

## The Localized Character of the "Metallic" State in High Tc Superconductors.

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### Abstract

The resistivity behaviour of a large series of polycrystalline samples at different defect (carrier) concentrations is discussed using the form  $\rho_0 \exp(T_0/T)^b$  in which  $\rho_0$  is a temperature-dependent parameter. This equation allows to examine the gradual and characteristic change of  $\rho(T)$  as a function of carrier concentration observed in single-crystals as well as in polycrystalline superconductors within an single mechanism. A cross-over between the  $b=1/2$  and the  $b=1/4$  regimes is found. The "metallic" dependence of the normal resistivity state has a induced-disorder localized character.

### 1. Introduction

The Metal-Insulator Transition (MIT) is a common feature of all high Tc superconductors. It is achieved by doping a parent compound and results in a resistivity behaviour  $\rho \sim T$  at sufficiently high carrier density/temperature as for electrons coupled to Debye phonons in a metal. The high Tc superconductors are therefore called "metallic" although the origin of the linear behaviour is not yet known [1-3].

On the other hand, in the insulating state (at low carrier concentration) [4] and in the vicinity of the metal-insulator transition [5,6], Variable-Range Hopping (VRH) conduction has been claimed to occur. All these measurements have shown that a hopping mechanism, eventually overwhelmed by activated conduction on localized states induced by disorder, is established even in the region of the phase diagram where these materials are expected to be strongly correlated. Variable-Range Hopping mechanism has been also reported in the normal state of the superconducting  $Ba_{1-x}K_xBiO_{3-y}$  and  $La_{2-x}Sr_xCuO_{4-y}$  systems [7,8]. This further detection of hopping in the normal state suggests that a system of localized electrons (eventually correlated by Coulomb Gap (CG) mechanisms) could form the basic Fermi liquid in which the superconductivity occurs. From that assumption, a quantum percolation theory based on localized states has been developed and has shown to

account correctly the normal state properties, including the  $\rho \sim T$  dependence [9]. More recently, a quantum percolation model has been used to explain the characteristic dome-shaped dependence of Tc on carrier concentration. A percolation threshold was identified suggesting that superconductivity occurs within percolative clusters [10-12]. The critical exponent found for the localization length, around 0.5, is the value currently obtained in different experiments on the metal-insulator transition of disordered systems and normally attributed to coulomb repulsions [13-15]. Other measurements as the thermoelectric power have also indicated the possibility that correlated electrons (correlated holes) play a role in the superconductivity mechanism [15,16].

### 2. Results

In this work, we focus our attention on the behaviour of the resistivity as a function of temperature around the MIT. We discuss few prepared samples but the aim of this paper is to evaluate the general T-dependence of the resistivity of high Tc materials. A common feature is the existence of a temperature,  $T_{min}$ , at which the  $\rho(T)$  curve presents a minimum, which is a function of the carrier concentration and which appears to be correlated with the slope,  $d\rho/dT$ , of the metallic region. These properties

have been reported in polycrystalline and in single-crystals samples indicating an intrinsic feature of these materials [17,18,19]. When  $T_{\min}$  is quite high, the resistivity curve exhibits only the insulating trend in the temperature range often reported, from few K to 300K. Measurements performed at higher temperatures supported this assumption [8]. On the other hand, when  $T_{\min}$  is very small, only the metallic trend is observed (see fig.1).

Our samples are polycrystalline pellets of  $\text{YBa}_2\text{Cu}_{3-x}\text{Li}_x\text{O}_{6.5+y-x/2}$  for  $0 < x < 0.30$  (samples A). The sample preparation method, the oxygen stoichiometry determination, the average Cu charge,  $[\text{Cu-O}]^{\text{p}}$ , calculation as well as the technique used for the resistivity determination were reported in a previous paper [20]. A degradation of the  $T_c$  increasing the Li content was observed and attributed to the oxygen vacancies induced in the  $\text{CuO}_2$  planes by the Li introduction. Moreover, in the insulating range, 3D variable-range hopping on localized states induced by disorder has been observed which suggests a  $T_{\min}$  greater than the maximum temperature measured, 300K [21]. Some pellets of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_{2-x}\text{Li}_x\text{O}_{8+y-x/2}$  (samples B) will also be discussed. Some results of the resistivity measurements are plotted in fig.1 (samples A) and fig.2 (samples B) as a function of temperature. The oxygen content of the samples A is reported in Table I.

In the insulating range, the resistivity data have been fitted with the following equation:

$$\rho = \rho_0 \left( \frac{T}{T_0} \right)^{2b} \exp\left( \frac{T_0}{T} \right)^b \quad (1)$$

where the exponent can assume values of  $b = 1/4$ ,  $1/3$  and  $1/2$  [22,23,24]. The temperature dependence of the pre-exponential factor has particular importance.

