

Pairing correlations with s^* and $d_{x^2-y^2}$ symmetry in a disordered Cu_4O_8 cluster

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Recently we have shown [V. F. Elesin, A. V. Krasheninnikov, and L. A. Openov, *Sov. Phys. JETP* **79**, 789 (1994)] that in the hole-doped Cu_4O_8 cluster pairing correlations with s^* symmetry are nearly twice as strong as those with $d_{x^2-y^2}$ symmetry, while in the electron-doped cluster pairing correlations seem to be present in the s^* channel only. In this paper the effect of on-site disorder on the pairing correlators with s^* and $d_{x^2-y^2}$ symmetry in the Cu_4O_8 cluster is studied numerically through an exact diagonalization of the Emery-Anderson Hamiltonian. It is shown that at a nearly optimal doping level (0.25 excess holes per copper atom) the disorder weakens pairing correlations in the $d_{x^2-y^2}$ channel and has much less influence on pairing correlations in the s^* channel. Based on the results obtained, the “superconducting” components of pairing correlators are estimated to be 10–30 % of their full values, with the remaining parts of correlators being contributions from a finite-size effect. These results indicate that cluster calculations may be relevant for the study of high- T_c superconductivity.

Much attention has been paid lately to the symmetry of the pairing state in high- T_c superconductors. The knowledge of the underlying symmetry might shed light on the mechanism of high- T_c superconductivity and reduce the size of the list of theoretical models debated. Unfortunately, experimental data are still controversial. There is evidence for $d_{x^2-y^2}$ symmetry^{1,2} as well as for s^* symmetry.^{3,4} The most consistent theoretical approach to the problem is the analysis of suitable model Hamiltonians. But strong Coulomb correlations prevent analytic solutions of even simplified two-dimensional (2D) models. In such a situation, great importance is attached to numerical calculations on finite clusters. For example, quantum Monte Carlo methods have been used to calculate the pairing correlators with s , s^* , and $d_{x^2-y^2}$ symmetry.^{5,6} While in the 2D Hubbard model the pairing correlations have been found in the $d_{x^2-y^2}$ channel only,⁵ the correlations with both s^* and $d_{x^2-y^2}$ symmetry have been shown to take place in the 2D Emery model.⁶ The variational Monte Carlo calculations have revealed mixed $s+id$ symmetry of the superconducting state in the Emery model.⁷ In Ref. 8 the pairing correlators in different channels have been calculated by means of exact diagonalization of the Emery Hamiltonian, and correlations with s^* symmetry have been shown to dominate. All these numerical results favor the purely nonphonon mechanisms of high- T_c superconductivity. However, the weak point of cluster calculations is the small size of clusters studied. Though a very short coherence length in high- T_c cuprates indicates that studies on finite Cu-O clusters may be relevant in describing the physics of the cuprates and may lead to a qualitative understanding of the properties of the infinite CuO_2 plane, it is still not clear whether the pairing correlations found are intrinsic to a particular model Hamiltonian or are just a finite-size effect.

One way to learn something more about the presence or absence of “superconducting” components in pairing correlators of finite Cu-O clusters is to study the influence of Anderson disorder on pairing correlators with different symmetries. Indeed, Anderson disorder mimics nonmagnetic im-

purities, which are known to have much stronger effect on $d_{x^2-y^2}$ -wave superconductors as compared with s - or s^* -wave superconductors. Hence, numerical calculations on disordered clusters might help us to separate “superconducting” components of pairing correlators from finite-size ones and thus to check the relevance of cluster calculations for the study of high- T_c superconductivity.

We should stress that we use the term “superconducting component” to mean the pairing-correlation-induced part of the total pairing correlator. It is needless to say that true long-range superconducting order may be found in the infinite system only. However, the superconducting order, if it exists in a large system, should manifest itself in small clusters. So, it may be hoped that numerical investigations of even tiny clusters can provide at least qualitative information on the characteristics of the infinite system.

