Effect of disorder on the resonating-valence-bond model of high-temperature superconductivity: Relationship to experiments

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Nonmagnetic disorder is shown to be pair breaking in the resonating-valence-bond model which has been proposed as a theoretical description of the recently discovered high-temperature superconductors. We calculate its effect on the superconducting transition temperature T_c and on the excitation gap in the superconducting density of states. We also include a discussion of the large number of recent experiments investigating suppression of T_c and discuss the relevance of the present calculation to these experiments.

I. INTRODUCTION

The recent discovery of high-temperature superconductors with transition temperatures in the 90 K range (the $Y_1Ba_2Cu_3O_{7-y}$ series) and also in the 40 K range [the $(La_{1-x}(Ba,Sr)_x)_2CuO_{4-y}$ series] has provoked an intense experimental effort to elucidate their properties. Several theoretical models[1-6] have been proposed as starting points for describing the superconductivity in these materials based on pairing mechanisms that do not include the conventional electron-phonon coupling of standard Bardeen-Cooper-Schrieffer (BCS) theory. The need to consider exotic pairing mechanisms is motivated by the very high transition temperatures in these materials and by the very weak isotope effect associated with the oxygen atoms.[7,8] In this paper, we will concentrate on several closely related theoretical models which are based on a pairing mechanism that is magnetic in origin and can be loosely described as being mediated by the superexchange interaction between neighboring electrons.

We use the name resonating valence bond (RVB) model[1] for this group of theoretical models because of the proposal that under certain conditions, i.e., where frustration might inhibit the establishment of long-range antiferromagnetic order, the normal state described by these models consists of a superposition of singlet bonds resonating between different sites.[1]

This group of theoretical models is based on the Hubbard Hamiltonian and all lead to superconducting order parameters which are momentum dependent and some of which can be anisotropic on the Fermi surface. Therefore, an obvious issue to explore is the extent to which nonmagnetic disorder is pair breaking in these models and to examine the possibility of how this could explain the observation of T_c suppression in the experimental investigations mentioned above.

This paper examines this issued by examining the nature of pair breaking as a result of nonmagnetic disorder in the RVB model with a calculation of the effect of disorder on T_c and on the excitation gap in the superconducting density of states. Then we present an overview of the large number of experiments investigating variations in T_c. These experimental studies can be divided into three groups, those investigating the role of oxygen content on the superconducting properties, those investigating the effect of substitutions for Cu on superconductivity, and the influence of fast neutron irradiation on the materials. We list the explanations that have been put forward to account for the results of these experiments and indicate those features that are relevant to the pair breaking mechanism proposed in this paper.

II. THEORY

A. Review of the RVB model

The Hubbard model in the nearly-half-filled limit has been proposed as a starting point to describe the new high-T_c materials, this choice being motivated by the very high normal-state resistivities ρ_N of the materials just above T_c indicating that they are close to a metal-insulator transition.

Stronger motivation for considering a strongly correlated model follows from a comparison of the experimental Hall coefficients and thermopower with expectations from band-structure calculations.[9] The latter give a half-filled electron band for La_2CuO_4 which would give Hall coefficients and thermopowers corresponding to negative carriers; experiment gives positive carriers with vanishing inverse Hall coefficients at half filling. As there appears to be no gap opening transition giving this behavior, the more likely origin is a Mott-Hubbard metal-insulator transition at half filling.

The Hubbard Hamiltonian is given by

$$H = -t\sum_{\langle ij\rangle,\delta}(c_{i\delta}^{\dagger}c_{j\delta}+\text{H.c.})+U\sum_i n_{i\uparrow}n_{i\downarrow}\ , \qquad (1)$$

where t is the intersite hopping matrix element, U is the intrasite Coulomb repulsion, and $c_{i\delta}^{\dagger}$ creates a charge carrier on site i. The sum over $\langle ij\rangle$ is over nearest neighbors.

