Quantitative test of a microscopic mechanism of high-temperature superconductivity

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One of the main challenges to theoretical attempts to understand the microscopic mechanism of high-transition-temperature (high-\(T_c\)) superconductivity is to account quantitatively for the superconducting condensation energy, the energy by which the normal state differs from the superconducting state. A microscopic model commonly used to describe the superconducting copper oxides, the \(t-J\) model, is thought to capture the essential physics of the phenomenon: the interplay between the electrons’ kinetic energy and their antiferromagnetic exchange interaction. Within the \(t-J\) model the condensation energy can be related to the change in the dynamical spin structure between the superconducting and the normal states. Here we propose a microscopic mechanism for the condensation energy of high-\(T_c\) superconductors. Within this mechanism, the appearance of a resonance in the superconducting state enables the antiferromagnetic exchange energy in this state to be lowered relative to the normal state. We show that the intensity of the resonant neutron-scattering peak observed previously in YBa\(_2\)Cu\(_3\)O\(_7\) when it undergoes the transition to the superconducting state is in quantitative agreement with the condensation energy of these materials.

One reason for the absence of a generally accepted microscopic explanation of high-\(T_c\) superconductivity (HTSC) is the lack of quantitatively precise definition of a ‘mechanism’. In the traditional BCS superconductors, the phonon mechanism is quantitatively verified by isotope substitution and single particle tunnelling experiments. It is a widely held view that HTSC involves strong electronic interactions rather than phonon-mediated electron pairing. To date, many different ‘mechanisms’ have been proposed, but very few quantitatively falsifiable predictions have been checked against experimental data.

A system undergoes a transition from the normal to the superconducting state because it can lower the total free energy. The condensation energy \(E_c\), defined as the energy difference between the normal state, extrapolated to zero temperature, and the superconducting state \(E_s\), can be directly measured through the thermodynamical critical field \(H_c\) by the following relation:

\[
E_c = E_s - E_n = \frac{H_c^2}{4\pi} V_0
\]

Here we choose \(V_0 = a \times b \times c\) to be the volume of a unit cell (in the high-\(T_c\) copper oxides, \(a = b\) with reasonably good accuracy) and define the energies inside one unit cell. Alternatively, the condensation energy can also be found by integrating the difference in specific heats in the (extrapolated) normal and superconducting states from \(T = 0\) to the superconducting transition temperature \(T_c\) (refs 2, 3).

On the other hand, the condensation energy can, in principle, be computed from a microscopic hamiltonian. Ideally, one would like to start from the full hamiltonian involving electronic kinetic energy, the Coulomb interaction energy and the electron lattice coupling energy. Chester has studied the condensation energy of such a hamiltonian and showed how various contributions to the condensation energy could in principle be determined experimentally. Among many theories of HTSC, only the interlayer tunnelling mechanism made a quantitatively falsifiable prediction about the condensation energy. More recently, Leggett showed that the change in the interlayer Coulomb energy can be directly related to the frequency and momentum integral of the dynamic charge susceptibility, a quantity which can be measured experimentally. He argued that a microscopic theory of HTSC should quantitatively predict the frequency and the momentum range at which the change of the dynamical susceptibility occurs, and quantitatively account for the condensation energy.

But the energy scale involved in HTSC is much smaller than that of the Coulomb interaction. To understand the mechanism for HTSC, it is useful to start with an effective hamiltonian which correctly describes the basic physics below the Coulomb energy scale. Recently, Scalapino and White initiated the investigation of condensation energy in the \(t-J\) model, which is defined by:

\[
H = -t \sum_{\langle ij \rangle} \epsilon_i c_{i\sigma}^\dagger c_{j\sigma} + J \sum_i S_i^x S_i^y
\]

Here \(c_{i\sigma}\) is the electron creation operator on site \(i\) with spin \(\sigma\), \(S_i^x, S_i^y\) are the electron spin operators, \(\langle ij \rangle\) denotes a pair of near-neighbour sites and the hamiltonian does not act on the space of doubly occupied sites. Equation (2) describes the hamiltonian of one layer only. In a bilayer system like YBa\(_2\)Cu\(_3\)O\(_7\), there are two layers per unit cell, with additional antiferromagnetic coupling \(J\) between the layers. If a system described by this hamiltonian undergoes a superconducting transition away from half-filling of the electron band, the kinetic energy \(E_k\) is expected to increase slightly, but the decrease in the exchange energy \(E_J\) may be significantly larger, so that a superconducting ground state is realized.

