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Variation of the superconducting transition temperature of $\text{YBa}_2\text{Cu}_3\text{O}_x$ with oxygen content

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Résumé.- A partir de mesures thermogravimétriques sous pression d'oxygène variable suivies de mesures de l'effet Meissner nous déterminons le diagramme de phase de la température de transition T_c du composé $\text{YBa}_2\text{Cu}_3\text{O}_x$ pour $6 < x < 7,0$. Pour x compris entre 6,0 et 6,6 nous trouvons que ce système est biphasé, seule une faible partie du volume étant supraconducteur avec $T_c \sim 50$ K. Pour x compris entre 6,6 et 7,0 la phase observée est supraconductrice et sa température de transition varie très rapidement avec x . Nous obtenons un accord qualitatif avec la théorie BCS en supposant l'existence d'une bande rigide à 3D. De cet accord nous tirons la valeur de 320 ± 60 K pour la température de Debye et le paramètre de couplage $NV = 0,8 \pm 0,1$. L'analyse de la dépendance du taux x en oxygène en fonction de la pression d'oxygène permet de déduire une interaction répulsive de 0,6 eV entre sites d'oxygène.

Abstract.- Systematic thermogravimetric measurements under variable oxygen pressure followed by magnetic determination of the transition temperature of the superconducting compound $\text{YBa}_2\text{Cu}_3\text{O}_x$ yield the phase diagram of T_c versus the oxygen content for $6 < x < 7.0$. For $6 < x < 6.6$ the compound is found mainly non superconducting although a small amount of a superconducting phase with $T_c \sim 50$ K is present. For $6.6 < x < 7.0$ a single superconducting phase is evidenced by the Meissner effect whose transition temperature increases very rapidly with x in rough agreement with BCS theory, assuming a three dimensional rigid band model and a parabolic density of states above $x = 6.5$. From this fit we get a Debye temperature of 320 ± 60 K and the dimensionless parameter $NV = 0.8 \pm 0.1$. A repulsive interaction $\Delta W = 0.6 \pm 0.05$ eV between oxygen sites is inferred from the dependence of oxygen content on oxygen pressure.

1. Introduction.

In this paper we present an experimental investigation of the dependence of the superconducting transition of the compound $\text{YBa}_2\text{Cu}_3\text{O}_x$ as a function of the oxygen content x .

Indeed, soon after the initial discovery by Bednorz and Muller [1] of the new family of high T_c superconducting oxides and the subsequent characterization of their crystal structure [2,3] a large number of investigation have concerned the effect on T_c of substitution of either alkaline earths for Ba or trivalent rare earths for Y[4,5]. Despite the fact that most of the rare earth atoms are strongly magnetic as evidenced by their susceptibility, the net result of

these substitutions was a $\pm 10\%$ change of T_c around the initial value of 91 K without correlation with the size of the magnetic moment of the rare earth atom. On the contrary, ever since the early investigations a clear influence on T_c of the annealing conditions was observed, namely that vacuum annealing destroyed superconductivity and oxygen or air annealing restored the initial value of T_c or even increased it. Furthermore not only the annealing state was necessary but the rate of cooling and removal from the furnace was seen to be critical. All these observations pointed out the role of the stoichiometry of the oxygen atoms in $\text{YBa}_2\text{Cu}_3\text{O}_x$. We have undertaken a systematic quantitative study of the effect of oxygen content on T_c on this

compound by measuring the oxygen variation by thermogravimetry. Since the magnetic measurements involved for the determination of the transition temperature through the Meissner effect could be carried out on samples of the same size as those used in the thermogravimetric method without alteration (such as that involved when attaching contacts for resistivity) we have systematically operated on the *same sample* for both type of measurements thus avoiding possible spread due to inherent differences between samples. This fact turned out to be crucial in order to reliably set a phase diagram of the variation of T_c with the oxygen stoichiometry.