The intrasite Coulomb repulsion is believed to be large in these materials and, therefore, to proceed further with Eq. (1) the constraint of no double occupancy on site i is imposed. This is done by performing a canonical transformation on H yielding an effective Hamiltonian that operates on the space of nondoubly occupied sites.[10] A new quasiparticle operator is introduced, denoted by $f_{i\delta}$, related to the original $c_{i\delta}$ by $c_{i\delta}=b_i^{\dagger}f_{i\delta}$ where b_i is a boson

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operator that enforces the single occupancy constraint via $\sum_\delta f_{i\delta}^\dagger f_{i\delta}+b_i^\dagger b_i=1$. Performing a Hartree-Fock factorization[1,2] yields an effective Hamiltonian that we work with from now on:

$$H=\sum_{k\delta}\xi(k)f_{k\delta}^\dagger f_{k\delta}-J\sum_k\tau(k)(\Delta^* f_{-k\downarrow}f_{k\uparrow}+\text{H.c.}) \ . \tag{2}$$

Equation (2) describes a system of interacting quasiparticles $f_{k\delta}$ with normal-state quasiparticle energy $\xi(k)=-t\delta\tau(k)-\mu$ where $\tau(k)=2[\cos(k_xa)+\cos(k_ya)]$. μ is the chemical potential of the system determined by δ, which defines the deviation of each site i in the original Hubbard model from unity where we are using the mean-field identification of $b_i=\delta^{1/2}$. Thus, δ is given by $\langle n_i\rangle=\sum_\delta\langle f_{i\delta}^\dagger f_{i\delta}\rangle=1-\delta$. The $f_{k\delta}$ quasiparticles which exist in an energy band of width $8t\delta$ experience an attractive interaction $J=4t^2/U$ between the time reversed states $f_{-k\downarrow}$ and $f_{k\uparrow}$. Thus, the Hamiltonian described by Eq. (2) has a superconducting instability built into it. It should be noted that the attractive pairing interaction J exists over the full bandwidth $8t\delta$. A contribution from pair hopping can also be including in Eq. (2), leading to a term in the pairing interaction which is dependent on δ.[2] This does not alter the basic conclusions of this calculation.

Before discussing the superconducting state, the nature of the normal state particularly at $\delta=0$ is worth discussing. At $\delta=0$ the bandwidth shrinks to zero and the system is that of a set of localized spins interacting via J. The detailed nature of the ground state is not completely clear. On a two-dimensional square lattice the possibility of long-range antiferromagnetic order exists in the original Hubbard model.[11] With frustration, however, Anderson has proposed a state of singlet bonds resonating between sites, the resonant valence bond (RVB) state.[1] The excitations of this system would be spin fluctuations whose detailed character has not been completely worked out.[12] However, it is claimed that they would give rise to a linear term in the specific-heat capacity which appears to be seen experimentally.

The density of states of the two-dimensional system in the normal state described by Eq. (2) is obtained from $N_n(\varepsilon)=\sum_k\delta[\varepsilon-\xi(k)]$ yielding

$$N_n(\varepsilon)=\frac{1}{2\pi^2\delta t}K(y) \ , \tag{3}$$

where $y^2=1-|(\varepsilon+\mu)/(4\delta t)|^2$ and $K(y)$ is the complete elliptic integral.

Away from the half-filled case we can investigate the superconductivity indicated by Eq. (2) by diagonalizing the Hamiltonian to yield

$$H=\sum_{\alpha=0,1,k}E(k)\gamma_{k\alpha}^\dagger\gamma_{k\alpha}$$

where

$$E(k)=[\xi^2(k)+J^2\Delta^2\tau^2(k)]^{1/2} \ ,$$

and where T_c is obtained from

$$\Delta=\left[\sum_k\tau(k)\langle f_{-k\downarrow}f_{k\uparrow}\rangle\right]\Big/4 \ .$$

