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The functional form of the $T_c(x)$ line in the phase diagram of high temperature superconductors

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The critical temperature T_c in high temperature superconductors is proposed to be governed by the geometrical correlations between carriers. A model is put forward for these correlations and the dependence of T_c on the doping x in the phase diagram of $La_{2-x}(Sr)_xCuO_4$ is derived near $T=0$. The model links T_c explicitly to the observed fraction of diamagnetic phase $p(x)$. It explains the observed opposite curvatures of $T_c(x)$ and $p(x)$ for heavy doping and agrees with other existing observations.

The exhaustive effort invested in the study of high temperature superconductors has led to an increase in the understanding of these compounds. Nevertheless, there are still many gaps in the jigsaw puzzle that these systems represent. In particular the form of the boundary $T_c(x)$ of the superconducting phase in the T(temperature)–x(doping concentration) plane, proved to be very elusive. All these materials can be described in terms of weakly coupled two-dimensional (2D) planes [1], and here the compound $La_{2-x}(Sr)_xCuO_4$(LSCO) is taken as a representative example. It has been recently proposed [2] that geometrical correlations between the planar holes induced by doping, play a central role in the determination of the phase diagram. Specifically, it has been proposed that the pairs are bound together by an excitation and its anti-excitation, each of which occupies not much more than one plaquette in the underlying antiferromagnetic 2D square lattice of copper atoms. The pairs exist in a mixture of two real-space states that occupy, respectively, two adjacent and next adjacent plaquettes in the plane. This state was found to give a planar density of oxygen holes $x_0 \approx 0.15$, which corresponds to the doping concentration when the critical temperature T_c is maximal. In this picture when the global doping matches this value the plane is completely covered with overlapping pair excitations. For the purpose of the present discussion overlap of pair excitations is the vehicle through which superconductivity appears and hence this maximal coverage of the plane yields in principle an entirely superconducting system. This accounts for measurements of highest diamagnetism at x_0 [3,4] as well as for observations of phonon softening when T is reduced towards T_c in this range [2,5]. Each oxygen hole that is added onto the plane at this stage pushes in between pairs and overcrowds them. The forced proximity of more than two holes disturbs the pair excitations, destroying locally the carrier of the supercurrent and thus suppressing the local superconducting order parameter. So if locally $x(\boldsymbol{r}) > x_0$, a small domain around $\boldsymbol{r}$ goes normal and ceases to belong to the superconducting phase. Further doping results in increasingly large islands of such normal domains even at $T=0$. When x exceeds a critical value x_{max}, the spread of the normal phase is large enough to prohibit any superconducting path between the boundaries of the system. Using percolation ideas [6] this situation occurs at the percolation threshold p_c, namely, when the superconducting cluster ceases to span the system. Consequently the value of x_{max} could be calculated, $x_{max} \approx 0.3$ [2], in good agreement with experimental observations [4,7,8] (site- or bond-percolation models give $x_{max}=0.29$ or 0.32, respectively).

Hypothesising that for $x<x_0$ at $T=0$ superconductivity appears when a superconducting cluster (SC-cluster) of paris spans the system (i.e., when

the area occupied by pairs exceeds a fraction p_c of the entire available surface) and assuming that the percolation model still applies, enabled to calculate the lowest doping at which superconductivity can be observed, $x_{min} \approx 0.075$ [2]. This is in reasonable agreement with heat capacity [4] and other measurements [7,9].

The applicability of the percolation model usually hinges on the geometrical structure of clusters being quenched. For $x \geq x_0$ this is true within an extended range of time scales, due to the low mobility of pairs in the normal background [10] which keeps the boundaries of the SC-clusters fairly stationary. This low mobility is not to be confused with the supercurrent, which corresponds to the non-dissipative transport of pairs *within the SC-cluster*. For $x < x_0$ it was argued that single holes may be less restricted than pairs in the normal background [10], and so some correlations may develop in the formation process of the clusters. Nevertheless, this picture can still be applied (see below for discussion on this point).