In this paper we use the exact diagonalization technique to investigate the effect of Anderson disorder on pairing correlations with s^* and $d_{x^2-y^2}$ symmetry in the Cu_4O_8 cluster. We use the two-dimensional Emery model⁹ combined with the diagonal on-site disorder. The Hamiltonian has the form

$$\begin{aligned}
 H = & -t \sum_{\langle ik \rangle, \sigma} (d_{i\sigma}^+ p_{k\sigma} + \text{H.c.}) + \epsilon \sum_{k, \sigma} n_{k\sigma} + U_d \sum_i n_{i\uparrow} n_{i\downarrow} \\
 & + U_p \sum_k n_{k\uparrow} n_{k\downarrow} + V \sum_{\langle ik \rangle, \sigma \sigma'} n_{i\sigma} n_{k\sigma'} \\
 & + \sum_{j=i,k} w_j (n_{j\uparrow} + n_{j\downarrow}), \quad (1)
 \end{aligned}$$

where w_j are the increments in the site potentials of the copper and oxygen atoms randomly distributed in an energy interval of width W , other notations being standard (see, e.g., Refs. 8 and 10). The parameter W characterizes the degree of disorder (the case $W=0$ corresponds to the absence of disorder) and plays a role of defect concentration.¹⁰

We consider the two-dimensional Cu_4O_8 cluster with periodic boundary conditions. We study in detail the case of "optimal" hole doping, when there are five holes in the cluster (one doped hole in the parent dielectric state). For the relative (per copper atom) concentration x of excess holes we have $x=0.25$, this value being close to the optimal doping level at which T_c reaches its maximum in p -type high- T_c superconductors. To solve numerically the many-electron Schrödinger equation $H\Psi = E\Psi$ we make use of the Lanczos algorithm. The exact ground-state wave function is then used to calculate the pairing correlator P_α in α channel ($\alpha = s^*$ or $d_{x^2-y^2}$):

$$P_\alpha = \sum_{\mathbf{r}, \mathbf{r}'} \langle \Delta_\alpha^+(\mathbf{r}) \Delta_\alpha(\mathbf{r} + \mathbf{r}') \rangle, \quad (2)$$

where

$$\Delta_\alpha^+(\mathbf{r}) = N_0^{-1/2} \sum_{\boldsymbol{\rho}} g_\alpha(\boldsymbol{\rho}) d_{\mathbf{r}, \uparrow}^+ d_{\mathbf{r} + \boldsymbol{\rho}, \downarrow}^+, \quad (3)$$

N_0 is the number of CuO_2 unit cells (for the cluster considered $N_0=4$), summation over \mathbf{r} and \mathbf{r}' is carried out over all the copper sites. The form of the function $g_\alpha(\boldsymbol{\rho})$ is determined by the symmetry of the pairing state: $g_{s^*}(\boldsymbol{\rho})=1$ when $\boldsymbol{\rho} = \pm a\mathbf{e}_x$ or $\boldsymbol{\rho} = \pm a\mathbf{e}_y$, and $g_{s^*}(\boldsymbol{\rho})=0$ for other values of $\boldsymbol{\rho}$; $g_d(\boldsymbol{\rho})=1$ when $\boldsymbol{\rho} = \pm a\mathbf{e}_x$, $g_d(\boldsymbol{\rho})=-1$ when $\boldsymbol{\rho} = \pm a\mathbf{e}_y$, and $g_d(\boldsymbol{\rho})=0$ for other values of $\boldsymbol{\rho}$. Here a is the lattice constant, and the averaging $\langle \dots \rangle$ is carried out with respect to the ground state (i.e., at $T=0$).

To minimize the finite-size effect,^{6,8} we subtract the quantity

$$\begin{aligned} \bar{P}_\alpha = N_0^{-1} \sum_{\mathbf{r}, \mathbf{r}', \boldsymbol{\rho}, \boldsymbol{\rho}'} g_\alpha(\boldsymbol{\rho}) g_\alpha(\boldsymbol{\rho}') \langle d_{\mathbf{r}, \uparrow}^+ d_{\mathbf{r} + \mathbf{r}', \uparrow} \rangle \\ \times \langle d_{\mathbf{r} + \boldsymbol{\rho}, \downarrow} d_{\mathbf{r} + \mathbf{r}' + \boldsymbol{\rho}', \downarrow} \rangle \end{aligned} \quad (4)$$