The superconducting order parameter is defined as

$$J\Delta\tau(k)=A\xi+\Lambda \ , \tag{4}$$

where $\Lambda=-J\mu\Delta/\delta t$ and $A=-J\Delta/\delta t$ denotes the slope of the order parameter with respect to energy $\xi(k)$. The energy dependence of the RVB order parameter produces a more complex T_c equation than the BCS theory and is the origin of pair breaking due to nonmagnetic disorder. The chemical potential μ is derived from the filling condition $\langle n_i\rangle=\sum_{k,\delta}\langle f_{i\delta}^\dagger f_{i\delta}\rangle$ which yields

$$\delta=\int_{-4t\delta-\mu}^{4t\delta-\mu}d\xi N_n(\xi)\tanh\frac{\xi}{2T_c} \ . \tag{5}$$

The RVB theory predicts a nonzero $T_c=J/4$ at $\delta=0$ where the system should be insulating and should therefore display no superconductivity. Fluctuations around the mean-field solution described above may cause T_c to drop to zero continuously as δ approaches zero. A more sophisticated development of the RVB theory[13] describes it in terms of a local U(1) gauge symmetry which, upon doping away from half filling, may be broken by a superconducting transition at a temperature proportional to δ. An alternative hypothesis[14] indicates that at $\delta=0$ antiferromagnetic long-range order develops and is favored over superconductivity driving T_c to zero at $\delta=0$. Another approach,[15] starting with the RVB Hamiltonian, involves the use of coherent-potential-approximation (CPA) to evaluate the particle-particle kernel in the T_c equation and leads to T_c which is zero for sufficiently small carrier density. The key idea of the present calculation of disorder effects lies in the $\xi(k)$ dependence of the order parameter and this general feature is not dependent on any particular resolution of the $\delta=0$ issue.

B. Effect of disorder on superconductivity in the RVB model

In the presence of disorder, the superconducting order parameter is defined by the ansatz

$$\tilde\Delta=A\xi+\tilde\Lambda \ , \tag{6}$$

which provides a consistent way to calculate the effect of disorder on the order parameter. The quasiparticle frequency ω_n is also renormalized. The effect of disorder is calculated in the self-consistent Born approximation where the disorder is modeled by a scattering potential V, which is assumed constant in momentum space.[16]

In order to obtain some insight into the effects of pair breaking, we examine the region away from half filling approximately, replacing the normal-state density of states by its value at the chemical potential and temporarily extending the bandwidth from minus to plus infinity. More exact numerical results will be presented shortly. For the moment, this gives a crude idea of the effects of disorder on the superconducting density of states $N_s(\omega)$. The coupled self-consistent equations for $\tilde\omega_n$, where $\omega_n=(2n+1)T\pi$ is the quasiparticle frequency, and

$\tilde{\Lambda}$ are[16]

$$\tilde{\omega}_n = \omega_n + V^2 N_n(\mu) \int_{-\infty}^{\infty} d\xi \frac{\tilde{\omega}_n}{\tilde{\omega}_n^2 + \xi^2 + (A\xi + \tilde{\Lambda})^2} , \quad (7)$$

and

$$\tilde{\Lambda} = \Lambda + V^2 N_n(\mu) \int_{-\infty}^{\infty} d\xi \frac{(A\xi + \tilde{\Lambda})}{\tilde{\omega}_n^2 + \xi^2 + (A\xi + \tilde{\Lambda})^2} . \quad (8)$$

Equations (7) and (8) can be rewritten as

$$\frac{\tilde{\omega}_n}{\tilde{\Lambda}} = u(\omega_n) = \frac{\omega_n}{\Lambda} + \frac{1}{2\tau\Lambda} \frac{A^2}{1+A^2} \frac{\tilde{\omega}_n}{[\tilde{\omega}_n^2(1+A^2) + \tilde{\Lambda}^2]^{1/2}} , \quad (9)$$

where $1/2\tau = \pi V^2 N_n(\mu)$. Thus, in the case of a constant order parameter (in this case this would mean $A = 0$), the pair-breaking effect indicated by Eq. (9) is zero as expected from Anderson's theorem. Note also that as Δ approaches zero the pair breaking effect in Eq. (9) also disappears. Finally, it is worth noticing that as $\delta \rightarrow 0$, $N_n(\mu)$ diverges and a full T matrix approach for treating the scattering due to disorder is required.

