Scientific Research Publishing

World Journal of Condensed Matter Physics, 2024, 14, 67-76
https://www.scirp.org/journal/wjcmp
ISSN Online: 2160-6927
ISSN Print: 2160-6919

High-Temperature Superconductivity—An Electron Transfer Phenomenon

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How to cite this paper: Sonntag, J. (2024) High-Temperature Superconductivity—An Electron Transfer Phenomenon. *World Journal of Condensed Matter Physics*, **14**, 67-76.
https://doi.org/10.4236/wjcmp.2024.144007

Received: August 15, 2024
Accepted: October 29, 2024
Published: November 1, 2024

Abstract

The *increase* of the critical temperature T_c for superconductivity in $Al_{1-x}(SiO_2)_x$ cermets with increasing x correlates with a *decrease* of the electron density n due to electron transfer, expressed by $T_c/T_{c,\max} = 1-\gamma\cdot n^2$ (*). Behind the formula (*) and $T_c/T_{c,\max} = 1-82.6(P-0.16)^2$, which is characteristic of hole-doped cuprat high-temperature superconductors, lies a general phenomenon, namely electron transfer, which equalizes potential differences in the material and leads to a strong reduction of n. P is the fraction of holes filled by the transferred electrons. A quantitative consideration gives $T_c(x)/T_{c,\max} = 1-\left(\frac{1-x}{1-x_0}\right)^2$ (**), where x is the doping concentration and x_0 is the concentration at which superconductivity begins. At $x = x_{\max} = 1$ the electron source is completely depleted and with further growth of x the hole density p starts to increase and T_c decreases until superconductivity disappears completely at $x = 2-x_0$. Taking into account the formula (**), the hypothesis arose that for $x > x_{\max}$ $T_c/T_{c,\max} = 1-\gamma\cdot p^2$ (***), an analogue of the formula (*), and that superconductivity is possible not only by electron-Cooper pairs but also by paired holes. The mechanisms described here for HTSC suggest an analogy to the physics of semiconductors and that of nanocomposites: Electron-hole duality. The "$P = 1/8$" anomaly in $YBa_2Cu_3O_{6+x}$ is caused by the simultaneous presence of electrons and holes, a consequence of incomplete electron transfer.

Keywords

High-Tc Superconductor, Electron Transfer, Electron Density, Hole Density, "P = 1/8" Anomaly, Jahn-Teller Effect

1. Introduction

Since the discovery of high-temperature superconductivity (HTSC) by Bednorz & Müller [1] in 1986, the underlying mechanism has remained an unsolved mystery to this day, although the physics community is certain that the mechanisms crucial for superconductivity take place in the CuO_2 levels and the CuO_2 layers serve as a charge carrier reservoir. For hole-doped HTSC it is called "hole conduction" because the high T_c is caused by O_2 doping, which provides holes. There is a simple relationship connecting the superconducting critical temperature T_c with P, the number of doped holes per Cu atom in the CuO_2 planes [2],

$$T_c/T_{c,\max} = 1 - 82.6\left(P - P_{\max}\right)^2, \tag{1}$$

where $T_{c,\max}$ is the maximum of the curve, which appears at $P = P_{\max} = 0.16$.

In 2023 the editor of the publication by Wang *et al.* [3] about the superconductors $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ wrote a forward to it: "The mechanism of high-temperature superconductivity in copper oxide materials remains a mystery more than 30 years after its initial discovery. One way to shed light on this is to look for correlations between different observables in cuprate families…"

Such a correlation mentioned is, for instance, the correlation between T_c and the electron density n found in $Al_{1-x}(SiO_2)_x$ cermets, shown in a separate paper,

$$T_c/T_{c,\max} = 1 - \gamma \cdot n^2, \tag{2}$$

where γ is a parameter, which is a constant for a superconductor. The special thing about this is that the change in n is caused by electron transfer, which compensates for potential differences in the material. These two aspects, Equation (2) and electron transfer, are important for an understanding of HTSC.

