

NORMAL PROPERTIES OF HTS-SYSTEMS

A. GLODEANU

Faculty of Physics – University of Bucharest
doina.banciu@meteoimh.ro

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Abstract. Normal resistivity, the anisotropy of resistivity and the Neel temperature for high- T_c 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 localised 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 $\text{Cu}^{3+}\text{-Cu}^{2+}$ pairs (which may or may not be hybridized by oxygen ions), $\text{Cu}^{2+}\text{-O}^{2-}$ together with $\text{Cu}^{1+}\text{-O}^{1-}$ pairs appropriate for $\text{La}_{2-x}(\text{Ba,Sr,Ca})_x\text{CuO}_{4-\delta}$ and $\text{ABa}_2\text{Cu}_3\text{O}_{7-\delta}$ (where $A = \text{Y, La, Nd, Sm, Eu, Gd, Ho, Er, Lu}$) systems or by small cluster (of $\text{O}^{2-}, \text{O}^{1-}, \text{Cu}^{2+}, \text{Cu}^{3+}$ ions) as in [4], for all class of HT_c -supraconductors.

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 μ is the mobility, k_B – Boltzmann constant, T – temperature, e – electron charge and D – diffusion coefficient), combined with the probability

$$P = \nu \exp\left(-\frac{E_a}{k_B T}\right) \quad (1)$$

where ν is

$$\nu = \frac{E_{ab} - E_b}{h} \quad (2)$$

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 ρ is given by

$$\rho = \rho(T, T_a, n, d_{AD}) = \frac{\pi \hbar k_B T \exp\left(\frac{T_a}{T}\right)}{e^2 n d_{AD}^2 (V_2^2 + V_3^2)^{1/2}} \quad (3)$$

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 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 $[T_c - T] = 300$ K. So far in order to obtain V_2 and V_3 we considered small cluster formed by two ions (Cu^{3+} - Cu^{2+}), (O^{2-} - 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:

$$T_a = \frac{(1 - S^2)V_0 / k_B}{\left[1 + (1 - S^2)\left(\exp\frac{2V_0}{k_B T} - 1\right)\right]^{1/2} + 1} \quad (4)$$

where S is an order parameter, $S = \frac{1}{2}(1 + x)$, x being the concentration of O^{2-} and $2V_0$ is the work required to replace two $[A D]$ pairs by AA pairs and 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 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$:

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

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

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

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

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

$$T_a \in [0 \div T_{a,\max}] \quad (7)$$

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

The corresponding average is:

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

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

Table 1

T_c [K]	50	90	110	120	150	Obs.
\bar{a}_{calc}	3.99	2.40	2.15	1.88	1.75	
\bar{a}_{exp}	4.20	2.28	1.75	1.80	?	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:

$$[T_a \bar{a}]_{13\text{K}} \approx [T_c \bar{a}]_{40\text{K}} \approx [T_c \bar{a}]_{90\text{K}} \approx [T_c \bar{a}]_{110\text{K}} \approx [T_c \bar{a}]_{120\text{K}} \approx \dots = \text{const} \quad (9)$$

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 ρ 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.

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

where:

$$\rho_a = \rho_{pd}^0(a) \frac{\exp\left[\frac{T_{0,pd}(a)}{T}\right]}{1 + \gamma_a \exp\left[\frac{T_{0,pd}(a) - T_{0,dd}(a)}{T}\right]}, \quad (11)$$

$$\rho_b = \frac{2}{3} \rho_{pd}^0(b) \exp\left[\frac{T_{0,pd}(b)}{T}\right], \quad (12)$$

$$\rho_{pd}^0 = \frac{2}{3} \frac{\pi m k_B T}{e^2 h n |\eta_{dd}|} \left(\frac{d_{pd}}{r_d}\right)^{3/2}, \quad (13)$$

$$\rho_{dd}^0 = \frac{4}{3} \frac{\pi m k_B T}{e^2 h n |\eta_{dd}|} \left(\frac{d_{dd}}{r_d}\right)^3, \quad (14)$$

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

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

$$A_{a,b}(T) = \frac{\rho_a(T)}{\rho_b(T)} \in \left[0 \div \frac{A_{a,b}^0}{1 + \gamma_a}\right] \quad (15)$$

for

$$\begin{aligned} T &\in [0 \div \infty], \\ A_{a,b}^0 &= \frac{3}{2} \frac{\rho_{pd}^0(a)}{\rho_{pd}^0(b)} \approx 1.535, \\ \gamma_a &\approx 0.12. \end{aligned}$$

Hence for YBa₂Cu₃O₇-...