In the absence of disorder, the superconducting density of states is

$$N_s(\omega) = N_n(\mu) \operatorname{Re} \left(\frac{\omega}{[\omega^2(1+A^2) - \Lambda^2]^{1/2}} \right) , \quad (10)$$

where $\Lambda = \mu A$. Thus, Eq. (10) implies an excitation gap given by $\Delta_{\text{gap}} = |\mu A| / (1+A^2)^{1/2}$ in the absence of disorder. When disorder is present, Eq. (9) shows that the excitation gap is reduced according to the usual pair breaking form familiar from magnetic scattering[16,17] as

$$\tilde{\Delta}_{\text{gap}} = \Delta_{\text{gap}} \left[1 - \left(\frac{1}{2\tau\Lambda} \frac{A^2}{(1+A^2)} \right)^{2/3} \right]^{3/2} . \quad (11)$$

Note that as was stated earlier, pair breaking effects in the density of states vanish as $\Delta \rightarrow 0$.

Even though pair breaking effects on $N_s(\omega)$ vanish as $\Delta \rightarrow 0$, the T_c equation is modified by pair breaking due to the structure of the equation itself which is given by

$$1 = \frac{T}{4\delta t} \sum_n \int_{-4t\delta-\mu}^{4t\delta-\mu} \frac{N_n(\mu)[\xi^2 J/\delta t - \tilde{\Lambda}\mu/\Delta - \xi(\tilde{\Lambda}/\Delta - J\mu/\delta t)]}{\tilde{\omega}_n^2 + \xi^2} . \quad (12)$$

As was noted earlier from Eq. (9) at T_c, $\tilde{\omega}_n/\tilde{\Lambda} = \omega_n/\Lambda$. Thus, using this fact and replacing $\tilde{\omega}_n$ by $\omega_n + 1/2\tau$ yields a T_c equation

$$1 = \frac{T_c J}{4\delta^2} \int d\xi N_n(\xi) [\mu^2(S_1 + S_2/2\tau) + \mu\xi(2S_1 + S_2/2\tau) + \xi^2 S_1] , \quad (13)$$

where

$$S_1 = \frac{1}{t^2} \sum_n \frac{1}{(\omega_n + 1/2\tau)^2 + \xi^2} , \quad (14)$$

which can be summed to give

$$S_1 = \frac{i(Y_- - Y_+)}{2t^2 \xi T_c \pi} , \quad (15)$$

and where

$$S_2 = \frac{1}{t^2} \sum_n \frac{1}{\omega_n [(\omega_n + 1/2\tau)^2 + \xi^2]} , \quad (16)$$

which can be summed to give

$$S_2 = i \frac{1/2\tau(Y_+ - Y_-) - i\xi(Y_+ + Y_-) + 2i\xi\Psi\frac{1}{2}}{2t^2\pi\xi T_c[(1/2\tau)^2 + \xi^2]} , \quad (17)$$

where

$$Y_- = \Psi[\tfrac{1}{2} + 1/(2\pi T_c)(1/2\tau - i\xi)]$$

and where

$$Y_+ = \Psi[\tfrac{1}{2} + 1/(2\pi T_c)(1/2\tau + i\xi)] .$$

In the small δ limit, the term in Eq. (13) that contributes most is

$$1 = \frac{T_c J}{4\delta^2} \int d\xi \xi^2 N_n(\xi) S_1 , \quad (18)$$

which yields

$$1 = \frac{2J}{(4\delta t)^3} \int d\xi \frac{i\xi(Y_- - Y_+)}{2\pi} , \quad (19)$$

where the density of states $N_n(\xi)$ has been approximated by $1/(8t\delta)$. Equation (19) can be examined analytically in the small scattering limit $1/2\tau \ll T_c$, and also using $\xi \ll T_c$. Expanding the digamma function yields[18]

$$\frac{\delta T_c}{T_{c0}} \simeq \frac{1.0 + 8.85(t\delta/J)^2}{\tau J} . \quad (20)$$

