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

JAN STANKOWSKI[1*], MARCIN KRUPSKI[1], ROMAN MICNAS[2]

[1]Institute of Molecular Physics, Polish Academy of Sciences,
M. Smoluchowskiego 17, 60-179 Poznań, Poland

[2]Institute of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland

The $T_c(x)$ dependence of high-temperature superconductors shows that superconductivity occurs above a critical concentration x_1. For concentrations exceeding x_1, 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 $YBa_2Cu_3O_{6+x}$. 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-

[*]Corresponding author, e-mail: janstank@ifmpan.poznan.pl

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_{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].

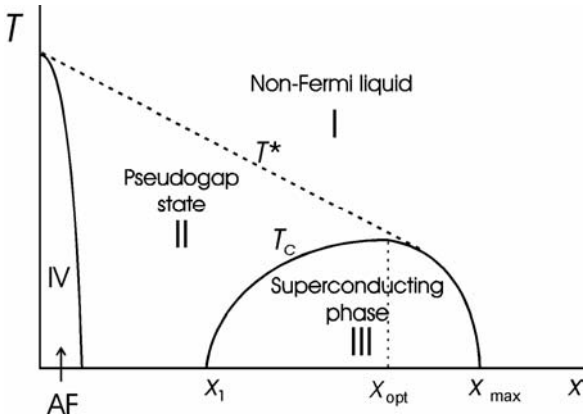

Fig. 1. Phase diagram of a high-temperature superconductor (after Ref. [2])

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 $La_{2-x}Sr_xCuO_{4-y}$ and YBCO, the equation has the form given by Labbé and Bok [6]:

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

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 $D^2 = \gamma^2/[(E_d$

$-E_p)^2 + 16\gamma^2]^{1/2}$. The parameter γ 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.

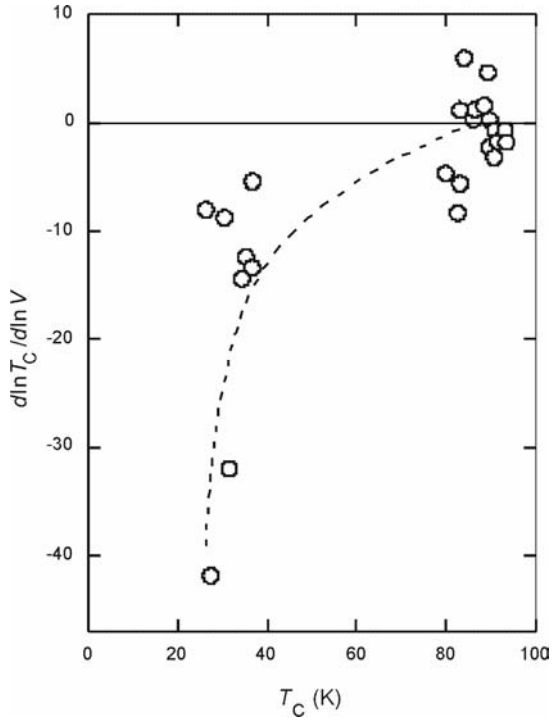

Fig. 2. $d\ln T_c/d\ln V$ versus critical temperature (after Ref. [4])

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

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

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 λ, 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:

$$k_B T_c = 1.13\hbar\omega_0 \exp\left(-1/\bar{\lambda}\right) \tag{3}$$

where $\bar{\lambda} = (8/\pi)(t/U)\Phi(x)$. The transfer integral t and the on-site interaction U satisfy the relation $U >> t$, 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:

$$T_c \approx t\delta \exp\left(-U\delta/t\right) \tag{4}$$

where $\delta = t/U$ 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, $(T_{co} - T_{cf}) \propto p$.