2. Experimental.

The samples were prepared from stoichiometric amounts of reagent grade powders of CuO , Y_2O_3 and BaCO_3 . After grinding and cold pressing this mixture into a bar $5 \times 5 \times 30\text{mm}^3$, sintering was operated at 950°C in air for 10 hours in an alumina boat. This was followed by an annealing stage of 2 hours at 500°C under 1 atm oxygen and slow cooling in the furnace down to room temperature. This method gave consistently black, dense, highly polycrystalline and mechanically tough material. Upon analysis by a scanning electron microscope only traces of other phases were found (the « green » phase Y_2BaCuO_5 and a red one BaCuO_2) [6]. X ray spectra were consistent with the known orthorhombic structure of the material [3]. The thermogravimetric measurements were made in two ways: firstly, *in situ* in a thermobalance in order to set the oxygen content as a function of oxygen partial pressure and temperature and, most important, to determine the order of magnitude of the time involved for oxygen exchange in various conditions of temperature and partial pressure of oxygen. Secondly, using this thermogravimetric determination we defined a systematic annealing procedure of 2h30' at 500°C followed by weighing after natural cooling of the furnace (at an initial rate of $2^\circ\text{C}/\text{min}$). This was carried out in a furnace equipped with a vacuum facility down to 10^{-7}mm Hg of air. Variable pressure could be set in the system by adjusting a needle valve attached to the pumping line.

The weight of the sample, typically 400 mg was measured before and after the anneal within 0.1 mg on a separate balance prior to the magnetic measurement. The changes of weight were found reproducible if the annealing conditions were kept identical. No systematic loss of weight (due to handling for instance) was observed and complete reversibility of oxygen intake was observed after a dozen annealing operations at different oxygen pressures. The main source of errors rested in the limited accuracy of the weighing procedure. Finally it was observed that the

sample weight, i.e. its oxygen content, was stable for days at room temperature with a slight tendency to pick up weight (0.15 % in two weeks) for the most deoxidized state corresponding to $\text{YBa}_2\text{Cu}_3\text{O}_6$.

The magnetic measurements were made using a vibrating sample magnetometer (PAR-FMI) equipped with a variable temperature 3.5 K-300 K Oxford Inst. cryostat and circulating liquid He system.

The temperature at the sample position was measured using a calibrated 50Ω Pt resistor (Rosemount) linked to a four probe Keithley mΩ meter. The absolute precision was not better than ± 0.25 K. The sensitivity of the magnetometer system was better than 10^{-4} emu which was amply sufficient to detect the (partial) Meissner effect of a sample of 0.1 cm^3 in the remanent field of a Varian 6" electromagnet (30 gauss) or to measure a magnetization curve when needed. Good reversibility was observed between heating and cooling curves at constant field. Good reproducibility was obtained over a large number of runs made on the same sample and was limited only by small parasitic vibrations at the basic frequency of the system.

Resistivity measurements were carried out with a four probe geometry using mechanical CuBe wire spring contacts on special plate like samples ($2 \times 7 \times 0.6\text{ mm}^3$) cut from the bulk with a diamond saw. The measurements were either ac or dc with typical currents of 1 to $100\ \mu\text{A}$ either in a regular He cryostat or in a specially built variable temperature insert adequately positioned in a liquid He container. Several problems appeared at low temperature on the more deoxidized forms which were attributed to the existence of a non-reproducible temperature dependent contact resistance quite similar to the observation of reference [7].

3. Results.

A first series of thermogravimetric measurements showed that it was possible to remove reversibly oxygen from the « as prepared » compound $\text{YBa}_2\text{Cu}_3\text{O}_7$ by heating at 700°C for 7 hours in a vacuum of 10^{-6} mm Hg . The resulting relative loss of weight of 2.45 % is very close to the calculated value of 2.40 % corresponding to the decrease in the oxygen content of the compound from O_7 to O_6 . Two similar further annealing operations of the same sample in air and in vacuum reproduced essentially the same weight change and did restore superconductivity in the O_7 form. We conclude from this that the amplitude of the reversible oxygen variation is at least 1.0 ± 0.05 and could possibly be extended by the use of higher pressures [8]. A detailed thermogravimetric measurement essentially revealed the features observed simultaneously by Tarascon *et al.* [5] and Capponni *et al.* [3], namely