In a tight-binding model, the mean kinetic energy \(E_k\) can be expressed as a frequency integral of the optical conductivity \(\sigma(\omega)\) (refs 17–19). Then the contribution of \(E_k\) to the condensation energy can be measured by comparing \(\sigma(\omega)\) in the normal and the superconducting states. In the low-frequency regime, the Drude peak in the normal state collapses into a \(\delta\)-function peak in the superconducting state, usually with conserved weight. Therefore, the change in the kinetic energy has to be determined from \(\sigma(\omega)\) in the higher-frequency range.

Scalapino and White made the insightful observation that the change in the \(J\) term in equation (2) can also be directly expressed as a frequency and momentum integral of the dynamic spin structure factor \(S(q,\omega)\). For bilayer materials such as YBa\(_2\)Cu\(_3\)O\(_{6+\delta}\), it is convenient to separate the even and odd parts of \(S(q,\omega)\) with respect to bilayer interchange within a unit cell:

\[
S(q,\omega) = S_{\text{even}}(q,\omega) \cos^2 \left( \frac{q \cdot d_{\text{CuO}}}{2} \right) + S_{\text{odd}}(q,\omega) \sin^2 \left( \frac{q \cdot d_{\text{CuO}}}{2} \right)
\]

Here \(d_{\text{CuO}}\) is the distance between nearest-neighbour Cu–O planes, so \(S_{\text{even}}\) and \(S_{\text{odd}}\) describe the in-phase and out-of-phase spin fluctuations in the two planes constituting one bi-layer. Then \(\Delta E_j = E_j^0 - E_j^1\), defined as a difference between exchange energies in the normal \((E_j^0)\) and the superconducting \((E_j^1)\) states, may be obtained (per unit cell) as:

\[
\Delta E_j = \frac{3}{2} \left[ \frac{1}{2\pi} \int_{-\pi/a}^{\pi/a} dq \right] \int_0^{\hbar \omega} dq \frac{d\langle\omega\rangle}{\pi} \left[ S_{\text{even}}(q,\omega) - S_{\text{odd}}(q,\omega) \right]
\]

\[
\times \left[ \frac{1}{2} f(\cos(q,a) + \cos(q,a)) + \frac{1}{4} J \right]
\]

\[
\times \left[ S_{\text{even}}(q,\omega) - S_{\text{odd}}(q,\omega) \right]
\]

\[
\times \left[ \frac{1}{2} f(\cos(q,a) + \cos(q,a)) - \frac{1}{4} J \right]
\]

Here \(q = (q_x, q_y)\) is a two-dimensional in-plane momentum and...
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$S_{\text{even/odd}}$ and $S_{\text{odd/even}}$ correspond to the dynamic spin structure factors in the normal and the superconducting states, respectively. It is known\cite{12,13} that $J_2$ is much smaller than $J_1$ so the $J_1$ term in equation (4) may be safely neglected. Scalapino and White pointed out\cite{14} that as $S(q,\omega)$ can be measured directly in neutron-scattering experiments, $\Delta E_j$ can therefore in principle be measured. If $\Delta E_j$ turns out to be much smaller than the experimentally measured condensation energy $E_c$, this gives a convincing way to rule out any mechanism of high-$T_c$ superconductivity based on the $t$-$J$ model. On the other hand, if $\Delta E_j$ turns out to be greater than $E_c$, one would have identified an important driving force for superconductivity, and can quantitatively test any theoretical mechanism of HTSC based on the $t$-$J$ model, which should predict where in frequency and momentum space the change of $S(q,\omega)$ occurs.