2. Physical Model

Applying a 35-year-old theory [4] [5], the present article proposes a mechanism that can explain HTSC. It is based on the assumption that the charge carrier densities in HTSC are largely influenced by electron transfer, which compensates for potential differences. The Hall effect plays a key role in confirming this assumption: In $YBa_2Cu_3O_{6+x}$ (YBCO), in addition to the *hole* Fermi surface, small electron pockets [6] were also detected in the underdoped region, indicating that electrons and holes are present simultaneously.

The parabolic curve $T_c/T_{c,\max}$ versus n, Equation (2), looks like the right part of Equation (1) ($P > P_{\max}$), and with its left part ($P < P_{\max}$) when mirrored on the vertical at $P_{\max}$. However, while in Equation (2) the maximum of T_c occurs at $n = 0$, in Equation (1) the maximum occurs on the P axis at $P_{\max}$. And the question arizes, what is the reason for this shifting of $T_{c,\max}$ on the P-scale?

Let us assume that the 4*s* orbitals of the Cu atoms in the lowest layer in the unit cell (**Figure 1**) form a narrow 4*s* band. This band we call band *A*. The 2*p* orbitals of the O atoms and the 3*d* orbitals of the Cu atoms overlapp forming a common *pd* band, called band *B*. The additional O atoms introduced by doping in this

lowest layer produce holes in band *B*. Electron transfer now takes place from the band *A* into these holes. As a consequence, the electron density *n* in the band *A* decreases more and more as *x* increases. For $Yba_2Cu_3O_{6+x}$ at $x=0.30$ (corresponding to $P=0.05$), *n* has reduced to such an extend that superconductivity can occur. And as *x* continues to increase, *n* decreases further and T_c increases until band *A* is completely free of "free" electrons. This is the case at $x=1$ (corresponding to P_{max}). As *x* increases further, T_c begins to decrease again.

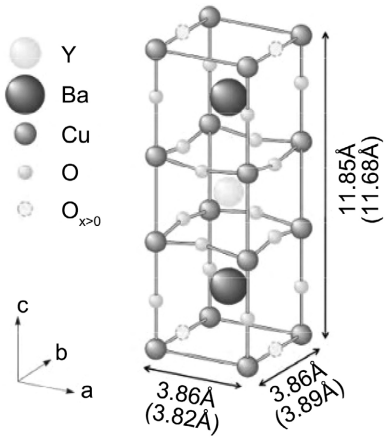

Figure 1. Unit cell of $YBa_2Cu_3O_{6+x}$, taken from Buttler ([7], p. 19). For an arbitrarily given oxygen concentration *x*, this unit cell is slightly modified. The lengths shown in the figure correspond to the extreme values $x=0$ and $x=1$ (values in brackets).

To the left and right of P_{max}, T_c decreases with increasing distance from P_{max} because the carrier density increases; to the left of P_{max}, *n* increases with increasing distance to P_{max}, to the right of P_{max}, the hole density *p* increases with increasing distance to P_{max}. In other words, T_c decreases (parabolically) with increasing distance from the T_c maximum in the same sense as the carrier density increases, both to the left of P_{max} and to the right of P_{max}. This commonality of the two parabolic dependencies is expressed by Equation (1).

3. Quantitative Consideration

For the following calculations we assume a one-to-one correspondence between *x* and *P* in oxygen doped HTSC. In $YBa_2Cu_3O_{6+x}$ such a one-to-one correspondence between *x* and *P* is only approximately fulfilled, which is the consequence of the so-called "$P=1/8$" anomaly, which will be discussed later.

Let $N_{A,0}$ be the "free" number of electrons available for electron transfer per unit cell within the band *A*. Then the remaining number of "free" electrons per unit cell in band *A* after electron transfer is given by

$$N_A(x)=N_{A,0}\left(1-\frac{x}{x_{max}}\right) \tag{3}$$

for $0\le x\le x_{max}$, but $N_A(x)=0$ for $x\ge x_{max}$. x_{max} is the concentration where the maximum of T_c occurs. $N_A(x)=0$ at $x=x_{max}$, which specify the complete

emptying of the band *A* due to electron transfer.

