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Enhanced transition temperature in a quantum confined high-$T_c$ superconductor

L. Menon
University of Nebraska - Lincoln

D. Yu
University of Nebraska - Lincoln

Yi Liu
University of Nebraska-Lincoln, yliu@unl.edu

B. Jayaram
University of Nebraska-Omaha

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There is considerable controversy about the effect of quantum confinement on superconductivity. There are reports of both increase and decrease of the transition temperature in nanometer-sized superconductors compared to bulk superconductors. Almost all of these studies have involved exclusively low-\(T_c\) superconductors since it is easier to fabricate ultra-small structures of low-\(T_c\) superconductors than the high-\(T_c\) oxide superconductors.

In low-\(T_c\) superconductors, the coherence length is comparable to, or larger than the Fermi wavelength of carriers. Hence any sample small enough to exhibit quantum confinement effects (i.e. comparable to the Fermi wavelength) is also smaller than the coherence length. Thus, inevitably, there will be a size-effect perturbation of the Cooper pairing and it will never be clear as to whether any modification of \(T_c\) is due to this perturbation, or a quantum confinement effect leading to a discretization of the quasi-particle density-of-states.

High-\(T_c\) superconductors (HTSCs) are more appropriate candidates for quantum confinement studies since they have strong binding energies and small coherence length that is typically a fraction of a nanometer. In these materials, the coherence length is much smaller than the Fermi wavelength of carriers, which are a few tens of nanometers. Hence, it is possible to make structures of a few tens of nanometers, which are comparable to the Fermi wavelength, but much larger than the coherence length. Any modification of \(T_c\) will then have accrued most likely from a modification of the density of quasi-particle states caused by quantum confinement, as opposed to any effect on the Cooper pairs.

The standard BCS formalism, applied to delocalized quasi-particles with a well defined density-of-states, leads to the following relation for \(T_c\) in any superconductor if we neglect band-structure effects [1]:

\[
\frac{2}{V} = \int_{-\kappa_B \theta_D}^{\kappa_B \theta_D} N(E) \frac{1}{E} \tanh \left( \frac{E}{2k_B T_c} \right) dE
\]  

where \(V\) is the effective coupling potential for Cooper pairs, \(k\) the Boltzmann constant, \(\theta_D\) a cut-off temperature (e.g. Debye temperature for phonon-mediated coupling), \(E\) the quasi-particle energy measured from the...
Fermi level and $N(E)$ the energy-dependent normal density of quasi-particle states (here $\Delta$ is the superconducting gap).

It was pointed out by Labbé [2] and Friedel [3] that such expressions can lead to transition temperatures far in excess of the BCS standard result for bulk structures [4], namely

$$1.76k_{\text{c}} = \Delta = 2k_{\text{B}} \theta D \exp \left( - \frac{1}{N(0) V} \right)$$  \hspace{1cm} (2)

if $N(E)$ in the normal state does not follow a square-root dependence on energy and peaks strongly around the Fermi level.

If $N(E)$ has a singularity within an energy range $k\theta_D$ of the Fermi level, i.e. $N(E) = g\delta(E \pm k\theta_D)$ ($g$ is a degeneracy factor) and $\theta \leq \theta_D$, then Equation (1) reduces to

$$k_{\text{c}} = \frac{k\theta D}{2 \tanh^{-1} \left( \frac{2k\theta D}{gV} \right)}$$

$$\lim_{\theta \to 0} k_{\text{c}} = k_{\text{c}}(\text{max}) = \frac{gV}{4} \hspace{1cm} (3)$$

Since the pairing potential $V$ in HTSCs is relatively large as a result of the small coherence length, one can hope to achieve a very high transition temperature (given by Equation (3)), if we can force the normal density-of-states within an energy range $k\theta_D$ of the Fermi level to be singular, or at least much larger than what it is in bulk. Thus, appropriate modification of the density-of-states can enhance $T_c$.

The above claim is predicated on the applicability of the BCS theory to HTSCs. There are multiple theories for HTSCs, but most of them are similar to BCS [5] and consistent with the above claim. Kresin and Wolf [6, 7, 8 and 9], who take into account the two-dimensional (2D) nature of superconductivity in the Cu–O plane of typical HTSCs, have shown that in the strong coupling limit, the bulk BCS result is modified to

$$k_{\text{c}} = \frac{0.25\Omega}{\sqrt{\exp[2/\lambda] - 1}} \hspace{1cm} (4)$$

where $\Omega$ is a cut-off energy and $\lambda$ is effectively the product $N(0)V$. Even this expression predicts that a larger $N(0)$ will lead to a higher $T_c$.