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

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 ρ_{ab} of (10) and ρ_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], $A_{c,ab}(T \rightarrow \infty) \approx 37.5$, which is almost 30 times higher than $A_{a,b}(T \rightarrow \infty)$, 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 oxigens ions, arranged in a perovskite-type lattice are spin oriented (up and down) and they can be devided 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 $\text{Cu}^{3+}\text{--Cu}^{2+}$, $\text{Cu}^{2+}\text{--O}^{2-}$, $\text{Cu}^{1+}\text{--O}^{1-}$, 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 oxigen 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

$$E = E_0 + p^2V \quad (21)$$

where:

$$E_0 = \frac{N}{4} \sum_{n=1}^m Z_n \left[\left(V_{AA,n}^a + V_{AA,n}^p \right) c^2 + \left(V_{BB,n}^a + V_{BB,n}^p \right) (1-c)^2 + \right. \\ \left. + 2 \left(V_{AB,n}^a - V_{AB,n}^p \right) c(1-c) \right] \quad (22)$$

$$V = \frac{N}{4} \sum_{n=1}^m (-1)^{n+1} Z_n \left[\left(V_{AA,n}^a - V_{AA,n}^p \right) c^2 + \left(V_{BB,n}^a - V_{BB,n}^p \right) (1-c)^2 + \right. \\ \left. + 2 \left(V_{AB,n}^a - V_{AB,n}^p \right) c(1-c) \right] \quad (23)$$

m being the order of coordination sphere, V_{AA}^a , 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 $p \rightarrow 0$ is

$$T_N = -\frac{V_0}{k_B} = -\frac{1}{2k_B} \sum_{n=1}^m (-1)^{n+1} Z_n \left[J_{AA,n} c^2 + J_{BB,n} (1-c)^2 + 2J_{AB} c(1-c) \right] \quad (24)$$

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

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

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 Cu^{2+} ions are in d^9 configuration, the total spin $S = 1/2$ and a magnetic moment exists. The Cu^{1+} ions are, at first sight in d^{10} configuration no spin and no magnetic moment. However the 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 Cu^{2+} and O^{2-} ions such that the tendency will be that an electron from Cu^{1+} will leave the ion because of vacancy attraction. Then we can suppose that a magnetic impurity is formed with a radius $r_s \approx d$ (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 $y \rightarrow 0$, for both studied systems, $T_N \rightarrow 0$ and the metallic regim 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 antiferromagnetic 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 polycrystalline 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

1. A. Glodeanu, V. Iancu, Rev. Roum. Phys. **33**, 619–624 (1988).
2. A. Glodeanu, V. Iancu, Rev. Roum. Phys. **34**, 75–81 (1989).
3. A. Glodeanu, Rev. Roum. Phys. **36**, 831–835 (1991).
4. A. Glodeanu, G. Stan, Proc. Suppl. BPL, **5**, 313–316 (1997).
5. W. A. Harrison, *Electronic Structure and the properties of Solids*, W. H. Freeman and Company, San Francisco, 1980, p. 21 also Dover Publication Inc. New-York, 1989, p. 18–21.
6. R. H. Fowler, E. A. Guggenheim, Proc. Roy. Soc. A **174**, 189 (1939).
7. P. W. Anderson, Z. Zou, Phys. Rev. Lett. **60**, 132 (1988).
8. S. W. Tozer *et al.*, Phys. Rev. Lett. **59**, 1768 (1987).
9. N. P. Ong *et al.*, Phys. Rev. B, **35**, 8807 (1987).
10. Yu. A. Ossipyan *et al.*, Physica C, 153–155, 1133 (1988).
11. L. Forro *et al.*, Physica C, 153–155, 1357 (1988).
12. L. Ya. Vinnikov *et al.*, Physica C, 153–155, 1359 (1988).
13. Gy. Hutiray *et al.*, Physica C, 153–155, 1361 (1988).
14. A. M. Gorayeb *et al.*, Physica C, 153–155, 1363 (1988).
15. M. Konezukowsky *et al.*, Physica C, 153–155, 1365 (1988).
16. M. Gurrinch *et al.*, Physica C, 153–155, 1371 (1988).
17. K. Murata *et al.*, Physica C, 153–155, 1373 (1988).
18. T. Murakami *et al.*, Physica C, 153–155, 1691 (1988).
19. T. Yasuda *et al.*, Jap. Journ. Appl. Physics, **27**, L 1910 (1988).
20. J. M. Tranquada *et al.*, Phys. Rev. Lett. **60**, 156 (1987).
21. S. Mitsuda *et al.*, Phys. Rev. B, **36**, 822 (1987).
22. T. Freltoft *et al.*, Phys. Rev. **36**, 826 (1987).
23. J. H. Brewer *et al.*, Phys. Rev. Lett. **60**, 1073 (1988).
24. N. Nishida *et al.*, Jap. Journ. Appl. Physics, **26**, L 1856 (1987).
25. H. A. Bethe Proc. Roy. Soc. A, **150**, 552 (1935).
26. T. Kasuya, A. Yanase, 5 Appl. Phys. **39**, 430 (1968).