To go beyond the small δ limit and for larger values of $1/2\tau$ Eq. (13) must be solved numerically in conjunction with Eq. (5) for μ. Disorder can be incorporated into μ by replacing $\tanh(\xi/2T)$ by $(Y_+ - Y_-)/(\pi i)$. However, this results in negligible changes in the results. T_c curves for $J/4 = 0.2$ and 0.3, and $1/(2t\tau) = 0$, 0.02, 0.1 are shown in Fig. 1. At δ close to 0, Eq. (20) is a good approximation for the effect of disorder for $1/2\tau$ values, measured in units of t, even as large as 0.1.

The inclusion of the recently proposed d-wave solution for the order parameter in the RVB theory[19] produces qualitatively similar results with changes in the numerical coefficients in Eq. (20), and a less rapid suppression with increasing δ.[18] However, the inclusion of pair hopping[2] reverses the stability of the extended s- and d-wave states for low δ leading us back to the same qualitative conclusions discussed above.

A group theoretical classification[20] of possible superconducting order parameters in the case of orthorhombic

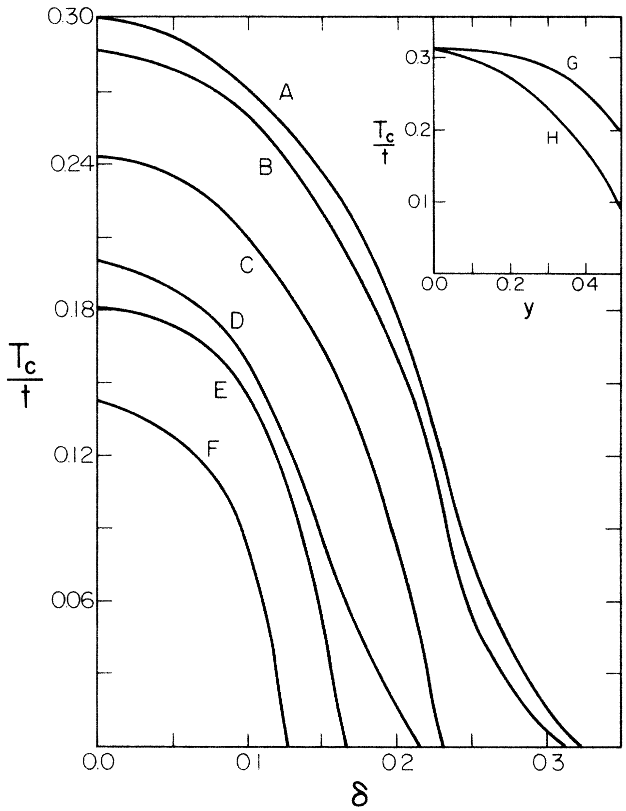

FIG. 1. T_c vs δ for several values of $J/4$ and $1/2\tau t$. Curves A, B, and C correspond to $J/4=0.3$ and $1/2\tau t=0.0$, 0.02, 0.1, respectively. Curves D, E, and F correspond to $J/4=0.2$ and $1/2\tau t=0.0$, 0.02, 0.1, respectively. In the inset T_c is shown as a function of oxygen content y in $Y_1Ba_2Cu_3O_{7-y}$ calculated from Eq. (13) with $J/4=0.5$ and $1/2\tau_0 t=1.0$, and 1.25 in curves G and H, respectively.

symmetry concludes that extended s-wave and d-wave states occur within the same representation of the point group D_{2h} for this symmetry. This would result in mixing between extended s- and d-wave-type order parameters and, thus, both types of order parameters would need to be considered in a more complete calculation of pair-breaking effects.

