 0, \mu = 0) = 0$.

By calculating the trace of the *r*-matrix, we obtain the expression

$$\Omega(\Delta,\mu) = -\frac{V}{\beta} \sum_{n=-\infty}^{\infty} \int \frac{d^2k}{(2*\pi)^2} \left[\ln \frac{\omega_n^2 + (\varepsilon - \mu)^2 + \Delta^2}{\omega_n^2 + \varepsilon^2} - \frac{\Delta^2}{\omega_n^2 + (\varepsilon - \mu)^2 + \Delta^2} \right]$$
(83)

By using the formula

$$\sum_{n=-\infty}^{\infty} \ln \frac{\omega_n^2 + b^2}{\omega_n^2 + a^2}$$
$$= \int_0^\infty dx \left[\frac{\beta}{2\sqrt{a^2 + x}} th \frac{\beta\sqrt{a^2 + x}}{2} - \frac{\beta}{2\sqrt{b^2 + x}} th \frac{\beta\sqrt{b^2 + x}}{2} \right]$$
$$= 2 \ln \frac{ch(\beta b/2)}{ch(\beta a/2)}$$
(84)

we get the equation for the thermodynamic potential:

$$\Omega(\Delta) = V \int \frac{d^2k}{(2\pi)^2} \left\{ -\frac{2}{\beta} \ln \frac{\operatorname{ch}(\beta/2)\sqrt{(\varepsilon-\mu)^2 + \delta^2}}{\operatorname{ch}(\beta\varepsilon/2)} + \frac{\Delta^2}{2\sqrt{(\varepsilon-\mu)^2 + \Delta^2}} \operatorname{th} \frac{\beta\sqrt{(\varepsilon-\mu)^2 + \Delta^2}}{2} \right\} (85)$$

By making some transformations and calculating the traces of Γ matrices, we arrive at the equation

$$\Omega(\Delta) - \Omega(0) = \frac{V}{2} \int_{C} \frac{dw}{2\pi i} \int \frac{d^{2}k}{(2\pi)^{2}} \Delta_{i}^{4}(\mathbf{k}, w)$$
$$\times \frac{1}{e^{Bw} + 1} \frac{1}{[w^{2} - (\varepsilon(\mathbf{k} - \mu)^{2}]^{2}} \qquad (86)$$

By expanding the contour C and calculating the contribution to the integral at poles $w = \pm(\varepsilon(k) - \mu)$, we get

$$\Omega(\Delta) - \Omega(0) = \frac{V}{8} \int \frac{d^2k}{(2\pi)^2} \frac{\Delta_i^4(\mathbf{k})}{[\varepsilon(\mathbf{k}) - \mu]^2} \\ \times \left\{ \frac{\beta}{2} \left(1 - \text{th}^2 \frac{\beta(\varepsilon(\mathbf{k}) - \mu)}{2} \right) - \frac{1}{(\varepsilon(\mathbf{k}) - \mu)} \text{th} \frac{(\varepsilon(\mathbf{k}) - \mu)}{2} \right\}$$
(87)

where $\varepsilon(k)$ describes the spectrum of two-dimensional electrons, the free energy *F* is connected with the thermodynamic potential Ω by the relation $F = \beta \Omega$; $\Omega(\Delta)$ and $\Omega(0)$ are the thermodynamic potentials at $T < T_c$ and $T > T_c$, respectively; and *V* is the two-dimensional volume (the area of a cuprate layer).

It is easy to verify that, despite the presence of the factors $(\varepsilon(\mathbf{k}) - \mu)$ in the denominator in formula (87), no singularity on the Fermi surface $\varepsilon(\mathbf{k}) - \mu$ is present.

Equations (85) and (87) (at $T \sim T_c$) can be a basis for calculations of various thermodynamic quantities, including a jump of the heat capacity.

A similar method of calculations was developed by St. Weinberg.⁴⁹

7.6. Heat Capacity of the *d*-Pairing

Equation (85) yields the following formula for the thermodynamic potential $\Omega(\Delta)$:⁴³

$$\Omega(\Delta) = V \int \frac{d^2k}{(2\pi)^2} \left\{ -\frac{2}{\beta} \ln \frac{\operatorname{ch}(\beta/2)(\sqrt{(\varepsilon(\mathbf{k}) - \mu)^2 + \Delta(\mathbf{k})^2})}{\operatorname{ch}(\beta\varepsilon/2)} + \frac{\Delta(\mathbf{k})^2}{2\sqrt{(\varepsilon(\mathbf{k}) - \mu)^2 + \Delta(\mathbf{k})^2}} \times \operatorname{ch}\frac{\sqrt{(\varepsilon(\mathbf{k}) - \mu)^2 + \Delta(\mathbf{k})^2}}{2} \right\}$$
(88)

Here, V is the two-dimensional volume (the area of a cuprate layer), $\Delta(\mathbf{k})$ is the superconductor gap, **k** is the momentum of an electron, and $\varepsilon(\mathbf{k}) = -2t[\cos(k_x a) + \cos(k_y a)]$ gives the spectrum of two-dimensional electrons. The heat capacity is calculated by the formula

$$C = -T \frac{\partial^2 \Omega}{\partial T^2} \tag{89}$$

The results of calculations of the heat capacity *C* are given in work.⁴⁵ We have carried out the computerbased calculations of the heat capacity of the compound $YBa_2Cu_3O_{6.63}$. The equation for the superconductor gap Δ was obtained in Subsection 7.5.

