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The effect of on-site disorder on the critical temperature in a model of high T_c superconductivity with oxygen vacancies

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Abstract. *We consider a simple model for* $La_{2-x}Sr_xCuO_{4-\delta}$ *type superconductors to describe the holes in the Cu–O plane in the presence of a dilute random distribution of oxygen vacancies and randomly distributed non-magnetic impurities in an attempt to model the high degree of spatial anisotropy found in these high temperature superconductors. The superconducting order parameter is self-consistently evaluated in the neighbourhood of the vacancies via the mean field Gorkov equations in real space. The numerical analysis suggests that high critical temperatures are conceivable within this model and indicates that significantly lower* T_c*s may be possible in the presence of non-magnetic impurities.*

1. Introduction

The new high T_c superconductors (HTSCs) are believed to possess spatial disorder at length scales comparable to the superconducting coherence length [1–3]. This issue, which may be an important feature of the HTSCs as addressed, for example, in [4], is often not addressed in simple theoretical models. This has prompted the present study of the dependence of superconductivity on the system disorder. It is perhaps easy to see that this is a difficult problem to solve, at least given the present state of knowledge on the HTSCs. We therefore attempt to make a toy model to obtain some qualitative understanding of the relationship between disorder and superconductivity in these systems. We focus our attention on $La_{2-x}Sr_xCuO_{4-\delta}$ and related substances in this article [5].

We consider a tight binding t–J type model (where J is assumed to be unrelated to the $U \rightarrow \infty$ limit of the Hubbard model) for oxide-deficient hole superconductors with a dilute random distribution of oxygen vacancies and a distribution of holes in the Cu–O plane arising from acceptor defects (see for example [6] and [7]). It has recently been shown that the oxygen vacancies may provide a plausible mechanism for pairing between such holes in the neighbourhood of the vacancies in real space (discussed in some detail in [7, 8]). This idea has already been used to obtain some insight into the high critical temperatures in these systems.

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However, it is often found that there are non-magnetic impurities (such as zinc among copper ions) in the Cu–O plane [4]. The earlier analysis [7] can be extended to include a case where there is a random distribution of non-magnetic impurities in the system. The presence of such impurities is expected to affect the on-site hole energies and their hopping integrals. To model the presence of these impurities we assume that the holes now acquire a random distribution of on-site energies and that the hopping integral remains essentially unaffected in the presence of the impurities. We further suppose that the on-site energies may be described by a probability distribution of width ε uniformly distributed about zero (like in the Anderson model of localization). A small fraction (few percent) of oxygen vacancies are assumed to act as pairing centres between the holes.

We find that a mean-field treatment of the system considered here leads to superconductivity provided the on-site disorder in hole energies is small compared with the exchange interaction between the copper ions across the random missing oxygen sites.

The presentation is arranged as follows. Section 2 focuses briefly on the Hamiltonian of our model and derives the mean-field Gorkov equations in real space for the superconducting order parameter using the standard Zubarev Green's function formalism [9]. The exchange interaction across the oxygen vacancies is unknown. Section 3.1 assumes a simple binary distribution of the exchange interaction—a strong exchange interaction across the vacancies and zero elsewhere. The model is used to present a rough estimate of the superconducting order parameter across the oxygen vacancies. Section 3.2 contains a description of an approximation scheme that enables us to calculate the superconducting order parameter self-consistently across the vacancy sites. Section 3.3 presents our numerical results and section 4 concludes with a brief discussion of our results.

2. The 'disordered *t–J* type' model

We choose a tight binding *t–J* type model (where J is assumed to be unrelated to the $U \to \infty$ limit of the Hubbard model) in the hole representation with the creation (annihilation) operators for these holes denoted by $c_{i\sigma}^{\dagger}$ ($c_{i\sigma}$) where σ is the spin index and i is the position of the hole on the Cu–O plane. The non-magnetic impurities are assumed to affect the on-site energies of the holes at the copper sites. It is difficult to determine how the hole energies may be altered due to the non-magnetic impurities. For our model we simply assume that a random distribution of hole energies with width ε uniformly distributed about zero on the copper sites adequately accounts for the on-site disorder due to such impurities.