However, one should apply this line of reasoning with extreme care. The quantity $S(q,\omega)$ in equation (4) is not the normal state spin structure factor above $T_c$, but rather an extrapolated normal state quantity at $T = 0$. Experimentally, one has to carefully identify features in $S(q,\omega)$ which change abruptly at $T_c$. Theoretically, one has to identify contributions to $S(q,\omega)$ which are absent in the normal state and only present in the superconducting state, so that the difference in equation (4) can be rigorously defined. A resonant neutron peak has been discovered in the family of YBa$_2$Cu$_3$O$_y$ superconductors\cite{15,16}. In the optimally doped YBa$_2$Cu$_3$O$_7$ superconductor with $T_c = 91$ K, the resonance peak occurs in the spin scattering channel at energy $\omega_c = 41$ meV. It is centred around momentum $Q = (\pi/a, \pi/a)$ and it occurs in the odd channel with respect to bilayer interchange. Perhaps the most remarkable feature of the resonance peak is its onset at the superconducting transition temperature $T_c$. Above $T_c$, there is no experimentally identifiable spectral weight in this frequency and momentum range. This experiment is therefore ideally suited for analysing the contribution to the condensation energy due to the exchange interaction.

We constructed a theory\cite{9} of the neutron resonance peak by first identifying a resonance in the spin-triplet particle-particle (p-p) channel defined by the following operator:

$$\pi^I = \sum_k \cos(k_x - k_y) \hat{c}_{k}^{\dagger} \hat{c}_{-k}$$

(5)

where $\hat{c}_{k}$ creates a spin-up electron at momentum $k = (k_x, k_y)$. In a series of exact diagonalization studies on the Hubbard and $t$-$J$ models, Meixner, Hanner and the two of us\cite{17}, and Eder, Hanner and one of us (S.-C.Z.)\cite{18}, demonstrated the existence of such a triplet p-p resonance for all doping ranges. A triplet p-p resonance cannot be detected in neutron-scattering experiments on the normal state. However, below $T_c$, the d-wave superconducting order parameter mixes a p-p resonance into the dynamical spin structure factor, leading to a sharply defined collective mode in the triplet particle-hole (p-h) channel (the so-called $\pi$-resonance). The contribution from the p-p resonance to the p-h channel below $T_c$ is given\cite{19} by:

$$\int d(\omega) S(q,\omega) = \frac{2(\Delta_{\pi})^2}{1 - n}$$

(6)

where $\Delta_{\pi}$ is the dimensionless $d$-wave superconducting order parameter (not the energy gap) and $n$ is the density of electrons. This simple estimate of the spectral weight of the $\pi$ resonance at $q = Q$ agrees reasonably well with the absolute intensity measured by Feng et al.\cite{12,13}. On the other hand, the width of the $\pi$ resonance in momentum space cannot be calculated reliably. Within the $SO(5)$ theory\cite{13}, the $\pi$ resonance has been interpreted as a pseudo-Goldstone boson of the spontaneous $SO(5)$ symmetry breaking in the superconducting state. Its existence is therefore directly correlated with the existence of the superconducting long-range order.

Because the coupling to a p-p resonance is only possible in the superconducting state, it indeed contributes to the difference in $S(q,\omega)$ as required by equation (4). We point out here that the logic leading to our explanation of the $\pi$ resonance below $T_c$ can be reversed to provide a microscopic mechanism of HTSC. On one hand, the existence of the $\pi$ resonance is a unique property of the superconducting state; on the other hand, its existence around $q$ lowers $E_c$, as we see from equation (4). Therefore, the system undergoes a superconducting transition, so that a $\pi$ resonance mode can emerge, which in turn lowers $E_c$. In other words, no matter how antiferromagnetically correlated is the normal state, a superconducting state can always further lower the exchange energy by coupling a p-p resonance into the dynamic spin structure factor $S(q,\omega)$. Our mechanism for HTSC makes a quantitatively precise prediction which can be checked experimentally. Once we assume that the HTSC is dominantly driven by the emergence of a new collective mode, the $\pi$ resonance, this mechanism predicts that the condensation energy is determined by the zero-temperature spectral weight of the $\pi$ resonance, and the energy saving occurs precisely in the frequency and momentum range of the $\pi$ resonance.