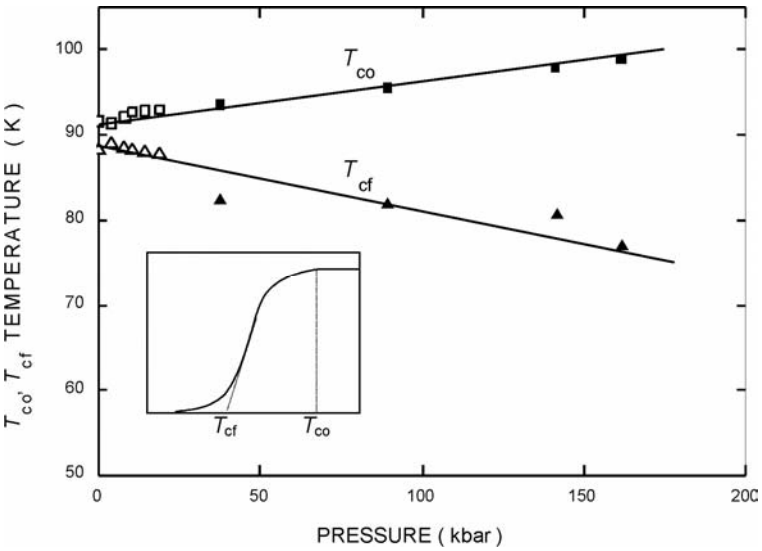

Fig. 3. Dependence of T_{co} and T_{cf} on pressure for YBCO [9].
Inset: T_{co} – critical onset temperature and zero-resistivity T_{cf} temperature

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: $YBa_2Cu_3O_{6+x}$, $Y_{1-x}Ca_xBa_2Cu_3O_6$, $La_{2-x}Sr_xCuO_4$, $La_{2-x}Sr_xCaCu_2O_6$, as well as for $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$ 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 $YBa_2Cu_3O_{6+x}$ 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.

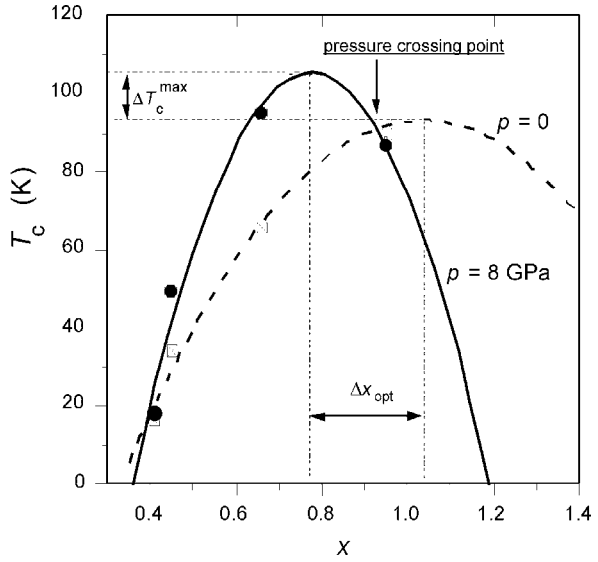

Fig. 4. T_c versus oxygen content in $YBa_2Cu_3O_{6+x}$ for p = 0 and under the pressure p = 8 GPa
The plots are a parabolic approximation to the experimental data taken from Ref. [12]

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 $YBa_2Cu_3O_{6+x}$ 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]:

$$T_c = T_c^{\max}\left[1 - A\left(x - x_{\text{opt}}\right)^2\right] \tag{5}$$

where $T_c^{\max}$, A, x, and x_{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:

$$\left(\frac{dT_c}{dp}\right) = \left(\frac{\partial T_c}{\partial x}\right)\left(\frac{\partial x}{\partial p}\right) + \left(\frac{dT_c}{dp}\right)_{\text{noCT}} \tag{6}$$

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 $T_c^{\max}$, A, and x_{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 $T_c^{\max}$, A, and x_{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 $YBa_2Cu_3O_7$. 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).