that the oxygen intake of a previously deoxidized sample starts above 200°C for 1 atm O_2 , peaks around 450°C and, upon further heating is followed by a quasi reversible loss of oxygen. Upon cooling from 700°C, an oxygen intake is observed down to about 360°C where a plateau is reached (see Fig.1 insert). The final oxygen content defined by the difference between the initial weight of the sample and this final plateau depends on both the partial pressure of oxygen and the cooling rate.

When operating at constant temperature in presence of a variable oxygen partial pressure it was possible to measure the characteristic times necessary to reach an apparent equilibrium situation at each stage. Whereas it was found that 5 minutes were sufficient at 720°C for oxygen pressures larger than 0.1 atm, much longer times (up to one hour)

were necessary at lower oxygen pressures. At 480°C these times increase by one order of magnitude.

A practical consequence of these results is that long time annealings at temperatures above 500°C are unnecessary to obtain a sample in a maximum oxidation state. Upon cooling at a rate of 3°C/minute in air the gain of oxygen from approximately 6.5 at 700°C to 6.0 was no longer appreciable below 360°C indicating that the oxygen exchange became very slow or that the reaction was complete. (Fig.1, insert).

Further thermogravimetric determination of oxygen were carried out by a systematic annealing of 2h30' at 500°C (except otherwise see Table I) at several values of air pressure down to 10^{-6} mm Hg, followed by weighing the sample after natural cooling in the furnace.

The results are presented in figure 1 and table I where the weight loss in terms of oxygen O_x is plotted *versus* the log of the partial pressure of oxygen during the anneal. An approximate logarithmic relation is observed, such that a ten fold increase in oxygen partial pressure increases x by 0.1. However, since the diffusion time involved at low oxygen pressure may become fairly long the lower part of the straight line drawn in figure 1 will be shifted to lower values of x when complete equilibrium is reached.

We have chosen to attribute in figure 1 and in the remaining part of our analysis of the data the value 7.0 for the oxygen content of the most oxidized state of the sample i.e. after annealing under 1 atm of oxygen. Although the exact absolute value should

