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The design of high-T_c superconductors – Room-temperature superconductivity? ☆

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ABSTRACT

This year is the centennial of the discovery of superconductivity and the 25th anniversary of the discovery of high-T_c superconductors (HTS). Though we still do not fully understand how HTS work, the basic rules of design can be determined from studying their systematics. We know what to do to increase T_c and, more importantly, what to do to increase critical current density J_c. This in turn lays down a challenge for the chemist. Can the ideal design be synthesized? More importantly, what are the limits? Can one make a room-temperature superconductor? In fact fluctuations place strict constraints on this objective and provide important guidelines for the design of the ideal superconductor.

1. Introduction

A quarter of a century on from the discovery of cuprate high-T_c superconductors (HTS) there is still no agreed mechanism for the pairing of carriers. In principle this could be expected to prevent the rational design of better HTS. But in fact we know enough about their behavior to assemble some clear guidelines as to how to increase T_c and in practical terms how to increase the critical current density, J_c. A much talked about goal, even here at this conference, is the grand hope of room temperature superconductivity. But is this possible? And would such materials be useful? These important issues are the focus of this paper.

HTS cuprates are indeed remarkable materials but they are complex and it is this complexity that compromises both their understanding and their optimization. At first sight they seem clearly to be non-BCS superconductors. But is this really true? There are other complicating factors that conspire to obscure the true situation. We list these and then illustrate how these various factors play out in the complex phenomenology of HTS.

2. What determines T_c?

In a conventional weak-coupling *d*-wave superconductor one can say rather simplistically that T_c is determined by the magnitude of the anisotropic *d*-wave gap, Δ_0, which can be considered to be identical to the superconducting (SC) order parameter, Δ_0'. The relation is:

$$2.14k_BT_c^{mf} = \Delta_0 = 2\hbar\omega_B \exp[-1/(N(E_F)V)], \quad (1)$$

where usually one would just write T_c but it is necessary to emphasize that it is in fact the mean-field (mf) T_c value, T_c^{mf}, because fluctuations play such an important role in HTS physics. In Eq. (1) $\hbar\omega_B$ is the energy scale of the pairing boson, $N(E_F)$ is the density of states (DOS) at the Fermi level and V is the pairing interaction.

Some of the complications include: (i) In the underdoped region there is a pseudogap which depletes the DOS around the $(\pi,0)$ antinodes. (ii) In the overdoped region the 2D electronic structure leads to a van Hove singularity (vHs) which strongly enhances the DOS, which in fact diverges at the singularity. Clearly this can have a major effect on T_c through the exponential dependence on $\lambda = N(E_F)V$. (iii) The pairing boson is generally considered to be AF spin fluctuations or paramagnons, so that the energy scale $\hbar\omega_B$ is likely to be of the order of J the magnetic superexchange interaction energy. This is an order of magnitude higher than the Debye energy so it is easy to see that in combination with the vHs it is quite possible, using Eq. (1) to achieve room-temperature superconductivity. It is this possibility that we wish to assess. Finally, (iv) as noted, there are strong SC fluctuations present both above and below T_c which suppress T_c below T_c^{mf}.

Fig. 1 summarizes these effects in the Y123 system, $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$. Data points show Δ_0 (red) and the pseudogap energy, E_g, (blue) determined from specific heat studies [1].[1] Infrared *c*-axis ellipsometry studies confirm this data in all respects [2]. Using Eq. (1) we can thus calculate the doping dependent $T_c^{mf}(p)$ from $\Delta_0(p)$ – solid red curve – which reveals an expected T_c for this system of 150 K if weak-coupling BCS were to apply. However, with the opening of the pseudogap at $p \approx 0.19$ holes/Cu the order param-

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[1] For interpretation of color in Figs. 1, 2, 4, 5, and 6 the reader is referred to the web version of this article.

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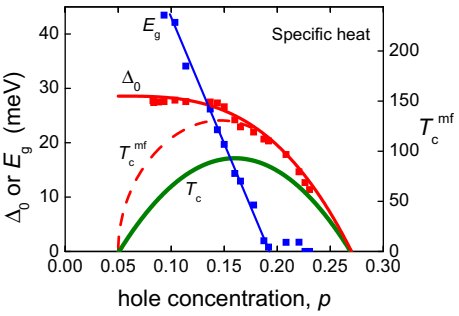

Fig. 1. Red data points show the SC energy gap Δ_0 and blue the pseudogap energy E_g from specific heat studies on $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$. For a BCS d-wave superconductor T_c is given by Eq. (1) and hence the solid red curve with right-hand scale. A T_c of 150 K is expected based on the energy gap. But the pseudogap suppresses T_c (dashed curve) with maximum T_c now of 125 K. Moreover, SC fluctuations suppress T_c even further giving $T_c^{max} \approx 90$ K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

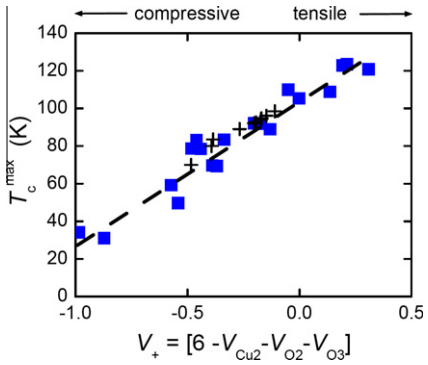

Fig. 2. T_c^{max} plotted versus the bond-valence sum (BVS) parameter $V_+ = 6 - V_{Cu} - V_{O_2} - V_{O_3}$ for 19 different HTS cuprates (filled squares) and for $LnBa_2Cu_3O_{7-\delta}$ and $Y(Ba_{1-x}Sr_x)_2Cu_3O_{7-\delta}$ (crosses) which show a progressive decrease in T_c^{max} as the basal plane is compressed due to reduction in ion size.