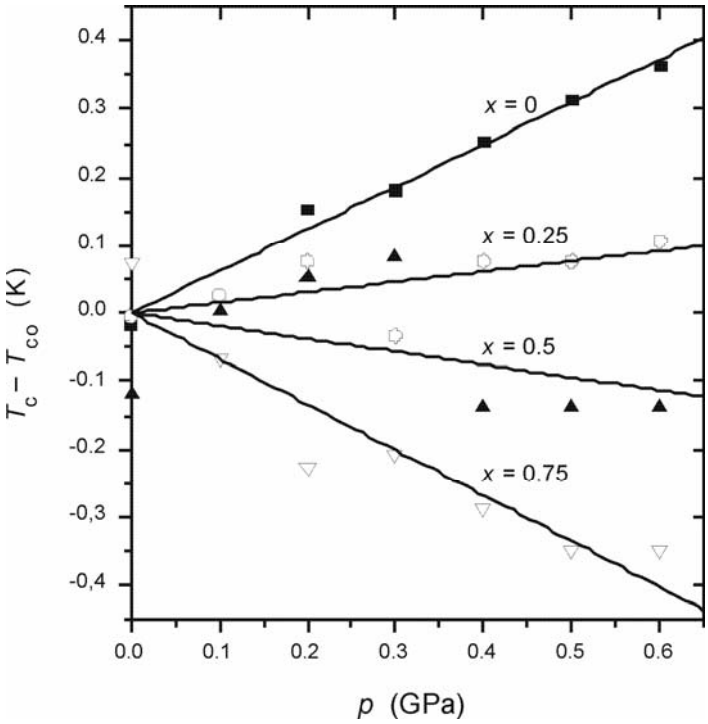

Fig. 5. Pressure dependence of the critical temperature shift, $T_c(p) - T_c(0)$, in composite $YBCO_{1-x}$ PST_x for different concentrations of PST [19]

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_{co} on x was also confirmed. This suggests that the pressure effect depends on whether the underdoped 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_{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].

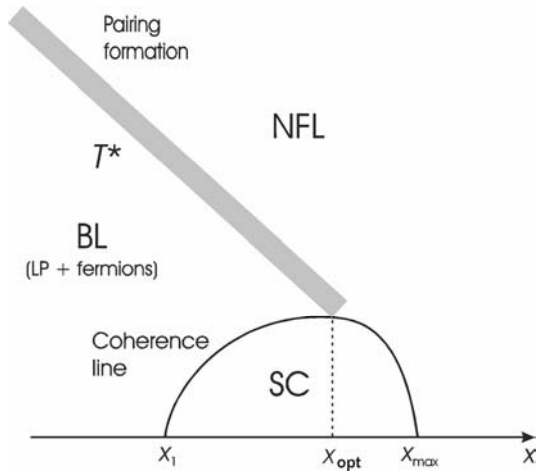

Fig. 6. A line pair correlation T_{LP} separating the Fermi liquid (FL) and Bose liquid (BL) regions (the latter is formed by nearly free LP) and the phase correlation line, T_c, enclosing the superconducting condensate (SC)

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.

For low carrier concentrations ($x_1 < x < x_{opt}$) at T^*, fermions start to bind into LP's (composite bosons), which condense at T_c. For large concentrations ($x_{opt} < x < x_{max}$), 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_{opt}. The transfer integral rises with increasing pressure. Therefore, the pressure coefficient is positive below x_{opt}, since T_c scales like $t^2/|U|$. However, T_c scales like $1/2zt$ above x_{opt}, which implies that the pressure coefficient is negative (like in the BCS model) (Fig.7).

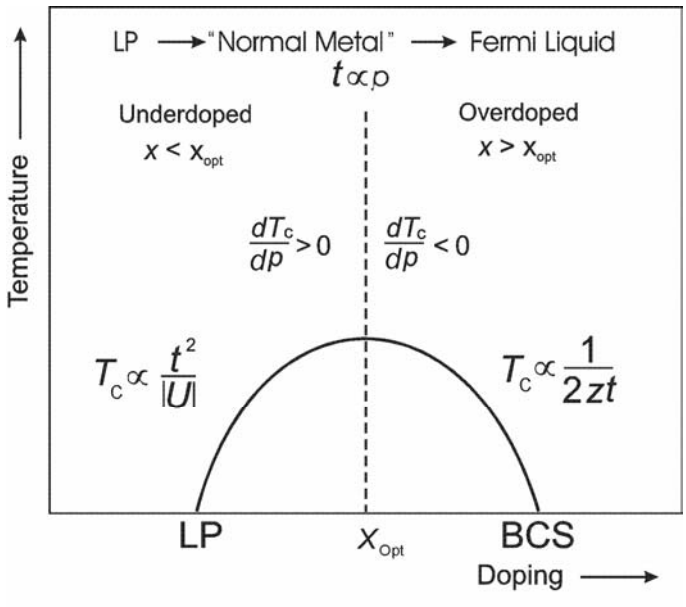

Fig. 7. Scaling of the pressure effect below ($x < x_{opt}$) and above ($x > x_{opt}$) the optimal carrier concentration