We assume that this picture qualitatively captures the essential features of spatial disorder in the Cu–O plane at length scales comparable to the superconducting coherence length. The Hamiltonian for the model is

$$H - \mu N = \sum_{i} \varepsilon_i c_{i\sigma}^{\dagger} c_{i\sigma} + \sum_{ij} (b_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \text{Hermitian conjugate}) - \sum_{(ij)} (J_{ij}/2)(c_{i\uparrow}^{\dagger} c_{i\downarrow}^{\dagger} - c_{i\downarrow}^{\dagger} c_{j\uparrow}^{\dagger})(c_{i\downarrow} c_{i\uparrow} - c_{j\uparrow} c_{i\downarrow}) \quad (1)$$

where $\mu = \varepsilon_F$ is the Fermi energy, ε_i is the on-site hole energy, b_{ij} is the hopping integral, ij implies nearest neighbours (NNS), J_{ij} is the antiferromagnetic exchange between Cu ions and N is the total number of holes in the system.

We define the superconducting order parameter as follows

$$\Delta_{ij} \equiv \langle c_{i\uparrow} c_{j\downarrow} - c_{i\downarrow} c_{j\uparrow} \rangle \tag{2}$$

where $\langle \ldots \rangle$ implies an ensemble average in the *disordered system*. A mean-field factorization of (1) readily yields

$$H - \mu N = \sum_i \varepsilon_i c_{i\sigma}^{\dagger} c_{i\sigma} + \sum_{(ij)} (b_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \text{Hermitian conjugate})$$
$$- \sum_{(ij)} (J_{ij}/2)[\Delta_{ij}^{*} (c_{j\uparrow} c_{i\downarrow} - c_{j\downarrow} c_{i\uparrow}) - (c_{i\uparrow} c_{j\downarrow} - c_{i\downarrow} c_{j\uparrow}) \Delta_{ji}]. \tag{3}$$

To derive the mean-field Gorkov equations we start with the Green's functions for the hole operators and write as follows:

$$G_{ij}(t) = -i\Theta(t) \langle \{c_{i\uparrow}(t), c_{j\uparrow}^{\dagger}(0)\} + \{c_{i\downarrow}(t), c_{j\downarrow}^{\dagger}(0)\} \rangle \tag{4}$$

$$F_{ij}(t) = -i\Theta(t) \langle \{c_{i\uparrow}^{\dagger}(t), c_{j\downarrow}^{\dagger}(0)\} - \{c_{i\downarrow}^{\dagger}(t), c_{j\uparrow}^{\dagger}(0)\} \rangle. \tag{5}$$

The equations of motion for these Green's functions close for the mean-field Hamiltonian in (3) to yield [9],

$$i\hbar \dot{G}_{ij}(t) = 2\hbar\delta(t)\delta_{ij} + \varepsilon_i G_{ij}(t) + \sum_{\{q\}} b_{qi} G_{qi}(t) + \sum_{\{q\}} (J_{qi}/2) \Delta_{qi} F_{qi}(t) \tag{6}$$

$$i\hbar \dot{F}_{ij}(t) = -\varepsilon_i F_{ij}(t) - \sum_{\{q\}} b_{qi} F_{qi}(t) + \sum_{\{q\}} (J_{qi}/2) \Delta_{qi}^{*} G_{qi}(t) \tag{7}$$

where the overdots on the LHS of (6) and (7) mean time derivatives and $\{q\}$ represents the set of NN Cu ions with respect to site i. Equations (4) and (5) lead to the initial conditions $G_{ij}(0) = -i2\hbar\delta_{ij}$ and $F_{ij}(0) = 0$. Using these conditions, (6) and (7) may be self-consistently integrated over time to yield $\Delta_{ij}(T)$, the temperature dependent NN gap function:

$$\Delta_{ij}(T) = -i \int_{-\infty}^{\infty} \frac{\{F_{ij}(w + i\varepsilon) - F_{ij}(w - i\varepsilon)\}}{e^{\beta w} + 1} dw \tag{8}$$

where

$$F_{ij}(w + i\varepsilon) = (1/2\pi) \int_{-\infty}^{\infty} F_{ij}(t) \exp(iwt)\, dt. \tag{9}$$

The central problem in determining the superconducting order parameter for our Hamiltonian in (3) therefore concerns the self-consistent evaluation of $F_{ij}(t)$ at all lattice sites and the subsequent evaluation of (8) above.