Thus this model reproduces the three numbers x_{min}, x_0 and x_{max} quite accurately. Encouraged by this, the aim here is to deduce the functional form of the $T_c(x)$ line in the T–x phase diagram of LSCO near $T=0$. The underlying idea is that when the plane is only partially covered by the SC-cluster there are channels through which the supercurrent is forced to flow. These channels narrow down when x approaches x_{min} (from above) and x_{max} (from below). So to destroy superconductivity, at a given x, thermal fluctuations need only disconnect these channels rather than turn the entire cluster normal. The closer is the planar structure to p_c, the narrower are these superconducting bridges and the smaller is the temperature needed to upset them. Reciprocally, increasing the temperature, larger regions go normal until, at T_c, the typical size of a locally upset region becomes comparable to the width of the smallest channels that bridge between larger superconducting blobs. When this happens those bridges are "cut" and the boundaries are no longer connected by the SC-cluster. This leads to appearance of finite resistance, whose onset defines T_c for our present purpose.

We first discuss the regime $x \geq x_0$ and find an expression for $T_c(x)$ and then continue with a slight modification to describe the regime $x < x_0$. The logical steps of the arguments presented here are the following:

(1) Determine the typical linear size ζ_T of the superconducting area that thermal fluctuations can upset at temperature T;

(2) Express the dependence of the typical width w of the narrowest bridges between superconducting blobs on the area fraction of pairs p and relate p to the doping concentration x to find $w(x)$;

(3) T_c is the smallest temperature needed to turn these bridges normal, hence equate $w(x)$ with ζ_T at T_c to obtain $T_c(x)$.

We first consider step 1. As the temperature is raised thermal fluctuations begin to agitate the pairs in an attempt to disrupt them. Since the normal domains in this regime are denser in holes than the SC-cluster, the fluctuations actually press pairs in until at some temperature, comparable to the binding energy between holes, a substantial part of the pairs begins to collapse. To estimate the linear size of a typical normal domain ζ_T in this range of temperatures we have to estimate the energy invested in breaking the pairs in it. The planar concentration of the holes in the superconducting phase is $n = x_0/(2d^2)$, where d is the separation between Cu atoms in the underlying lattice. The total energy needed to upset a domain of size $(\zeta_T)^2$ is then roughly $kT \approx nE_b(\zeta_T)^2$, where k is Boltzmann's constant and E_b is the characteristic energy needed to destroy one pair. This gives

$$\zeta_T \approx \sqrt{2kT/x_0 E_b}\, d \sim T^{1/2}. \qquad (1)$$

Having estimated ζ_T we move to step 2 that poses a *purely geometrical question*: how does the typical width of the narrowest bridges depend on the geometrical disorder in the plane? This question has been hardly addressed in the context of the percolation model, mainly due to the difficulty to define properly this width, and so presently it has no definite answer [11]. In our context the locally narrowest neck may be identified by the locally highest (super)current density. When $T=0$ and x is close to x_{max}, the SC-cluster is only barely connected and the fraction of area occupied by the pairs is just above p_c. It is reasonable to assume that, as most quantities near the percolation threshold [6] $w(p)$ is a power of the geometrical order parameter $|p-p_c|$.

$$w(p) \sim |p-p_c|^{\theta}, \tag{2}$$

where θ is a (currently unknown) critical exponent.

At T_c $w(p)$ is comparable to ζ_T, which gives upon comparing eqs. (1) and (2) $T_c(p) \sim |p-p_c|^{2\theta}$. To obtain $T_c(x)$ one needs to find first $p(x)$, whose general properties we now consider. The overall doping concentration can be written as an average over the normal and the superconducting parts

$$x = p(x)x_o + [1-p(x)]x_n, \tag{3}$$

where x_n is the mean doping concentration of the single holes in the normal domains (the holes need not be uniformly distributed within these domains). In particular, at $x_{max}p(x_{max}) = p_c$ and $x_n(x_{max}) = x_H{}^2 x_n$ increases with x, while the concentration within the SC-cluster remains constant x_o, since no further in-cluster doping is possible without overcrowding pairs and suppressing the superconducting order parameter. Thus we can use eq. (3) to gain insight on the behaviour of $p(x \geq x_o)$.

