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Suppression of superconductivity in high-T_c cuprates due to nonmagnetic impurities: Implications for the order parameter symmetry

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Abstract. We studied the effects of nonmagnetic impurities on high-temperature superconductors by solving the Bogoliubov-de Gennes equations on a two-dimensional lattice via exact diagonalization technique in a fully self-consistent way. We found that s-wave order parameter is almost unaffected by impurities at low concentrations while $d_{x^2-y^2}$-wave order parameter exhibits a strong linear decrease with impurity concentration. We evaluated the critical impurity concentration $n_{\rm i}^{\rm c}$ at which superconductivity ceases to be 0.1 which is in good agreement with experimental values. We also investigated how the orthorhombic nature of the crystal structure affects the suppression of superconductivity and found that anisotropy induces an additional s-wave component. Our results support $d_{x^2-y^2}$-wave symmetry for tetragonal and $s + d_{x^2-y^2}$-wave symmetry for orthorhombic structure.

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The symmetry of the order parameter (OP) in high $T_{\rm c}$ cuprates is important both for understanding the mechanism of superconductivity and also for technological applications [1]. For example, d-wave symmetric OP effectively refutes phonon mechanism and for a device made of a d-wave superconductor having no gap in energy spectrum, no refinement would get rid of the dissipation at low frequencies, even at low temperatures. $3d$ metal (Zn, Ni, Al, Ga, Fe, ...) atom substitution for Cu atoms in high-$T_{\rm c}$ cuprates may identify the symmetry of the OP [2]. It is a well known fact that for conventional superconductors having isotropic order parameter, nonmagnetic impurities with small concentrations have no effect on critical temperature [3–6] while magnetic impurities act as strong pair breakers, and as a result of this superconductivity is suppressed very rapidly [7–9]. On the other hand, nonmagnetic impurities are very effective in anisotropic superconductors [10–12]. For a pure superconductor, anisotropy leads to increase in $T_{\rm c}$ [10,13,14] and the critical temperature suppression rate with increasing impurity concentration is proportional to the strength of anisotropy [10–12]. Unlike the conventional superconductors, in hole-doped [15] high-$T_{\rm c}$ cuprates both magnetic (Ni) and nonmagnetic (Zn) impurities suppress $T_{\rm c}$ very effectively.

Dependence of the superconducting properties (critical temperature, order parameter, density of states, ...) on impurity or point defect concentration is a subject of ongoing research. So far, most of the experiments have been performed to investigate effects of Zn and Ni substitution in $YBa_2Cu_3O_{7-\delta}$ compounds [16–39]. Alternatively, disorder can also be introduced by creating defects with ion irradiation [40–44], but in this case affected region is often uncontrollable.

In spite of the complexity of the high-$T_{\rm c}$ cuprates (boundaries, defects, ...), insufficient control of the actual impurity or point defect concentration, solubility, and homogeneity of the distribution of the dopants which may lead to contradictory data, we can summarize some of the experimental results as follows:

- For $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ compounds, at small concentrations, $x < 0.04$, Zn ions occupy preferably Cu-sites in the CuO_2 planes, however for $x > 0.04$ the substituent starts to occupy Cu-sites in the chain [16,19,45–47]. Since this compound has two planes and one chain in a unit cell, for $x < 0.04$ the actual (effective) impurity concentration $n_{\rm i}$, *i.e.* the number of impurities per unit cell per CuO_2 plane, becomes $3x/2$.
- The critical temperature decreases linearly with increasing impurity concentration in substitution [16,29] (for $x > 0.04$ the drop rate decreases due to partial occupancy of Zn at chain sites) and point defect concentration in irradiation [44] experiments.
- Due to orthorhombicity of YBCO material, CuO_2 planes exhibit an anisotropic behavior and admixture of d- and s-wave is possible [35,48–50].
- Zn substitution does not alter the carrier concentration in CuO_2 planes [32].