The calculation has up to now only considered nonmagnetic disorder. An obvious issue in light of some of the experiments which we will discuss next is the effect of pair-breaking from magnetic impurities. In the small δ limit, T_c is determined mainly by Eq. (18), which, as can be seen, depends only on $\omega_n+1/2\tau$. Therefore, the effect of magnetic pair breaking will be additive in this limit with $1/2\tau$ being replaced by $1/2\tau+1/2\tau_{\text{magnetic}}$. At larger values of δ the other terms in Eq. (13) make a contribution in the calculation of T_c but the observation that the magnetic pair breaking adds linearly to $1/2\tau$ should be a good approximation still.

III. RELATIONSHIP TO EXPERIMENTS

Several experimental studies examining variations in superconductivity in the new high-T_c materials have also observed reductions in the transition temperature which may be partly explained by a pair-breaking mechanism. These experiments can be divided into three groups, those involving substitutions for Cu in both $(La_{1-x}(Sr,Ba)_x)_2CuO_{4-y}$ and $Y_1Ba_2Cu_3O_{7-y}$, irradiation by fast neutrons and variations in oxygen content y.

A. Results for T_c suppression: Comparison with Cu substitution experiments

A quantitative link between reductions in T_c and the predictions of the present theory can be established by using Eq. (20). As can be seen from Fig. 1, this provides a good estimate of the extent of T_c suppression due to disorder over a wide range of values of $1/2\tau$ at small δ. From Eq. (20), the transition temperature will be reduced to half of its original value T_{c0}, when the mean-free path for scattering from disorder $l=v_F\tau$ decreases to half the superconducting coherence length $\xi_0=v_F/T_{c0}$. Estimates for ξ_0 for $Y_1Ba_2Cu_3O_{7-y}$ in particular have been obtained from an analysis of upper critical-field measurements, yielding a value of ξ_0 of between 7 and 34 Å,[21] for superconductivity perpendicular to and parallel to the basal plane, respectively. For the present discussion, we use the value 20 Å as an approximate guide for ξ_0 for both the $(La_{1-x}(Ba,Sr)_x)_2CuO_{4-y}$ and $Y_1Ba_2Cu_3O_{7-y}$ superconductors. Anisotropy of the superconductivity in the basal plane relative to the c axis of $Y_1Ba_2Cu_3O_{7-y}$ is an interesting complication which we have not yet incorporated in the present pair-breaking mechanism but which will not affect the present discussion.

Using a simple Drude expression for the resistivity in the normal state just above T_c, $\rho_N=(3\pi/2)h/[(ek_F)^2 l]$ and estimating k_F from $k_F^3/3\pi^2=n$ where n is the carrier concentration, which from Hall coefficient measurements has been estimated as approximately 10^{21} cm^{-3},[22] we see that an increase in ρ_N due to disorder of 1000 $\mu\Omega$ cm would correspond to a value for l of 10 Å approximately. Therefore, the observation of an increase in ρ_N of 1000 $\mu\Omega$ cm should coincide with an approximate reduction in T_c from 40 to 20 K in the case of $La_{2-x}Sr_xCuO_{4-y}$ or from 90 to 45 K in $Y_1Ba_2Cu_3O_{7-y}$. Approximate values for ρ_N are obtained from estimates of the resistivities just about T_c. This estimate for the suppression of T_c is in reasonable agreement with Cu substitution experiments on $(La_{1-x}(Ba,Sr)_x)_2CuO_{4-y}$, where in substituting Ni for Cu, an increase in ρ_N from approximately 200 to 700 $\mu\Omega$ cm is accompanied by a decrease in T_c from 39.3 to 22.6 K.[23] Similarly, in substituting Zn for Cu, an increase of ρ_N from 200 to 1000 $\mu\Omega$ cm is accompanied by a decrease in T_c from 39.3 to 15 K.[23] In substituting Ni for Cu in $Y_1Ba_2Cu_3O_{7-y}$, T_c drops from 90 to 50 K with an accompanying rise in ρ_N from 1000 to 2000 $\mu\Omega$ cm approximately.[23] While the agreement between the present theory and the experiments is only approximate, it is evident that a semiquantitative explanation of some of the observed reductions in T_c is within the scope of the present pair breaking mechanism.

