Remarks on the phase diagram of high-temperature superconductors: pressure dependence

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The $T_c(x)$ dependence of high-temperature superconductors shows that superconductivity occurs above a critical concentration $x_c$. For concentrations exceeding $x_c$, $T_c$ increases until an optimal concentration $x_{opt}$ is reached and drops with further increase of $x$. Above $x_{opt}$, i.e., in the overdoped region, there exists a single $T_c$ which can be taken as the temperature of the Cooper pair formation and, simultaneously, of their condensation (BEC) to the superconducting state. For carrier concentrations below the optimal value, $x < x_{opt}$, there are two characteristic temperatures, $T^* > T_c$. At $T^*$, phase incoherent local pairs (LP’s) are formed and only at $T_c$ the system undergoes the superconducting phase transition. The existence of these two characteristic temperatures, $T^*$ and $T_c$, reflects various phenomena related to strong electron correlations. We review the pressure effects in the cuprate family YBCO and propose their explanation within the Hubbard model and crossover from BCS cooperative pairing to Bose–Einstein of preformed pairs. The scaling of the pressure effects above and below $x_{opt}$ is analyzed in terms of two parameters: the transfer integral $t$ and on-site energy $U$. With increasing pressure, $t$ increases and the density of states at the Fermi level decreases. Above $x_{opt}$, $T_c \sim 1/2zt$ and $dT_c/dp < 0$. Below $x_{opt}$, however, the derivative $dT_c/dp > 0$, since $T_c \sim t^2/U$.

Key words: high $T_c$ cuprates; pressure effect; Cooper pairs; local pairs; phase diagram

1. Introduction

High-temperature superconductivity (HTSC) discovered by Bednorz and Miller [1] in layered structures of copper oxides is well seen for YBa$_2$Cu$_3$O$_{6+x}$. An increase in the oxygen concentration $x$ causes a controlled change in concentration of carriers (holes). This unique feature of YBCO allows spin and charge correlations to be monitored in the antiferromagnetic (AF) insulator state for $x < 0.5$ and in the superconduct-
ing (SC) state when $x$ varies from 0.5 to 1. A general phase diagram of the cuprates [2] (Fig. 1) exhibits two characteristic concentrations: $x_1$, at which the superconducting phase occurs and $x_{\text{max}}$, where this phase disappears. For very low concentrations of carriers (holes/electrons), the material exhibits antiferromagnetism, and spin and charge are localized. With increasing carrier concentration, pair correlations develop and almost free bosonic-like local pairs occur. The origin of a pseudogap temperature $T^*$ is still discussed. In particular, NMR data on $T_1$ anomaly ascribe this temperature to a spin gap [3].

Fig. 1. Phase diagram of a high-temperature superconductor (after Ref. [2])

In this paper, we review the pressure effects in HTSC and propose their explanation within the concept of preformed pairs and BCS-BEC crossover scenario.

2. Pressure effect theory and experimental results

The pressure effect in HTSC has been analyzed in detail by Griessen [4]. The data collected for YBCO showed that the pressure coefficient $dT_c/dp$ is large and positive for materials with $T_c$ close to 25 K, and its absolute value tends to zero when the critical temperature attains its highest value: $T_c = 90$ K (Fig. 2). Theoretical explanation of the pressure effect explored various models, among them 3D and 2D BCS models [5, 6], the Resonating Valence Bond (RVB) approach [7] and multipolaronic models [8].

The starting point for the first two models is the equation for $T_c$ well known in BCS theory. Under the assumption of two-dimensional transport in La$_{2-x}$Sr$_x$CuO$_{4-y}$ and YBCO, the equation has the form given by Labbé and Bok [6]:

$$k_B T_c = 1.13 D \exp\left(-1/\lambda^{1/2}\right)$$

(1)

where $k_B$ is the Boltzmann constant, $\lambda = N(E_F)U_{el-ph}$ is the effective parameter of the electron-phonon coupling, and $D$ is the width of the van Hove singularity $D^2 = \gamma^2/(E_d$
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\[-E_p^2 + 16\gamma^2\]^{1/2}. The parameter \(\gamma\) is the overlap integral of \(3d_{x^2-y^2}\) and \(2p_x\) orbitals. \(E_d\) and \(E_p\) are the electron site energies of 3d copper and 2p oxygen orbitals, respectively.