3. The calculations

3.1. Choosing the numbers for our model

Solving (6) and (7) for a completely self-consistent evaluation of $\Delta_{qi}(T)$ for every pair of lattice sites is a very intensive computational problem. We therefore must make some assumptions to simplify the problem and yet capture the temperature dependent behaviour of the superconducting order parameter $\Delta_{ij}(T)$.

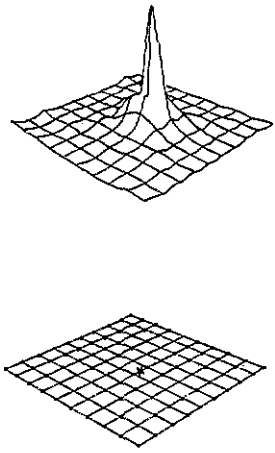

Figure 1. The upper plane presents a picture of Δ_{qi} as a function of position on the Cu–O plane. The peak height is 0.98 eV. The lower plane depicts a cross at the position of the missing oxygen site.

Let us now return to the assumption of enhanced pairing across the oxygen vacancies mentioned in section 1; this implies that the J_{ij}s are enhanced across the vacancies rather than elsewhere. As far as the author is aware, the value of J_{ij} across the oxygen vacancies is not known. In an effort to simplify the problem we select a binary distribution of values for the exchange coupling J_{ij}. We set J_{ij} equal to zero at every lattice site which is not a neighbour of a vacancy and assign it a suitable number at those lattice sites that area. Thus, if i and $\underline{i}$ are sites adjacent to a vacancy we set $J_{i\underline{i}}$ non-zero along the Cu–vacancy–Cu bonds and set it zero elsewhere. While this asssumption is qualitatively correct it is clearly an oversimplification of the problem.

The binary distribution of J_{ij} does indeed lead to superconductivity for reasonable choices of other parameters. In fact, with a constant $\varepsilon_i = 0.5$ eV, $\mu = 0$ and hopping integral $b_{ij} = 1$ eV it can be shown that the system remains superconducting at very high temperatures (~0.1 eV) when $J_{i\underline{i}} > 1.6$ eV (and zero elsewhere) for 5% vacancies on a 50×50 lattice [7]. Further dilution of the vacancy concentration and a smaller $J_{i\underline{i}}$ reduces T_c to a level consistent with experimental findings. A calculation with smaller $J_{i\underline{i}}$ [10], however, is difficult to perform self-consistently. We shall return to this point in section 3.3.

It is possible to make a qualitative estimate of the superconducting order parameter $\Delta_{i\underline{i}}$ at $T = 0$. To make such an estimate, we chose values of the parameters used in [7] (and summarized above) and performed an estimate of $\Delta_{i\underline{i}}$ on a 10×10 lattice with a single vacancy and periodic boundary condition (PBC). For large $J_{i\underline{i}}$, $F_{i\underline{i}}(t)$ decays rapidly in time. We performed a study of the short time behaviour of $F_{i\underline{i}}(t)$ and hence estimated $\Delta_{i\underline{i}}$ qualitatively. The result shows a sharply peaked function with a fast fall off to 20% of the peak value at the next nearest neighbours (NNNs) surrounding the vacancy (see figure 1). It may be noted that a completely self-consistent evaluation of $\Delta_{i\underline{i}}$ for a single vacancy in a small lattice (e.g., 10×10) with PBC does not lead to superconductivity. Superconductivity does arise, however, when there are several vacancies. The above observation may be a result of the mean field nature of the approximation [11].

