# Influence of Anderson disorder on superconducting pairing correlations with $s^*$ and $d$ symmetry in high-$T_c$ superconductors

V. F. Elesin, A. V. Krasheninnikov, and L. A. Openov

*Moscow State Engineering-Physics Institute, 115409 Moscow, Russia*
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The influence of Anderson disorder with degree $W$ on pairing correlation functions with $s^*$ and $d_{x^2-y^2}$ symmetry in a $Cu_4O_8$ cluster, which is an elementary fragment of a $CuO_2$ plane (a common structural element of high-$T_c$ superconductors), has been investigated by exact diagonalization. It has been shown that at a nearly optimal level of hole doping (0.25 excess carriers per copper atom) enhancement of the disorder results in significantly faster weakening of the correlations in the $d_{x^2-y^2}$ channel than in the $s^*$ channel. The "superconducting" contribution to the $d_{x^2-y^2}$ correlation and the critical value $W_c$, at which the superconducting correlations in the $d_{x^2-y^2}$ channel vanish, have been evaluated. The results obtained are qualitatively consistent with experiments on the influence of nonmagnetic defects on high-$T_c$ superconductors and attest to the mixed $s^*+d$ symmetry of the gap in $p$-type high-$T_c$ superconductors for which the superconducting correlations in the $s^*$ channel dominate. In the case of electron doping of the $Cu_4O_8$ cluster, superconducting correlations with $d_{x^2-y^2}$ symmetry are apparently completely absent, and the pairing correlators in the $s^*$ channel are weakly dependent on $W$. © *1995 American Institute of Physics.*

## 1. INTRODUCTION

At the present state of the investigation of high-$T_c$ superconductors, one of the most pressing questions is the symmetry of the superconducting order parameter $\Delta(\mathbf{k})$ ($\mathbf{k}$ is the momentum) in the $ab$ crystallographic plane, i.e., in two-dimensional (2D) $CuO_2$ layers, which are generally believed to be responsible for high-$T_c$ superconductivity. The resolution of this question is extremely important, since it will significantly shorten the list of discussible theoretical models, which can be hypothetically divided into two groups: models with $s^*$-wave symmetry and those with $d$-wave symmetry of the order parameter $\Delta(\mathbf{k})$ (see, for example, Refs. 1 and 2).

The final word, of course, must be given by experiment. However, the experimental data are, unfortunately, equivocal: there is evidence in support of both the $s^*$ (Refs. 3 and 4) and $d$ (Refs. 5 and 6) symmetry of $\Delta(\mathbf{k})$ in high-$T_c$ superconductors. Moreover, it has not been ruled out that these results do not contradict one another at all, if the order parameter can have mixed $s+d$ symmetry.[7,8] The only thing which is certain is the singlet character of the pairing and the strong anisotropy of $\Delta(\mathbf{k})$ (Refs. 9–13) [we stress that here and below we are dealing with the "2D anisotropy" of $\Delta(\mathbf{k})$ in the $ab$ plane]. The possibility of the realization of $d_{x^2-y^2}$ pairing in high-$T_c$ superconductors is of special interest, since just this symmetry is predicted by the presently popular model of a nonphonon mechanism,[2,14] in which the pairing interactions are caused by the exchange of antiferromagnetic fluctuations with the spectrum taken from experiment (for example, using inelastic neutron scattering). However, this model is essentially phenomenological, and the $d_{x^2-y^2}$ symmetry of the order parameter in it is actually stipulated by choice of the interaction.

The most systematic approach to investigating the possibility of a nonphonon mechanism in high-$T_c$ superconductors is to analyze the pertinent model Hamiltonians (for example, the Hubbard or Emery Hamiltonian). However, an analytical treatment of these models is exceptionally difficult due to the need to take into account the strong Coulomb correlations. In this situation numerical calculations based on the Monte Carlo method and exact diagonalization take on great importance. For example, the quantum and variational Monte Carlo methods have been used repeatedly to study pairing correlations with $s$, $s^*$, and $d_{x^2-y^2}$ symmetry in the Hubbard and Emery models,[7,15–20] and in Ref. 21 pairing correlations with different symmetries were calculated by means of exact diagonalization of the Emery Hamiltonian.

What do the results of the numerical investigations say about the symmetry of the order parameter? It turns out that there are only pairing correlations with $d_{x^2-y^2}$ symmetry in the 2D Hubbard model,[16] while there are pairing correlations with both $d_{x^2-y^2}$ and $s^*$ symmetry in the Emery model[17] (there are no superconducting correlations in the $s$ channel, which is natural, since the charge carriers experience strong Coulomb repulsion at the lattice points, which prevents the local pairing characteristic of the usual phonon mechanism). However, investigations of clusters of different size (scaling) in the Hubbard[18,19] and Emery[19,20] models showed that the pairing correlators in configuration space diminish rapidly with the distance. We note, however, that the quantum Monte Carlo method, whose error increases abruptly with decreasing temperature, was used in Refs. 18 and 19. Therefore, the temperature at which the calculations were performed might not be low enough to reveal superconducting order in the system (although there are pairing correlations already at these temperatures[16,17]).

The presence of pairing correlations with $s^*$ and $d_{x^2-y^2}$ symmetry in the Emery model is also supported by the calculations performed for the $T=0$ case using the varia-

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tional Monte Carlo method. For example, it was established in Ref. 15 that the ground-state energy of a Cu–O cluster consisting of 36 $CuO_2$ unit cells is minimal, if the variational wave function corresponds to an $s^*$- or $d_{x^2-y^2}$-wave superconducting state. Enhancement of the Coulomb repulsion between carriers on neighboring copper and oxygen sites causes the $s^*$ wave to become energetically more favorable than the $d_{x^2-y^2}$ wave. In Ref. 7 the variational Monte Carlo method was used to investigate the superconducting characteristics of the 2D Hubbard model. It was found that the absolute energy minimum is achieved, if the order parameter has mixed $s+d$ symmetry.

However, the error of the variational Monte Carlo method is also quite large,[7,15] and the results obtained by this method can depend on how successfully the form of the variational wave function was selected. For this reason there is interest in calculations of pairing correlations performed by exact diagonalization, which, while not permitting the investigation of Cu–O clusters as large as those investigated by the quantum and variational Monte Carlo methods, makes it possible to perform exact calculations for the $T=0$ case. Hopefully, owing to the small value of the coherence length in high-$T_c$ superconductors, the investigation of even small Cu–O clusters will make it possible to compose a qualitatively true picture of the characteristics of an infinite $CuO_2$ plane.

In Ref. 21 we used exact diagonalization to calculate the pairing correlation functions in the 12-site $Cu_4O_8$ cluster. It was shown that at realistic values of the parameters of the 2D Emery model and a nearly optimal doping level ($x=0.25$ excess carriers per copper atom) there are no pairing correlations with $s$ symmetry and the correlations with $s^*$ symmetry are considerably stronger than the correlations with $d_{x^2-y^2}$ symmetry (this is true for both hole and electron doping).

Thus, the numerical calculations attest to the presence of superconducting correlations with $s^*$ and $d_{x^2-y^2}$ symmetry in the Emery model and to dominance of the $s^*$ channel over the $d_{x^2-y^2}$ channel.