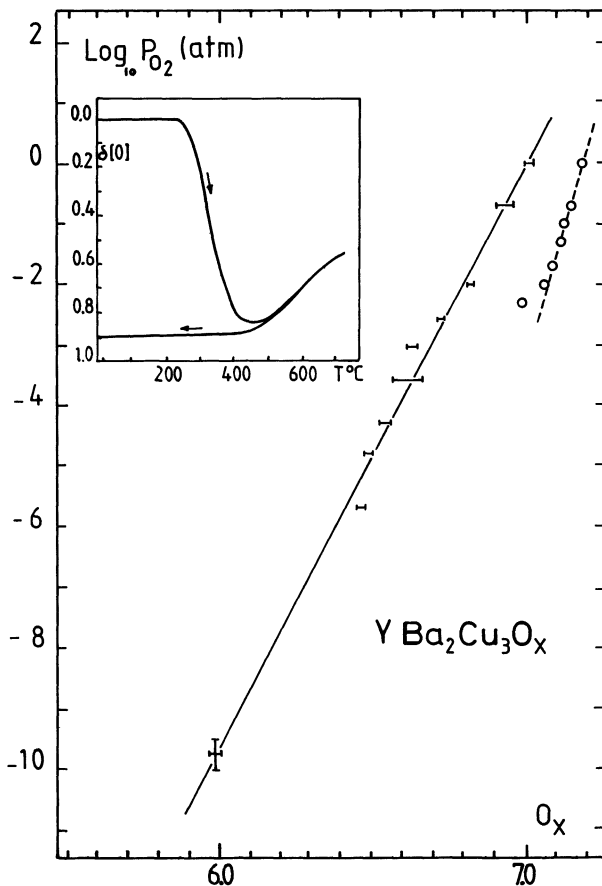


Fig.1.- Oxygen content O_x of $YBa_2Cu_3O_x$ as a function of the partial pressure of oxygen after our annealing procedure [2h30' at 500°C followed by natural cooling in the furnace]. For $x > 6.6$ the annealing procedure is compatible with a homogeneous distribution of oxygen whereas for $x < 6.6$ a longer time should be spent (or a smaller cooling rate). The points (O) are taken from Michel and Raveau [9] and apply to $La_3Ba_3Cu_6O_{14+\delta}$.

Insert: Thermogravimetric recording of oxygen intake in air of a sample previously deoxygenated. The rate of heating is about 6°C/min. The cooling rate is 3°C/min.

Table I.-Relation for oxygen annealing of $YBa_2Cu_3O_x$, between oxygen pressure P_{O_2} , oxygen content O_x (determined by thermogravimetry) and transition temperature T_c at mid height of Meissner effect. The width ΔT_c of the transition is determined from respectively 10 % and 90 % of Meissner effect at low temperature. The standard annealing conditions are 2h30' at 500°C followed by natural cooling of the furnace.

P_{O_2} (atm)	O_x	T_c (K)	ΔT_c (K)	$T_c/\Delta T_c$	Observations
1.0	7.0	89.5	7	13	
0.2	6.94	88.5	14.5	6.1	
1×10^{-2}	6.83	65	11	5.9	
2.6×10^{-3}	6.73	56.5	15	3.8	
2.6×10^{-4}	6.67	57	11	5.2	
2.6×10^{-4}	6.63	50	16	3.1	
2.6×10^{-4}	6.55	23	20	1.1	10 h anneal
8×10^{-5}	6.54	28	26	1.1	
1.6×10^{-5}	6.50	34	39	0.9	
2×10^{-6}	6.47	28	44	0.6	
2×10^{-5}	6.40	23	20	1.1	
2.6×10^{-6}	6.38	20	20	1.0	40 h anneal
2.6×10^{-10}	5.95	18	20	0.9	

await a direct determination of oxygen content by an appropriate method, there exists a converging set of evidence that the value 7.0 is not far off [3-5]. Since all other lower values of oxygen content are related to this initial value by weight difference, should this initial value be modified, a rigid translation of the scale of oxygen content would follow. Also present in figure 1 are the points resulting from a similar study by Michel and Raveau [9] on the compound $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14+\delta}$ isostructural with $\text{YBa}_2\text{Cu}_3\text{O}_7$. The relation between the oxygen pressure and oxygen content in that case appears to be very similar to our work. This compound however, is not superconducting [10].

The Meissner effect measurements of the transition temperature are presented in figure 2 for a selected number of different oxygen content states (indicated by the numbers attached to each set of symbols) of the same sample. The data are collected in table I. We characterize the transition temperature T_c by usual criterion of the temperature at mid height of the Meissner amplitude and the transition width ΔT_c by the temperature difference between the magnetization points at 10 % and 90 % of the Meissner amplitude. The sharpness of the transition, given by $T_c/\Delta T_c$, is also reported in table I.