Every O atom introduced by doping provides $N_{B,0}$ holes per unit cell. At $0 \le x \le x_{\max}$, these holes are immediately filled with electrons transferred from band *A*, but at $x \ge x_{\max}$ there are $N_B(x)$ residual (unfilled) holes per unit cell in the band *B*, given by

$$N_B(x) = N_{B,0}\left(\frac{x}{x_{\max}} - 1\right) \tag{4}$$

for $x > x_{\max}$, but $N_B(x) = 0$ for $x \le x_{\max}$.

The concentration dependences of $N_A(x)$ and $N_B(x)$ are shown in Figure 2. As a result of the electron transfer, the number of electrons per unit cell, $N_A(x)$, decreases with increasing *x*, according to Equation (3) ($x \le x_{\max}$), whereas the number of holes per unit cell, $N_B(x)$, increases with increasing *x*, according to Equation (4) ($x > x_{\max}$).

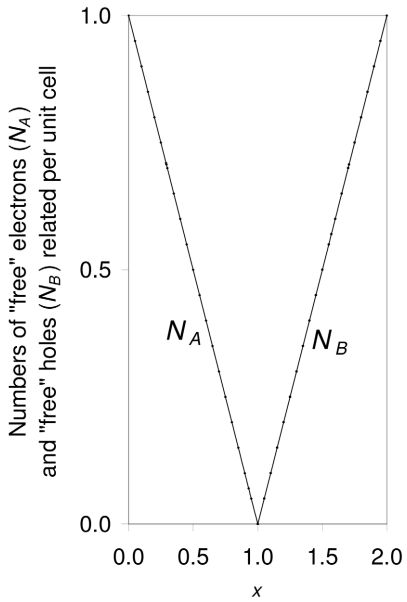

Figure 2. $N_A(x)$ and $N_B(x)$, the numbers of "free" electrons and "free" holes per unit cell, Equations (3) and (4), respectively, versus *x* for $N_{A,0} = N_{B,0} = 1$ and $x_{\max} = 1$.

For the electron density and hole density related to the cross-sectional area of the unit cell, n_f and p_f, it follows:

$$n_f = N_A(x)/F, \tag{5}$$

$$p_f = N_B(x)/F, \tag{6}$$

where $F \approx 1.49 \times 10^{-15}$ cm^2 is the average cross-sectional area vertical to *c* in the unit cell of YBCO, see Figure 1.

Because the electrostatic Coulomb interaction acts in the volume, we are interested in the electron density and hole density related to the unit cell, *n* and *p*,

$$n = N_A(x)/v_{UC}, \tag{7}$$

$$p = N_B(x)/\upsilon_{UC}, \tag{8}$$

where the average volume of the unit cell of YBCO is $\upsilon_{UC} \approx 1.74\times10^{-22}$ cm^3. The concentration dependences of n, p, n_f and p_f are shown in **Figure 3**.

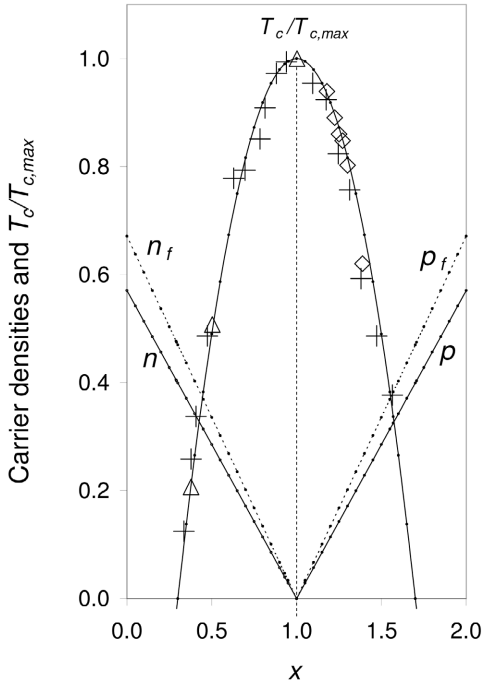

Figure 3. $T_c(x)/T_{c,\max}$ of hole-doped HTSC calculated using Equation (12) and compared with experimental data for $La_{2-x}Sr_xCuO_4$(+), $La_{2-x}Sr_xCaCu_2O_6$(Δ), and $Y_{1-x}Ca_xBaCu_3O_{7-\delta}$ with $\delta \approx 0.04$ (diamonds) (taken from Tallon *et al.* [2], **Figure 2** therein), using $x = P\cdot(x_{\max}/P_{\max})$ with $P_{\max} = 0.16$ and $x_{\max} = 1$. n and p in units of 10^{22} cm^{-3}, equations (7) and (8), n_f and p_f in units of 10^{15} cm^{-2}, Equations (5) and (6).

