$YBa_2Cu_3O_{7-x}$: Transport Properties and Defects at High Temperature

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Electrical resistivity measurements were carried out on polycrystalline $YBa_2Cu_3O_{7-x}$ at temperatures $300 \le T \le 1023$ K and oxygen partial pressures $5 \cdot 10^{-7} \le p_{O_2} \le 1$ atm. The samples, equilibrated in the p_{O_2} range from $5 \cdot 10^{-4}$ to 1 atm, show metallic behaviour, the one equilibrated at $p_{O_2} = 2 \cdot 10^{-5}$ shows a transition between metallic and semiconducting behaviour at 920 K, and that equilibrated at $p_{O_2} = 5 \cdot 10^{-7}$ shows semiconducting behaviour: for the latter the relevant resistivity is due to the oxygen-ion migration. The isotherms log σ vs. log p_{O_2} (in the temperature range from 723 to 1023 K) show slopes of about 1/6 at 723 K (orthorhombic phase) and about 1/2 at 1023 K (tetragonal phase). These results are discussed in terms of appropriate defect models.

Key words: Superconductors, electrical properties, defects.

1. Introduction

Since 1987, the year of the discovery of superconducting $YBa_2Cu_3O_{7-x}$ [1], many papers have been published on the characterization of this compound but only a few concern the transport properties and defect structure at temperatures high enough for the crystal-gas (oxygen) equilibria to be set up, and where the mobilities of the ionic carriers are remarkable.

However, some important "electrical" features are already known, such as the facts that holes are the majority carriers and that the conductivity between 300 and 1000 K is correlated with the deficiency of oxygen, x [2]. Moreover, it is known [3] that the temperature of the second order transition T_{O-T}, orthorhombic ($YBa_2Cu_3O_7$, Fig. 1 a) to tetragonal ($YBa_2Cu_3O_6$, Fig. 1 b), can be precisely detected with resistance measurements, in the temperature range from 600 to 1050 K. This transition is characterized by a loss of oxygen from the O_1 sites of the basal plane. Also, the dependence of T_{O-T} on the oxygen partial pressure [4], and of the critical temperature (T_c) on the x values, has been reported [5].

On the other hand very little is known about the correlation between the electrical conductivity and the oxygen partial pressure (p_{O_2}) for both the orthorhombic and tetragonal phases, whose knowledge is required to determine the defect structure. Secondly, the oxygen ion contribution to the total conductivity is not yet explained.

Also the kinetics of the oxygen exchange related to the vacancy ordering in the basal plane of the structure of both phases, which has a fundamental importance for superconductivity, has not yet been clarified.

The present work aims at yielding a contribution to these open problems, through resistance measurements carried out with a D.C. four-probe method between 80 and 1023 K and in the p_{O_2} range $5 \cdot 10^{-7} \div 1$ atm, using metal or solid oxygen-ion conducting electrodes.

2. Experimental

The $YBa_2Cu_3O_{7-x}$ was prepared by a solid state reaction from $BaCO_3$ (99.98%), CuO (99.999%) and Y_2O_3 (99.999%) (all Aldrich products). The wet mixed powders were pressed in disk form (diameter 12 mm, height 4–5 mm) and heated under a flux of oxygen, for successive periods of 12 h at 1123, 1173, and 1223 K, respectively. This thermal cycle was repeated twice on pellets obtained by grinding, mixing and pressing again the specimens.

After equilibration at 673 K for 12 h in a dry oxygen flow, the pellets were slowly cooled to room temperature. These final samples exhibited X-ray reflections due to only the orthorhombic phase and an x value near zero, as reported earlier [6].