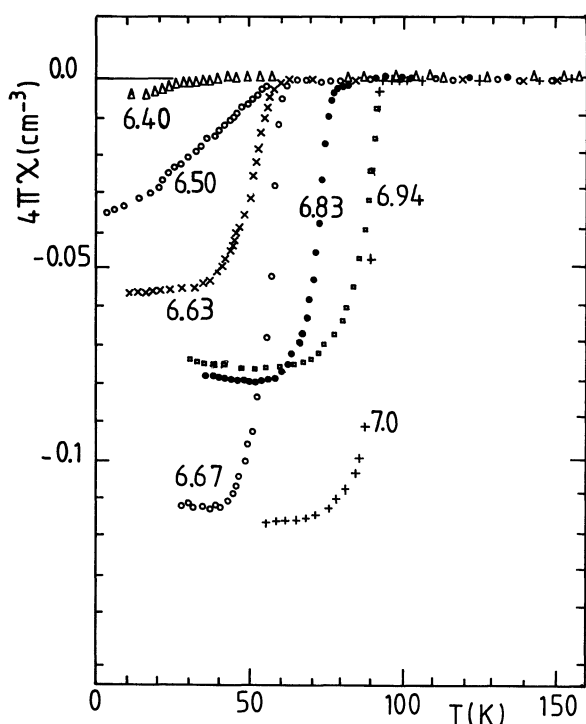


Fig.2.- Selected data of Meissner effect measurements corresponding to various states of oxidation of $\text{YBa}_2\text{Cu}_3\text{O}_x$. For $x > 6.6$ the Meissner transition is step like and involves more than 5% of the sample volume. For $x < 6.6$ the Meissner effect amplitude is reduced and the transition temperature linearly spreads. This is interpreted as due to an inhomogeneous distribution of the remaining oxygen in the compound.

Mere inspection of table I or figure 2 reveals immediately that the superconducting transition falls into two categories, depending on the oxygen content of the sample. For $6.6 < x < 7.0$ the sharpness of the transition increases from 3.1 to 13 and the amplitude of the Meissner effect varies from 6 % to 12 %, although this variation is not monotonous [11]. Quite an opposite behaviour is observed for $6.0 < x < 6.6$: the transition no longer appears as « step like » but rather as a sloping wedge originating below 55 K. The amplitude of the Meissner effect measured at 10 K decreases drastically with oxygen content and is barely measurable below $x = 6.40$. However we now observe that the amplitude of the Meissner effect decreases when the annealing time increases for the lower values of the oxygen partial pressure. Furthermore we have consistently observed that a large diamagnetic shielding signal (up to 50 % or 70 % of the total Meissner effect) was present (when increasing the magnetic field at low temperatures) only for the more oxidized states $x > 6.6$. For $x < 6.6$ little or no differences was noticed between the field cooled state magnetization (flux expulsion) and the zero field cooled state magnetization (diamagnetic shielding). In order to condense these observations on a diagram of T_c versus the oxygen content x in figure 3, the representative point of each transition for $x > 6.6$ is drawn as a rectangular box barred at T_c with a height set by ΔT_c . For $x < 6.6$ we have split the representative point into i) a square at $T = 0$ to express that a large fraction of the sample is not superconducting and ii) a vertical line of height ΔT_c characteristic of the remaining distribution of superconducting phase. The area below 50 K and $x = 6.6$ has been hatched since most likely a two phase system is prevailing in this part of the diagram [12].

In order to investigate the possible inhomogeneous oxygen concentration distribution in samples annealed according to the above mentioned procedure, a special 40 h anneal at 380°C under 10^{-2} mmHg air was performed on a sample corresponding to $x = 6.38$. After this anneal no change of weight was detected but the amplitude of the Meissner effect became less than 0.1 % as compared to about 10 % for the more oxidized states. This fact shows that indeed fairly long times are necessary in order to reach an equilibrium distribution of oxygen at low oxygen content.

The results of resistivity versus temperature for three samples are reported in figure 4. These samples labelled A, B and C have been annealed respectively under 1 atm O_2 , 10 mm Hg and 1 mm Hg air for 3 h at 600°C . Since no thermogravimetric measurement was performed on these samples (because of their small size) the determination of their oxygen content relies on the use of figure 1 which links this quantity to the oxygen pressure during the annealing