There is one more factor which makes it possible to determine the symmetry of a superconducting state: nonmagnetic impurities and radiation defects, which influence the critical temperature $T_c$ of superconductors with $s$, $s^*$, and $d_{x^2-y^2}$ pairing differently. Considerable experimental material on the influence of impurities (see, for example, Ref. 22) and radiation defects (see, for example, the review in Ref. 23 and the references cited therein) on high-$T_c$ superconductors has been accumulated. It has been established that $T_c$ decreases when there is increased atomic disorder (i.e., when the relaxation time $\tau$ decreases) and vanishes when $1/\tau \approx E_F$ (Refs. 23 and 24), where $E_F$ is the Fermi energy and Planck's constant $\hbar$ is set equal to unity.

At the same time, it is known from theory that in the weak-coupling limit nonmagnetic impurities do not influence the value of $T_c$ of superconductors with $s$ pairing[25] (Anderson's theorem), have a very strong effect on $d_{x^2-y^2}$ superconductors (causing $T_c$ to vanish when $1/\tau \approx T_{c0}$, where $T_{c0}$ is the value of $T_c$ in the absence of impurities[26]), and have a significantly weaker effect on the value of $T_c$ of superconductors with $s^*$ symmetry of the order parameter.[21,27]

The situation in the case of tight binding is less clear. The general conclusion[26] is that the characteristic value of $\tau$ for $d_{x^2-y^2}$ symmetry, at which superconductivity is completely suppressed by the defects, decreases when the interaction is strengthened by a factor of $(1+\lambda_Z)$, where $\lambda_Z = 1 - \langle \mathrm{Im}\Sigma(\mathbf{k}, i\omega_0)\rangle/\omega_0$ and $\Sigma(\mathbf{k}, i\omega_0)$ is the self-energy part of the boson field at the minimum fermionic Matsubara frequency $\omega_0 = \pi T_{c0}$ ($\langle ... \rangle$ denotes averaging over the Fermi surface). However, $\lambda_Z$ is fairly indefinite (see, for example, 26). As for $s^*$ symmetry, we do not know of any studies in which the strong-coupling effects were systematically taken into account.

Thus, it would be useful to study the influence of disorder on superconducting correlations with $s$, $s^*$, and $d_{x^2-y^2}$ symmetry using the approach which we previously employed in Ref. 21, i.e., an *ab initio* approach. The purpose of the present study to numerically investigate the influence of Anderson disorder (an analog of nonmagnetic defects) on pairing correlators with $s$, $s^*$, and $d_{x^2-y^2}$ symmetry in the $Cu_4O_8$ cluster by exact diagonalization.

We have studied the case of nearly "optimal" electron and hole doping (0.25 charge carriers per copper atom) It shown that in the case of hole doping of the $Cu_4O_8$ cluster, enhancement of the disorder results in decreases in the pairing correlators in the $d_{x^2-y^2}$ channel. The pairing correlators in the $s^*$ channel remain practically unchanged when there is weak disorder and begin to decrease significantly only when the disorder becomes so strong that it suppresses the antiferromagnetic correlations. The results obtained attest to the presence of a "superconducting component" in the pairing correlators of finite Cu–O clusters and permit evaluation of the contribution of this component to the pairing correlators. Along with the data from our previous paper[21] and the experimental findings presented in this paper, the results of the numerical calculations attest to the mixed $s^*+d$ symmetry of the order parameter $\Delta(\mathbf{k})$ in $p$-type high-$T_c$ superconductors in which the correlations in the $s^*$ channel dominate. In the case of electron doping, it appears that there are pairing correlations only in the $s^*$ channel, in agreement with the experimental investigations of $n$-type high-$T_c$ superconductors.

## 2. ALGORITHM FOR CALCULATING PAIRING CORRELATORS IN THE EMERY–ANDERSON MODEL

To describe a system of correlated charge carriers in a $CuO_2$ plane, we used the Emery model,[28] whose Hamiltonian has the form

$$H_E = -t\sum_{\langle ik\rangle,\sigma}(d_{i\sigma}^{+}p_{k\sigma}+\text{h.c.})+\varepsilon\sum_{k,\sigma}n_{k\sigma}+U_d\sum_i n_{i\uparrow}n_{i\downarrow}$$

$$+U_p\sum_k n_{k\uparrow}n_{k\downarrow}+V\sum_{\langle ik\rangle,\sigma,\sigma'}n_{i\sigma}n_{k\sigma'}, \qquad (1)$$

where all the notation is standard (see, for example, Ref. 21).

The influence of nonmagnetic impurities on the electronic characteristics of $CuO_2$ layers was simulated by diagonal Anderson disorder. This approach was previously employed repeatedly to numerically investigate the combined effect of atomic disorder and Coulomb correlations in

one-dimensional[29–31] and two-dimensional[32] systems. The corresponding term in the Hamiltonian has the form

$$H_A=\sum_j w_j(n_{j\uparrow}+n_{j\downarrow}), \tag{2}$$

where the $w_j$ are additions to the site potentials of the copper and oxygen atoms, which take on random values in an energy range of width $W$ with the distribution function

$$P(w_j)=\begin{cases} 1/W, & |w_j|\leq W/2 \\ 0, & |w_j|>W/2 \end{cases}$$

so that $\langle w_j\rangle=0$ and $\langle w_j w_k\rangle=\delta_{jk}W^2/12$. The parameter $W$ characterizes the degree of disorder ($W=0$ corresponds to the absence of disorder).

The many-electron Schrödinger equation

$$(H_E+H_A)\Psi=E\Psi$$

was solved numerically using the Lanczos algorithm (for further details see Ref. 33). The relative error of the calculations did not exceed $10^{-12}$. The two-dimensional $Cu_4O_8$ cluster was considered with periodic boundary conditions. In the present work we thoroughly investigated the case of "optimal" hole (five holes in the cluster) and electron (three holes in the cluster) doping,[21] which correspond to the addition of one excess hole or one excess electron, respectively, to the original insulating state (four holes in the cluster) (the carrier concentration is then $x=0.25$ per copper atom, which is close to the values of $x$ at which the maximum $T_c$ is achieved in $p$-type[34] and $n$-type[35] high-$T_c$ superconductors).

Numerically finding the many-electron wave function $\Psi$ of the ground state (in the site representation), we calculated the correlators $P_\alpha$ and $\tilde{P}_\alpha$ in the $\alpha$ pairing channel ($\alpha=s^*$ or $d_{x^2-y^2}$) from the formulas[18,21]

$$P_\alpha=\sum_{r,r'}\langle\Delta_\alpha^+(r)\Delta_\alpha(r+r')\rangle, \tag{3}$$

$$\tilde{P}_\alpha=N_0^{-1}\sum_{\substack{r,r'\\ \rho,\rho'}} g_\alpha(\rho)g_\alpha(\rho')\langle d_{r,\uparrow}^+ d_{r+r',\uparrow}\rangle \times\langle d_{r+\rho,\downarrow}^+ d_{r+r',\rho',\downarrow}\rangle, \tag{4}$$

where

$$\Delta_\alpha^+(r)=N_0^{-1/2}\sum_\rho g_\alpha(\rho)d_{r,\uparrow}^+ d_{r+\rho,\downarrow}^+, \tag{5}$$

$N_0$ is the number of $CuO_2$ unit cells (for the cluster under consideration $N_0=4$), the summation with respect to $r$, $r'$, $\rho$, and $\rho'$ is carried out over the copper sites, and the form of the function $g_\alpha(\rho)$ is determined by the symmetry of the pairing state: for $s^*$ pairing we have $g_\alpha(\rho)=1$ for $\rho=\pm ae_x$ and $\rho=\pm ae_y$ ($a$ is the period of the square lattice), and $g_\alpha(\rho)=0$ when $\rho$ has other values; for $d_{x^2-y^2}$ pairing we have $g_\alpha(\rho)=1$ for $\rho=\pm ae_x$, $g_\alpha(\rho)=-1$ for $\rho=\pm ae_y$, and $g_\alpha(\rho)=0$ when $\rho$ has other values (we did not consider the case of local $s$ pairing, since there are no pairing correlations in the $s$ channel[21]).