As $n \propto N_A$ we get with Equations (2) and (3)

$$T_c(x)/T_{c,\max} = 1-\gamma'\left(N_{A,0}\cdot\left(1-\frac{x}{x_{\max}}\right)\right)^2 \tag{9}$$

for the left side of the bell curve, where $\gamma' \propto \gamma$.

At $x = 0$, there is one "free" electron per unit cell in band A, and in band B each doped O atom contributes one hole per unit cell, *i.e.* $N_{A,0} = 1$ and $N_{B,0} = 1$. $x_{\max} = 1$, because at $x = 1$ the number of holes due to doping agrees with the number of electrons in the band A at $x = 0$. Therefore Equation (9) can be replaced by

$$T_c(x)/T_{c,\max} = 1-\gamma'\cdot(1-x)^2. \tag{10}$$

Superconductivity begins at $x = 0.30 \equiv x_0$. By setting $T_c(x)/T_{c,\max} = 0$ in Equation (10), we obtain

$$\gamma' = \frac{1}{(1-x_0)^2} \tag{11}$$

and, introduced in Equation (10),

$$T_c(x)/T_{c,\max} = 1 - \left(\frac{1-x}{1-x_0}\right)^2. \tag{12}$$

In Figure 3, the concentration dependence of $T_c(x)/T_{c,\max}$ calculated by Equation (12) is drawn and compared with the experimental data of $La_{2-x}Sr_xCuO_4$, $La_{2-x}Sr_xCaCu_2O_6$ and $Y_{1-x}Ca_xBaCu_3O_{7-\delta}$ with $\delta \approx 0.04$ (taken from Tallon *et al.* [2]). There is a relatively good agreement between the experimental data and Equation (12).

Although Equation (12) was derived using Equations (2) and (3) only for $x \le 1$, the experimental data also follow Equation (12) very well for $x > 1$. How is this possible? According to Equations (3) and (4) and in consistency with Figure 2, for $x > 1$ there should only be "free" holes but no "free" electrons.

Considering the relatively good agreement between the experimental data and equation (12) also for $x > 1$, we dare to hypothesize that superconductivity is possible not only by *electron*-Cooper pairs but also by *hole*-Cooper pairs consisting of two holes and that there is a complete analogy between *electron*-Cooper pairs and *hole*-Cooper pairs. This includes the hypothesis that, for symmetry reasons, there is also an analogue to Equation (2), namely

$$T_c/T_{c,\max} = 1 - \gamma \cdot p^2. \tag{13}$$

Since $p \propto N_B$, using Equations (13) and (4) we get

$$T_c(x)/T_{c,\max} = 1 - \gamma'\left(N_{B,0} \cdot \left(\frac{x}{x_{\max}} - 1\right)\right)^2 \tag{14}$$

for the right side of the bell curve. And if $N_{B,0} = 1$, $x_{\max} = 1$ and Equation (11) are considered, the identic Equation (12) follows. That means, Equation (12) follows from the Equations (2) & (3) as well as from the Equations (13) & (4), independently of each other.

If $T_c(x)/T_{c,\max} = 0$ is set, Equation (12) has two solutions, $x = x_0$ and $x = 2 - x_0$, which define the limits within which superconductivity occurs. Superconductivity exists in the range $x_0 < x < 2 - x_0$. For $x_0 < x < 1$, superconductivity is realized by *electron*-Cooper pairs, for $1 < x < 2 - x_0$ by *hole*-Cooper pairs.

While Equation (2) corresponds to the left part of the $T_c(x)/T_{c,\max}$ bell curve in Figure 3, Equation (13) corresponds to the right part of it.

The electrostatic repulsion of like charges, electron-electron repulsion or hole-hole repulsion, is responsible for the decrease of T_c with increasing carrier density. This is reflected by the parabolic bell-shaped curve with the T_c maximum.