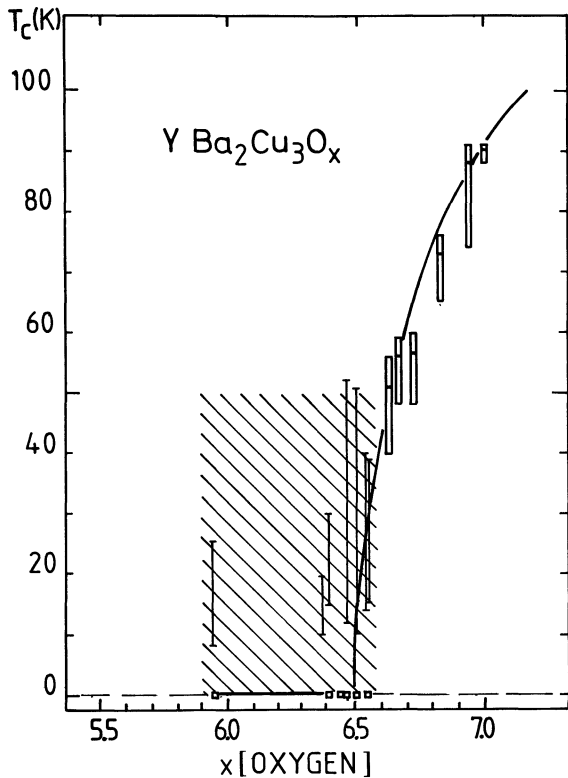


Fig.3.- Phase diagram of the superconducting transition temperature and width (at 10% and 90% of the Meissner effect) versus the oxygen content of $YBa_2Cu_3O_x$ (rectangles). For $x < 6.6$ the representative point is split into a bar spanning 10% and 90% of the distribution of T_c and a zero temperature point representing the non-superconducting part of the sample. The hatched area indicates a two-phase region. BCS fit is indicated by the solid line.

operation. We get $x(A)=7.0$, $x(B)=6.76 \pm 0.05$, $x(C)=6.67 \pm 0.05$ where the error in x is mainly due to the limited accuracy of this procedure. The effect on the resistivity of oxygen depletion from $YBa_2Cu_3O_7$ is fairly apparent : in the normal state at 100 K there is a 10 fold increase of resistivity together with a change of sign of the temperature derivative $\Delta\rho/\Delta T$ when x decreases from 7.0 to 6.67 ± 0.05 . Concerning the superconducting transition temperature and transition width we observe the same pattern as for the Meissner effect determination : samples A and B have a well defined transition temperature and a relative transition width $T_c/\Delta T_c$ of 150 and 15 respectively. In contrast, sample C has a relative transition width of 1.0 in agreement with the Meissner measurements. Thus the resistivity measurements tend to reinforce the conclusions drawn from those of the Meissner effect concerning the effect of oxygen depletion.

No attempt has been done here to study the crystallographic structure of our compounds by X-ray or neutron diffraction as a function of oxygen. Clearly the determination of the orthorhombic-tetragonal transition and the possible occurrence of a mixed phase system [12] should be investigated in a systematic way in conjunction with our measurements.

4. Discussion.

A simple interpretation of the relation between the oxygen content x of $YBa_2Cu_3O_x$ and the oxygen pressure at equilibrium is as follows :

We assume that W the enthalpy of formation of the oxide for $6 < x < 7$, depends on the stoichiometry of oxygen δ through

$$W = W_0 - \delta \Delta W \text{ with } x = 6.5 + \delta$$

where W_0 is the enthalpy of formation of the compound for $x = 6.5$ and ΔW is a repulsive interaction between near neighbour oxygen sites. The existence of an average enthalpy W assumes a mean field type of description of the interactions between the oxygen, analogous to that of elementary order-disorder transformations.