As our mechanism predicts an additional spectral weight around $q = Q$ in the superconducting state, one may wonder what happens to the spectral sum rule, which states that $S(q,\omega)$ integrated over both $q$ and $\omega$ (without the $f(q) = \cos(q, a) + \cos(q, b)$ factor in equation (4)) should be a constant, independent of the nature of the ground state. Our additional spectral weight should, of course, be compensated by a depletion of spectral weights from other parts in the momentum space. However, because $f(q)$ has an absolute minimum at $q = Q$, their contributions to (4) cannot completely cancel the $\pi$ resonance contribution. In fact, depletion of the spectral weight near $q = 0$ would lead to additional enhancement of the condensation energy.

Both the condensation energy and the spectral weight of the neutron resonance peak have been measured experimentally, so it is straightforward to check this prediction. Within Landau–Ginzburg theory, $H_s = \Phi_1(2\sqrt{2}\pi n\lambda)$, where $\Phi_1 = hc/2\lambda$ is the superconducting flux quantum, $\xi$ is the coherence length and $\lambda$ is the London penetration depth. In YBa$_2$Cu$_3$O$_y$, these two length scales are determined to be in the range of $\xi = 12-20$ Å and $\lambda = 1,300-1,500$ Å. Using $a = b = 3.85$ Å and $c = 11.63$ Å, this gives a condensation energy of $E_c = 3.3-12$ K per unit cell. On the other hand, $E_c$ can also be measured directly in specific-heat experiments. Loram et al. reported (see page 251 of ref. 2 and page 247 of ref. 3) a value of $E_c = 6$ K per unit cell for YBa$_2$Cu$_3$O$_y$. We now turn to the experimental measurement of $\Delta E_j$ given by equation (4). In practice, it is very hard to measure the change of $S(q,\omega)$ throughout the frequency and momentum range. However, because our mechanism predicts that most of the condensation energy is saved in the range of $\omega_c = 41$ meV and a two-dimensional momentum transfer $Q = (\pi/a, \pi/a)$, we can analyse the neutron scattering data by assuming that the contributions of the other parts do not change significantly at $T_c$. Indeed, for frequencies above the resonance the neutron-scattering intensity does not change as the system goes from normal to superconducting. For frequencies below and in the resonance range, the normal state intensity $S_{\text{normal}}(q,\omega)$ is below the experimental sensitivity limit in both even and odd channels. Because of the sum rule discussed above we may assume that it vanishes identically, so we make an assumption that in this frequency range the spectral weight $S_{\text{normal}}(q,\omega)$ is spread uniformly in momentum space and therefore does not contribute to equation (4). Below $T_c$, a neutron resonance peak emerges in the odd channel, and $S_{\text{odd}}(q,\omega)$ has been measured in absolute units in the range of the resonance. The dimensionless quantity $\int d(\omega) S_{\text{odd}}(Q,\omega)$ is measured to be 0.52 at $T = 10$ K by Feng et al.\cite{18}. (A theoretical estimate based on references 9 and 12 gives 0.32 for this value.) The resonance has a lorentzian profile centred at $q = Q$ with a width $\kappa_{\pi} = 0.23$ Å$^{-1}$ (ref. 16), so the two-dimensional momentum integral can be easily estimated.

$$\Delta E_j = \frac{3}{2} \pi \left( \frac{\kappa_{\pi}}{2} \right)^2 \frac{1.052}{2} \frac{2\pi}{\pi} 0.016f$$

(7)

Taking $f = 100$ meV we obtain $\Delta E_j = 18$ K. The actual condensa-
tion energy should be smaller than $\Delta E_J$ as the kinetic energy is expected to increase below the superconducting state. Taking this into account, we see that the spectral weight of the $\pi$ resonance peak can quantitatively account for the condensation energy measured from $H_c$ and specific-heat experiments, in reasonable agreement with the prediction based on our mechanism.