4. Discussion

4.1. The "*P* = 1/8" Anomaly

As shown in Figure 4, for $YBa_2Cu_3O_{6+x}$ there are larger deviations between the experimental data and Equation (12). This is related to the "$P = 1/8$" anomaly.

The cause is an incomplete electron transfer, caused by the fact that the potential equalization is already achieved at lower electron transfer, before the band A is completely emptied. The potential difference ΔV is obviously smaller than in other HTSC where such a "$P=1/8$" anomaly does not occur. This means that for $0.09<P<0.16$ in YBCO there are carriers in both bands, electrons in band A and holes in band B. This view is supported by observations of quantum oscillations in underdoped YBCO, combined with their negative Hall coefficient R_H at low temperature T in this concentration range [6] and [9] (including the "Supplementary material" in [9]). It reveals that the Fermi surface in the underdoped YBCO also includes small electron pockets.

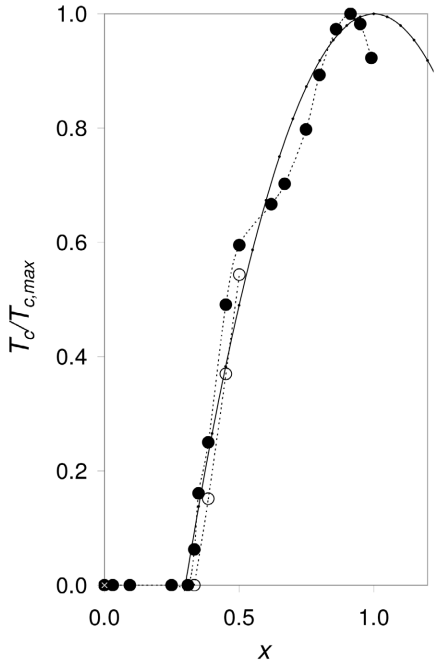

Figure 4. $T_c/T_{c,\max}$ vs. x for $YBa_2Cu_3O_{6+x}$ using the measured value $T_{c,\max}=94\,\mathrm{K}$, compared with Equation (12) (solid line). The experimental data are from Buttler ([7], there page 26, Abbildung 3.8.). The maximum of the experimental data is not at $x=1$, but at 0.93, a consequence of the "$P=1/8$" anomaly. The two types of points, open and filled circles, come from different theoretical models [7] [8], in which different arrangements of the oxygen atoms are assumed by doping.

At low temperatures $R_H<0$, but $R_H>0$ at higher temperatures. This finding can be explained by the fact that electrons and holes are present simultaniously, but their contributions to R_H change with temperature, resulting in sign reversal of R_H with increasing T. This is accompanied by a reduction in T_c compared with a situation where all holes would be filled by transferred electrons. Therefore, in YBCO the maximum value measured for T_c, $T_{c,\max}=94\,\mathrm{K}$, is smaller than what would be theoretially possible, if all electrons were transferred. Assuming a theoretically possible maximum value of $T_{c,\max}=120\,\mathrm{K}$ (for complete electron transfer), we obtain a relatively good agreement of the theoretic

curve with the experimental data $x \le 0.5$ as shown in Figure 5. While there is excellent agreement with the model represented by the filled circles (for $x \le 0.5$), there is a slight parallel shift for the model represented by the open circles. For the two models, see [7] and [8].

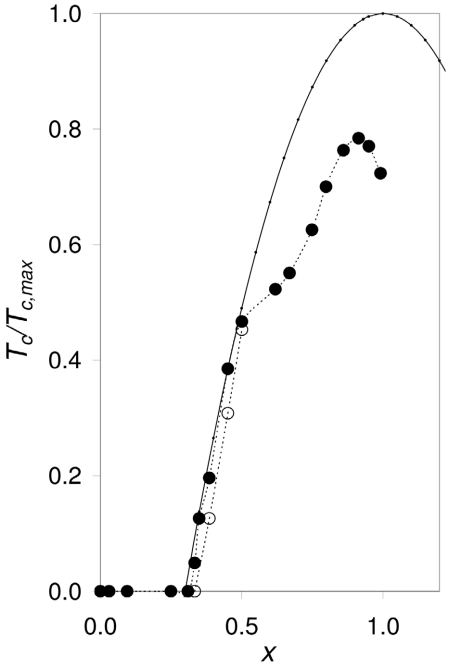

Figure 5. The same as Figure 4, but $T_{c,\max} = 94$ K was replaced by $T_{c,\max} = 120$ K.