Close to T_c^{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_{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 $x > x_{opt}$. For $x > x_{opt}$, $T^* \approx T_c$, because fluctuations are negligible. For $x < x_{opt}$, $T^* > T_c$ 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_{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_{max} towards lower concentrations still remains unexplained.

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References

[1] BEDNORZ J.G., MILLER K.A., Z. Phys., B64 (1986), 189.
[2] ANDERSON P.W., Science, 288 (2000), 480.
[3] BRINKMANN D., MALI M., *NMR Basic Principles and Progress*, Springer-Verlag, Berlin, 1994, Vol. 31, p. 171.
[4] GRIESSEN R., Phys. Rev., B36 (1987), 5284.
[5] ALLEN P.B., DYNES R.C., Phys. Rev., B12 (1975), 905.
[6] LABBÉ J., BOK J., Europhys. Lett., 3 (1987), 1225.
[7] ANDERSON P.W., Science, 235 (1987), 1196.
[8] ALEXANDROV A. S., RANNINGER J., ROBASZKIEWICZ S., Phys. Rev., B33 (1986), 4526.
[9] DRIESSEN A., GRIESSEN R., KOEMAN N., SALOMONS E., BROUWER R., DE GROOT D.G., HEECK K., HEMMES H., RECTOR J., Phys. Rev., B36 (1987), 5602.
[10] TALLON J.L., BERHNARD C., SHAKED H., HITTERMAN R. L., JORGENSEN J.D., Phys. Rev., 51 (1995), 12911.
[11] GOLDSCHMIDT D., KLEHE A.-K., SCHILLING J.S., ECKSTEIN Y., Phys. Rev., 53 (1996), 14631.
[12] SADEWASSER S., SCHILLING J.S., PAULIKAS A.P., VEAL B.W., Phys. Rev., B61 (2000), 741.

[13] LIAROKAPIS E., LAMPAKIS D., NISHIZAKI T., PANAGOPOULOS C., High Pressure Res., 18 (2000), 109.
[14] KALDIS E., RÖHLER J., LIAROKAPIS E., POULAKIS N., CONDER K., LOEFFEN P.W., Phys. Rev. Letters, 79 (1997), 4894.
[15] NUEMEIER J. J., ZIMMERMANN H.A., Phys. Rev., B47 (1993), 8385.
[16] JOVER D.T., WILHELM H., WIJNGAARDEN R.J., LIU R.S., Phys. Rev., B55 (1997), 11832.
[17] GUPTA R. P., GUPTA M., Phys. Rev., B50 (1994), 9615.
[18] PICKETT W.E., Physica, C289 (1997), 51.
[19] KRUPSKI M., STANKOWSKI J., PRZYBYŁ S., ANDRZEJEWSKI B., KACZMAREK A., HILCZER B., MARFAING J., CARANONI C., Physica C320 (1999), 120.
[20] EMERY V.J., KIVELSON S.A., ZACHAR O., Phys. Rev., B56 (1997), 6120.
[21] DE MELLO E.V.L., ACHA C., Phys. Rev., B56 (1997), 466.
[22] CAIXEIRO E.S., DE MELLO E.V.L., Physica, C383 (2002), 89.
[23] MICNAS R., ROBASZKIEWICZ S., [in]: *High-T_c Superconductivity 1996: Ten Years after the Discovery*, E. Kaldis, E. Liarokapis, K.A. Miller (Eds.), NATO ASI Series E, Kluwer Academic Publishers, The Netherlands, Vol. 343 (1997), p. 31.
[24] ABRIKOSOV A.A., Phys. Rev., B63 (2001), 134518; ibidem B64 (2001), 104521.
[25] MICNAS R., TOBIJASZEWSKA B., Acta Phys. Polon. B, 32 (2001), 3233.

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