One further indication that a nonmagnetic pair-breaking mechanism is the source of the observed T_c

reduction arises in the Cu substitution experiments where nonmagnetic Zn produces a more rapid decline in T_c than Ni which normally does have a magnetic moment.[24–26] This has been linked to the observation that while La_2ZnO_4 exists, it does so with a structure different to La_2NiO_4, hinting that the source of the T_c suppression has its origin in disorder that may accompany lattice distortion. It has been observed that lattice distortion does indeed accompany T_c reduction in these experiments, as measured by a decreasing c/a ratio and changes in unit cell volume.[24] However, it should be noted that possible long-range strain fields introduced by strong distortion of the lattice may not be linear in the impurity concentration and, thus, may not be realistically treated within the present simplified model. An orthorhombic-to-tetragonal lattice transition is also observed when substituting Fe, Co, Ni, and Ga in the 90 K materials.[26] Substituting both Zn and Ni for Cu does eventually appear to induce a magnetic moment in the samples,[23] as deduced from susceptibility measurements; however, these moments do not appear to be detectable in the samples until the superconductivity is almost completely destroyed.

B. Effect of fast neutron irradiation on T_c

Another group of experiments makes use of irradiation by fast neutrons to study variations in T_c. This should provide the cleanest method to study the effect of disorder on T_c, in conjunction with the predictions of the present theory, since other complications such as changes in carrier concentration or magnetic moments would not be induced in the samples. In these experiments, it is observed that T_c decreases linearly with increasing neutron flux, and hence increasing disorder, from 90 to 65 K in $Ho_1Ba_2Cu_3O_7$ and from 40 to 0 K in $La_{2-x}Sr_xCuO_4$.[27] For irradiation on $Y_1Ba_2Cu_3O_{7-y}$ at a lower temperature the reduction in T_c is less pronounced, going from 90 to 86 K.[28] It would be interesting to accompany irradiation by neutrons with measurements of ρ_N in order to test the proposed pair-breaking mechanism further.

C. Effect of oxygen depletion and oxygen order-disorder on T_c

The influence of variations in oxygen content on the superconducting properties of $Y_1Ba_2Cu_3O_{7-y}$ and $[La_{1-x}(Sr,Ba)_x]_2CuO_{4-y}$ has been the subject of a large number of experiments.[29–33] In $Y_1Ba_2Cu_3O_{7-y}$, it is experimentally observed that as y increases from 0 to 1, T_c drops from 90 K to less than 20 K.[29,30] The rate at which T_c decreases depends on the way in which the oxygen content is varied, with experiments involving gettering with Zr observing a saturation of T_c at about 60 K for y between 0.2 and 0.4,[29] while studies using samples produced by quenching see a steady decrease.[33] All these studies indicate a lattice structural transition from orthorhombic-to-tetragonal symmetry at approximately y greater than 0.5, accompanied by an increase in the Hall coefficient. Furthermore, as the oxygen content is decreased the resistivity ρ_N increases in the case of $Y_1Ba_2Cu_3O_{7-y}$ jumping from 0.5 mΩ cm where T_c is 90 K to 9.0 mΩ cm when T_c has dropped to about 25 K.[29]

The removal of oxygen from $Y_1Ba_2Cu_3O_{7-y}$ creates randomly distributed oxygen vacancies along the one-dimensional Cu-O1 chains. In the vicinity of the orthorhombic-to-tetragonal lattice transition in this material, when y increases beyond 0.5, both of the oxygen sites in the basal plane become equally occupied. The disorder introduced by the random configuration of oxygen vacancies would play a role in suppressing T_c via a pair breaking mechanism of the kind discussed in the present calculation.