Here $P_\alpha$ is the pairing correlator, and $\tilde{P}_\alpha$ is obtained from $P_\alpha$ when the anomalous averages are not taken into account. The subtraction of $\tilde{P}_\alpha$ from $P_\alpha$ makes it possible to at least partially take into account the effects caused by the restricted size of the cluster.[16] A positive value of the difference $P_\alpha-\tilde{P}_\alpha$ may be regarded as evidence of the presence of superconducting correlations in a cluster. As was noted in the introduction, it should be borne in mind that $P_\alpha-\tilde{P}_\alpha$ is always finite in a cluster. The presence of long-range off-diagonal order in a system can be evaluated only from the divergence of $P_\alpha$ in the thermodynamic limit.[18] Nevertheless, we assume that if there is superconducting order in the infinite $CuO_2$ plane described by the Emery model, it must have some influence on the value of $P_\alpha-\tilde{P}_\alpha$ in the $Cu_4O_8$ cluster.

Our goal was to find the dependence of $P_\alpha-\tilde{P}_\alpha$ on the degree of disorder $W$ for assigned parameters of Hamiltonian (1). It should be noted here that when the value of $W$ in (2) is fixed, the characteristics of the ground state (including $P_\alpha-\tilde{P}_\alpha$ depend on the specific form of site disorder, i.e., on the specific set $\{w_j\}$ in (2). A correct description of the influence of defects on the electronic structure of small clusters requires averaging over the different disorder configurations and determination of both the mean values and the standard deviations.[32] For this reason, we performed the calculation in the following manner: for each of the $L$ different random sets $\{w_j^l\}$ ($l=1, ..., L$) with $W=$const we calculated the values of $(P_\alpha-\tilde{P}_\alpha)^l$, and then we determined the value of $P_\alpha-\tilde{P}_\alpha$ (for the particular value of $W$) as the arithmetic mean for the $L$ configurations. The standard deviation was calculated using the standard formula from mathematical statistics. We usually restricted ourselves to $L=30$ disorder configurations, since the results in that case scarcely differed from those obtained for $L=100$.

However, as our calculations showed, averaging over the different configurations $\{w_j^l\}$ is insufficient. This is because in the absence of disorder the ground state of the $Cu_4O_8$ cluster with one excess carrier (a hole or an electron) is quadruply degenerate: doubly with respect to the total spin projection and doubly with respect to the total quasimomentum $(\mathbf{K}_x,\mathbf{K}_y)=(0,\pi/a)$ and $(\pi/a,0)$. For this reason, for example, when $P_\alpha-\tilde{P}_\alpha$ is calculated for $W=0$, the appropriate averaging must be performed over these degenerate states[21] [actually, it is sufficient to average over two states with different quasimomenta and the same spin projection: $\varphi_{0,\pi/a}(\mathbf{r})$ and $\varphi_{\pi/a,0}(\mathbf{r})$].

Any disorder, no matter how weak (any small, but finite value of $W$), violates translational invariance and results in removal of the degeneracy with respect to the quasimomentum. Then one of the states which are close in energy (but differ strongly with respect to the structure of the wave function) turns out to be the ground state, and the value of $P_\alpha-\tilde{P}_\alpha$ consequently differs sharply from its value for $W=0$ (since the averaging was performed over these two states when $W=0$). The variation of $P_\alpha-\tilde{P}_\alpha$ is random because the disorder results in the random (but dependent on the specific disorder configuration) "selection" of one of the two states which were originally degenerate with respect to the quasimomentum.

In this situation we used the following technique to obtain physically reasonable results (more specifically, a

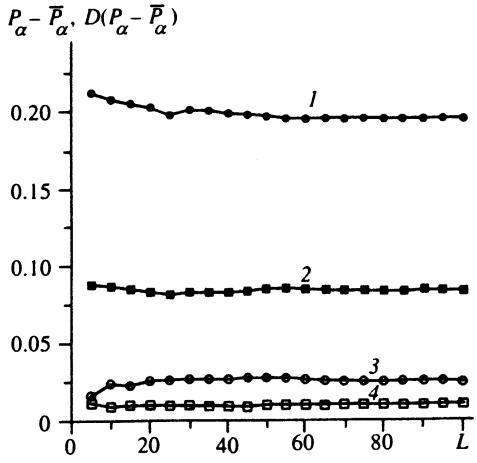


FIG. 1. Mean values of the pairing correlators $P_\alpha - \bar{P}_\alpha$ (curves *1* and *2*) and the standard deviations $D(P_\alpha - \bar{P}_\alpha)$ (curves *3* and *4*) versus the number of Anderson disorder configurations $L$ in the case of hole doping for $\varepsilon/t=2$, $U_d/t=6$, $U_p/t=2.5$, $V/t=1.5$, and $W/t=2$; ■ and □, $\alpha=d_{x^2-y^2}$; ● and ○, $\alpha=s^*$.

smooth dependence of $P_\alpha - \bar{P}_\alpha$ on $W$ as $W \to 0$). Finding the wave function $\Psi$ for a certain (random) set $\{w_j\}$, we performed a repeated calculation for the set $\{w'_j\}$, where $w'_j = w_{j'}$ holds and site $j'$ is obtained from site $j$ by a 90° rotation of the cluster $Cu_4O_8$ (which is equivalent to the replacement of axes $x \to y$, $y \to x$ in coordinate space). If, for example, the function $\Psi$ is similar to the function $\varphi_{0,\pi/a}(\mathbf{r})$, $\Psi'$ turns out to be similar to $\varphi_{\pi/a,0}(\mathbf{r})$ and vice versa (of course, we are referring here to only an approximate correspondence between $\Psi$ and $\varphi$, since the quasimomentum is no longer a "good" quantum number when there is disorder). As in the case of $W=0$ we ultimately obtained two states with different wave functions $\Psi$ and $\Psi'$, which are energetically degenerate. Averaging over these two states, we found $P_\alpha - \bar{P}_\alpha$ for the particular disorder configuration, and, as described above, we then performed averaging over different configurations.

We stress that the procedure described for calculating $P_\alpha - \bar{P}_\alpha$ in a disordered cluster is essential at small values of $W$ (i.e., when $W/t \ll 1$). When $W$ is large, the ground-state wave function differs strongly from both $\varphi_{0,\pi/a}(\mathbf{r})$ and $\varphi_{\pi/a,0}(\mathbf{r})$; therefore, the additional averaging of $P_\alpha - \bar{P}_\alpha$ with respect to $\Psi$ and $\Psi'$ is not necessary. Nevertheless, to maintain uniformity, we performed this averaging at all values of $W$, even when $W/t \gg 1$.

## 3. CALCULATION RESULTS

We performed calculations of the pairing correlators $P_\alpha - \bar{P}_\alpha$ in the disordered $Cu_4O_8$ cluster for three different sets of parameters of the Emery Hamiltonian: I) $\varepsilon/t=1$, $U_d/t=8$, $U_p=V=0$; II) $\varepsilon/t=2$, $U_d/t=6$, $U_p=V=0$ (in the absence of doping these two sets correspond to an insulating "charge-transfer" state); III) $\varepsilon/t=2$, $U_d/t=6$, $U_p/t=2.5$, $V/t=1.5$ (these values of the parameters are used most often by different investigators; they were taken from Ref. 36).