![Graph](image)

Fig. 2. \(\frac{d\ln T_c}{d\ln V}\) versus critical temperature (after Ref. [4])

By differentiating Eq. (1), one obtains the volume dependence of \(T_c\):

\[
\frac{d \ln T_c}{d \ln V} = \frac{d \ln D}{d \ln V} + \frac{1}{2\lambda^{1/2}} \frac{d \ln \lambda}{d \ln V}
\]  

(2)

For \(d \ln D / d \ln V = 4\), \(d \ln \lambda / d \ln V = -3\) and \(D = 0.3\) eV, Eqs. (1), (2) qualitatively describe the experimental data. The value of the parameter \(\lambda\), determined from Eq. (1), strongly depends on volume, which means that electron-phonon interaction remarkably changes with increasing pressure.

In the RVB model [7], the \(3d_{x^2-y^2}\) orbital of the copper ion \(Cu^{2+}\) is hybridized with the \(2p_x\) oxygen orbital, forming the so-called Zhang–Rice singlet. The critical temperature has a BCS-like form:

\[
k_BT_c = 1.13h\omega_b \exp\left(-1/\overline{\lambda}\right)
\]  

(3)

where \(\overline{\lambda} = (8/\pi)(t/U)\Phi(x)\). The transfer integral \(t\) and the on-site interaction \(U\) satisfy the relation \(U \gg t\), and \(\Phi(x)\) is some function depending exclusively on the
carrier concentration. In this model, the cutoff energy $\hbar \omega_0$ is defined by the transfer integral $t$. Taking $\hbar \omega_0 = 0.08$ eV and $\lambda = 0.4$ yields $T_c = 95$ K for a nearly half-filled band ($x = 1$). For heavy hole carriers, the expression for the critical temperature assumes the form:

$$T_c = t \delta \exp \left( -U \frac{\delta}{t} \right)$$

(4)

where $\delta = tU$ is the admixture of the Cu$^{3+}$ state in the main state of Cu$^{2+}$. The critical temperature scales as $t^2/U$ [7]. The theory of bipolaronic superconductivity yields the largest value of the pressure coefficient $dT_c/dp$ [8, 4].

In complex oxides, the pressure coefficient can not only take different values but it can also change the sign. Driessen et al. [9] have shown that the pressure coefficients at the onset temperature $T_{co}$ and critical temperature $T_{cf}$, defined as the intersection of the tangent to linear part of the resistivity $R(T)$ curve with the $T$-axis, have opposite signs (Fig. 3). The pressure coefficient $dT_{co}/dp > 0$, and $dT_{cf}/dp < 0$, have opposite signs over the entire pressure range, from 0 to 170 kilobars. The change of sign in the pressure coefficient is associated with strong fluctuations above $T > T_c$. For a low concentration of the Cooper pairs, the pressure coefficient is positive, while it is negative at the critical point for high contents of the superconducting phase. This shows that the pressure expands the fluctuation region, $(T_{co} - T_{cf}) \propto p$.

In cuprate HTSC, the empirical relation between $T_c$ and hole concentration $x$ (the number of holes per one Cu atom in the CuO$_2$ plane) is approximately described by a parabolic dependence [10, 11]. This dependence correctly describes $T_c(x)$ for such
Compounds as: YBa$_2$Cu$_3$O$_{6+\delta}$, Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_6$, La$_{2-x}$Sr$_x$CuO$_4$, La$_{2-x}$Sr$_x$CaCu$_2$O$_6$, as well as for (Ca$_x$La$_{1-x}$)(Ba$_{1.75-x}$La$_{0.25+x}$)Cu$_3$O$_y$ for various oxygen contents $y$.