In the two series, the least-square fits, using eq. 1, have indicated a change from  $b=1/4$  to  $b=1/2$  approaching the metallic region. This cross-over is accompanied by  $T_0'$  values from  $b=1/2$  becoming larger than  $T_0$  values obtained from the  $b=1/4$  fits and by a progressive increase of the localization length,  $a$  (see Table I). Since this is due to the metallic character of  $\rho \sim T$  such a cross-over is expected to be a general trend at the MIT.

The monotonous behaviour of  $T_0$  and the gradual change of  $\rho$  as a function of the doping level (Table I) may suggest that the Fermi level lies within the mobility gap without substantial excitation of carriers through the mobility edge and that the MIT could be a result not of the fact that the Fermi level crosses the mobility edge on varying the doping level, but a result of correlations and transport at long localization lengths.

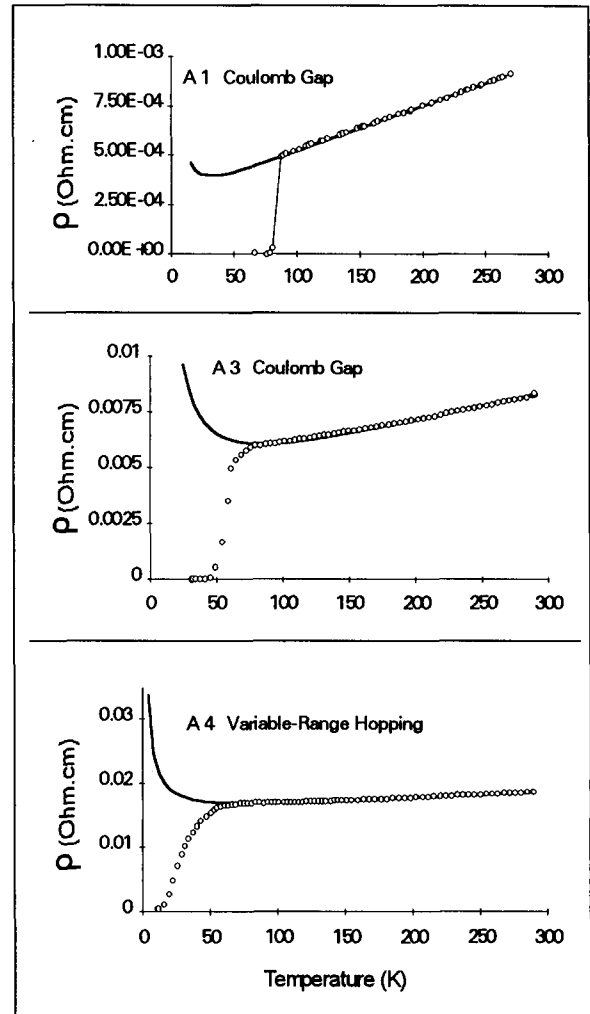


Figure 1. The resistivity behaviour as a function of temperature for three samples of  $\text{YBaCuO}$  at different Li contents (A1=1.35%, A3=6.7% and A4=10%at. Li). The solid lines represent the theoretical fits using eq.1.

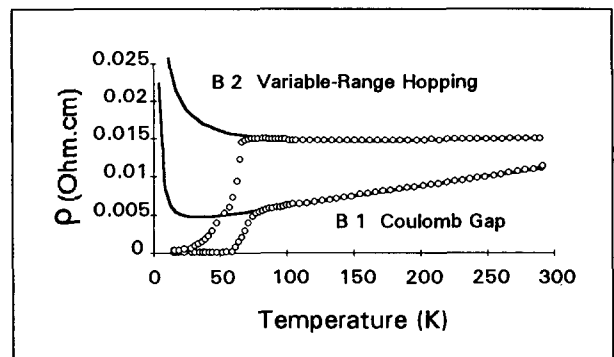


Figure 2. The resistivity behaviour as a function of temperature for two samples of  $\text{BiSrCaCuO}$  (2212) at different Li contents (B1=2.5%, B2=5%at. Li). The solid lines represent the theoretical fits using eq. 1.

Table I. The activation energies,  $T_0'$  and  $T_0$  obtained using in eq. 1, respectively, the exponent value  $b=1/2$  and  $b=1/4$  as a function of Li content. The localization lengths,  $a$ , have been calculated for the best fit results underlined using eq. (2) with  $N_F=10^{21}$  (eV.cm<sup>3</sup>)<sup>-1</sup> and eq. (3) with a dielectric constant value  $\epsilon=10$ . The  $T_{\min}$  are calculated using eq. 4 and the best fit results. The  $\rho_0$  values and the oxygen stoichiometry are reported as a function of Li content.