Observe that a plot of the order parameter $\Delta_{i\underline{i}}$ for the more interesting case of multiple vacancies close to and far from the superconducting transition temperature (which itself is difficult to find) would undoubtedly be desirable to obtain. Such a plot would provide a clear description of the highly anisotropic nature of the order parameter

between the copper sites in the neighbourhood of, and away from, the oxygen vacancies. This would illustrate the role played by the order parameter in bringing about the superconducting transition within the context of this model. However, the making of such a plot requires a completely self-consistent evaluation of Δ_{ij} *for all* NN *copper sites* on the lattice. Such a calculation, estimating the relief of the order parameter on the 2D lattice for multiple vacancies, would be very difficult for a lattice of reasonable size and hence is not available at the present time.

Our choice of parameters for the disordered t–J model is based on the calculations described at the beginning of this section. We will return to the details of our results in section 3.3 below.

3.2. The random phase averaging technique

As pointed out in section 1 it is computationally intensive to evaluate Δ_{qi} self-consistently across every pair of NN Cu sites. Thus, it is essential to further simplify our problem. We therefore choose to calculate Δ_{qi} self-consistently only across the sites adjacent to oxygen vacancies. Such a calculation does not imply that Δ_{qi} is zero everywhere except across the vacancies, but that it is self-consistent across the vacancies only. Since we already qualitatively know that Δ_{ij} is large across the vacancies compared with elsewhere, the above calculation should yield an order parameter and a T_c that is reasonable and perhaps comparable to a fully self-consistent calculation.

We peform our calculations under the above mentioned simplification using the well known 'random-phase averaging technique'. This method has often been used in computing properties of disordered systems (see for example [7, 12, 13]). In this technique the total number of equations to be self-consistently solved is reduced by solving directly for

$$F_i(t) = \sum_j c_j F_{ij}(t) \qquad G_i(t) = \sum_j c_i G_{ij}(t)$$

instead of $F_{ij}(t)$ and $G_{ij}(t)$, respectively. Thus, the initial conditions now become $F_i(0) = 0$ and $G_i(0) = -i2\hbar c_i$. To calculate Δ_{ij} self-consistently the c_is are chosen as follows: all c_is with i not adajacent to a vacancy are set to zero and to the rest a random phase φ_i, uniformly distributed between 0 and 2π, are assigned. To see this, consider a pair of Cu sites next to a vacancy and label them 1 and 2. Now, set $c_1 = \exp(i\varphi_2)$ and $c_2 = \exp(i\varphi_1)$, etc. These phase factors are merely calculational devices and the above choice of phases reflects our intention to evaluate Δ_{ij} self-consistently only at the vacancy sites [7, 12, 13]. With $F_r(t) \equiv \Sigma_i \exp(-i\varphi_i)F_i(t)$ the gap equation may be written as [7]

$$\Delta_{ij}^{*}(T, N_v) = (-1/2N_v\beta h)\int_0^{\infty} [F_r(t)/\sinh(t\pi/\beta h)]\,dt \tag{10}$$

where N_v is the number of oxygen vacancies and $\beta = 1/k_B T$, k_B being the Boltzmann constant.

3.3. Results

We have solved for Δ_{ij} self-consistently in (6) and (7) using the random phase averaging technique described in section 3.2. The lattice size was chosen to be 50×50 (i.e., 50 Cu ions along each side) and PBC was used.

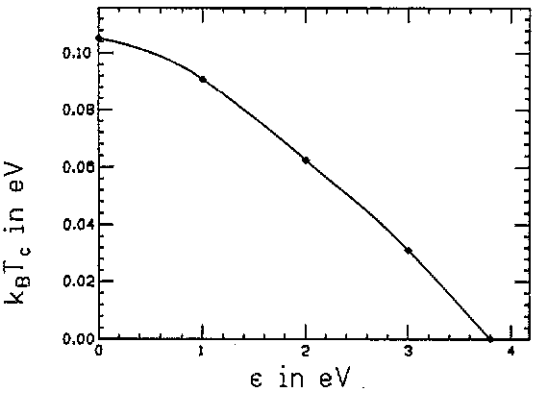

Figure 2. Graph of $k_B T_c$ versus the disorder parameter ε in eV. Each of the T_cs are averaged over several independent calculations. The values of the model parameters are given in the text. The T_cs for $0 \leqslant \varepsilon \leqslant 3$ eV are more reliable than that for T_c at $\varepsilon = 3.8$ eV.