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On the theoretical side, the existing pair-breaking models overestimate the suppression of critical temperature and predict an increasing slope with increasing impurity concentration [51–54] which contradicts the observed linear dependence of T_c on n_i. The effects of neither magnetic (Ni) nor nonmagnetic (Zn) impurities on the superconducting properties of the cuprates have been explained clearly. The main reason for the discrepancy between theory and experiment is that the conventional Abrikosov-Gor'kov (AG)-type pair-breaking models ignore the position dependence of the order parameter near impurity sites. Recently, Franz and his coworkers [55], and Zhitomirsky and Walker [56] argued that spatial variation of the order parameter must be taken into account for short coherence length superconductors.

In the present paper, we investigate effects of nonmagnetic impurities on high-T_c cuprates for both tetragonal and orthorhombic phases by solving the Bogoliubov-de Gennes (BdG) equations [57,58] in a fully self-consistent way. In particular, we address the possibility of extracting the OP symmetry by examining the effects of nonmagnetic impurities. Our results support $d_{x^2-y^2}$-wave pairing symmetry for tetragonal and $s+d_{x^2-y^2}$-wave for orthorhombic structure. The possibility of admixture of s- and d-wave symmetries have already been proposed in various experimental [49,50] and theoretical works [59–61,51].

The BdG equations on two-dimensional lattice have the following form [58,62]

$$\sum_j \begin{pmatrix} H_{ij} & \Delta_{ij} \\ \Delta_{ij}^\star & -H_{ij}^\star \end{pmatrix} \begin{pmatrix} u_n(j) \\ v_n(j) \end{pmatrix} = E_n \begin{pmatrix} u_n(i) \\ v_n(i) \end{pmatrix}, \quad (1)$$

where $u_n(i)$ and $v_n(i)$ are quasiparticle amplitudes at site i with eigenvalue E_n, and Δ_{ij} is the pairing potential. The normal-state part of the Hamiltonian can be written as

$$H_{ij} = (t_{ij} + U_{ij} n_{ij}/2)(1-\delta_{ij}) + (V_i^{\rm imp} - \mu + U_{ii} n_{ii}/2)\delta_{ij}, \quad (2)$$

where t_{ij} is the hopping amplitude, μ is the chemical potential, $U_{ij}n_{ij}/2$ and $U_{ii}n_{ii}/2$ are the Hartree-Fock potentials with on-site interaction U_{ii} and off-site interaction U_{ij}, respectively. Finally $V_i^{\rm imp}$ is the impurity potential. The pairing potentials are defined by

$$\Delta_{ij} = -U_{ij} F_{ij}. \quad (3)$$

The charge density n_{ij} in the Hartree-Fock potentials and the anomalous density F_{ij} in the pairing potential are determined from

$$n_{ij} = \sum_\sigma \langle \Psi_\sigma^\dagger(i) \Psi_\sigma(j) \rangle, \quad (4)$$

$$F_{ij} = \langle \Psi_\uparrow(i) \Psi_\downarrow(j) \rangle, \quad (5)$$

where σ is spin index, and $\Psi_\sigma^\dagger(i)$ and $\Psi_\sigma(i)$ are related to the quasiparticle creation ($\gamma_{n\sigma}^\dagger$) and annihilation ($\gamma_{n\sigma}$) operators

$$\begin{bmatrix} \Psi_\uparrow(i) \\ \Psi_\downarrow^\dagger(i) \end{bmatrix} = \sum_n \left[\gamma_{n\uparrow} \begin{pmatrix} u_n(i) \\ v_n(i) \end{pmatrix} + \gamma_{n\downarrow}^\dagger \begin{pmatrix} -v_n^\star(i) \\ u_n^\star(i) \end{pmatrix} \right], \quad (6)$$

where γ and $\gamma^\dagger$ satisfy the Fermi commutation relations. The self-consistency conditions can be written in terms of u_n, v_n, and E_n

$$n_{ij} = 2\sum_n u_n^\star(i) u_n(j) f(E_n) + v_n(i) v_n^\star(j)[1-f(E_n)], \quad (7)$$

$$F_{ij} = \sum_n u_n(i) v_n^\star(j)[1-f(E_n)] - v_n^\star(i) u_n(j) f(E_n), \quad (8)$$

where $f(E_n) = 1/[\exp(E_n/k_{\rm B}T) - 1]$ is the Fermi distribution function.

