NORMAL PROPERTIES OF HTS-SYSTEMS

A. GLODEANU
Faculty of Physics – University of Bucharest
doina.banciu@meteoinmh.ro
(Received December 7, 2004)

Abstract. Normal resistivity, the anisotropy of resistivity and the Neel temperature for high-Tc superconductors are calculated using a localized model in which the charge transfer has an important role. The dependence of temperature and oxygen vacancy concentration is explained.

Key words: superconductivity, normal resistivity, antiferromagnetism, Neel temperature.

Since the discovery of high-\(T_c\) superconductors a great effort has been made to understand the normal properties of these materials. The knowledge of electrical resistivity as a function of temperature, the anisotropy, the magnetic properties, especially the anti-ferromagnetic ones, are important steps in understanding the mechanism for such \(T_c\) -systems.

The aim of this paper is to put together the main results published in a series of papers, all of them based on a localized picture \([1]–[4]\).

I. First, in order to explain the resistivity in \(HT_c\) -materials, our idea is, \([1]\), that the electrical conduction is a charge transfer process in which the electrons or holes are tunnelling (or hopping) from a donor to an acceptor site. These donor-acceptor complexes may be formed by \(Cu^{3+}–Cu^{2+}\) pairs (which may or may not be hybridized by oxygen ions), \(Cu^{2+}–O^{2-}\) together with \(Cu^{1+}–O^{1-}\) pairs appropriate for \(La_{2–x}(Ba,Sr,Ca)_xCuO_4–\delta\) and \(ABa_2Cu_3O_7–\delta\) (where \(A = Y, La, Nd, Sm, Eu, Gd, Ho, Er, Lu\) ) systems or by small cluster (of \(O^{2-}, O^{1-}, Cu^{2+}, Cu^{3+}\) ions) as in \([4]\), for all class of \(HT_c\)-superconductors.

In other words the donor-acceptor complexes form “bi-atomic molecules” and the charge carriers are oscillating between the bonding and antibonding states of molecules with a finite probability. If an external field is applied the charge particle is hopping from an ion to another, in the direction of the field, giving rise to an electric current.

Besides the above picture we use some other approximations such as:

a) the Einstein relation \(\mu k_B = eD / T\) (where \(\mu\) is the mobility, \(k_B\) – Boltzmann constant, \(T\) – temperature, \(e\) – electron charge and \(D\) – diffusion coefficient), combined with the probability
\[ P = \nu \exp \left( \frac{E_a}{k_b T} \right) \]  

(1)

where \( \nu \) is

\[ \nu = \frac{E_{ab} - E_b}{\hbar} \]

(2)

\( E_{ab} \) and \( E_b \) being the antibonding and bonding energies, corresponding to the donor-acceptor complex and \( E_a \) is an activation energy;

b) the transfer matrix elements are calculated using Koster-Slater’s procedure and Harrison’s universal parameters [5].

Then, the normal resistivity \( \rho \) is given by

\[ \rho = \rho(T, T_a, n, d_{AD}) = \frac{\pi \hbar k_B T \exp \left( \frac{T_a}{T} \right)}{e^2 n d_{AD}^2 (V_2^2 + V_3^2)^{1/2}} \]

(3)

where \( T_a = \frac{E_a}{k_B} \), \( n \) – concentration of carriers (electrons and holes), \( V_2 \) – Harrison’s covalent energy, \( V_3 \) – the polar energy and \( d_{AD} \) – the distance between donor and acceptor.

The relation (3) is valid for all classes of \( \text{HT}_c \)-superconductors (13 K, 40 K, 90 K, 110 K, 120 K, 150 K, …), and the value of the calculated resistivity, with proper activation energy \( T_a \), is in good agreement with the experimental data in the range \([T_c - T] = 300 \text{ K}\). So far in order to obtain \( V_2 \) and \( V_3 \) we considered small cluster formed by two ions (\( \text{Cu}^{3+}-\text{Cu}^{2+} \)), (\( \text{O}^{2-}-\text{O}^{1-} \)) and the largest by 13 atoms (7 O and 6 Cu ions).

II. To calculate the activation energy \( T_a \), [4], we consider a quasi-chemical (superlattice) model as in [6], which leads to:

\[ T_a = \frac{(1 - S^2) V_0 / k_B}{\left[ 1 + \left( 1 - S^2 \right) \left( \exp \left( \frac{2V_0}{k_B T} \right) - 1 \right) \right]^{1/2}} + 1 \]

(4)

where \( S \) is an order parameter, \( S = \frac{1}{2}(1 + x) \), \( x \) being the concentration of \( \text{O}^2- \)and \( 2V_0 \) is the work required to replace two \([A D]\) pairs by \( \text{AA} \) pairs and \( \text{DD} \) pairs (in the case of spin fluctuation the pairs are formed by spin).