Had the concentration x_n been independent of x, with all added holes used to disrupt pairs, p would have decreased linearly with x. But, besides destroying pairs, doping also compresses the holes in the normal domains, and hence $p(x)$ decreases *slower than linearly*. Therefore, if $p(x)$ is well-behaved between x_o and x_{max} we have $\partial_x p < 0$ and $\partial_{xx} p > 0$. Only when x_n saturates at its highest value x_H for $x > x_{max}$, and further doping only eats into the pairs clusters, does $p(x)$ settle into a constant linear decay, the rate of which is determined below. Similar considerations can be applied to x_n: As x increases x_n follows monotonically $\partial_x x_n > 0$. Differentiating eq. (3) with respect to x we obtain

$$1 = (x_o - x_n)\partial_x p + (1-p)\partial_x x_n, \tag{4}$$

from which $\partial_x x_n$ and $\partial_{xx} x_n$ can be analysed. Considering the regime $x > x_{max}$ (4) yields

$$\partial_x p(x > x_{max}) = -1/(x_H - x_o). \tag{5}$$

The above information, combined with the values $p(x_o) = 1$ and $p(x_{max}) = p_c$, yields the qualitative behaviour of $p(x)$. Knowing its curvature we can set an upper bound on p in this regime, which can be written in the form

$$(1-p_c)/(x_{max}-x_o) > (p-p_c)/(x_{max}-x). \tag{6}$$

Substituting the numbers from measurements [4,7] and from ref. [2] into eq. (6) yields that the r.h.s. is bounded by a number around 4. A good approximation for $p(x)$ is then by the form

$$p(x) = p_c + (1-p_c)\left[\frac{x_{max}-x}{x_{max}-x_0}\right]^{\alpha}$$

$$\equiv p_c + K(x_{max}-x)^{\alpha}, \tag{7}$$

with α the only available parameter (to be determined below from experimental data). To give the above right sign of $\partial_{xx} p$ we have $\alpha > 1$. Using eq. (7) in relation (3) one can solve for x_n to get

$$x_n(x) = x_o + (x-x_o)/[1 - p_c - K(x_{max}-x)^{\alpha}]. \tag{8}$$

From eqs. (2) and (7) we obtain the typical behaviour of the width of the critical necks

$$w[p(x)] \sim (x_{max}-x)^{\alpha\theta}. \tag{9}$$

Upon comparing with ζ_T (step 3), we finally find

$$T_c = T_o[(x_{max}-x)/(x_{max}-x_o)]^{2\alpha\theta}, \tag{10}$$

where T_o is, in principle, a constant to be determined by measurements.

Let us now turn to experimental evidence to determine the powers α and θ. The fraction of the superconducting phase p asserts itself through measurements of the Meissner diamagnetism, which have already been reported [3,4]. Assuming that the oxygen holes distribute uniformly amongst Cu–O planes, the diamagnetic fraction should be a direct measure of $p(x)$. Inspecting these measurements, one can see that although $T_c(x \geq x_o)$ curves downwards (implying $0 < 2\alpha\theta < 1$), $p(x)$ has an *opposite* curvature ($\alpha > 1$), conforming with the above arguments. Figure 3 in ref. [4] (p is termed there f_s) shows such an effect, although no attempt has been made to connect between the two curvatures. Analysing that plot we can deduce that (to the available accuracy) $\alpha \approx 2.0 \pm 1$ and $2\alpha\theta \approx 0.8 \pm 0.5$, yielding $\theta \approx 0.2 \pm 1$. A similar analysis carried out on the noisier data shown in ref. [7] gives $2\alpha\theta \approx 0.7 \pm 0.2$, again in agreement with the above.

Since the form of $w(p)$ proposed in eq. (2) is valid only for p not too far from p_c, eq. (10) should hold only in the vicinity of x_{max}. Nevertheless, to obtain

a simple expression for $T_c(x)$ and to check the extension of the validity of this description, we ignore this limitation and upon extending eq. (10) down to x_0, the coefficient T_0 becomes $T_c(x_0) \approx 40$ K.