from P_α . Pairing correlations in the α channel are thought to persist if $P_\alpha - \bar{P}_\alpha > 0$.^{6,8} Our aim is to calculate $P_\alpha - \bar{P}_\alpha$ as a function of disorder parameter W at given values of other parameters of the Hamiltonian (1). Note that at a fixed value of W , the ground-state characteristics depend on the specific realization of the site disorder, i.e., on the specific set $\{w_j\}$ in (1). A correct description of the influence of defects on the electronic structure of small clusters requires taking a suitable average over various disorder configurations and determining both mean values and mean-square deviations.¹⁰ Under such circumstances, we carried out calculations in the following manner: For each of L different random sets $\{w_j^l\}$ ($l=1, \dots, L$), at fixed values of all the other parameters of the Hamiltonian, we calculated $(P_\alpha - \bar{P}_\alpha)^l$. Mean values of $P_\alpha - \bar{P}_\alpha$ at a fixed value of W were then found as the arithmetic means over L configurations. Mean-square deviations $D(P_\alpha - \bar{P}_\alpha)$ were calculated using the standard formula of mathematical statistics. In most cases we restricted the calculations to $L=30$ disorder configurations as results obtained were practically the same as for $L=100$. The following parameters sets have been used: (i) $\epsilon/t=1$, $U_d/t=8$, $U_p=V=0$; (ii) $\epsilon/t=2$, $U_d/t=6$, $U_p=V=0$; (iii) $\epsilon/t=2$, $U_d/t=6$, $U_p/t=2.5$, $V/t=1.5$.

Figure 1 presents plots of the dependences of

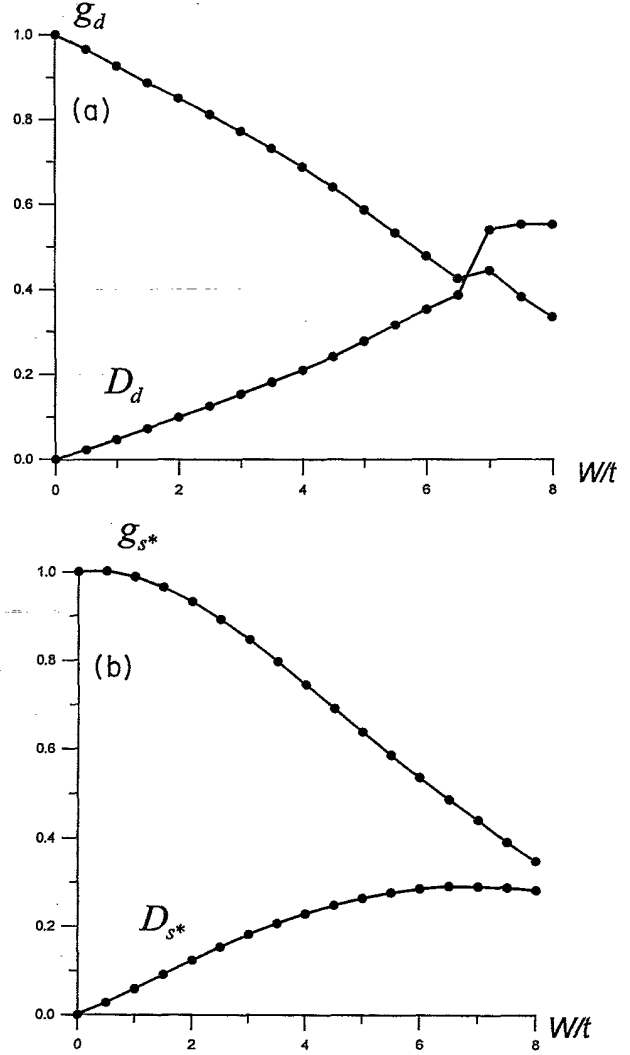


FIG. 1. Plots of normalized pairing correlators $g_\alpha = (P_\alpha - \bar{P}_\alpha)/(P_\alpha - \bar{P}_\alpha)_0$ and of their mean-square deviations $D_\alpha = D(P_\alpha - \bar{P}_\alpha)/(P_\alpha - \bar{P}_\alpha)_0$ versus the disorder parameter W/t in the hole-doped Cu_4O_8 cluster for the parameters set (iii) $\epsilon/t=2$, $U_d/t=6$, $U_p/t=2.5$, $V/t=1.5$. (a) $\alpha = d_{x^2-y^2}$, (b) $\alpha = s^*$.