We start out from the case of hole doping. Figure 1 presents typical plots of the mean values of the pairing correlators $P_\alpha - \bar{P}_\alpha$ and the standard deviations $D(P_\alpha - \bar{P}_\alpha)$ in the $d_{x^2-y^2}$ and $s^*$ channels versus the number $L$ of Anderson disorder configurations included in the averaging. It is seen that $P_\alpha - \bar{P}_\alpha$ and $D(P_\alpha - \bar{P}_\alpha)$ reach constant values quite quickly as $L$ increases, allowing us to restrict ourselves to $L=30$ in most cases.

We now proceed to a description of the dependence of the pairing correlators on $W$, which specifies the degree of disorder and plays the role of the concentration of nonmagnetic (for example, radiation) defects in cluster calculations. Figure 2 presents plots of $g_\alpha = (P_\alpha - \bar{P}_\alpha)/(P_\alpha - \bar{P}_\alpha)_0$ and $D_\alpha = D(P_\alpha - \bar{P}_\alpha)/(P_\alpha - \bar{P}_\alpha)_0$ versus $W$ in the $d_{x^2-y^2}$ and $s^*$ pairing channels for parameter set (III), where $(P_\alpha - \bar{P}_\alpha)_0$ is the value of $P_\alpha - \bar{P}_\alpha$ when $W=0$. As follows from Fig. 2a, the correlator $g_d$ in the $d_{x^2-y^2}$ channel decreases monotonically as $W$ increases. For $W/t \gg 1$ $g_{s*}$ in $s^*$ channel qualitatively similarly depends on $W$ (see Fig. 2b). The standard deviations $D_\alpha$, which play the role of the errors caused by the sensitivity of $g_\alpha$ to the specific disorder configuration, increase with increasing $W$ in each channel.

A fundamental difference between the dependences of $g_\alpha$ and $D_\alpha$ on $W$ in the $d_{x^2-y^2}$ and $s^*$ channels is that $g_{s*}$ remains unchanged for $W/t<1$, while $g_d$ decreases already for $W/t \ll 1$. This is graphically illustrated by Fig. 3, in which the values of $D_d$ are depicted in the form of vertical lines. We note that $g_d$ decreases linearly as a function of $W$. The

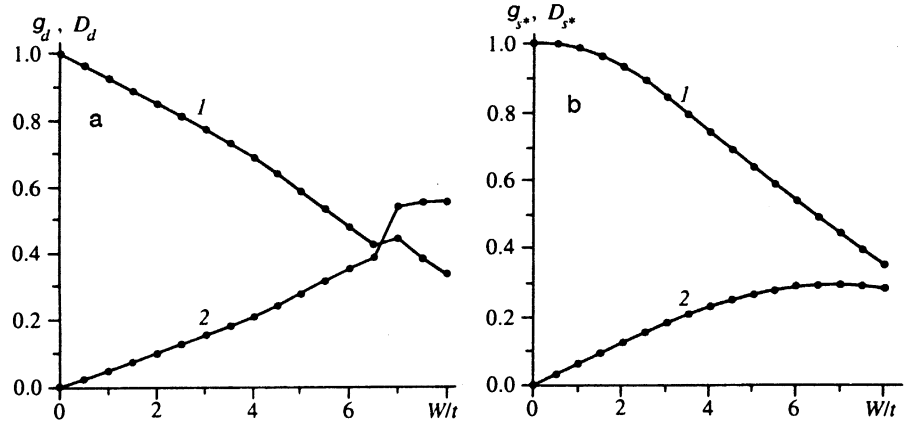


FIG. 2. Mean values of the normalized pairing correlators $g_\alpha = (P_\alpha - \bar{P}_\alpha)/(P_\alpha - \bar{P}_\alpha)_0$ (curves *1*) and the normalized standard deviations $D_\alpha = D(P_\alpha - \bar{P}_\alpha)/(P_\alpha - \bar{P}_\alpha)_0$ (curves *2*) versus the strength of the Anderson disorder $W/t$ for hole doping with $\varepsilon/t=2$, $U_d/t=6$, $U_p/t=2.5$, $V/t=1.5$, and $L=30$: a) $\alpha=d_{x^2-y^2}$; b) $\alpha=s^*$.

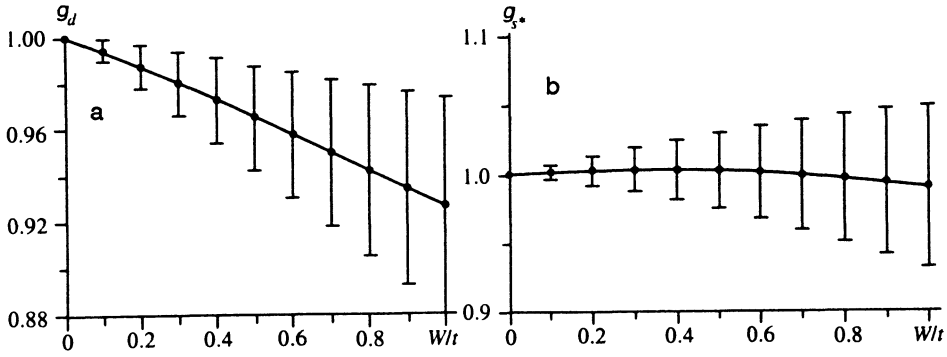


FIG. 3. As in Fig. 2. The values of $D_\alpha$ are depicted as vertical error bars for $L=30$: a) $\alpha=d_{x^2-y^2}$; b) $\alpha=s^*$.

reason for such a dependence of $g_d$ on $W$ will be discussed below, but now we note that qualitatively similar results were obtained for sets (I) and (II).

We stress that a significant (40–50%) decrease in the pairing correlators in the $d_{x^2-y^2}$ and $s^*$ channels is observed only for $W/t>5$ (see Fig. 2), i.e., for a degree of Anderson disorder such that suppression of the antiferromagnetic correlations occurs (the influence of atomic disorder on the antiferromagnetic correlators in the $Cu_4O_8$ cluster was studied by exact diagonalization in Ref. 32). This indicates that, along with the pairing interactions, a significant contribution to the correlators is made by nonsuperconducting interactions, and the finite-size effect is consequently very significant (thus, this contribution cannot be taken into account completely even by subtracting $P_\alpha-\bar{P}_\alpha$; see Sec. 2). Apparently, the main role is played here by magnetic interactions. We previously noted the existence of a "magnetic contribution" to $P_\alpha-\bar{P}_\alpha$ in Ref. 21.

Let us now turn to the case of electron doping. Our calculations showed that as the disorder becomes stronger (i.e., as $W$ increases), $g_d$ increases sharply even for $W/t<1$, the standard deviation $D_d$ exceeding the mean value. This is true of all the sets of parameters of Hamiltonian (1) that we investigated. Figure 4a presents the plots for set (I), where the binding energy of the two excess electrons is negative.[37]

Conversely, as follows from Fig. 4b, in the case of electron doping, as in the case of hole doping, the pairing correlators in the $s^*$ channel scarcely vary for $W/t<2$ (there is even a small maximum in the vicinity of $W/t=1$, whose height, however, is less than the standard deviation). A significant decrease in $g_{s*}$ occurs only for $W/t>3$, although the values of $D_{s*}$ are then so large that $g_{s*}\approx$ const holds "within the range of error" in this range of $W/t$ as well.