We solve the BdG equations on a 20×20 square lattice (hence, we diagonalize a 1600×1600 matrix) with periodic boundary conditions by exact diagonalization technique using IMSL subroutines. After choosing a suitable initial guess for OP, we solve equation (1). Next, we calculate the new charge density n_{ij} and anomalous density F_{ij} *via* equations (7, 8) and iterate this procedure until a reasonable convergence is achieved. The BdG equations are solved self-consistently. Self-consistency conditions (Eqs. (7, 8)) lead to 10 separate equations. The first five (obtained from Eq. (7)) renormalize on-site energies and hopping matrix elements while the last five (obtained from Eq. (8)) affect the on-site and nearest-neighbor interaction terms. Although, the first five of these self-consistency conditions can be neglected for conventional superconductors where $U/t \ll 1$, for strong interaction case we should keep them, since they play important role especially in the presence of impurities. The impurity potential $V_i^{\rm imp}$ is treated in the unitary limit, *i.e.* $V_i^{\rm imp} \gg t$, and taken nonzero for randomly chosen lattice sites.

We first solve the BdG equations for tetragonal case $t_x = t_y = t$ where t_x and t_y are nearest-neighbor hopping amplitudes along x and y directions, respectively. For s-wave OP symmetry we assume that on-site (attractive) interaction is $U_{ii} = -1.7t$ and there is no nearest-neighbor interaction. In the case of d-wave OP symmetry on-site (repulsive) interaction is $U_{ii} = 1.4t$ and nearest-neighbor (attractive) interaction is $U_{ij} = -1.4t$. With this choice of parameters we fix the chemical potential μ so that the band filling factor is $\langle n \rangle \simeq 0.8$ and the zero temperature coherence length is $\xi_0 \simeq 4a$. These values are in good agreement with the commonly accepted experimental values.

Figure 1 shows that, at low impurity concentrations s-wave OP symmetry is almost unaffected by the impurities or point defects. Although we use several on-site interaction values by keeping the band filling factor and zero temperature coherence length constant, we do not get any qualitative change. This result is consistent with Anderson theorem [5] and AG theory [8]. However, experimental data for high-T_c cuprates exhibit a much stronger suppression of superconductivity with increasing disorder.

On the other hand, our d-wave calculations give results similar to the behavior observed in experiments. For d-wave symmetry we find that on-site pairing potential is negligibly small. In Figure 1, Δ_d is amplitude of the nearest-neighbor pairing potential. We obtain a linear

Table 1. The critical temperature T_{c0} and the initial drop $\chi = [(T_{c0} - T_c(x))/T_{c0}]/x$ in various Zn doped YBCO compounds. In constructing the table, we used $T_c(x)$ values at $x < 0.04$ for which χ is almost x independent.

Material	T_{c0} [K]	χ	Reference
$YBa_2(Cu_{1-x}Zn_x)_3O_7$	92	-13	[16]
$YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$	90	-12.3	[18]
$YBa_2(Cu_{1-x}Zn_x)_3O_7$	90	-10.5	[19]
$YBa_2(Cu_{1-x}Zn_x)_3O_7$	92	-12.3	[23]
$YBa_2(Cu_{1-x}Zn_x)_3O_7$	92	-15	[25]
$YBa_2(Cu_{1-x}Zn_x)_3O_7$	87	-8.7	[29]
$YBa_2(Cu_{1-x}Zn_x)_3O_{6.9}$	93.6	-6.8	[34]
$YBa_2(Cu_{1-x}Zn_x)_3O_{6.9}$	93	-15	[35]