$g_\alpha = (P_\alpha - \bar{P}_\alpha)/(P_\alpha - \bar{P}_\alpha)_0$ and $D_\alpha = D(P_\alpha - \bar{P}_\alpha)/(P_\alpha - \bar{P}_\alpha)_0$ on W in $d_{x^2-y^2}$ and s^* channels for the set (iii). Here $(P_\alpha - \bar{P}_\alpha)_0$ is the value of $P_\alpha - \bar{P}_\alpha$ at $W=0$. For the set (iii) the value of $(P_{s^*} - \bar{P}_{s^*})_0$ has proven to be roughly twice as large as that of $(P_d - \bar{P}_d)_0$. The ratio $(P_{s^*} - \bar{P}_{s^*})_0/(P_d - \bar{P}_d)_0 \approx 2$ holds also for other parameters sets.⁸ As follows from Fig. 1, g_d decreases monotonically with increasing W . The same is true for the dependence of g_{s^*} on W , but only at $W/t > 1$. Mean-square deviations D_α increase with W in both channels.

The qualitative difference between the functions $g_\alpha(W)$ in s^* and $d_{x^2-y^2}$ channels consists in that the correlator g_{s^*} remains almost unchanged at $W/t < 1$ within the uncertainty D_{s^*} , whereas g_d decreases already at $W/t \leq 1$. This is clearly illustrated in Fig. 2 where mean-square deviations D_d are plotted as vertical lines. The same results were obtained for parameters sets (i), (ii). Thus, $d_{x^2-y^2}$ wave pairing is more sensitive to the disorder than s^* pairing, as expected. We

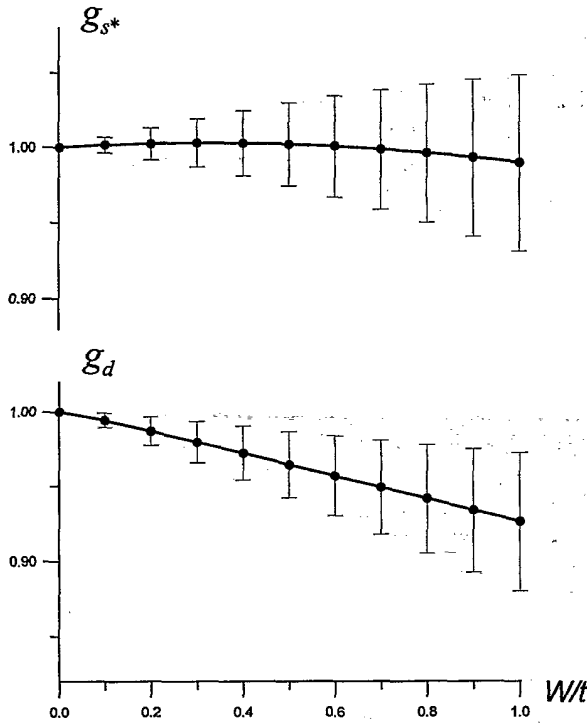


FIG. 2. The same as in Fig. 1. Mean-square deviations D_α are shown as vertical lines.

would like to stress that a substantial (40–50 %) decrease of pairing correlators in both $d_{x^2-y^2}$ and s^* channels occurs only at $W/t > 5$ (see Fig. 1), i.e., at such values of W when the disruption of the antiferromagnetic correlations takes place.¹⁰ This fact attests to the essential contribution of non-superconducting (probably, magnetic) interactions, along with the superconducting ones, to the pairing correlators. This contribution is apparently conditioned by finite-size effects and should be absent in a large system. To determine the *relative* weights of superconducting components in total pairing correlators, we assume that finite-size effects equally

contribute to the *normalized* pairing correlators in both channels, i.e., $g_{s^*}(W) = g_{s^*}^{\text{SC}}(W) + g_{\text{FS}}(W)$ and $g_d(W) = g_d^{\text{SC}}(W) + g_{\text{FS}}(W)$ were g_α^{SC} are the superconducting components (different in $\alpha = s^*$ - and $d_{x^2-y^2}$ channels at $W > 0$) and g_{FS} is the finite-size contribution (the same in both channels).