The foregoing discussion focused on the doping regime $x \geq x_0$. We now extend it to $x_{min} < x < x_0$, using the general relation eq. (3), which holds in both regimes. As holes are added to the dilutely doped system more and more pairs are formed until, at x_{min}, a spanning SC-cluster appears. Further doping may, in principle, lead both to increasing concentration of single holes within the normal domains x_n (now $x_n < x_0$) and to expansion of the superconducting part. Thus we first have $\partial_x p > 0$ and $\partial_x x_n \geq 0$. Further, if x_n were constant then p would have increased linearly with x, but since in principle x_n may also increase then part of the doping may go into the normal domains, causing p to *increase slower than linearly*, implying $\partial_{xx} p \leq 0$ (equality corresponds to constant x_n). The same argument, applied to x_n yields $\partial_{xx} x_n \leq 0$. All this limits the freedom we have in describing $p(x)$ and we again assume a general power law form

$$p(x) = p_c + (1 - p_c)[(y - y_{min})/(1 - y_{min})]^{\beta},$$

where for brevity we have defined $y \equiv x/x_0$ and $y_{min} \equiv x_{min}/x_0 = p_c$. Again the only available parameter is the power β, whose value is determined below from experimental data. Substituting into eq. (3) an explicit expression for x_n can be obtained, but it is of no immediate interest here.

Note that due to the low density of normal domains around the clustered pairs in this regime, thermal fluctuations upset pairs now by separating them rather than by squeezing them in as for $x > x_0$ (This difference has significant ramifications which are beyond the scope of this paper, and are currently under study). Nevertheless, to calculate ξ_T we can follow a procedure similar to the above, replacing E_b by a different characteristic energy, which results again in $\xi_T \sim \sqrt{T}$. Repeating the steps that led to eq. (10), we obtain now the corresponding expression for T_c in this regime

$$T_c = T_1[(y - p_c)/(1 - p_c)]^{2\beta\theta}, \qquad (11)$$

where T_1 is a constant to be determined. To evaluate β we refer again to the data in ref. [4] that show a fairly accurate linear increase in the fraction of the diamagnetic phase with x, $\beta = 1.0 \pm 0.1$. This linearity has another significant implication discussed below. Reanalysing the data from ref. [4] we find $2\beta\theta = 0.24 \pm 0.1$, giving a value for θ that agrees within the error bars with that found near x_{max}. Analysing similarly the data of ref. [9] we find $2\beta\theta = 0.36 \pm 0.1$, giving again $\theta = 0.2 \pm 0.1$. In principle, there is no reason why the prefactors T_1 in eq. (11) and T_0 in eq. (10) should be related. Nevertheless, to check the range of validity of the present picture, as done for T_0, we take the experimental value $T_1 = T_c(x_0) \approx 40$ K. The $T_c(x)$ line that results from expressions (10) and (11) with $\theta = 0.2$ on both sides, is plotted in fig. 1 together with data from ref. [4] for comparison. The agreement is reasonable, considering the usual large fluctuations in the preparation of samples of LSCO. Expecting the curve to be inadequate away from x_{min} and x_{max}, we find that the curve deviates from the data only for $0.11 < x < 0.18$, implying a surprisingly extended range of validity.

Before concluding let us discuss the validity of the assumption of quenched structure in the plane. For $x > x_0$ it is plausible that this is the case due to the "pressure" of the single holes in the normal domains, which restricts the pairs to the SC-cluster. Namely, the boundaries of the SC-cluster can be considered practically stationary. In the regime $x < x_0$ one might expect some mobility of the single holes in the normal domains due to the large free volume available (e.g. by the mechanism proposed in ref. [2], which is available to single holes but not to paired holes), which may effect the picture. Randomly quenched clusters and single holes permit using $p(x_{min}) = p_c$, while high mobility allows dipolar attraction between the SH excitations to effect clustering and reduce $p(x_{min})$. This reservation gains in importance with increasing temperature. The linearity of $p(x)$, evidenced by the measurements in ref. [4] indicates that x_n is practically constant within an extended range above x_{min} (see eq. (3)). This supports the idea that single holes in the normal domains are mobile [10] and diffuse to pair (at least on the time scales of the measurements). It thus substantiates the assumption in ref. [2] and here that practically *all* single holes pair for $x \approx x_{min}$. But although single holes may move, the pairs, once formed, have very low mobility in the normal back-