Now we arrive at the fundamental question. Why and how do the phase diagram and $T_c(x)$ change when a pressure is applied? The answer was given in the paper by Sadewasser et al. [12], who present a complete description of recent investigations of the pressure dependence of $T_c$ in YBa$_2$Cu$_3$O$_{6+\delta}$ in function of the concentration of oxygen defects in CuO$_2$. From their data (Fig. 2 in [12]), the parabolic dependence $T_c(x)$ for various pressures may be obtained. The dependence is shown in Fig. 4 for atmospheric pressure and for $p = 8$ GPa.

![Fig. 4. $T_c$ versus oxygen content in YBa$_2$Cu$_3$O$_{6+\delta}$ for $p = 0$ and under the pressure $p = 8$ GPa](image)

The plots are a parabolic approximation to the experimental data taken from Ref. [12].

The critical temperature depends not only on carrier concentration, but also on the degree of buckling of the CuO$_2$ planes, on the occurrence of structural phase transformations, and on pressure induced relaxational phenomena. The latter highly interesting effect is related to the ordering of mobile oxygen defects in the lattice; an increase in pressure reduces the mobility of defects and simultaneously increases the degree of ordering of oxygen defects. This is particularly well observed in YBCO samples with reduced oxygen contents [12], where the increase of $T_c$ with pressure, and hence the values of $dT_c/dp$, strongly depend on the temperature at which the pressure is varied. For example, the pressure coefficient of a sample with $x = 0.41$, subject to the effect of different pressures at low temperatures ($T < 200$ K), is $(dT_c/dp)_{LT} = +2.1$ K/GPa. However, a much larger value of $dT_c/dp$ is obtained if the sample is subject to the same pressure at room temperature for a period sufficiently long to allow a full relaxation. A well oxygenated sample ($x = 0.95$) does not exhibit relaxation effects and its pressure coefficient $dT_c/dp = +0.24$ K/GPa.
Changes induced by hydrostatic pressure on oxygen-chain ordering were observed by Liarokapis et al. [13] in Raman spectra of YBa$_2$Cu$_3$O$_{6-x}$ single crystals ($x = 0.5$ and overdoped) in the temperature range 77–300 K. In the overdoped compounds ($x > 0.92$), pressure tends to decrease the transition temperature, reducing the disorder. This is probably connected with a structural phase transformation in the CuO$_2$ planes observed for $x \geq 0.95$ [14].

As was mentioned above, the dependence of $T_c$ on carrier concentration approximately satisfies the following parabolic type relation [12]:

$$T_c = T_c^{\text{max}} \left[ 1 - A \left( x - x_{\text{opt}} \right)^2 \right]$$

(5)

where $T_c^{\text{max}}$, $A$, $x$, and $x_{\text{opt}}$ are functions of pressure. In YBCO, the carrier concentration $x$ can be varied by changes in oxygen concentration, by cation replacements or by applying a pressure. In a simple “charge transfer model”, $T_c$ can increase only by increasing $x$, with all other parameters constant. According to such a model, $dT_c/dp = 0$ at the optimal concentration $x = x_{\text{opt}}$. In reality however, the pressure coefficient is nonzero and positive, and varies from $+1$ to $+2$ K/GPa. In the modified charge transfer model [15], the total pressure derivative consists of two parts:

$$\left( \frac{dT_c}{dp} \right) = \left( \frac{\partial T_c}{\partial x} \right) \left( \frac{\partial x}{dp} \right) + \left( \frac{dT_c}{dp} \right)_{\text{noCT}}$$

(6)

The first term stands for normal charge transfer to the CuO$_2$ planes caused by increasing pressure, while the second term accumulates contributions from the pressure dependences of $T_c^{\text{max}}$, $A$, and $x_{\text{opt}}$. However, this model is not capable of explaining all the changes observed experimentally. The experimental changes in $T_c$ as a function of pressure and $x$ can be explained only if one assumes that $T_c^{\text{max}}$, $A$, and $x_{\text{opt}}$ are quadratic functions of pressure, as demonstrated by Jover et al. [16] for the thallium compound. A very large anisotropy of the coefficient $dT_c/dp$ as a function of axial pressure was observed in YBa$_2$Cu$_3$O$_7$. If the axial pressure was applied along the $a$ axis, the coefficient was equal to $-2.0$ K/GPa. Along the $b$ axis it was $1.9$ K/GPa and along the $c$ axis $-0.3$ K/GPa [17, 18]. Compression along the $b$ axis yields a reduction in hole density, while compression along the $a$ axis enhances this density.