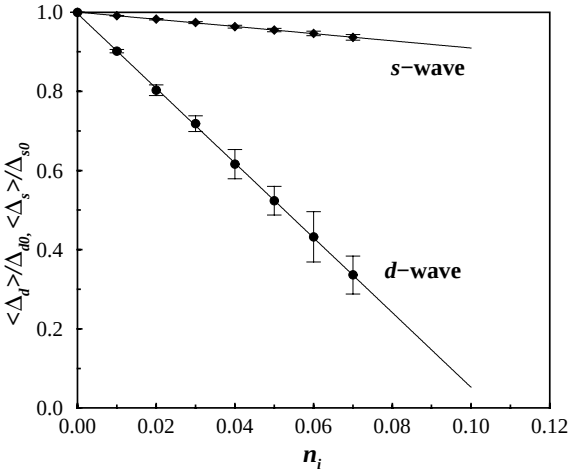

Fig. 1. Normalized s- and d-wave order parameters, $\langle \Delta_d \rangle / \Delta_{d0}$ and $\langle \Delta_s \rangle / \Delta_{s0}$, *versus* impurity concentration n_i for tetragonal structure. Δ_{d0} and Δ_{s0} are the magnitudes of the order parameters in the absence of the impurities, and $\langle \cdots \rangle$ is taken over 20 different impurity distributions. Solid lines represent the best linear fit to the data.

decrease in the mean OP, which is assumed to be proportional to the critical temperature T_c [67], and the slope of the straight line is in good agreement with the experimental data summarized in Table 1. The critical impurity or point defect concentration n_i^c at which superconductivity ceases is also near to experimental value $\simeq 0.1$. In comparing our results with experimental data we should keep the following point in our mind. For $x < 0.04$, substitutional impurities go preferentially to CuO_2 planes [16,19,45–47] and hence the actual concentration is $3x/2$. However for higher concentrations some of the Zn atoms occupy the chain sites, and in this case we cannot relate the in plane concentration to the actual one. Therefore, we used the initial points, *i.e.* $x < 0.04$, to evaluate the initial drop in Table 1. To obtain the experimental value for critical impurity concentration n_i^c, we extrapolated the linear parts of the experimental curves to intersect the impurity concentration axes.

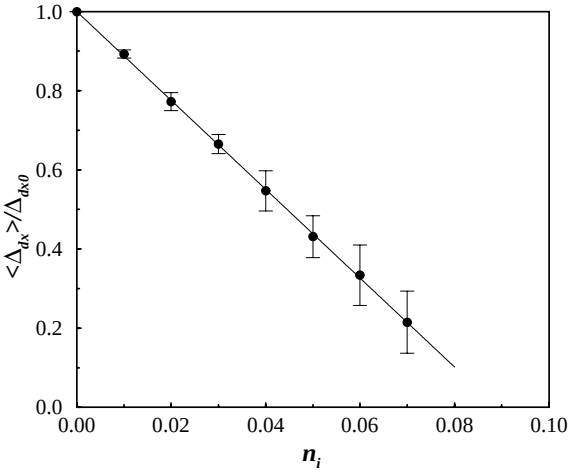

Fig. 2. Normalized order parameter *versus* impurity concentration for orthorhombic structure. Δ_{dx0} is x component of the order parameter in the absence of impurities. Solid line represents the best linear fit to the data.