Remembering that 2 oxygen vacancies are created for each molecule of oxygen we can write the chemical equilibrium between the non stoichiometric oxide and the oxygen pressure by :

$$P_{O_2}^{1/2} = A \exp - (W_0 - \delta \Delta W)/kT$$

where we assume that the prefactor depends on δ in a non-exponential way. The energy of interaction ΔW between oxygen is obtained by

$$\Delta W = \frac{1}{2} kT \frac{d \log_e P_{O_2}}{d \delta}$$

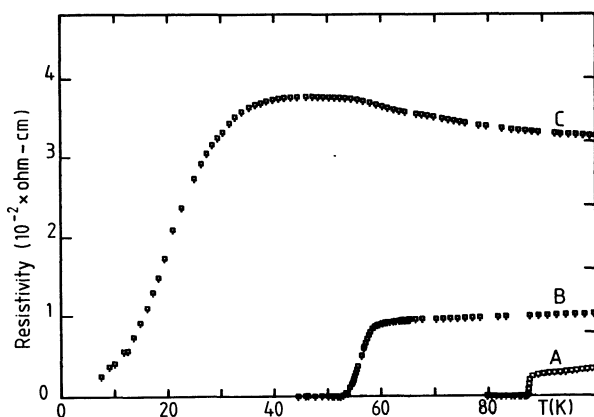


Fig.4.- Resistivity versus temperature for three samples of $YBa_2Cu_3O_x$ with different oxygen content : sample A was annealed under 1 atm O_2 ($x = 7.0$). Sample B was annealed under 10 mm Hg of air ($x = 6.76 \pm 0.05$) and sample C under 1 mm Hg of air ($x = 6.67 \pm 0.05$).

Referring to figure 1 with the numerical values for the slope $d \log_{10} P_{O_2} / d\delta = 9.5 \pm 0.5$ and $T = 630 \pm 30$ K (the last temperature at which the oxide is left at equilibrium upon cooling down) we get :

$$\Delta W = 0.6 \pm 0.5 \text{ eV}$$

This determination should provide a basis for the interpretation of the orthorhombic-tetragonal transformation in the framework of an order disorder phase transition within the oxygen lattice.

The ensemble of the coupled thermogravimetric, Meissner effect and resistivity measurements is rather straightforward to discuss : it appears that for oxygen content between 6.6 and 7.0 the distribution of oxygen is homogeneous and the superconducting transition remains well defined according to our criterion, although rapidly shifting down in temperature. On the contrary, for oxygen content below 6.6 our procedure did not produce a homogeneous distribution of oxygen, resulting in a large part of the sample being depleted and not superconducting, the remaining part becoming superconducting over a very large range of temperatures. The inability to detect diamagnetic shielding currents in this situation indicates further that the superconducting areas are in the form of islands surrounded by the normal phase.

A tentative quantitative interpretation of the variation of T_c with the oxygen content is presented in figure 5 where $\log T_c$ is plotted *versus* the oxygen content δ above 6.5.

Indeed, assuming that $x = 6.5$ corresponds to a stoichiometric semiconducting compound, it is possible to account for the presence of oxygen above that value by the progressive filling of a conduction band by holes. Assuming further a 3D character to this band (although the structure is more likely to be 2D or even 1D) one can simply relate the density of states $N(\delta)$ of this conduction band to the excess δ of oxygen above 6.5 by :

$$N(\delta) = \left(\frac{6}{\pi^4} \right)^{1/3} \frac{m}{\hbar^2} \delta^{1/3}$$

where we assume that each oxygen removes two electrons.

If a BCS type of mechanism is at play, then :

$$T_c = \theta \exp(-1/N(\delta)V)$$

where θ is some characteristic temperature and V an attractive potential for a Cooper pair. We then have the relation :

$$\text{Log } T_c = \text{Log } \theta - \alpha \left(\frac{1}{\delta} \right)^{1/3}$$

$$\text{with } N(\delta)V = \alpha^{-1} \delta^{1/3}.$$

The insert of figure 5 shows the determination of $\theta = 320 \pm 60$ K by a linear extrapolation of the above relation. From this fit we get $\alpha = 1.3$ and $N(0.5)V = 0.8 \pm 0.1$ for the highest $T_c = 91$ K (onset of Meissner effect). The continuous curve presented in figure 5 represents the variation of T_c according to this relation and is seen to be in rough agreement with the data. In particular it should be noted that the regime where a very large distribution of T_c is measured corresponds to the range $0 < \delta < 0.1$ where BCS theory predicts a very steep rise of T_c *versus* δ . This fact gives some credit to the hypothesis of a slight inhomogeneity in the distribution of oxygen concentration in the sample. It should be noted that although being oversimplified [1] this kind of check for the validity of 3D density of states associated with the usual BCS transition offers a mean to analyse our results and suggests how improvement in sample preparation and characterization may yield a more useful test of the theory. In conclusion, the main finding of this study is that