Samples	$T_0'$ (K) (CG)	$T_0$ (K) (VRH)	$a$ (Å)	$\rho_0$ (ohm.cm)	oxygen stoichiometry	$T_{\min}$ (K)
A1 YBaCuO (123) 1.35%at. Li	<u>124</u>	0.1	131	2.1E-04	6.86±0.01	31
A2 YBaCuO (123) 2%at. Li	<u>227</u>	4	72	2.3E-03	6.70±0.03	57
A3 YBaCuO (123) 6.7%at. Li	<u>336</u>	210	49	3.3E-03	6.59±0.03	84
A4 YBaCuO (123) 10%at. Li	505	<u>1250</u>	53	9.0E-03	6.53±0.03	78
A5 YBaCuO (123) pure	1350	<u>27000</u>	19	5.0E-02	6.38±0.02	1687
B1 BiSrCaCuO (2212) 2.5%at. Li.	<u>131</u>	0.2	124	2.6E-03		33
B2 BiSrCaCuO (2212) 5%at. Li	570	<u>2500</u>	42	7.6E-03		156

The resistivity behaviours of the more insulating samples (A4 and B2, respectively, in fig. 1 and 2, A5 in table I) are best fitted using a 3D Variable-Range Hopping (VRH) mechanism with  $b=1/4$ . Using the Mott parametrization [22]:

$$T_0 = \frac{16}{k N_F a^3} \quad (2)$$

where  $N_F$  is the density of states at the Fermi level and  $a$  the localization length, we can infer this latter using a current estimate of  $N_F = 10^{21}/\text{cm}^3$  eV. We find  $a \approx 50\text{\AA}$  as expected from the vicinity of the MIT.

For the "metallic" samples, we can use the Coulomb Gap (CG) relation [25]:

$$T_0' = \frac{e^2}{k a \epsilon} \quad (3)$$

where  $\epsilon$  is the dielectric constant.

Using current values of  $\epsilon = 10$  [18] and the experimentally  $T_0'$ , we find  $a \approx 100\text{\AA}$ . The cross-over from  $b=1/4$  to  $b=1/2$  is estimated experimentally at a  $T_0$  corresponding to a localization length  $a \approx 50\text{-}60\text{\AA}$  (see Table I).

### 3. Discussion

Previous study has suggested that the linear dependence of the resistivity could be the result of the crossing of the Fermi level through the mobility edge [18]. However, from the gradual change of  $\rho(T)$  from the insulator to the metal, it may be argued that a single mechanism takes place, i.e. quantum percolation leading to eq. (1). In this case, the equation (1) should be valid not only in the strongly insulating state when  $T_0$  is large but also at lower  $T_0$  values. From eq.(1), we deduce the existence of a minimum of  $\rho(T)$  at:

$$T_{\min} = \frac{T_0}{2^{(1/b)}} \quad (4)$$

and a U-shaped  $\rho(T)$  whose exact form depends on  $b$ .

Of particular interest is the equation (1) when  $b=1/2$ . This corresponds to the correlated coulomb gap hopping (CG) of Efros and Shklovskii [25]. In this case,  $\rho_0(T) \sim T$  when  $T \gg T_{\min}$ .

The cross-over from VRH to CG occurs when the activation energy for non-correlated hopping  $\epsilon_{\text{VRH}} = kT^{3/4}T_0^{1/4}$  exceeds the coulomb gap  $\Delta = e^3 N_F^{1/2} / \epsilon^2$

[25-27]. The cross-over temperature is thus  $T^* = e^4 a N_p / \epsilon^2$ . For the value of the localization length  $a = 100 \text{ \AA}$  with  $\epsilon = 10$  [18], one gets  $T^*$  around 1000K which allows the observation of  $b = 1/2$  up to relatively high temperatures. Conversely, for small  $a = 10 \text{ \AA}$ , typically encountered in the insulator range [4], we have  $T^*$  around 10K leading to the observation of VRH at  $T > T^*$ . A rough estimate of this temperature can also be obtained by the cross-over values of the  $T_0$  [26]. The hopping distances,  $R$ , obtained in the present investigation are close to the value of  $a$ . Using the theoretical expression  $R = (1/4)a(T_0/T)^{1/2}$  for the CG case [27], we find that  $R/a \approx 1$  indicating a relevant overlapping of the hopping centres. In contrast, for a strongly insulating sample, one finds that  $R/a \gg 1$  leading to a dilute limit regime [27].