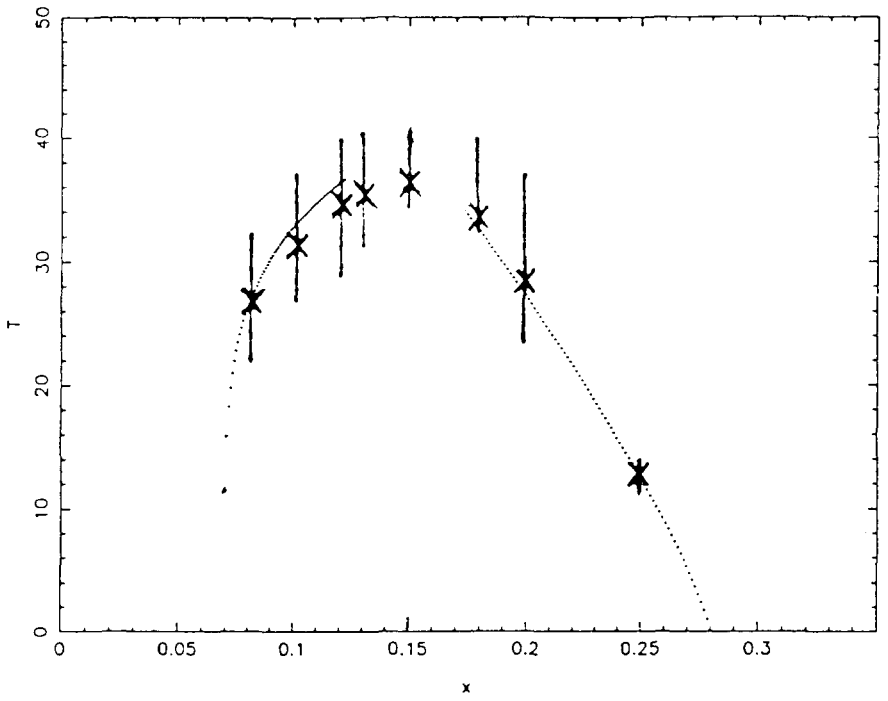

Fig. 1. The $T_c(x)$ curve that results from expressions (11) and (12) (dotted lines) together with data from ref. [4] (points with error bars) for comparison. The parameters used are $\theta=0.2$, $\alpha=2.0$, $\beta=1.0$ and $T_o=T_1=40$ K.

ground. Hence the boundaries of the clusters can be considered stationary even in this regime. It must be made clear that the mobility discussed here is not related to the transport of pairs *within* the SC-cluster, which is associated with the superconductivity.

Nevertheless, the mobility of single holes may in itself affect the results in the sense that the topological structure of the clusters that form in the plane may not follow a percolation-model pattern. Thus our model comprises a convenient modification by keeping $p(x_{min})=p_o$, and letting mobility modify only x_n for x close to x_{min}. This is justified by the close estimate the model yields for x_{min} and for T_c in its neighbourhood.

To conclude, a well-defined model has been proposed to study the effect of geometrical correlations amongst pairs in the Cu–O planes on the critical temperature. The qualitative, as well as the quantitative results agree with the available data reasonably well, but more data is needed to pinpoint the values of the exponents accurately. The model presented here links explicitly the (previously unclearly related) diamagnetic fraction and $T_c(x)$ and also accounts for the opposite curvatures of $p(x>x_o)$ and $T_c(x>x_o)$. It should be emphasised that the dependence of the width of the critical bridges on the superconducting fraction is a property that is governed mainly by the underlying geometry, rather than directly relating to superconductivity. As such it can be found from studies that are independent of the problem at hand (e.g., the percolation model, or some variation of it). Also note that if the same geometrical model applies both near x_{min} and x_{max}, the value of θ should be identical near both the intersects of T_c with the $T=0$ axis. This enables to test the model by examining $T_c(x)$ near these points independently, as well as by comparing to a tangential study of the pure geometrical problem. The temperature dependence of ξ_T. on the other hand, may differ between the two regimes, due to:

(1) the different densities of single holes surrounding superconducting domains, which leads to different interactions between the excitations in the plane, and

(2) the different mechanisms by which thermal fluctuations upset the pairs. These may in principle change the power of $(x/x_0 - p_c)$ in $T_c(x)$ near x_{min}, but analysing the data in refs. [4,7,9], such a difference could not be detected. It should be stressed that the parameters used to plot fig. 1 are not adjusted to fit the data and a better fit can be provided (e.g., by $T_0 = 40$ K, $T_1 = 42$ K and $\theta = 0.18$). Nevertheless, the agreement found by using experimental data is good enough even without adjusting the parameters.

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