3. Sign inversion of the pressure coefficient in composite PST-YBCO in the vicinity of the “pressure crossing point”

The parabolic dependencies $T_c(x,0)$ and $T_c(x,p)$, plotted in Fig. 4, show that there is a crossing of the parabolas in the “overdoped” regime, with $p = 0$ and $p \neq 0$, suggesting a change in the sign of the pressure coefficient from positive to negative. This
result is also suggested by the theory, since for low concentrations of holes in HTSC there are strong fluctuations of the condensate, which coexist with the local pairs (LP’s). When pressure is applied, the number of LP’s in the Fermi sea increases, causing an increase in $T_c$. For large concentrations $x$, these fluctuations are less important and the BCS theory can be applied, predicting a negative pressure effect. The "crossing point", which gives rise to the sign change of the pressure coefficient, has been observed in samples of composite YBCO$_{1-x}$PST$_x$ (PST – Pb(Sc$_{0.5}$Ta$_{0.5}$)O$_3$) [19]. For YBCO, a positive value of the pressure coefficient $dT_c/dp = 0.5$ K/GPa was obtained. The sign inversion of the pressure coefficient was also observed in composite PST-YBCO in the vicinity of "crossing" point (see Fig. 5).

![Fig. 5. Pressure dependence of the critical temperature shift, $T_c(p) - T_c(0)$, in composite YBCO$_{1-x}$PST$_x$ for different concentrations of PST [19]](image)

For the dispersed superconducting phase with increasing concentrations of PST (which is a reservoir of holes), the pressure coefficient decreased and changed its sign to negative, $dT_c/dp < 0$, for high values of $x$. The quadratic dependence of $T_c$ on $x$ was also confirmed. This suggests that the pressure effect depends on whether the under-doped or overdoped regime of the investigated material is considered.

The dispersion of superconducting YBCO in a PST composite leads to a change in the hole concentration of HTSC grains. Strontium in PST is a reservoir of holes in the PST-YBCO composite. When the fraction of PST increases, the hole concentration
inside the YBCO superconducting grain rises. Hence changes of the dispersion of the YBCO-PST composite make it possible to pass smoothly through the crossing point with the carrier concentration. The crossing point phenomena related to stable $x_1$ and $x_{\text{opt}}$ shifted towards lower temperatures can be related to changes in the symmetry of pairing mechanisms [7, 20].

4. Modelling the effect of pressure on $T_c$ in HTSC

The pressure effect has been recently discussed on the basis of the extended Hubbard model, in particular the influence of pressure on the parabolic character of the $T_c(x,p)$ dependence in HTSC [21]. It has been concluded that the pressure effect is related to a pressure induced charge transfer from the reservoir of holes to the CuO$_2$ planes. The data for the Hg-1201 material also suggest the existence of an intersection point that leads to the sign change of $dT_c/dp$. It has been found that the hopping integral depends on pressure and that $T_c$ is proportional to the pressure applied in the underdoped regime [22].

According to the model of local pairing, two important lines can be drawn on the phase diagram of HTSC (Fig.6): a line of pair correlations ($T^*$), at which carriers form LP's, and a coherence line ($T_c$), below which the superconducting condensate is formed [23].