## 4. DISCUSSION OF THE RESULTS

As follows from Figs. 2 and 3, in the case of hole doping, $g_d$ decreases with increasing $W$ even for $W/t\ll 1$, while $g_{s*}$ remains practically unchanged in this range of $W$. Thus, as expected (see the introduction), $d_{x^2-y^2}$ pairing is far more sensitive to disorder. The important point is the evaluation of the critical degree of disorder $W_c$, at which the superconducting correlations are destroyed. This requires knowledge of the size of the superconducting contribution (we use $g_d^{SC}$ to denote it) to the pairing correlator. We shall attempt to evaluate it on the basis of the following arguments.

Figure 5 presents plots of the dependence of the difference $\delta_{sd}=g_{s*}-g_d$ on $W$, which were constructed on the basis of the data presented in Fig. 2. It is seen that for each of the three sets of parameters considered $\delta_{sd}$ increases monotonically with increasing $W$ for $W/t<2$ and that for $W/t>2$ it reaches the constant values $\delta_{sd}^0\approx 0.28$ (I), 0.25 (II), and 0.07 (III) [the oscillations of $\delta_{sd}$ for set (III) are apparently due to the inadequate number of disorder configurations included in the averaging]. We note that starting at certain values of $W/t$ the standard deviations $D_d$ exceed the mean

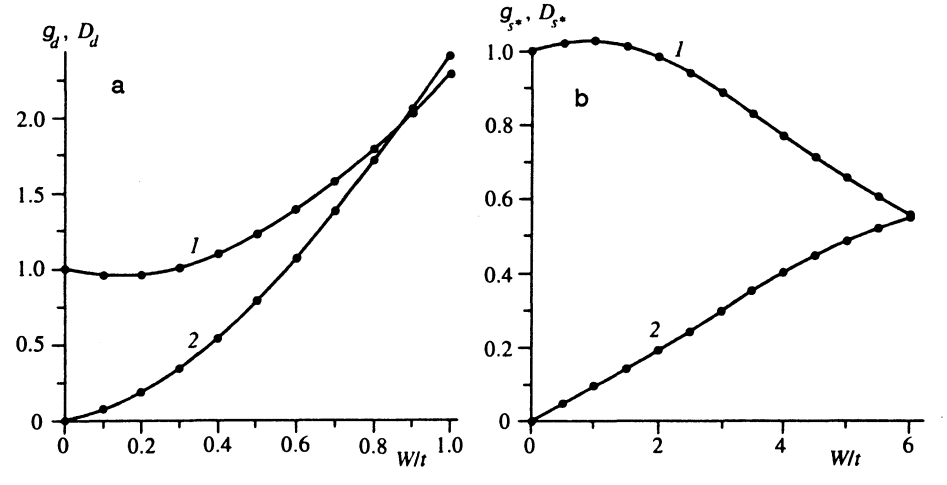


FIG. 4. As in Fig. 2 for electron doping with $\varepsilon/t=1$, $U_d/t=8$, $U_p=V=0$, and $L=30$: a) $\alpha=d_{x^2-y^2}$; b) $\alpha=s^*$.

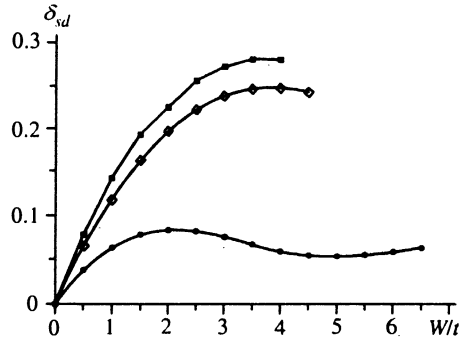


FIG. 5. Dependence of $\delta_{sd}=g_{s*}-g_d$ on $W/t$. The ranges of values of $W/t$ for each set of parameters were selected on the basis of the condition $D(P_d-\bar{P}_d)<P_d-\bar{P}_d$ for $L=30$. ■—$\varepsilon/t=1$, $U_d/t=8$, $U_p=V=0$. ◇—$\varepsilon/t=2$, $U_d/t=6$, $U_p=V=0$. ●—$\varepsilon/t=2$, $U_d/t=6$, $U_p/t=2.5$, $V/t=1.5$.

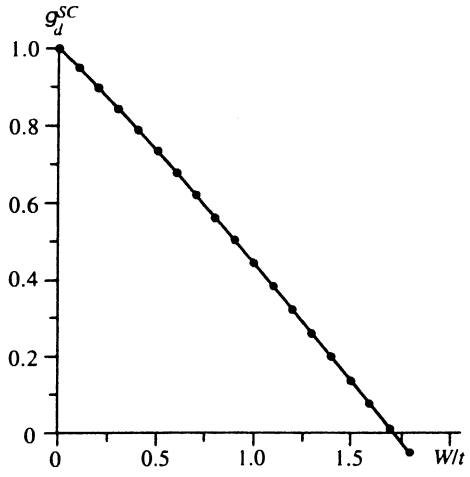


FIG. 6. Dependence of the superconducting component of the pairing correlator $g_d^{SC}$ on $W/t$ for hole doping with $\varepsilon/t=2$, $U_d/t=6$, $U_p=V=0$, and $L=30$.

values of $g_d$, producing an irregular dependence of $g_d$ on $W$ (see Fig. 2a). For this reason, the values of $W/t$ in Fig. 5 are restricted to the ranges $0\leqslant W/t\leqslant 4$ (I), $0\leqslant W/t\leqslant 4.5$ (II), and $0\leqslant W/t\leqslant 6.5$ (III), in which $g_d\geqslant D_d$.

The increase in $\delta_{sd}$ followed by the approach to a constant value indicates that in the $d_{x^2-y^2}$ channel the superconducting component $g_d^{SC}$ is suppressed more rapidly as $W/t$ increases than is the analogous quantity in the $s^*$ channel (this is consistent with Fig. 3). As a result, only nonsuperconducting interactions make a contribution to $g_d$ at large $W$. Therefore, $\delta_{sd}^0$ is approximately equal to $g_d^{SC}(0)$, i.e., to the relative contribution of the superconducting component to the total pairing correlator $g_d$ at $W=0$, which thus amounts to $\approx 0.28$ for (I), $\approx 0.25$ for (II), and $\approx 0.07$ for (III).

We stress that $g_d^{SC}(0)=0.1-0.3$ is comparatively low. This allows us to take another look at the[21] "contradiction" noted in our preceding paper, i.e., the fact that in the transition from optimal ($x=0.25$) to strong ($x=0.5$) hole doping the total correlator $g_d(0)$ decreases by only 10–20% [whereas it would be reasonable to expect $g_d(0)$ to vanish, since the state of a $CuO_2$ plane with $x=0.5$ is nonsuperconducting]. The reason why $g_d(0)$ has a finite value for $x=0.5$ is apparently that an increase in the concentration of holes (like an increase in the disorder parameter $W$) only suppresses the superconducting component $g_d^{SC}(0)$ to the total pairing correlator $g_d(0)$, but this contribution amounts to only 20%.