The advantage of an order parameter in the above expression is that it allows us to analyse the contribution to the activation energy of the thermal charge, spin fluctuations, etc.
The most important fluctuations which give a contribution to $T_a$ of (4) are the thermal ones but spin and charge fluctuations can not be neglected.

For perfect order $S = 1$ and $T_a = 0$ which leads to $\rho \propto T$ exactly as in Anderson’s model [7]. Also $T_a = 0$ for $V_0 = 0$. In both cases the metallic regime is realised as required.

The order parameter can be connected to oxygen excess or vacancies. For example for YBa$_2$Cu$_3$O$_{7-\delta}$:

$$\delta = \frac{1}{4}(1 - S)$$ \hspace{1cm} (5)

which means $\delta = 0$, $S = 1$ and $\delta = 0.25$ $S = 0$.

For La$_{2-x}$Ba$_x$CuO$_{4-\delta}$:

$$\delta = \frac{1}{2}\left(x - \frac{1}{2}(1 - S)\right), \text{etc.}$$ \hspace{1cm} (6)

From [4] it results that $T_a$ is a function of temperature. Of course $T_a$ can be negative, zero or positive. A priori it cannot be said which sign is realised but to make a superlattice stable $V_0$ must be positive. In this case we can suppose that

$$T_a = \epsilon [0 + T_{a,\text{max}}]$$ \hspace{1cm} (7)

Then we can calculate the average value of $a = \rho(T)/\rho(T_c)$, a parameter being very much used in the experiment.

The corresponding average is:

$$\bar{a} = \frac{1}{T_{a,\text{max}}} \int_0^{T_{a,\text{max}}} a dT_a = \frac{T_c^2}{T_c - T} \cdot \frac{1}{T_{a,\text{max}}} \left[1 - \exp\left(\frac{T - T_a}{T_{T_a,\text{max}}}ight)\right]$$ \hspace{1cm} (8)

The average calculated values compared with the experimental values, for $T = 300$ K, are given in Table 1.

<table>
<thead>
<tr>
<th>$T_c$ [K]</th>
<th>50</th>
<th>90</th>
<th>110</th>
<th>120</th>
<th>150</th>
<th>Obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{a}_{\text{calc}}$</td>
<td>3.99</td>
<td>2.40</td>
<td>2.15</td>
<td>1.88</td>
<td>1.75</td>
<td></td>
</tr>
<tr>
<td>$\bar{a}_{\text{exp}}$</td>
<td>4.20</td>
<td>2.28</td>
<td>1.75</td>
<td>1.80</td>
<td></td>
<td>?</td>
</tr>
</tbody>
</table>

The experimental data are very dispersed for $T_c = 150$ K.

As can be seen from Table 1 the agreement with the experimental data is quite satisfactory.

Also from Table 1, both for calculated and experimental values, it results:
\[ [T_{c\bar{\alpha}}]_{13K} \approx [T_{c\bar{\alpha}}]_{40K} \approx [T_{c\bar{\alpha}}]_{90K} \approx [T_{c\bar{\alpha}}]_{10K} \approx [T_{c\bar{\alpha}}]_{120K} \approx \ldots = \text{const} \quad (9) \]

with an error less than 10%!

The relation (9) is a very good criterion to say that the average lattice model is a good one and at the same time it can be used to predict even higher \( T_c \) superconductors.

III. As is well known from the measurements the resistivity in the normal state of \( HT_c \)-superconductors is very anisotropic and especially in the \( c \) direction compared with the resistivity of the (\( ab \)) plane.

In [3] we calculated this anisotropy for \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) to show, based on the same localised picture, how to proceed in order to explain the experimental data.

Using \( \rho \) of (3) first we calculated the resistivity in the (\( ab \)) plane and in the \( a \) and \( b \) directions, for pairs like \( \text{Cu}^{2+}--\text{Cu}^{3+}, \text{O}^{1-}-\text{Cu}^{2+}, \) etc.

\[
\rho_{\text{ab}} = \frac{1}{2}(\rho_a + \rho_b) \quad (10)
\]

where:

\[
\rho_a = \rho_{pd}^0(a) \frac{\exp\left[\frac{T_{0,\text{pd}}(a)}{T}\right]}{1 + \gamma_a \exp\left[\frac{T_{0,\text{pd}}(a) - T_{0,\text{dd}}(a)}{T}\right]},
\]

\[
\rho_b = \frac{2}{3} \rho_{pd}^0(b) \exp\left[\frac{T_{0,\text{pd}}(b)}{T}\right],
\]

\[
\rho_{pd}^0 = \frac{2}{3} \pi m k_B T \frac{(d_{pd})^{3/2}}{e^2 h n |\eta_{dd}| (r_d)},
\]

\[
\rho_{dd}^0 = \frac{4}{3} \pi m k_B T \frac{(d_{dd})^3}{e^2 h n |\eta_{dd}| (r_d)},
\]

\[
\gamma_a = \frac{\rho_{pd}^0(a)}{\rho_{dd}^0(a)}, \quad T_{0,\text{dd}} \quad \text{and} \quad T_{0,\text{pd}} \quad \text{are the activation energies when the particles are transferred from a “}d\text{” state to another “}d\text{” state or from a “}p\text{” state to a “}d\text{” state, respectively, and }\eta_{pd}, \eta_{dd}, r_d \text{ are given in [5].}
\]