The task of solving the integral equation was reduced to that of an algebraic equation which was solved by the method of iterations. The equation for the superconductor gap depends on the spin correlation function. For it, the necessary data were taken from works Refs. [35, 36]. In calculations, we used the following values of parameters of the correlator: $\omega_{\rm SF}(T_C) \approx 7.7$ meV, $\chi_S(Q) = 44$ eV, $\xi/a \approx$ 2.5, t = 2 eV, $\mu = 0.25$, $T_c = 95$ K.

We chose such a value of the constant g which satisfies the relation $2\Delta/kT_c = 3.4$ like that in works Refs. [32, 33]. The results of numerical calculations are presented in Figure 15, where we can see the temperature dependence of the electron heat capacity: (1)—the curve which is an approximation of the results of computer-based calculations (crosses); (2)—the curve which describes the exponential BCS dependence. These results are in good agreement with experiments made by the group of Kapitulnik⁵⁰ at low temperatures.

The calculations showed a square dependence of the heat capacity on the temperature in the temperature range from zero to the superconducting temperature. It was shown,⁴³⁻⁴⁶ that the dependence has the form

$$C = AT^2 \tag{90}$$

where $A = 0.126 \text{ J/K}^3$ mole.

7.7. Heat Capacity Jump in Superconductors

In what follows, we present the results of calculations of a jump of the heat capacity near the critical temperature,

$$\Delta C = -T \frac{\partial^2 \Delta \Omega}{\partial T^2}, \quad \beta = \frac{1}{T}$$
(91)

and evaluate the parameter $R = \Delta C / \gamma T_c$. Omitting the awkward and quite complicated details, we will give the final results.

We obtained R = 1.6. This value of the parameter is larger than that in the BCS theory, where R = 1.43. It is worth noting that the heat capacity jump is very sensitive to the doping. Figure 16 shows the results of recent calculations of one of the authors Ref. [45] for R as a function of the doping. It is seen that this parameter depends strongly on the doping. By using these results of calculations, it is possible to evaluate the condensation energy for high-temperature superconductors which is proportional to R^2 (see Ref. [51]).

The calculations imply that the heat capacity depend on the temperature as T^2 . Analogous results were obtained for the physics of heavy fermions.53 It was shown in this work that *d*-symmetry leads to a linear dependence of C/T on the temperature, whereas the s-symmetry is related to the exponential dependence of this quantity on the temperature. The linear dependence of C/T on the temperature was observed in the experimental works^{52, 54-56} for YBaCuO superconductors, The experimental results are presented in Figure 17. As was mentioned above, the problem of the determination of the symmetry of a gap in cuprate superconductors is urgent at the present time. Many experiments have confirmed the d-symmetry of the pairing.^{33,34} In particular, we mention new experiments,³⁴ in which the researchers have studied the quantization of magnetic flows in a ring which includes three



Fig. 16. Temperature dependence of the electron heat capacity, where (1) —the curve which is an approximation of the results of computerbased calculations (crosses); (2)—the curve which describes the exponential BCS dependence, points give the experimental data.⁵⁰

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Fig. 17. Parameter $R(T_c)$ characterizing the heat capacity jump as a function of the doping for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-x}$. The solid curve presents the results of theoretical calculations, the points mark the experimental data.⁵²

Josephson junctions. These works supporting the existence of *d*-pairing in high-temperature superconductors were marked by the Barkley prize. It was also shown that the sign of the order parameter in YBa₂Cu₃O_{7- δ} depends on the direction. This dependence corresponds to the $d_{x^2-y^2}$ -symmetry.

The temperature dependence of the electron heat capacity obtained in our calculations^{43,44} is related to the *d*-pairing. These thermodynamic calculations can be a supplementing test in the determination of the pairing symmetry in high-temperature superconductors.

It should be noted that the thermodynamic calculations clarifying the behavior of high-temperature superconductors have been also performed in Refs. [57, 58, 59, 60] in the frame of the other mechanisms of pairing.

8. SUMMARY

The high-temperature superconductivity is a dynamical field of solid-state physics which is intensively developed by theorists and experimenters. By summarizing the physical properties and the mechanisms of superconductivity in new high-temperature superconductors, we should like to separate the main properties and the theoretical problems arising in the studies of high-temperature superconductors.

In order to comprehend the nature of the superconducting state, it is necessary to construct a consistent microscopic theory which would be able to describe superconductive and normal properties of high-temperature superconductors. It is seen from the above-presented survey that many mechanisms of pairing in high-temperature superconductors, which pretend to the explanation of this phenomenon, have been advanced. On the whole, the most probable seems to be the "synergetic" mechanism of pairing, whose constituents are the electron–phonon interaction, spin-fluctuation, and other types of interaction in cuprate planes.

We believe that the known challenging properties, which are contradictory to a certain extent, of many chemical compounds in the superconducting and normal phases can be explained only by considering the interaction of all the degrees of freedom such as lattice-, electron-, and spinrelated ones. In this case, it is also necessary to take the complicated structure of high-temperature superconductors into account. The further development of the theory will require not only the execution of bulky numerical calculations, but also the solution of a number of fundamental problems concerning the strong electron correlations.

It seems to us that one of the key problems in the field of superconductivity is the mechanism and the symmetry of pairing.

Above, we have shown that some thermodynamical problems of high-temperature superconductivity, in particular the problem of antiferromagnetic spin fluctuations, can be efficiently solved within the method of continual integrals.

The paper deals with a specific organization form of matter. Other forms are described for example in the Refs. [61–63]. In most cases quantum theory is necessary for the description of the organization forms of matter. But even the interpretation of modern quantum theory seems still to be an open question, as is demonstrated in Refs. [64–69].

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