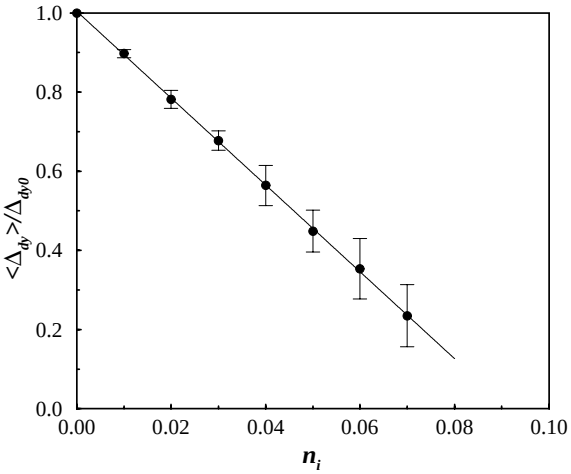

Fig. 3. Normalized order parameter *versus* impurity concentration for orthorhombic structure. Δ_{dy0} is y component of the order parameter in the absence of impurities. Solid line represents the best linear fit to the data.

Similar equations have already been solved by Xiang and Wheatley [63], however our additional self-consistency conditions and choice of parameters lead to a correct prediction for the critical impurity concentration. It is important to note that we can not have a self-consistent solution of the OP for extended s-wave by using any physical values for the above model parameters. This fact was pointed out by Wang and MacDonald [64], and they found that extended s-wave component is smaller than d-wave component by about two orders of magnitude.

When we introduce an orthorhombic distortion by taking $t_y = 1.5t_x$, as suggested by experimental data [35,48], we observe that an s-wave component (of approximately ten percent of d-wave components) is induced. Figures 2 and 3 show the variation of Δ_{dx} and Δ_{dy} components,

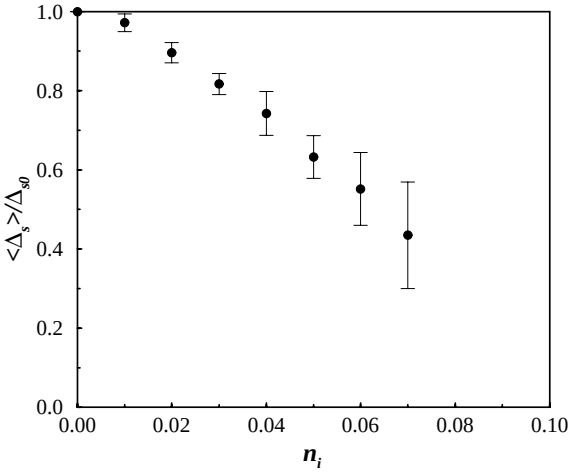

Fig. 4. Normalized s-wave component of the order parameter *versus* impurity concentration for orthorhombic structure. Δ_{s0} is the magnitude of the order parameter in the absence of impurities.

respectively. In the absence of disorder, $\Delta_{dy}/\Delta_{dx} \simeq 1.5$ with $\Delta_{dx} = 0.082t$. With increasing disorder, the larger one, *i.e.* $\langle\Delta_{dy}\rangle$, is suppressed faster. When we reach the critical impurity concentration both components vanish simultaneously. Moreover, d-wave components of the OP decrease linearly with $n_{\rm i}$ and vanish at $n_{\rm i} \simeq 0.1$ as in the case of pure d-wave symmetry. Here $\langle\cdots\rangle$ denotes averaging over 20 different impurity configurations.

As can be seen from Figure 4, s-wave component also decreases with $n_{\rm i}$, however while d-wave components exhibit a linear dependence on impurity concentration s-wave component shows a downward curvature similar to prediction of the AG theory.

In conclusion, we investigated the effects of nonmagnetic impurities and point defects within a BCS mean-field framework by means of BdG equations. For tetragonal structure, we found out that the observed suppression of superconductivity, when impurities are substituted or point defects are introduced, can be explained only if the OP is $d_{x^2-y^2}$-wave symmetric. In case of s-wave symmetry, superconductivity is almost unaffected by disorder. When a slight anisotropy is introduced by distorting copper oxide planes from a square to rectangular lattice we observed that a small amount of s-wave contribution is induced. For both tetragonal and orthorhombic structures we evaluate the critical concentration at which superconductivity ceases to be very near to experimental value $\simeq 0.1$.

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