Our choice of the model parameters is described as follows. The random on-site energies are chosen to be $\varepsilon_i = \varepsilon(R_i - 0.5)$, $0 \leqslant \varepsilon \leqslant 4$ eV, R_i being a random number between zero and one. We chose $b_{ij} = 1$ eV and a binary distribution of J_{ij}s with $J_{ji} = 1.65$ eV across the vacancies and zero elsewhere on the lattice. The Fermi energy was chosen to be zero and the vacancy concentration was kept at 3%. The choice of parameters was similar to those in [7] except for that of ε_i [14].

The time integration was carried out in steps of 0.0225 in units of $1/b_{ij}$ up to 400 time steps. We have also carried out these calculations by reducing the step size to 0.012 $(1/b_{ij})$. The results remain invariant under such refining. By evaluating $\Delta_{ji}(T)$ self-consistently with an accuracy of one part in 10^{-4} at progressively higher temperatures starting from $T = 0$ it is possible to establish a critical temperature T_c such that for $T \geqslant T_c$, $\Delta_{ji}(T) = 0$. We found that for $\varepsilon \geqslant 3.8$ eV it is difficult to calculate a non-vanishing $\Delta_{ji}(T)$ self-consistently for the chosen set of parameters in this model. The behaviour of T_c versus ε is given in figure 2. The calculations presented here can be further improved by averaging over a very large number of disorder configurations which has been kept small for practical computational reasons. Some preliminary calculations using a very large number of disorder configurations indicate that figure 2 will remain essentially invariant under such refinement.

Observe that the choice of $J_{ji} = 1.65$ eV across the vacancies and zero elsewhere is possibly large in view of the small J_{ij} values that are usually considered ($J_{ij} \sim 0.1$ eV or so [15] when there are no vacancies, the value of J_{ji} across oxygen vacancies is presently unknown). As mentioned in section 3.1, it is computationally difficult to calculate $\Delta_{ji}(T)$ self-consistently for small J_{ij}s. Some of our insights and expectations, albeit qualitative, for small J_{ji} values are sketched below.

We have already performed some preliminary calculations of $F_r(t)$ for $\mu = 0$, $b_{ij} = 1$ eV and $2 \leqslant \varepsilon \leqslant 4$ eV, $1 \leqslant J_{ji} \leqslant 4$ eV, where the on-site energies were kept constant (i.e., the effects of magnetic impurities were ignored). The results show that $F_r(t)$ is strongly oscillatory with a weak power law decay in time for small J_{ji} and given ε. Furthermore, it appears that $F_r(t)$ possesses a progressively weaker peak at $t = 0$ as well as a slower power law decay with decreasing J_{ji} for constant ε. The long lived nature of $F_r(t)$ renders the computational problem of the self-consistent calculation of Δ_{ji} (which involves an integration of $F_r(t)$ over all positive times, see (10)) very difficult. Precise numbers for T_c are hence difficult to estimate.

Our preliminary analysis based on the nature of the area cancellations in the $F_r(t)$ versus t plot suggest that T_c may be much lower than the high estimates obtained from

the calculations reported here with high values of J_{ii}. The decrease in T_c can be 40% or more compared with the estimates presented in figure 2, and thus are in a regime that is close to the experimentally observed T_c. Because of these difficulties it may be said that providing a curve such as the one in figure 2 for J_{ii} values as small as 1.0 eV or 0.5 eV requires solving a problem that turns out to be intrinsically more challenging than the one described here. Such an effort will only be warranted if a direct comparison between the calculations and experiments is possible.

It is important to note the simplicities and drawbacks of the simple model discussed in this work. We summarize these in the following paragraphs.