From the above pellets, bar-shaped samples (length 10 mm, diameter 4 mm) were obtained by cutting:

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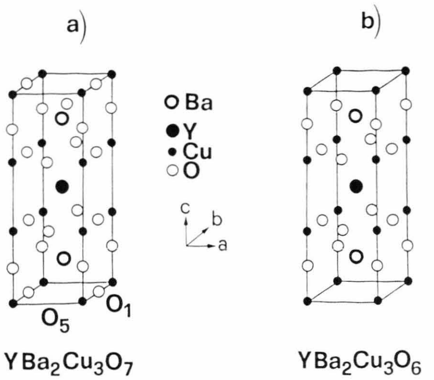

Fig. 1. Unit cell of $YBa_2Cu_3O_7$ (a) and $YBa_2Cu_3O_6$ (b).

these were employed in the electrical resistivity measurements, performed with a D.C. four-probe method by means of a potentiostatic Solartron 1286 Electrochemical Interface in combination with a Keithley 180 Digital Nanovoltmeter. In order to estimate the total conductivity, Ag-paint was used as electrodes. To obtain the oxygen-ion contribution, two slices of monocrystalline $ZrO_2 - 10\% Y_2O_3$ were put between the two probes applied at both sides of the bar as current elelctrodes and the sample itself.

Great attention was paid to reach the equilibrium of the specimens with the oxygen gas for all the oxygen partial pressures employed: 1; 0.2; $1 \cdot 10^{-2}$; $5 \cdot 10^{-4}$; $2 \cdot 10^{-5}$ and $5 \cdot 10^{-7}$ atm. These values were obtained by a flux of O_2 and N_2 mixtures, whereas the total pressure was kept at 1 atm in all the experiments.

For each p_{O_2}, the resistivity measurements were first taken on a cooling run, from 1023 K down to room temperature (RT) in steps of about 30 K, after complete equilibration of the samples at each chosen temperature; a similar heating run was then carried by stepwise increasing the temperature up to again 1023 K.

3. Results and discussion

Fig. 2 depicts the trend of the conductivity σ ($\Omega^{-1} \cdot cm^{-1}$) obtained for $YBa_2Cu_3O_{7-x}$ samples in the temperature range 300–1023 K at given p_{O_2} values.

The results may be summarized as follows:

a) For p_{O_2} between $5 \cdot 10^{-4}$ and 1 atm, the electrical behaviour detected with silver electrodes is metallic. At a given temperature, the conductivity decreases with decreasing p_{O_2}, which confirms that the carriers are holes. At $p_{O_2} = 2 \cdot 10^{-5}$ atm, the behaviour is still metallic from RT up to 920 K, but becomes semiconducting above that temperature. Finally, at $p_{O_2} = 5 \cdot 10^{-7}$ atm the semiconducting trend is shown over the whole temperature range. Remarkably, at this p_{O_2}, the σ values obtained between 923 and 1023 K are the same as those at $p_{O_2} = 2 \cdot 10^{-5}$ atm; a coincident value is also shown for $p_{O_2} = 5 \cdot 10^{-4}$ atm at 1023 K. In other words, at the above temperature and p_{O_2}, i.e., when the samples have semiconducting behaviour, the conductivity is independent of the oxygen partial pressure.

b) The curves for $p_{O_2} = 1$, 0.2, $1 \cdot 10^{-2}$, $5 \cdot 10^{-4}$, and $2 \cdot 10^{-5}$ atm show a change in slope corresponding to a structural phase transition (orthorhombic-tetragonal). The T_{O-T} values (determined by means of plots $d\log \sigma / dT$ vs. T), shown in Fig. 2 with arrows, are in good agreement with those reported in the literature [3].

c) The temperature of about 670 K marks a limit for all the isobares studied. Above this temperature, the interaction with the oxygen atmosphere becomes important. It can be inferred that at any p_{O_2} the samples have: (i) a constant oxygen content in the range $300 \leq T \leq 673$ K and (ii) x values increasing with temperature in the range $673 \leq T \leq 1023$ K. In particular, at $p_{O_2} = 5 \cdot 10^{-7}$ atm, the Arrhenius plot gives an activation energy of 0.4 and 0.65 eV in the temperature ranges 300–673 K and 673–1023 K, respectively.