We now compare our mechanism for HTSC with the spin fluctuation pairing mechanism\textsuperscript{[5-7]}. All these mechanisms are based on the antiferromagnetic exchange interaction $E_I$. Our analysis of the neutron data confirms that a large part of the condensation energy indeed arises from such an exchange interaction\textsuperscript{[3]}. However, our mechanism differs from the spin fluctuation pairing mechanism, both conceptually and quantitatively. The idea of spin fluctuation pairing is directly borrowed from the phonon-mediated pairing in the traditional BCS superconductors. It requires sizeable antiferromagnetic spin fluctuations in the normal state, in order to pair the Fermi liquid like quasiparticles. In contrast, in our mechanism, the antiferromagnetic spin fluctuations in the normal state do not play an important role in driving superconductivity. In the superconducting state, the $\pi$ resonance can be viewed as a kind of spin fluctuation in a particular frequency and momentum range. From the point of view of the SO(5) theory\textsuperscript{[3]}, the superconducting state is obtained from the antiferromagnetic state by a rotation, so it is natural to expect it to have more antiferromagnetic correlation than the normal state. The crucial conceptual difference between these two mechanisms therefore lies in the fact that normal state antiferromagnetic spin fluctuations are not required in our mechanism. This conceptual difference has a direct quantitative consequence. From equation (4), we see that the presence of spin fluctuation spectral weight in the normal state contributes negatively to the condensation energy. It is not clear why the spin fluctuation model would predict a change in the frequency-integrated weight of $S(q\omega)$ near $q = Q$. In fact, most theories of the neutron resonance peak based on the spin fluctuation models\textsuperscript{[6,7]} assume a pre-existing overdamped spin fluctuation mode in the normal state and only predict a reduction of damping below $T_c$ with essentially conserved weight.

Our mechanism provides a natural explanation for the doping dependence of the condensation energy. We attribute the condensation energy to the difference in exchange energies in superconducting and normal states. More-underdoped materials have considerably more antiferromagnetic correlations in the normal state, as known from neutron scattering\textsuperscript{[5,6]}. Although in the superconducting state the weight of the resonance is enhanced\textsuperscript{[3]}, the difference between the normal and the superconducting exchange energies becomes smaller. This is consistent with the results of Loram et al.\textsuperscript{[11]} who find a decrease in the condensation energy with decreased doping in Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{y+z}$. Until this point we have been discussing the relation between the condensation energy and the resonant peaks in neutron scattering at zero temperature. It would be interesting to see whether this idea also works at finite temperature. Without going into details, we would like to point out a striking similarity between the temperature dependence of $H_c$ (ref. 2) and that of the resonance intensity\textsuperscript{[28,29]} for the underdoped copper oxides: both quantities scale similarly below $T_c$ and both have ‘tails’ extending above $T_c$ presumably arising from significant pairing fluctuations in the pseudogap regime. These phenomena await future investigations.

Received 4 June; accepted 16 September 1998.

Acknowledgements. We thank P. Dai, H. Fong, S. Heyden, R. Keimer, H. Mook and D. Scalapino for discussions.

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**Moisture-induced ageing in granular media and the kinetics of capillary condensation**

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In 1773 Coulomb\textsuperscript{1} recognized that the static properties of granular systems can be discussed in terms of the frictional properties between different layers, leading to his relationship between the angle of repose of a granular pile ($\theta_0$) and the coefficient of static friction $\mu_s$: $\tan\theta_0 = \mu_s$. Two centuries later, solid friction and granular media still present many puzzles. One such is that the coefficient of static friction depends on the time during which the solids remain in contact before the measurement. Here we show that this ageing effect is manifested too in the angle of repose of granular media and originates from capillary condensation of water vapour between the packed particles, leading to the formation of water bridges. By assuming that the kinetics of this process are governed by the thermally activated nucleation of bridges, we can reproduce both the time- and humidity-dependence of the ageing behaviour. Our results also clarify the kinetics of adsorption in porous media more generally.

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