Fig. 6. A line pair correlation $T_{**}$ separating the Fermi liquid (FL) and Bose liquid (BL) regions (the latter is formed by nearly free LP) and the phase correlation line, $T_c$, enclosing the superconducting condensate (SC)

One should also add that Abrikosov [24], in his analysis of fluctuation effects, proposed the formation of superconducting filaments in one crystal direction only, i.e., of one-dimensional superconducting channels. Such channels that occur beyond the percolation threshold can induce the superconductivity of a sample. Nonuniform carrier distribution and strong fluctuations are essential phenomena in superconductors with low carrier concentration, for which there are two characteristic temperatures, $T^*$ and $T_c$, as well as charge and spin pseudogaps.
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For low carrier concentrations \((x_1 < x < x_{\text{opt}})\) at \(T'\), fermions start to bind into LP’s (composite bosons), which condense at \(T_c\). For large concentrations \((x_{\text{opt}} < x < x_{\text{max}})\), both characteristic lines eventually merge and \(T' = T_c\) which means that Cooper pair formation takes place at the same temperature at which the superconducting condensate emerges. A line of pair correlations can be considered as a formation line for bosons, attaining a macroscopic phase coherence only at \(T_c\), at which the whole system is described by a single wave function.

Within the model of local pairing by Micnas and Robaszkiewicz [23], the pressure effects, measured by \(dT_c/dp\), scale differently on both sides of the optimal carrier concentration \(x_{\text{opt}}\). The transfer integral rises with increasing pressure. Therefore, the pressure coefficient is positive below \(x_{\text{opt}}\), since \(T_c\) scales like \(t^2/|U|\). However, \(T_c\) scales like \(1/2zt\) above \(x_{\text{opt}}\), which implies that the pressure coefficient is negative (like in the BCS model) (Fig.7).

Close to \(T_{c_{\text{max}}}\), the pressure coefficient is nearly zero. Hence, the pressure causes an enhancement of \(T_c\) in the concentration regime where two distinct characteristic temperatures, \(T'\) and \(T_c\), are present. If \(T' = T_c\), the pressure coefficient is negative and \(T_c\) is reduced by pressure like in “classical” superconductors’. Such a dependence was confirmed by experiment in the case of the composite YBCO-PST [19], for which positive and negative pressure coefficients of \(T_c\) were observed.

The different scaling of the pressure effect below and above \(x_{\text{opt}}\) can also have an explanation in a nonuniform and fluctuating charge distribution for small \(x\), and
a homogeneous and relatively stable charge distribution for \( x > x_{\text{opt}} \). For \( x > x_{\text{opt}} \), \( T' = T_c \), because fluctuations are negligible. For \( x < x_{\text{opt}} \), \( T' > T_c \) and pressure shifts the equilibrium from the s- to the d-state. This difference can be explained by a possible occurrence of a structural instability, leading to a phase separation and self-organized stripe array. The stripes are one dimensional metallic objects, “topological defects” in the antiferromagnetic insulator. The stripe structure slowly fluctuates, which can be taken as the effect of the phase separation. Emery et al. [20] introduced two \( T' \) temperatures in their phase diagram. At \( T'_1 \) the stripe structure occurs. Charges are ordered along these stripes and charge correlations are 1D along the chain (there are no perpendicular correlations). At the temperature \( T'_2 \) a pairing takes place in metallic chains, giving rise to a spin gap. There is no coherence between neighbouring chains which suggests that one can observe “free Cooper pairs” in such a state. The phase coherence of these free pairs takes place at \( T_c \) and correlations between the pairs in neighbouring chains can result from Josephson coupling. The pressure effect is positive here, since the pressure increases the transfer integral \( t \) in the extended Hubbard model.

Recent calculations by Micnas and Tobijaszewska show that the expansion of the pseudogap region associated with mixing of s and d-wave components gives rise to an additional increase in \( T_c \) in the underdoped regime [25]. Above the concentration \( x_{\text{opt}} \), the lines \( T'(x) \) merge with the line \( T_c(x) \) and BEC takes place in the metallic region, where charge and phase fluctuations can be neglected like in the BCS model. Hence, the pressure effect is negative here. However, the experimentally discovered shift of \( x_{\text{mai}} \), towards lower concentrations still remains unexplained.

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**References**


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