In Fig. 3 we present the plots of the quantity $\delta_{sd} = g_{s^*} - g_d = g_{s^*}^{\text{SC}} - g_d^{\text{SC}}$ versus W . It is seen that for each of the parameters sets examined the value of δ_{sd} increases monotonically with W at $W/t < 3$, and approaches a constant value $\delta_{sd}^0 \approx 0.28$ (i), 0.25 (ii), 0.07 (iii) at $W/t > 3$ (oscillations of δ_{sd} for the set (iii) are probably due to insufficient number of disorder realizations used). Note that mean-square deviations D_d exceed mean values g_d starting with some W/t , thus giving rise to the nonregular dependence of g_d on W (see Fig. 1). In this connection, we have restricted the intervals of W/t values in Fig. 3 by the condition $g_d \leq D_d$, i.e., $0 \leq W/t \leq 4$ (i), $0 \leq W/t \leq 4.5$ (ii), $0 \leq W/t \leq 6.5$ (iii).

The initial increase of δ_{sd} reflects the fact that the superconducting component in the $d_{x^2-y^2}$ channel g_d^{SC} is being suppressed by disorder more quickly than that in the s^* channel, $g_{s^*}^{\text{SC}}$. The constant values of δ_{sd} at $W/t > 3$ indicate that superconducting interactions do not contribute to g_d at large W (i.e., $g_d^{\text{SC}} = 0$), while $g_{s^*}^{\text{SC}}$ remains almost unchanged, and the finite-size contribution g_{FS} is indeed the same in both channels. As a corollary, δ_{sd}^0 can be thought to be equal to $g_{s^*}^{\text{SC}}(W) \approx g_{s^*}^{\text{SC}}(0)$, or, equivalently, to $g_d^{\text{SC}}(0)$, as we supposed g_{FS} to be the same in both channels. In that way, $g_\alpha^{\text{SC}}(0) \approx 0.28$ for (i), 0.25 for (ii), and 0.07 for (iii). Now, having the values of $g_\alpha^{\text{SC}}(0)$, we are able to plot the dependence of g_d^{SC} on W/t by subtraction $g_{\text{FS}}(W) \approx g_{\text{FS}}(0) = 1 - g_\alpha^{\text{SC}}(0)$ from $g_d(W)$. This is done for set (ii) in Fig. 4. The critical value of W_c/t , derived from the condition $g_d^{\text{SC}}(W_c) = 0$, is equal to 1.7. At this value of W/t the correlator $g_{s^*}(W)$ does not differ much from $g_{s^*}(0)$, see Fig. 1, thus indicating a weak sensitivity of $g_{s^*}^{\text{SC}}$ and g_{FS} to the disorder at $0 < W/t < W_c/t$ and hence justifying the approximation $g_{\text{FS}}(W) \approx g_{\text{FS}}(0)$ at $W < W_c$ used by us when plotting $g_d^{\text{SC}}(W)$. The same linear dependences of g_d^{SC} on W take place for other parameters sets, the values of W_c/t being 1.6 and 1.0 for (i) and (ii), respectively.