In a quantum dot, the quasi-particle energy spectrum is completely discrete and the density-of-states is given by

$$N(E) = \sum_{n} g_n \delta(E - \epsilon_n) \hspace{1cm} (5)$$

at zero temperature, where $\epsilon_n$ is the energy of the $n$th subband bottom (in the conduction or valence band) measured from the Fermi level $E_F$. As long as $|\epsilon_n| \leq k\theta_D$, Equation (1) will reduce to Equation (3) and the $T_c$ will increase. At a finite temperature and for a finite amount of disorder, the delta functions in Equation (5) will be thermally and impurity broadened Lorentzians so that the $T_c$ will be less than what is predicted by Equation (3), but it will still be higher than what is predicted by Equation (1) for bulk structures.

Quantum dots of YBCO were formed in our laboratory somewhat serendipitously. YBCO powder produced by a sol–gel technique was sieved through a commercially available porous membrane (that has uniformly sized pores) and introduced into an RF plasma. Two different types of membranes were used: one with a pore diameter of 1 μm and the other with a pore diameter of 600 nm. The argon plasma was ignited by an RF generator supplying about 10 W of power at 13.6 MHz and the pressure was about 1 Torr.

Once the particles are in the plasma, they are negatively charged by collisions with mobile electrons and levitate in a quasi 2D layer above the driving electrode (see inset of Figure 1). The electrode is also negatively charged and hence repels the particles—balancing the

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**Figure 1.** (a) Optical micrograph of particles in a partially ordered Coulomb crystal. There is significant optical aberration in the upper left corner. The largest particle size is 600 nm. (b) The schematic of a plasma setup to self-assemble a Coulomb crystal of 600 nm YBCO particles.
forces of gravity and ion wind—causing them to levitate. Under proper conditions, the Coulomb interaction between the negatively charged particles, screened by the intervening positive ion cloud, leads to the formation of a more or less ordered array of particles in a floating 2D layer—a “Coulomb crystal” [10, 11 and 12]. We can levitate the Coulomb crystal in the plasma as long as we like and then transfer it to a silicon wafer for measurement. Transfer is accomplished by simply extinguishing the plasma and allowing the particles to fall freely on the substrate. The substrate is pre-coated with a sticky film that “glues” the fallen particles at sites where they land. This process destroys some of the ordering, but at least keeps the particles well separated from each other and prevents agglomeration. Figure 1 shows a micrograph of such an array in the plasma.

The particles formed by this technique have been extensively characterized by high resolution TEM, electron diffraction and energy dispersive analysis of X-rays (EDAX). High resolution TEM showed that only a 5 nm
layer on the outside edge of a particle is rendered amorphous by the plasma, but the central core remains crystalline. However, even within the crystalline core, the stoichiometry changes with position because of plasma-induced damage. Figure 2 shows the results of EDAX carried out at two different sites separated by about 50 nm inside a 200 nm particle that was exposed to a plasma for several minutes. The difference in the peak heights of various elements indicates that there is stoichiometry variation between these two sites. If we estimate the characteristic length scale for the variation of stoichiometry to be one-half of this distance, then we conclude that the superconducting YBCO regions (with the correct stoichiometry) are probably confined into quantum dots of diameter ~25 nm or smaller. The surrounding regions provide potential barriers for the carriers. In contrast, particles that have not been exposed to a plasma do not show such stoichiometry variations and hence contain no quantum dots.

To find the transition temperature in the plasma-damaged nanoparticles, their dc susceptibility was measured as a function of temperature in a SQUID magnetometer. Measurements are complicated by the presence of a nearly temperature-independent background susceptibility, which is always negative (diamagnetic) over all temperature ranges and is probably associated with the sticky film used to glue the particles on the substrate. This background susceptibility decreases very slowly (becomes more negative) with increasing temperature. Because of the background, it was not possible to observe the zero crossing of the susceptibility (paramagnetic to diamagnetic transition), which signals the onset of superconductivity.