Denoting the scattering rate due to the disorder introduced by each oxygen vacancy by $1/\tau_0$, $1/\tau$, appearing in Eq. (13) for T_c will be y/τ_0 where y, denoting the degree of oxygen depletion, is a measure of the number of scattering centers. The filling parameter δ appearing in the present theory can be related to y by denoting the formal charge state of Cu as $2+\delta$ and equating the net charge to zero in each unit of $Y_1Ba_2Cu_3O_{7-y}$ via $3+4+3(2+\delta)-2(7-y)=0$. Thus, $\delta=(1-2y)/3$. Substituting this expression for δ and the previous definition of $1/\tau$ into Eq. (13), the dependence of T_c on y can be calculated within the present pair-breaking mechanism for various values of J and $1/\tau_0$. For $J/4=0.5$ and $1/\tau_0=1.0$ and 1.25 the results are shown in the inset of Fig. 1. T_c decreases monotonically as y, and hence, $1/\tau$ increases. The rate of suppression of T_c increases markedly as y approaches 0.5. At lower values of y, there is a competition between the decline in T_c with decreasing y, and hence, increasing δ, in the present RVB theory and the disappearance of pair breaking as y approaches 0. This leads to the observed saturation near $y=0$. For a sufficiently small value of $1/\tau_0$, which we have not shown, T_c can have a broad maximum between $y=0$ and $y=0.5$. As can be seen from the inset of Fig. 1, the decrease of T_c with increasing y is quite similar to the results of the quenching experiments.[33]

In analyzing the data on T_c suppression with increasing oxygen depletion, it does not seem possible to use the measured resistivities above T_c as an estimate for the strength of pair breaking as was done when we discussed the Cu substitution experiment earlier. The measured increases in resistivities in the oxygen-depletion experiments probably reflect intergrain effects with variations in oxygen. This could explain the relatively small decreases in T_c coinciding with large jumps in the sample resistivities above T_c. Thus, the large and, in some instances, nonmonotonic changes in resistivity with increasing y probably do not directly reflect intragrain changes and are thus not directly related to the superconductivity in the samples.

D. Alternative explanations of T_c suppression

Several alternative hypotheses have been put forward to account for the observed T_c reduction in the oxygen-depletion experiments. These include changes in the carrier density, causing the Fermi level to move away from a peak in the density of states,[34] and decreases in the density of states at the Fermi energy due to the removal of energy bands from the vicinity of the Fermi energy as oxygen is removed from the one-dimensional Cu-O1 chains.[35] In conclusion, it is worth remembering that two issues appear to be operative in the oxygen-depletion experiments, one concerning the average oxygen content and the other concerning the degree of disorder of oxygen vacancies in the basal plane. It is the latter issue which is most relevant to the T_c reduction mechanism being proposed in this calculation.

E. Summary

To summarize, the experimental investigations of T_c suppression involve introducing disorder into the materials. This can be associated with the random positions of the oxygen vacancies in the Cu-O chains in the oxygen-depletion experiments, with lattice distortions and volume changes in the unit cell on substituting for Cu and finally with neutron irradiation experiments serving as a "pure" method of introducing disorder. The observed reductions in T_c can be then interpreted both qualitatively and semiquantitatively in terms of pair breaking due to this externally induced nonmagnetic disorder.

IV. CONCLUSION

We have carried out a calculation of the suppression of T_c due to pair breaking by nonmagnetic disorder in the resonating valence bond model. The origin of the pair breaking traces itself to the energy dependence of the order parameter over the energy band of width $8t\delta$ where the pairing takes place. Furthermore, we have indicated how the excitation gap in the density of states $N_s(\omega)$ is suppressed. The disorder is modeled by a simple scattering potential and the suppression of T_c calculated within a self-consistent Born approximation is linear in disorder.

The relationship of the large number of experiments on T_c variation to the present work has also been discussed and while some of these experiments introduce other complications such as changes in carrier concentration, density of states changes and magnetic moments, lattice disorder can be invoked as part of the explanation of the results.

In conclusion, it is possible that the observation of T_c suppression with disorder is a strong indicator that the new high-temperature superconductors possess an anisotropic and/or energy dependent order parameter and that these experiments could be interpreted as possible evidence for the RVB model.

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