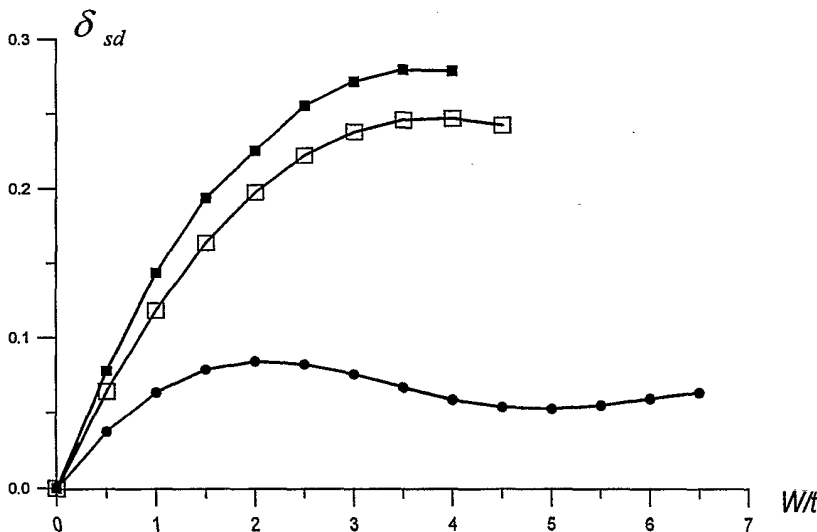


FIG. 3. Plots of $\delta_{sd} = g_{s^*} - g_d$ versus W/t . Intervals of W/t are chosen from the condition $D_d < g_d$ (see text). ■, (i) $\epsilon/t = 1$, $U_d/t = 8$, $U_p = V = 0$, □, (ii) $\epsilon/t = 2$, $U_d/t = 6$, $U_p = V = 0$, ●, (iii) $\epsilon/t = 2$, $U_d/t = 6$, $U_p/t = 2.5$, $V/t = 1.5$.

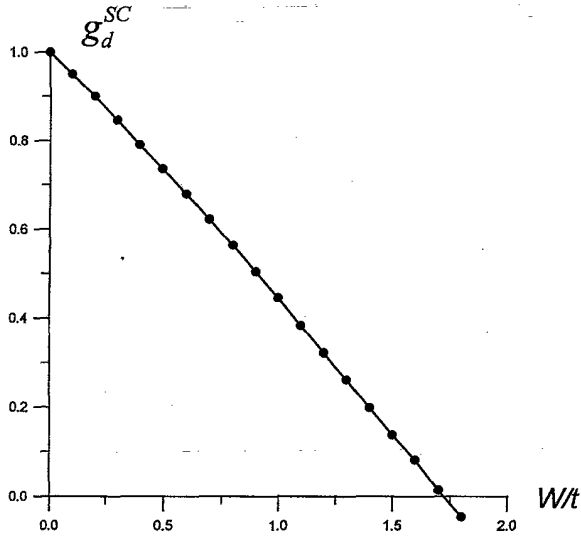


FIG. 4. Shows the superconducting component g_d^{SC} versus W/t in the hole-doped Cu_4O_8 cluster for the parameters set (ii) $\epsilon/t=2$, $U_d/t=6$, $U_p=V=0$.

In the case of s^* -wave pairing we are unable to estimate the value of W_c from our numerical calculations, since the function $g_{\text{FS}}(W)$ at large W is unknown. The only thing we can say is that the value of W_c in the s^* channel is apparently larger than that in the $d_{x^2-y^2}$ channel. Apart from the value of W_c , we can estimate the ratio $(P_{s^*}-\bar{P}_{s^*})_0^{\text{SC}}/(P_d-\bar{P}_d)_0^{\text{SC}} \approx (P_{s^*}-\bar{P}_{s^*})_0/(P_d-\bar{P}_d)_0 \approx 2$, where the first equality arises from our assumption that g_{FS} is the same in both channels, i.e., $g_{s^*}^{\text{SC}}(0) \approx g_d^{\text{SC}}(0)$, and the second one is the result of our numerical calculation. The presence of pairing correlations with both s^* and $d_{x^2-y^2}$ symmetries in the hole-doped Cu_4O_8 cluster points to a possible mixed symmetry of the order parameter in p -type high- T_c superconductors, with the prevalence of correlations in the s^* channel (see, also, Ref. 7).

We now proceed to a comparison of our results with theoretical studies of defects influence on the $d_{x^2-y^2}$ wave superconductors. For this purpose it is convenient to present the function $g_d^{\text{SC}}(W)$ in the following form (see Fig. 4):

$$g_d^{\text{SC}}(W) = 1 - b \frac{W}{t} = 1 - \frac{1}{\tau \epsilon}, \quad (5)$$