Now, knowing the contribution of $g_d^{SC}$ to $q_d$, we can construct the dependence of $g_d^{SC}$ on $W/t$ by subtracting the contribution of the nonsuperconducting interactions from the total normalized correlator $g_d$. The corresponding plot is presented in Fig. 6 for set (II). The critical value $W_c/t$ determined from the condition $g_d^{SC}=0$ is equal to 1.7. Similar plots of the dependence of $g_d^{SC}$ on $W$ can be constructed for the other sets of parameters. Then we have $W_c/T\approx 1.6$ and 1.0 for (I) and (III), respectively.

It would be interesting to discuss the comparative influence of Anderson disorder on the correlators $g_\alpha$ and the binding energy of the excess carriers $E_b$ (Ref. 32). We recall that the binding energy of two excess holes in the $Cu_4O_8$ cluster is given by the formula $E_b=E(4)+E(6)-2E(5)$, where $E(N)$ is the ground-state energy of the cluster with $N$ holes. A negative value of $E_b$ attests to the presence of effective attraction between the holes, i.e., the existence of a tendency to form a bound state.

It was shown in Ref. 37 that $E_b<0$ holds for parameter sets (I) and (II). As $W$ increases, the absolute value $|E_b|$ decreases linearly as a function of $W$, vanishing for $W_c'/t\approx 0.47$ (see Fig. 7). These results can be used to independently evaluate the superconducting contribution $g_d^{SC}$ to $g_d$. In fact, if the value of $g_d(W_c'/t)$ is found from Fig. 3a, the value of $g_d(0)-g_d(W_c'/t)$ will be approximately equal to $g_d^{SC}(0)$, since $g_d^{SC}(W_c')=0$. It is not difficult to see that the evaluation performed in this manner is qualitatively consistent with the determination of $g_d^{SC}(0)$ from the dependence of $\delta_{sd}$ on $W$ (see Fig. 5).

As was noted in Ref. 21, it is difficult to establish a unique correspondence between $E_b$ and $g_\alpha$ in the $Cu_4O_8$

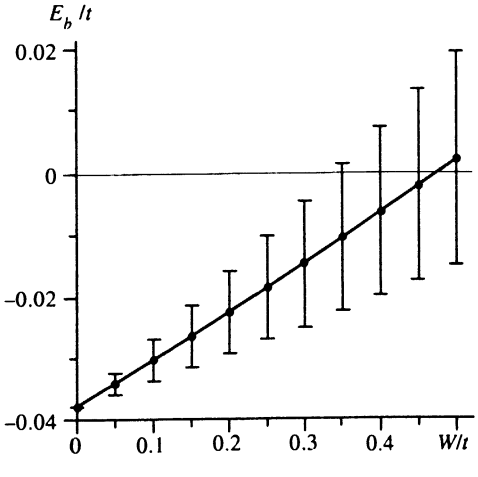


FIG. 7. Binding energy $E_b$ of two excess holes in the $Cu_4O_8$ cluster versus $W/t$ for $\varepsilon/t=2$, $U_d/t=6$, $U_p=V=0$, and $L=30$. The error bars show the standard deviations $D(E_b)/t$.

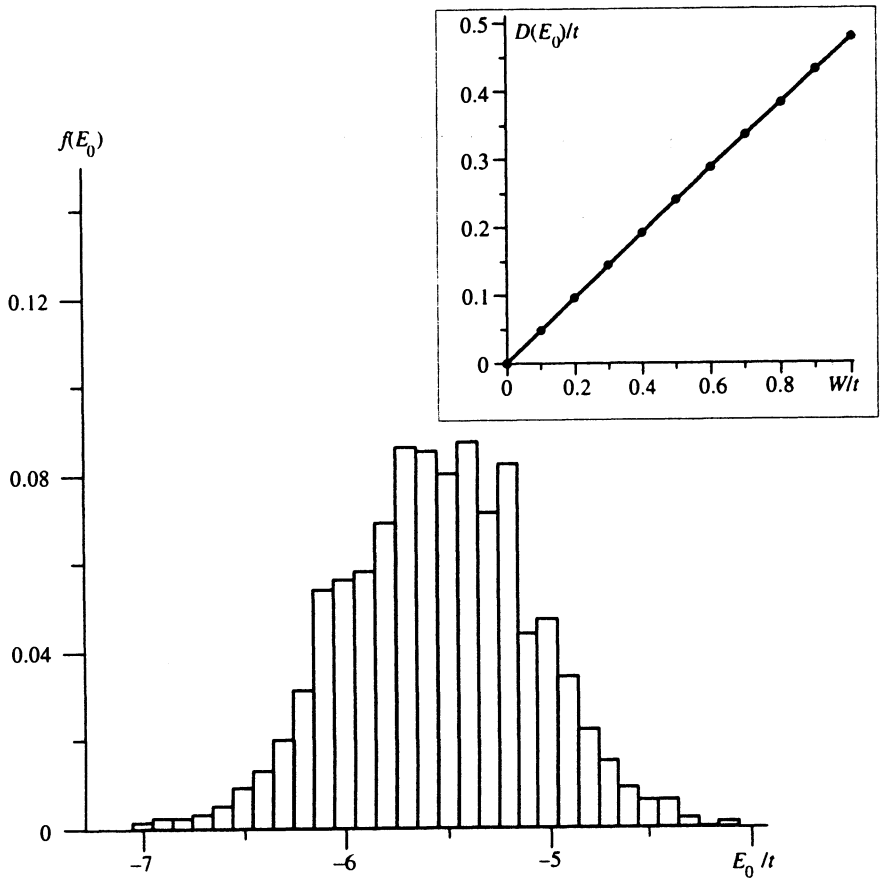


FIG. 8. Distribution function $f$ of the ground-state energy $E_0$ obtained by calculating $E_0$ for $L=1000$ different configurations of Anderson disorder in the case of hole doping for $\varepsilon/t=2$, $U_d/t=6$, $U_p=V=0$, and $W/t=1$. The standard deviation is $D(E_0)=0.45t$. The dependence of the standard deviation $D(E_0)/t$ on $W/t$ for $L=100$ is presented in the insert.

cluster. This is due, first, to the presence of a "nonsuperconducting" contribution to $g_\alpha$ and, second, to the very high sensitivity of $E_b$ (unlike $g_\alpha$) to the parameters of Hamiltonian (1). In particular, an increase in the Coulomb repulsion at the oxygen sites causes the sign of $E_b$ to change from minus to plus,[37] while the correlators $g_\alpha$ depend weakly on $U_p$. This is probably because the value of $E_b$ corresponds to a level of hole doping $n_h=0.25$ only "on the average" (since $E_b$ is a linear combination of the energies of three states with different occupation numbers), while the correlators $g_\alpha$ are calculated for the fixed value $n_h=0.25$.

Nevertheless, the qualitative correspondence between $E_b$ and $g_d$ noted above exists. In addition, it turns out that the superconducting contribution $g_d^{SC}(0)$ and the critical value $W_c$ are greater for parameter sets (I) and (II), for which $E_b<0$ holds and significantly smaller for set (III), for which $E_b>0$ holds i.e., when the effective interaction between the excess holes is repulsive.

To compare the results obtained with the existing theories and experiment, it is convenient to represent $g_d^{SC}(W)$ in the form (see Fig. 6)

$$g_d^{SC}(W)=1-b(W/t)=1-1/(\tau\varepsilon), \tag{6}$$

where $b$ is a numerical coefficient, which can be determined from the slope of $g_d^{SC}(W/t)$, $\varepsilon$ is the characteristic energy, and $1/\tau\sim W$ has the meaning of the inverse relaxation time of the hole carriers in a random potential of defects. In fact, $\tau$ should satisfy the uncertainty relation $\tau\cdot\delta E_0\sim 1$, where $\delta E_0$ is the uncertainty of the ground-state energy due to atomic disorder, whose degree is given by $W$.