The anisotropy in the (\( ab \)) plane is defined as:

\[
A_{a,b}(T) = \frac{\rho_a(T)}{\rho_b(T)} \in \left[ 0 \div \frac{A_{a,b}^0}{1 + \gamma_a} \right]
\]
for

\[ T \in [0 \div \infty], \]

\[ A_{a,b}^0 = \frac{3}{2} \frac{\rho_{pd}^0(a)}{\rho_{pd}^0(b)} = 1.535,\]

\[ \gamma_a \approx 0.12.\]

Hence for YBa\_2Cu\_3O\_7-…

\[ A_{a,b} \in [0 \div 1.37] \quad (16)\]

which is in a good agreement with the measured anisotropies.

Following the same way as above the resistivity in the \( c \) direction is:

\[ \rho_c = 4\rho_{pd}^0(c) \exp \left[ \frac{T_{0, pd}(c)}{T} \right] \left[ 1 + \frac{1}{4\gamma_c} \exp \left[ \frac{T_{0, dd}(c) - T_{0, pd}(c)}{T} \right] \right]. \quad (17)\]

Now, using \( \rho_{ab} \) of (10) and \( \rho_c \) of (17) the anisotropy is:

\[ A_{c,ab}(T) = \frac{\rho_c(T)}{\rho_{ab}(T)}. \quad (18)\]

If we suppose that the following inequalities are satisfied (which is to be expected)

\[ T_{pd}(c) > T_{pd}(a) > T_{pd}(b) > T_{dd}(c) > T_{dd}(a) \quad (19)\]

then for \( T \in [0 \div \infty] \) one gets:

\[ A_{c,ab} \in \left[ \infty \div \frac{2A_{c,b}^0(1 + \gamma_a)(1 + 4\gamma_c)}{\gamma_c(1 + \gamma_a + A_{a,b}^0)} \right] \quad (20)\]

which corresponds to experimental data [8]–[19]. In (20) \( \gamma_c = \frac{\gamma_a}{3} \) and \( A_{c,b}^0 = A_{a,b}^0/3. \)

To estimate \( A_{c,ab} \) we need the number of carriers in different directions. In general these are depending on temperature. For \( n_c(T) = n_a(T) \), which is in the range of experimental data [8]–[19], \( A_{c,ab}(T \to \infty) \approx 37.5 \), which is almost 30 times higher than \( A_{a,b}(T \to \infty) \), in satisfactory accord with observed values.

In the same way we proceed and for \( T \in [0 \div 300 \text{ K}] \) but in this case we need to use the activation energy of (4). For details see the papers [3]–[4].
The above procedure may be extended to other classes of superconductors in order to calculate the anisotropy.

**IV.** It was proved experimentally [20]–[24], for superconductor oxides, for some ranges of oxygen vacancy concentration, that these materials are in the normal state anti-ferromagnetic and semi-conductors – such that in [2] we calculated the transition temperature of the antiferromagnetic phase and we tried to correlate that with superconductivity.

In order to do that besides the above hypothesis we added some more, namely:

a) the anti-ferromagnetism of oxides ceramics is due to the same carriers as those which determine the superconductivity and the normal conductivity;

b) the $N$ copper and oxygen ions, arranged in a perovskite-type lattice are spin oriented (up and down) and they can be divided into two spin sublattices $a$ and $b$, each of them having $N/2$ sites [25]. The ions involved in forming pairs are of two types A (in concentration $c = \frac{N_A}{N}$) and B (in concentration $1 - c$). For example one might have Cu$^{3+}$–Cu$^{2+}$, Cu$^{2+}$–O$^{2-}$, Cu$^{4+}$–O$^{2-}$, etc. interacting pairs. As long as the charge carriers are localized the system might be anti-ferromagnetic and from the point of view of electrical conductivity it is a semiconductor. If a delocalization takes place in terms of temperature and oxygen vacancy concentration the pairs may condense and superconductivity rises.