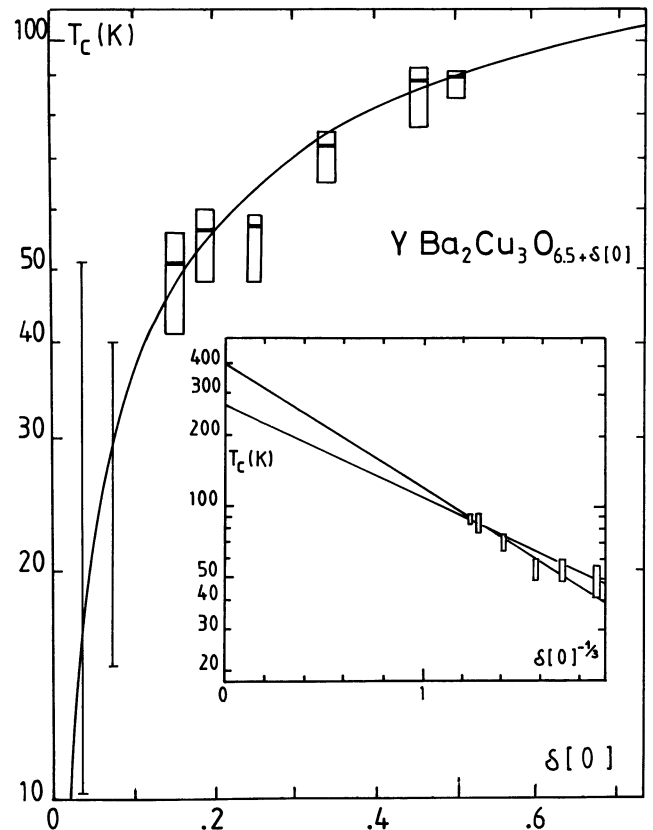


Fig.5.- Tentative fit of the dependence of T_c *versus* oxygen content with BCS theory. The experimental points are those of Fig.3 on a log scale. The solid line is $\log T_c = \log 320 - 1.03 (1/\delta)^{1/3}$. This fit assumes a rigid band model with parabolic density of states above $x = 6.5$.

Insert : Determination of the Debye temperature θ from plotting $\log T_c$ *versus* $\delta^{-1/3}$. This assumes an empty band at $\delta = 0$ i.e. $x = 6.5$.

there exists a range of solid solution of oxygen in $YBa_2Cu_3O_x$ for $6.6 < x < 7.0$.

The transition temperature appears to be well defined by Meissner effect measurements and decreases rapidly near zero for x approaching 6.6. However, although it is possible to produce samples containing nominally oxygen in lower quantities (down to $x = 6.0$) by annealing under a reduced oxygen pressure, the samples exhibit a mixed phase behaviour in this regime. While the major part of the sample remains normal, a small fraction revealed by the reduced amplitude of the Meissner effect continues to show superconducting response with T_c distributed below 50 K. This fraction can be

brought down to less than 1 % of the initial Meissner effect by long annealings under 10^{-6} atm of oxygen or less. Finally an attempt to fit the variation of T_c with the usual BCS theory in 3D is made consistent with a choice of a Debye-like temperature of 320 ± 60 K and the product $NV = 0.8 \pm 0.1$ for the highest superconducting transition temperature at 91 K.

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- [13] We neglect the effect of disorder on the density of states see : LABBE, J. and VAN REUTH, E.C., *Phys. Rev. Lett.* **24** (1970) 1232.