where b is a numerical coefficient, τ is associated with the relaxation time, ϵ is a characteristic energy ($\epsilon \approx \tau_c^{-1}$, where τ_c is a critical value of τ at which pairing correlations vanish). In cluster calculations, a value of τ may be estimated from the uncertainty principle $\tau \delta E_0 \sim 1$, where δE_0 is the uncertainty of the ground-state energy E_0 caused by the disorder. According to our calculations, $\delta E_0 \approx W$, so $\tau^{-1} \approx W$, i.e., $\tau_c^{-1} \approx W_c \approx t \sim 1$ eV. This value of τ_c^{-1} is at least an order of magnitude larger than that obtained for a $d_{x^2-y^2}$ -wave superconductor from numerical solution of Eliashberg equations.¹¹ We note, however, that the authors of Ref. 11 assumed an isotropic impurity scattering. As is discussed in Ref. 12, the

presence of the d -wave component in the impurity scattering can lead to a substantial increase of τ_c^{-1} .

In order to compare our calculations with existing experimental situation, we turn to a brief discussion of T_c degradation under particle irradiation. First, the value of T_c is known to decrease linearly in the irradiation dose, i.e., in the impurity concentration $n_{\text{im}} \sim \tau^{-1}$ (see, e.g., Ref. 13). This fact is in agreement with our result (5), as g_d^{SC} may be viewed to be proportional to Δ_d^2 , see (2). Next, experimentally observed critical value $\tau_c^{-1} \approx E_F$ at which T_c vanishes,¹³ is close to the calculated value of $\tau_c^{-1} \approx t$ in the $d_{x^2-y^2}$ channel since $E_F \approx t$. But then a question arises about the presence of the s^* -wave component in the order parameter. One should, however, keep in mind that strong disordering leads to the appearance of localization phenomena. It was shown in Ref. 13 that the condensate of Cooper pairs could be localized at $\tau^{-1} \approx E_F$, so that resistively measured T_c equals zero (as the supercurrent vanishes), while $\Delta \neq 0$. The transition of the Bose condensate of Cooper pairs into a localized state was apparently observed in Ref. 14 where the influence of radiation-induced defects on Δ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ was investigated by means of Andreev reflection. We can conform our calculations with the experimental facts if we assume that the contribution to Δ from the $d_{x^2-y^2}$ channel vanishes at $\tau^{-1} \approx E_F$ and then the localization of the remaining part of the Bose condensate with the s^* symmetry takes place.

Now let us consider briefly the case of the electron doping (three holes in the cluster, i.e., one extra electron in the parent state). As it was pointed out in Ref. 8, in the absence of disorder the value of $(P_{s^*}-\bar{P}_{s^*})_0$ for the electron-doped Cu_4O_8 cluster is an order of magnitude larger than the value of $(P_d-\bar{P}_d)_0$. This fact gives rise to strong doubts about the presence of the superconducting correlations with $d_{x^2-y^2}$ symmetry under electron doping. Moreover, according to our calculations, the pairing correlator g_d in the disordered cluster behaves rather unphysically: It increases substantially with W , while the mean-square deviation exceeds the mean value. This is true for all the parameters sets examined and points to a complete absence of $d_{x^2-y^2}$ -wave correlations in the electron-doped cluster. On the contrary, g_{s^*} is practically independent of W , thus indicating a weak sensitivity of pairing interactions with s^* symmetry to the disorder under electron doping as well as under the hole one. Hence, under electron doping, pairing correlations seem to be present in the s^* channel only, in accordance with experimental data.¹⁵ So, according to the model,¹³ we can expect radiation-induced defects in n -type cuprates to suppress resistively measured T_c , keeping the value of Δ , measured by means of Andreev reflection, almost unchanged up to $T_c=0$. This prediction may be checked experimentally.

In conclusion, we have separated the superconducting components of the pairing correlators with s^* and $d_{x^2-y^2}$ symmetry in the Cu_4O_8 cluster from the finite-size ones and have shown them to be 10–30 % of the total values. Our results indicate that purely nonphonon pairing correlations in s^* and $d_{x^2-y^2}$ channels are intrinsic for the two-dimensional Emery model. In the hole-doped cluster, the superconducting fraction of the pairing correlator in the s^* channel is a factor of 2 larger than that in the $d_{x^2-y^2}$ channel. Under electron

doping pairing correlations with the $d_{x^2-y^2}$ symmetry are absent.

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