A more accurate procedure can be applied. Figure 8 presents the distribution function $f(E_0)$, which describes the spread of the values of the ground-state energy $E_0$ for different disorder configurations. This distribution function was calculated for parameter set (II). The value of $\delta E_0$ actually specifies the half-width of this distribution function, i.e., the standard deviation $D(E_0)$. The dependence of $D(E_0)$ on $W$ is presented in the insert (see Fig. 8). It is seen that $D(E_0)$ increases linearly as $W$ increases, i.e., $\delta E_0\sim W$; therefore, $\tau\sim 1/\delta E_0\sim 1/W$ holds, and we arrive at (6). It follows from (6) that the characteristic energy is $\varepsilon\sim 1$ eV.

Let us compare our results with the known theoretical studies of the influence of defects on superconductors with $d_{x^2-y^2}$ gap symmetry. We assume that the superconducting component of the pairing correlator satisfies $g_d^{SC}\sim\Delta^2$ [see (3)], i.e, $g_d^{SC}\sim T_c^2$.

As we know (see, for example, Ref. 26), in the weak-coupling approximation the dependence of $T_c$ on the $\tau$ time for electrons to scatter on nonmagnetic impurities is described by the equation (for $\tau T_{c0}\gg 1$)

$$\frac{T_C}{T_{C0}}=1-\frac{\pi}{8}\frac{1}{\tau T_{C0}}, \tag{7}$$

the value of $T_c$ vanishing for $\tau_c T_{c0}\approx 1$, where $T_{c0}$ is the original critical temperature (in the absence of impurities).

Here the characteristic energy is of order $T_{c0}$ and amounts to ~0.01 eV for high-$T_c$ superconductors. However, if Eq. (7) were applicable to high-$T_c$ superconductors, $d_{x^2-y^2}$ pairing would be impossible in high-$T_c$ superconductors, since superconductivity would vanish at far smaller values of $\tau_c$. Therefore, attempts have been made to "weaken" the destructive action of impurities by taking into account the renormalization of $\tau$ due to strong electron–boson coupling.[26]

Let us now move on to $s^*$ pairing. Due to the weak dependence of the pairing correlator $g_{s*}$ on $W/t$, it is not possible to determine the corresponding value of $W_c$ from numerical calculations. To calculate the influence of impurities on the superconductivity in the $s^*$ channel, we shall utilize the analytical results obtained in Ref. 27 for an anisotropic superconductor with weak coupling [compare with (7)]:

$$\frac{T_c}{T_{cO}}=1-\frac{\pi}{8}\frac{\chi}{\tau T_{cO}} \quad \text{for} \quad \tau T_{cO}\gg 1, \tag{8}$$

where $\chi=\Delta-\langle\Delta\rangle^2/\langle\Delta^2\rangle$ is the anisotropy parameter, which is equal to zero in the special case of isotropic $s$ pairing ($\Delta$ =const);

$$\langle\ldots\rangle=\frac{\oint dl(\ldots)|\partial\varepsilon(\mathbf{k})/\partial\mathbf{k}|^{-1}}{\oint dl|\partial\varepsilon(\mathbf{k})/\partial\mathbf{k}|^{-1}}$$

denotes averaging over the Fermi surface.

The value of $\chi$ in a $p$-type high-$T_c$ superconductor can be determined on the basis of data from the photoemission spectroscopy of single crystals of $Bi_2Sr_2CaCu_2O_{8+x}$ (Ref. 12) ($\Delta=1-2$ meV in the $\Gamma-Y$ direction, 4–8 meV in the $\Gamma-X$ direction, and 14–20 meV in the $\Gamma-M$ direction) using the approximation formula proposed in Ref. 12

$$\Delta(\varphi)=\gamma_1\cos(2\varphi)+i\gamma_2\cos(\varphi+\varphi_0), \tag{9}$$

where the angle $\varphi$ is measured relative to the $\Gamma-M$ direction (a Cu–O bond in real space) and the parameters $\gamma_1$, $\gamma_2$, and $\varphi_0$ are determined from the condition that $|\Delta(\varphi)|$ agree with the experimental data (their values were presented in Ref. 12).

For anisotropic $s$ pairing we calculated $\chi$ by taking $\Delta(\varphi)$ equal to the absolute value of Eq. (9) and using (9) and a simplified 2D model of the energy spectrum with the dispersion law

$$\varepsilon(k)=-2t[\cos(k_xa)+\cos(k_ya)]+4t'\cos(k_xa)\cos(k_ya), \tag{10}$$

where the hopping of the carriers between nearest and next-nearest sites in a simple square lattice was taken into account, and the parameters $t$ and $t'=0.45t$ were selected using the requirement that $\epsilon(\mathbf{k})$ correspond to the photoemission experiments in Ref. 38. When the concentration of hole carriers was $n_h=0.25$ (per copper atom), we found $\chi\approx 0.12$. We note that a similar value of $\chi$ is obtained when the hopping of carriers only between nearest lattice sites is taken into account ($t'=0$), i.e., $\chi$ is only weakly sensitive to the values of $t$ and $t'$ in (10).

Thus, in the weak-coupling approximation the value of $T_c$ is an order of magnitude less sensitive to the effects of defects in the $s^*$ channel than in the $d_{x^2-y^2}$ channel, in qualitative agreement with our results. Consideration of the strong-coupling effects will apparently further weaken the influence of defects on the superconductivity in the $s^*$ channel. As for quantitative calculations, we do not know of any such work.

We now turn to the case of electron doping. As was noted in Ref. 21, in the case of electron doping, $g_{s*}$ is an order of magnitude greater than $g_d$ in the ordered $Cu_4O_8$ cluster (while in the case of hole doping we have $g_{s*}/g_d\approx 2$). This alone raises some doubt as to the presence of superconducting correlations in the $d_{x^2-y^2}$ channel. Moreover, the increase in $g_d$ with increasing $W$ (see Fig. 4a) attests to the complete absence of superconducting correlations in the $d_{x^2-y^2}$ channel in the case of electron doping (at the very least, these correlations are not displayed in the $Cu_4O_8$ cluster).

On the other hand, $g_{s*}$ scarcely depends on $W$ within the range of error (see Fig. 4b). Thus, while $g_{s*}$ contains a definite contribution specifically from superconducting correlations, our numerical calculations imply that of the pairing interactions in the $s^*$ channel are very insensitive to atomic disorder, as in the case of hole doping.

As far as we know there are no experimental data which might be interpreted as supporting the $d_{x^2-y^2}$ symmetry of $\Delta(\mathbf{k})$ in $n$-type high-$T_c$ superconductors. On the other hand, experiment provides convincing evidence that $\Delta(\mathbf{k})$ does not have zeros in the case of electron doping.[39] Nevertheless, it is unlikely that high-$T_c$ superconductors with different types of doping (hole and electron) would have different superconductivity mechanisms and, accordingly, different symmetries of $\Delta(\mathbf{k})$. In our opinion, this is further proof of the $s^*$ symmetry of $\Delta(\mathbf{k})$ in $p$-type high-$T_c$ superconductors, although their higher $T_c$ (in comparison with $n$-type high-$T_c$ superconductors) can certainly be a consequence of the presence of an "admixture" of a $d_{x^2-y^2}$ wave, i.e., the real symmetry of $\Delta(\mathbf{k})$ can be mixed.