The present model completely neglects any possible coupling between the vacancies via the copper spins. However, it is important to recognise that the concentration of the randomly distributed vacancies considered in this model is very low, typically not in excess of 5%. In the present work the vacancy concentration was kept at 3% which is also close to experimental numbers. Thus, the vacancies are too few and far between to have any significant adverse effect (due to any vacancy–vacancy coupling) on the estimation of the order parameter on the lattice.

The self-consistent calculation of the order-parameter is a difficult problem for high vacancy concentrations. The difficulties arise from the proximity of the vacancies to each other and from the subsequent corrections to the order prameter in the neighbourhood of the multiple vacancies. This is a difficult problem to handle and remains to be addressed.

Another important factor in our calculations has been the assumption that $J_{ij} = 0$ for (i, j) not adjacent to a vacancy. Allowing for a small J_{ij} between these copper sites will most likely enhance the order parameter throughout the system. Therefore, a calculation such as the one presented here (with self-consistency restricted to sites near the oxygen vacancies) is a sensible description of the real physical system only to the zeroth order in (J_{ij}/J_{ii}), where (i, j) are the copper sites not adjacent to a vacancy. A detailed calculation showing the effects of non-vanishing coupling between the copper sites, however, would complicate the self-consistency calculation significantly and still remains to be carried out. Given the assumption that enhanced pairing across the oxygen vacancies is the most important aspect of this model, it is possible that an increased J_{ij} for all sites not adjacent to a vacancy for fixed J_{ii} might suppress T_c for this model.

4. Discussion

To summarize, we observe that T_c is sensitive to the presence of non-magnetic impurities in the Cu–O plane in $La_{2-x}Sr_xCuO_{4-\delta}$ and related HTSCs. A wide distribution of on-site hole energies about zero tends to suppress and eventually kill superconductivity in these materials within the context of the present model. Further, T_c is quite sensitive to the magnitude of the exchange parameter J_{ij}. We emphasize that all the calculations reported here are mean-field in character and hence fail to treat the quantum fluctuations properly. One way to extend these calculations beyond the mean-field approximation would be to solve for $c_{i\sigma}(t)$ (or $c^{\dagger}_{i\sigma}(t)$) under certain simplifying conditions for the Hamiltonian in (1) and hence to calculate $\Delta_{ij}(T)$ for all T (for related work along these lines for other simple models see [16]). Such a calculation would be very difficult even with the rather

sophisticated modern tools of non-equilibrium many-body theory [17]. Approximate calculations along these lines are in progress.

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References

[1] Müller K A, Takashige M and Bednorz J G 1987 *Phys. Rev. Lett.* **58** 1143
[2] Maeno Y and Fujita T 1988 *Physica* C **153** 1105
[3] Cava R J, van Dover R B, Batlogg B and Rietman E A 1987 *Phys. Rev. Lett.* **58** 408
[4] Xiao G, Cieplak M Z and Chien C L 1990 *Phys. Rev.* B **42** 240
[5] Cheng S W, Thompson J D and Fisk Z 1989 *Physica* C **158** 109
[6] Jarrel M, Cox D L, Jayaprakash C and Krishnamurthy H R 1989 *Phys. Rev.* B **40** 8899
[7] Halley J W and Shore H B 1988 *Phys. Rev.* B **37** 525
[8] Halley J W, Davis S, Samsel P and Joynt R *Proc. of Int. Conf. On Superconductivity (Bangalore, India, 1990)* to be published
[9] Zubarev D N 1960 *Sov. Phys.–Usp.* **3** 320
[10] Sen S, Davis S and Halley J W unpublished
[11] Shore H B private communication
[12] Alben R, Blume M, Krakauer H and Schwartz L 1975 *Phys. Rev.* B **12** 4090
[13] Halley J W and Shore H B 1987 *Phys. Rev.* B **36** 6640
[14] Halley J W, Davis S and Sen S *Proc. of Int. Conf. on Low Temp. Phys. (Cambridge, 1990)* vol. LT **19** (Amsterdam: North-Holland)
[15] Mila F 1988 *Phys. Rev.* B **38** 11358
[16] Sen S 1990 *PhD Thesis* The University of Georgia
[17] Lee M H 1987 *Phys. Scr.* **T19** 497