#### 4. Conclusions.

In summary, our results show that it is reasonable to treat the resistivity data of high  $T_c$  materials in a wide range of temperature within a quantum percolation model based on the electron localization mechanism. These analyses allow a linear dependence of the resistivity as a function of the temperature and a cross-over from VRH to CG regimes. It is important to note that the resistivity behaviour discussed in this paper could also be shared by models based on granularity and/or conduction in band tails without existence of a true mobility edge [28,29]. Such models predict a  $b = 1/4$  regime at low temperatures and an increasing power,  $b = 1/2$ , at high temperatures. The cross-over temperature increases enhancing the dimensions of grains or decreasing the band tail width. Grains of the order of  $100 \text{ \AA}$  and bandwidths around  $0.2 eV$  are reported as necessary for the  $b = 1/2$  regime [28,29].

#### References

- 1 A. Virosztek and J. Ruvalds, Phys. Rev. B 42 (1990) 4064.
- 2 C.M. Varma, P.B. Littlewood, S. Schmitt-Rink, E. Abrahams, and A. Ruckenstein, Phys. Rev. Lett. 63 (1989) 1996.
- 3 P.W. Anderson and Z. Zhou, Phys. Rev. Lett. 60 (1988) 132.
- 4 M.A. Kastner, R.J. Birgeneau, Y. Chen, Y.M. Chiang, D.R. Gabbe, H.P. Janssen, T. Junk, C.J. Peters, P.J. Picone, T. Thio, T.R. Thurston, and H.L. Tuller, Phys. Rev. B 37 (1988) 111.
- 5 B. Ellman, H.M. Jaeger, D.P. Katz, T.F. Rosenbaum, A.S. Cooper and, G.P. Espinosa, Phys. Rev. B 39 (1989) 9012.
- 6 P. Mandal, A. Poddar, B. Ghosh and P. Choudhury, Phys. Rev. B 43 (1991) 13102.
- 7 B. Dabrowski, D.G. Hinks, J.D. Jorgensen, R.K. Kalia, P. Vashishta, D.R. Richards, D.T. Marx and A.W. Mitchell, Physica C 156 (1988) 24.
- 8 E.J. Osquiguil, L. Civale, R. Decca, and F. de la Cruz, Phys. Rev. B 38 (1988) 2840.
- 9 J.C. Phillips, Phys. Rev. B 39 (1989) 7536, B 41 (1990) 850.
- 10 V. Dallacasa and R. Feduzi, Phys. Lett. A 170 (1992) 153.
- 11 C.M. Soukoulis and G.S. Grest, Phys. Rev. B 44 (1991) 4685.
- 12 Th. Koslowski and W. von Niessen, Phys. Rev. B 42 (1990) 10342.
- 13 N.F. Mott, Conduction in Non-Crystalline Materials, Clarendon Press, Oxford, 1987.
- 14 M. Kaveh and N.F. Mott, Phys. Rev. Lett. 68 (1992) 1904.
- 15 D. Mandrus, L. Forro, C. Kendziora, and L. Mihaly, Phys. Rev. B 44 (1991) 2418.
- 16 K. Kitazawa, H. Takagi, K. Kishio, T. Hasegawa, S. Uchida, S. Tajima, S. Tanaka and K. Fueki, Physica C 153-155 (1988) 9.
- 17 D. Mandrus, L. Forro, C. Kendziora, and L. Mihaly, Phys. Rev. B 45 (1992) 12640.
- 18 C. Quitmann, M. Fleuster, C. Jarcho, D. Andrich, P.L. Paulose and G. Güntherodt, Physica C 185-189 (1991) 1337.
- 19 J.G. Bednorz and K.A. Müller, Z. Phys. B 64 (1986) 189.
- 20 R. Feduzi, F. Lanza and M.D. Giardina, Physica C 195, 177 (1992).
- 21 R. Feduzi and V. Dallacasa, accepted to Phil. Mag. Lett.
- 22 N.F. Mott and E.A. Davis, Electronic Processes in Non-crystalline Materials, Clarendon Press, Oxford, 1971.
- 23 V. Ambegaokar, B.I. Halperin and J.S. Langer, Phys. Rev. B 4, 2612 (1971).
- 24 F.D. Allen and C.J. Adkins, Phil. Mag. 26 (1972) 1027.
- 25 A.L. Efros and B.I. Shklovskii, J. Phys. C 8 (1975) L49.
- 26 A. Aharony, Y. Zhang and M.P. Sarachik, Phys. Rev. Lett. 68 (1992) 3900.
- 27 T.G. Castner, Hopping Transport in Solids, M. Pollak and B.I. Shklovskii (eds.), North-Holland, Amsterdam, 1991.
- 28 D. Adler, L.P. Flora and S.D. Senturia, Solid State Commun. 12 (1973) 9.
- 29 P. Sheng and J. Klafter, Phys. Rev. B 27 (1983) 2583.