## 5. COMPARISON WITH EXPERIMENT

We now turn to the results of experimental investigations of the influence of nonmagnetic impurities and radiation defects[23,24,40,41] on $p$- and $n$-type high-$T_c$ superconductors. To be specific, we shall dwell on radiation defects, which have an effect on high-$T_c$ superconductors that is qualitatively similar to the effect of nonmagnetic impurities.

An enormous body of experimental data that has been amassed provides evidence that the dependence of the reduced temperature $T_c/T_{c0}$ on the reduced fluence of ions, electrons, and other particles (i.e., on the concentration of defects) is a universal function of all high-$T_c$ superconductor systems.[23] This dependence is linear, and $T_c=0$ holds at a certain critical concentration of defects corresponding to the carrier relaxation time $\tau_c\approx 1/E_F\ll 1/T_{c0}$ ($E_F\approx t$ is the Fermi energy). Thus, the evaluation of $\tau_c$ is confirmed by the vanishing of $T_c$ at the beginning of the process of charge-carrier localization, as is indicated by the exponential increase in the

resistivity as $T_c \to 0$ (we note that $T_c$ is measured by resistive or inductive methods).

The results obtained here (see Fig. 6) for $d_{x^2-y^2}$ pairing are consistent, in order of magnitude, with the experimental data. On the other hand, for $1/\tau \approx 1$ eV the pairing correlators in the $s^*$ channel remain almost unchanged (see Figs. 2b and 3b), in apparent contradiction to experiment (to the vanishing of $T_c$ when $1/\tau \approx 1$ eV).

A self-consistent picture of the influence of impurities and defects on high-$T_c$ superconductors can be given, if the results in Refs. 42 and 43 are used. In Ref. 42 an investigation of the Ginzburg–Landau equation in a random field of defects revealed that for $1/\tau \approx E_F$, the condensate of Cooper pairs can be localized, and the superconducting current vanishes. This occurs at a certain temperature $T_s$, which decreases as the defect concentration increases and satisfies the inequality $T_s < T_c$ (we recall that $T_c$ is the temperature at which the density of the Bose condensate of Cooper pairs, which is proportional to $\Delta^2$, vanishes).

Thus, for $T_s < T < T_c$ the model in Ref. 42 predicts the existence of a localized condensate with $\Delta \neq 0$, which was apparently detected experimentally in Ref. 43. According to Ref. 43, in which Andreev reflection was employed to study the direct effect of radiation defects on $\Delta$ (rather than on $T_c$, as in the case of standard resistive and magnetic measurements), although the value of $\Delta$ in $YBa_2Cu_3O_{7-y}$ decreases by approximately a factor of two as the concentration of radiation defects increases, it remains finite up to $\tau \approx 1/E_F$, at which $T_s$ (defined by the condition that $R=0$) is already equal to zero. If it is now assumed that the contribution of the $d_{x^2-y^2}$ channel to $\Delta$ vanishes (or decreases significantly) at $1/\tau \approx E_F$ and that the Bose condensate with $s^*$ symmetry (and possibly with a small admixture of a $d_{x^2-y^2}$ wave) is then localized, all the available facts can, in principle, be reconciled. We note that the model in Ref. 42 provides qualitatively good descriptions of several observable features in the behavior of $T_s$, even for $n$-type high-$T_c$ superconductors (see also the experimental work reported in Refs. 40 and 41).

Thus, the results of our numerical calculations, together with an analysis of experiments involving the irradiation of high-$T_c$ superconductors, attest to the predominance of the pairing correlations in the $s^*$ channel over the correlations in the $d_{x^2-y^2}$ channel in the case of hole doping. However, as the calculations show, there are still pairing correlations in the $d_{x^2-y^2}$ channel (although they are weaker than those in the $s^*$ channel). This can apparently lead to an erroneous conclusion regarding the $d_{x^2-y^2}$ symmetry of $\Delta(\mathbf{k})$ in $p$-type high-$T_c$ superconductors in the interpretation of some experiments. Just this may be responsible for the ambiguity of the experimental data regarding the symmetry of the gap in $p$-type high-$T_c$ superconductors. In any case, when any experiments are analyzed, it must be taken into account that superconducting interactions are probably present simultaneously in both channels ($s^*$ and $d_{x^2-y^2}$) in the case of hole doping, the only question being their relative proportions.

It has not, however, been ruled out that the order parameter in $p$-type high-$T_c$ superconductors does, in fact, have a mixed $s^*+d$ symmetry, which has already been discussed in the literature (see, for example, Refs. 7 and 8). However, a numerical calculation of pairing correlators with mixed symmetry is beyond the scope of this paper.

## 6. CONCLUSIONS

In conclusion, we list the main results obtained in this work and the conclusions drawn on their basis.

1) In the case of hole doping of a $Cu_4O_8$ cluster, an increase in the Anderson disorder parameter $W$ results in a decrease in the pairing correlator $P_d - \bar{P}_d$ in the $d_{x^2-y^2}$ pairing channel even for $W/t \ll 1$, while the correlator $P_s - \bar{P}_s$ in the $s^*$ channel remains unchanged within the range of the "error" caused by the averaging over the different disorder configurations even when $W/t > 1$ The critical values of the disorder parameter ($W_c$) and the relaxation time $1/\tau_c \approx W_c$ are of order 1 eV. These results are consistent with experimental data on the effects of nonmagnetic impurities and radiation defects on $p$-type superconductors. With consideration of the conclusions drawn in Refs. 42 and 43, they make it possible to provide a consistent picture of the influence of atomic disorder on the critical characteristics of high-$T_c$ superconductors.

2) The evaluation of the size of the superconducting contribution to the pairing correlator $g_d$ with $d_{x^2-y^2}$ symmetry performed for the case of hole doping by comparing the dependences of $g_d$ and $g_{s*}$ on $W$ and on the basis of calculations of the binding energy in a disordered cluster[32] gives a value 0.1–0.3. Therefore, taking into account the presence of superconducting correlations in the $s^*$ channel, we can speak about a mixed $s^*+d$ symmetry in $p$-type high-$T_c$ superconductors.

3) In the case of electronic doping of the $Cu_4O_8$ cluster, there are apparently absolutely no superconducting correlations with $d_{x^2-y^2}$ symmetry, and the pairing correlators in the $s^*$ channel depend weakly on $W$. Therefore, the destruction of superconductivity by defects in $n$-type high-$T_c$ superconductors can be caused by localization of the Bose condensate of Cooper pairs.

As for $n$-type high-$T_c$ superconductors, the model of Bose-condensate localization[42] allows one to make a prediction amenable to direct experimental verification. If the order parameter for electron doping does in fact have pure $s^*$ symmetry and depends weakly on $1/\tau$ for $1/\tau \leqslant E_F$, as our calculations show, then when we study Andreev reflection in $n$-type high-$T_c$ superconductors we should find $\Delta(T_s) \approx$ const up to the point where the critical current goes to zero ($T_s = 0$). This behavior for $\Delta(T_s)$ differs qualitatively from that in $p$-type high-$T_c$ superconductors, where the presence of a $d_{x^2-y^2}$ component in the order parameter reduces $\Delta$ by about a factor of two when $T_s$ is decreased from $T_{CO}$ to zero[43] by suppressing pairing in the $d_{x^2-y^2}$ channel (but retaining superconductivity in the $s^*$ channel).

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