eter, Δ_0', is no longer equal to the SC gap Δ_0 [3] but is suppressed below Δ_0, and $T_c^{mf} = \Delta_0'/2.14k_B$ is also suppressed – dashed red curve. T_c^{max} falls to about 125 K and $T_c^{mf}(p)$ is now dome shaped. An idea of the suppression of Δ_0' can be derived from the model due to Bilbro and McMillan [3]. If $\Delta_0(\mathbf{k})$ and $E_g(\mathbf{k})$ have the same $\mathbf{k}$-space symmetry around the Fermi surface then

$$(2.14k_BT_c)^2 = \Delta_0'^2 = \Delta_0^2 - E_g^2 \qquad (2)$$

Next, there is the role of strong SC fluctuations. By an entropy balance procedure the suppression of T_c below T_c^{mf} has been determined for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ (Y123) and $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) [4]. The effects are of the order of only 5–10 K on the overdoped side but for optimal and underdoped samples the reduction in T_c is of the order of 30 K for Y123 and 60 K for Bi2212. The result is summarized in Fig. 1 by the solid green curve for Y123. In this way T_c^{max} is finally reduced from 125 K to around 90 K. In the light of these ideas, strategies to increase T_c would include reducing fluctuations (by e.g. increasing interlayer coupling or increasing external pressure) and reducing the impact of the pseudogap. Because $E_g \approx J(1 - p/0.19)$ [1] one approach might be to decrease J by for example increasing ion size and thereby decreasing orbital overlap. In fact increasing ion size is an established strategy for increasing T_c [5,6]. This is discussed in more detail in the next section.

Qualitatively, the above discussion describes the basic effects of the pseudogap and SC fluctuations in suppressing T_c. These issues can be addressed in rational ways. In addition one has the opportunity to control the DOS by shifting the vHs closer to the Fermi level. The location of the vHs has been shown to account for the differences in T_c^{max} observed in Bi2201, Bi2212 and Tl2201 by simply assuming the same pairing interaction in each case [7]. We now examine in more quantitative detail the effects of ion size and their impact on T_c.

3. Routes to increase T_c – ion-size correlations

Twenty years ago a remarkable correlation of T_c^{max} with a certain bond valence sum (BVS) parameter, V_+, was presented [8] that continues to represent the best correlation of T_c values with any structural parameter within the class of HTS cuprates. This is reproduced in Fig. 2 (solid squares) and includes 19 different cuprates. Here $V_+ = 6 - V_{Cu} - V_{O_2} - V_{O_3}$ where V_{Cu}, V_{O_2} and V_{O_3} are the planar copper and oxygen bond valence sums calculated using refined atomic coordinates from neutron diffraction. The parameter V_+ was introduced in an attempt to characterize the distribution of doped charge between copper and oxygen orbitals. Another parameter $V_-(= 2 + V_{Cu} - V_{O_2} - V_{O_3})$ was introduced to estimate the total doped charge.

In addition to describing charge distribution, this V_+ parameter is a measure of in-plane stress with large negative values indicating compression and positive values indicating tensile extension [9]. The correlation underscores the general rule that substitution of a larger ion results in an increase in T_c^{max} [5,6], as already noted.

To that early data we add additional data (crosses) for the series $LnBa_2Cu_3O_{7-\delta}$ where Ln = La, Nd, Sm, Gd, Dy and Yb [10], and for $Y(Ba_{1-x}Sr_x)_2Cu_3O_{7-\delta}$ [11]. This series exhibits a systematic in-plane compression as the size of the lanthanide rare earth is reduced and then Sr replaced for Ba. The correlation is conserved right across this series. The upshot of all this is that an overall strategy for increasing T_c lies in substituting, wherever possible, larger ions for those in the parent compound. It would suggest e.g. that the highest T_c (>150 K) might be found in the system $HgRa_2Ca_2Cu_3O_8$ were it possible, or safe, to synthesize.

4. Routes to increase T_c – apical oxygen

By way of introduction to this section we make two observations. Firstly, the top-most data points in Fig. 2 are for three-layer cuprates and here one has to choose whether to calculate V_+ for the inner CuO_2 layer or the outer CuO_2 layer. It turns out that the correlation breaks down completely if the calculation is done for the outer layer – values of V_+ are far too negative. The data shown are for the inner layer. This immediately suggests that it is the inner layer (where the apical oxygen is absent) that sets the magnitude of T_c^{max}.

Secondly, we consider the effects of external pressure. A profound paradox lies in the fact that, as we have just seen, *internal* pressure arising from ion-size effects decreases T_c^{max} while, in sharp contrast, *external* pressure is well known to raise T_c^{max} [12]. To anticipate the next section, it is quite possible that this external pressure effect is to reduce fluctuations so that T_c rises towards its upper ceiling of T_c^{mf}, while the ion-size effect probably involves a distortion of the Fermi surface so that the vHs moves closer to E_F.

But here we focus on a different effect arising from external pressure. In the case of optimally-doped $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ T_c was found to rise with increasing pressure from 110 K to a maximum at ≈125 K then fall before rising again towards 140 K [13]. The reason is that the inner CuO_2 layer is underdoped relative to the two outer CuO_2 layers in this three-layer cuprate. Application of pressure causes charge transfer from the Bi_2O_2 layer so that first the outer layers optimize (leading to a peak at $T_c \approx 125$ K) and then at higher pressure the otherwise less-doped inner layer optimizes with $T_c > 140$ K. Thus again the higher T_c value seems to be