Then we introduce a parameter $p$ to compute the probability to find the ions A and B (with spin up and down) on the two sublattices $a$ and $b$ and the corresponding number of pairs $N_{AA}$, $N_{BB}$, $N_{AB}$ in any order of the neighbouring ion-ion interaction. Then we calculate the total energy

$$E = E_0 + p^2 V$$

where:

$$E_0 = \frac{N}{4} \sum_{n=1}^{m} Z_n \left[ \left( V_{AA, n} + V_{AA, n} \right) c^2 + \left( V_{BB, n} + V_{BB, n} \right) (1 - c)^2 + 2 \left( V_{AB, n} - V_{AB, n} \right) c(1 - c) \right]$$

$$V = \frac{N}{4} \sum_{n=1}^{m} (-1)^{n+1} Z_n \left[ \left( V_{AA, n} - V_{AA, n} \right) c^2 + \left( V_{BB, n} - V_{BB, n} \right) (1 - c)^2 + 2 \left( V_{AB, n} - V_{AB, n} \right) c(1 - c) \right]$$

$m$ being the order of coordination sphere, $V_{AA}^p$, $V_{AA}^p$, etc. the contribution to the interaction energy from ions with anti-parallel and parallel spins correspondingly.

Using for entropy Stirling’s approximation, the free energy $F$ and the Neél temperature $T_N$ from $\frac{\partial F}{\partial p} = 0$ the Neél temperature $T_N$ for $p \to 0$ is
\[ T_N = -\frac{V_0}{k_B} = -\frac{1}{2k_B} \sum_{n=1}^{m} (-1)^{n+1} Z_n \left[ J_{AA,n} c^2 + J_{BB,n} (1-c)^2 + 2J_{AB} c(1-c) \right] \] (24)

where \( J = \frac{1}{2}(V_a - V_p) \) is the exchange integral between two ions for the \( n \)-th coordination sphere and \( Z_n \) is the number of neighbours for that sphere.

In general the sign in (24) is alternating from one sphere of coordination to another such that \( J < 0 \) and the effect of the next nearest neighbours is to diminish \( T_N \).

For the exchange integral the Anderson’s approach is used

\[ J = \sum_{R\neq R'} \left[ \frac{|t_{R-R'}|}{U} \left[ 2\hat{S}_R \hat{S}_{R'} - \frac{1}{2} \right] \right] \] (25)

where \( t \) is the transfer integral, \( U \) is Hubbard repulsive parameter and \( S_R \) is the spin on the site \( R \).

The transfer integral \( t \) is computed via [5] both for monocrystals and polycrystalline samples. These are done for \((\text{Cu}^{2+}–\text{Cu}^{2+})\), \((\text{Cu}^{1+}–\text{Cu}^{1+})\), \((\text{Cu}^{2+}–\text{Cu}^{1+})\) pairs hybridized by oxygen.

In our localized picture the \( \text{Cu}^{2+} \) ions are in \( d^9 \) configuration, the total spin \( S = 1/2 \) and a magnetic moment exists. The \( \text{Cu}^{1+} \) ions are, at first sight in \( d^{10} \) configuration no spin and no magnetic moment. However the \( \text{Cu}^{1+} \) ions are formed in the vicinity of oxygen vacancies and these vacancies are acting as positive centers. In the ionic picture the system seems to be more stable when there are \( \text{Cu}^{2+} \) and \( O^{2-} \) ions such that the tendency will be that an electron from \( \text{Cu}^{1+} \) will leave the ion because of vacancy attraction. Then we can suppose that a magnetic impurity is formed with a radius \( r_s \approx \frac{d}{2} \) \((d \) is the distance between two copper ions), like Kasuya magnetic impurity [26], although the F centers or Frenkel magnetic excitons are not excluded.

With all the above considerations and for \( U_{AA} = U_{BB} = U_{AB} = 4.5 \text{ eV} \) for \( T_N \) we obtained the values via relation (24), both for single and polycrystalline crystals of \( \text{La}_2\text{CuO}_{4-y} \) and \( \text{YBa}_2\text{Cu}_3\text{O}_{6.5-y} \).

The agreement with the experimental data is satisfactory even if the dispersion of the measured values is very high.

The most important results of the \( T_N \) calculation is the trend with the oxygen vacancy “\( y \)” such that for \( y \to 0 \), for both studied systems, \( T_N \to 0 \) and the metallic regime begins.

Of course the generalization for the system based on Bi and Tl is obvious in our model.
SOME CONCLUSIONS

1. The localised pictured discussed is a good approach to calculate the resistivity and the anisotropy for all classes of high $T_c$ superconductors.
2. The antiferomagnetic phase can be studied in the same localised limit with relevant results.
3. The quasi-chemical model for activation energy is working well too.
4. Our model seems to be more appropriate for polycristalline and doped HT$_c$-superconducting materials while Anderson’s model [7] is better for monocrystals.

Of course if for the order parameter we use $s = 0$, our model gives $\rho \propto T$ as in [7]. One of the advantages in our model is that all the parameters can be known via Harrison’s method.

REFERENCES