For the SQUID measurements, we were forced to use a minimum flux density of 1000 G because the SQUID signal became too noisy at lower fields. The amount of material in the particles is probably too small to produce adequate magnetic moment for measurement below 1000 G. Fortunately, the first critical magnetic field, $H_{c1}$, is significantly increased in powders containing small particles [13, 14] which is why the superconductivity is not quenched at 1000 G even though it is known that the values of $H_{c1}$ are 180 Oe for field parallel to the c-axis and 530 Oe for field perpendicular to the c-axis in

![Figure 3. Susceptibility of plasma-damaged YBCO particles (two different particle samples are shown in the top two panels) and undamaged bulk powder (bottom panel) as a function of temperature measured at 1000 Oe. The top panel also shows data at 5000 Oe. There is no transition at 5000 Oe since that is above the critical magnetic field. In the undamaged bulk powder, $T_c$ (for onset) is 92 K while the $T_c$ in the plasma-damaged particles prepared from the same bulk powder is >93 K. Since the transition in the bulk powder is very broad at 1000 G, we have included in the inset the transition at a field of 50 G (where the transition is narrower) to confirm that the bulk $T_c$ for onset is indeed 92 K.](image-url)
bulk YBCO [15]. An independent measurement of $H_{c1}$ in the powder showed it to be 2800 Oe at a temperature of 5 K.

The susceptibility data are shown in Figure 3. The transition temperature for the onset of superconductivity is defined as the temperature at which the susceptibility begins to drop [16]. In the upper two panels of Figure 3 (corresponding to plasma-damaged nanoparticles), $T_c \geq 93$ K, whereas in the bottom panel (bulk powder), $T_c = 92$ K. The transition in the powder is much broader than in sintered samples because of the lack of good electrical connectivity between neighboring grains. That is why we include (in the inset of the bottom panel) data taken at 50 G (where the transition is considerably narrower) to demonstrate that $T_c$ is indeed 92 K. The plasma-damaged nanoparticles exhibit at least a 1 K increase in $T_c$.

To confirm that the drop in susceptibility is indeed due to the onset of superconductivity, we measured the susceptibility of nanoparticles at a flux density of 5000 G, which is above the critical field. The susceptibility then increased with decreasing temperature (top panel of Figure 3) as expected.

We have measured several plasma-damaged samples and have found that all of them exhibited an increase in $T_c$. In some cases, the increase is only 1 K whereas in at least one sample, $T_c$ may have increased by 6 K (in the last case, the data are rather noisy).

The likely reason for this increase in $T_c$ is quantum confinement of carriers in ~25 nm regions of stoichiometric YBCO. This confinement will increase $T_c$ as long as the peaks in the density-of-states are not thermally smeared out to the extent that neighboring peaks overlap in energy. Thus, neighboring subbands must be separated in energy by more than $kT_c$, which is about 8 meV.

To estimate the subband separation in energy, we assume that the confining potential varies smoothly with distance, consistent with a gradually varying stoichiometry. A reasonable approximation then is to assume a parabolic confining potential $V(x) = (1/2)m^* \omega^2 x^2$ where the effective mass $m^*$ is assumed to be five times the free electron mass [17]. In this case, the subband separation in energy, $\hbar \omega$, will exceed $kT_c$ if the potential barrier rises to about 313 meV at 12.5 nm from the center (at the boundary of the ~25 nm region). A 313 meV barrier is very plausible since conduction/valence band offsets of this magnitude are routinely observed between semiconductor alloys of differing composition (an example is the ternary alloy Al$_x$Ga$_{1-x}$As where the maximum variation in bandgap as a function of the aluminum mole fraction $x$ far exceeds 300 meV). Any barrier higher than 313 meV will cause sufficiently strong quantum confinement to increase $T_c$.

It is also of interest to explore alternate mechanisms for $T_c$ increase. The $T_c$ of nanoscale superconductors may be influenced by the fluctuations of the order parameter [18–20] and also the shape of the particles [21]. Small particles of low-$T_c$ superconductors produced on a substrate by gas condensation techniques [22, 23] have always showed a decrease in $T_c$. However, there have been some report of a ~20% increase in $T_c$ in indium crystallites [24–26] that were smaller than or comparable to the zero-temperature coherence length of Cooper pairs. The increase was attributed to the increased surface to volume ratio in nanoparticles which could increase the electron–phonon coupling constant and hence $T_c$. This is not an issue in our experiment since the quantum dots are surrounded by acoustically like material which may present a potential barrier to carriers, but will not confine phonon modes or have any other serious effect on electron–phonon coupling.

Unusual phase transition effects are expected if the size of the superconductor approaches the characteristic size of the Cooper pairs (coherence length) [27], but since the coherence length of YBCO is only 1.4 nm along the $a$–$b$ plane and 0.2 nm along the $c$-axis [28], we do not expect to see such effects in our quantum dots which are much larger. Thus, quantum confinement remains the strongest candidate.

In conclusion, we have consistently observed a slight increase of $T_c$ in quantum confined superconductors which, we believe, accrues from a discretization of the quasi-particle density-of-states. To our knowledge, this is the first time that this effect has been observed in high-$T_c$ material.

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References