4.2. The Jahn-Teller Effect

The structural peculiarities of the HTSC can be compared with the material class "metal-insulator nanocomposites", in which electron transfer takes place from the metallic phase *A* to the insulator phase *B*, leading to a reduction of the electron density in the metallic phase (phase *A*) as shown in [5], there section V.

When comparing the HTSC with the $Al_{1-x}(SiO_2)_x$ cermets, it can be seen that the common feature is that in both systems, an electron transfer takes place, leading to a significant reduction of the charge carrier density, which is the prerequisite for relatively high T_c.

However, this electron transfer is only possible if there are free states in the insulator phase that the electrons can occupy. Since such free spaces are only present on the surface of the insulator phase, e.g. so-called dangling bonds, a special structure with a very large inner surface is created during the formation of the cermet, which is characterized by the fact that the insulator phase forms extremely thin layers and the metallic phase consists of very small spherical particles that are enveloped by the extremely thin insulator layers; this is called a granular structure. The situation is analogous with HTSC, with the only difference being that this possibility of such a structural "adaptation" (keyword "granular structure") does

not exist with HTSC single crystals. Instead, HTSC does have structural "adaptation" via the Jahn-Teller effect, but this does not create any empty spaces to accommodate transferred electrons; this structural adjustment only lowers the total energy of the system, which is not possible due to the absence of holes. The possibility for electron transfer opens only the creation of free holes by doping, *i.e.* $x > 0$.

A strong Jahn-Teller effect can support the chance for high values of T_c. It is an indication for a big ΔV and thus of the *complete* absorption of *all* electrons from band A by band B due to doping. If only a part of the electrons from the band B can be absorbed (due to a too small ΔV), this leads to a reduction in T_c as described.

4.3. BCS Theory and Electron-Hole Duality

The hypothesis put forward is simplified as follows: superconductivity is possible not only by electrons but also by holes, and there is a complete analogy between *electron*-Cooper pairs and *hole*-Cooper pairs, which is represented by Equations (2) and (13), among others. If so, then it is reasonable to assume that the BCS theory applies to HTSC and that the BCS theory applies to both superconductivity by electron pairs and superconductivity by hole pairs. This means that the question of the mechanism underlying the HTSC seems to be answered. However, there are arguments against it, the lack of an isotope effect and that an upper limit $T_c \approx 40\,\mathrm{K}$ is derived from the BCS theory. However, there are also classical superconductors in which no isotope effect occurs or even with "wrong sign" ([10], pp. 118). In addition, a strong isotope effect is also found in HTSC, which is even doping-dependent [11]. The 40K-limit was derived without assuming electron transfer, which is, however, a prerequisite for very high T_c in HTSC.

A paradox follows from Equations (2) and (13): While T_c continues to increase with ever decreasing carrier density, at $n = p = 0$ the conductivity should be zero and superconductivity should no longer be possible. However, this has not been found so far. One possible reason could be that the doping is not homogeneously distributed in the single crystal, so this case "$n = p = 0$" practically does not occur. Moreover, in practical experiment it should be extremely difficult to reach the maximum of the bell curve Equation (12).

The mechanisms for HTSC is intriguing in that it involves a symmetry with respect to electron-hole duality: the existence of both electron-Cooper pairs and hole-Cooper pairs. It bears an analogy to the physics of both semiconductors [12] and metal-metalloid alloys [4].

It is very likely that the mechanism in *electron*-doped HTSC is analoguous to that described in the present paper for *hole*-doped HTSC. That is, for *electron*-doped HTSC high T_c values are also expected to be the result of electron transfer. This is suggested by the finding by Kartsovnik *et al.* [13] that the Fermi surface for the electron-doped HTSC $Nd_{2-x}Ce_xCuO_4$ (NCCO) also contains electrons and holes.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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