d) The time required to reach the crystal-gas equilibrium depends on the p_{O_2} values. A preliminary kinetic study was performed on $YBa_2Cu_3O_{7-x}$ samples previously equilibrated at 743 K by increasing very rapidly the temperature to 773 K and then recording the resistivity, ϱ, vs. time, t, at constant $T = 773$ K. Whereas, for $p_{O_2} = 1$, 0.2, $5 \cdot 10^{-7}$ atm, the final equilibrium value was reached in the short time necessary to heat the samples to 773 K, for the remaining p_{O_2} values the rate was very low. The corresponding isotherms, well interpreted by the 1st order law, give the K (s^{-1}) values reported in the following table, along with the relevant p_{O_2} and x values.

p_{O_2} (atm)	x[+]	K (s^{-1})
$1 \cdot 10^{-2}$	0.23	$5.3 \cdot 10^{-3}$
$5 \cdot 10^{-4}$	0.43	$2.2 \cdot 10^{-4}$
$2 \cdot 10^{-5}$	0.60	$9.0 \cdot 10^{-5}$

[+] The x values were deduced from [4], utilizing, at 773 K, the x equilibrium data as a function of p_{O_2}.

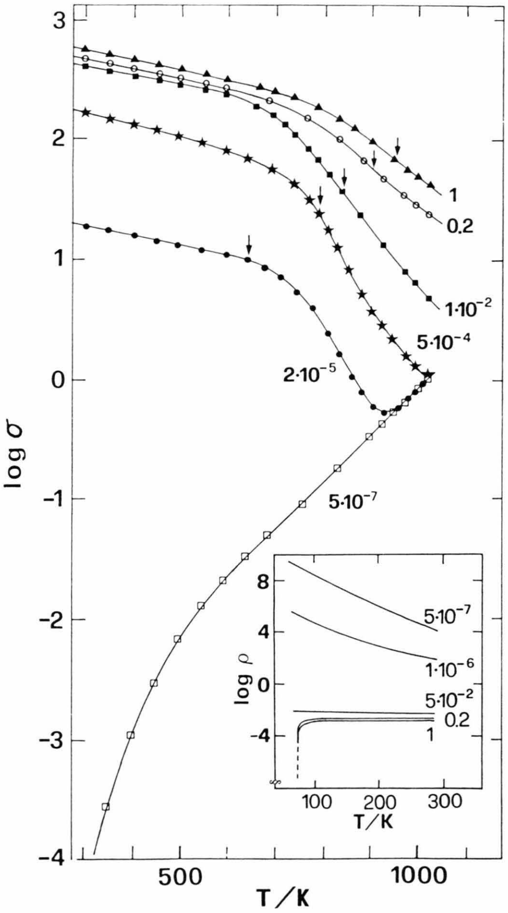

Fig. 2. Temperature dependence of the conductivity, σ, of $YBa_2Cu_3O_{7-x}$ under different p_{O_2} (indicated in atm). In the insert the trend of the resistivity, ϱ, in the temperature range 80–300 K, is shown.

e) When the electron blocking electrodes are used, the σ values obtained with $p_{O_2} = 5 \cdot 10^{-7}$ atm in the range $873 \leq T \leq 1023$ K are superimposed on those measured with silver electrodes; this clearly shows that, at this very low oxygen partial pressure, the conductivity is completely due to migration of the oxygen-ions. The ionic contribution is, on the contrary, negligible at higher p_{O_2} values except for the $p_{O_2} = 2 \cdot 10^{-5}$ atm isobar in the temperature range 923–1023 K where the conductivity is completely ionic, too.

In order to single out the superconducting samples, measurements were also performed in the temperature range 80–300 K. A T_c value of 95 K was detected on samples equilibrated at 673 K only when p_{O_2} is 1 and $1 \cdot 10^{-2}$ atm. At lower p_{O_2} ($5 \cdot 10^{-4}$, $1 \cdot 10^{-6}$ and $5 \cdot 10^{-7}$ atm), on the contrary, the samples cooled down to 80 K present resistivity values which increase with decreasing p_{O_2} (Fig. 2, insert).

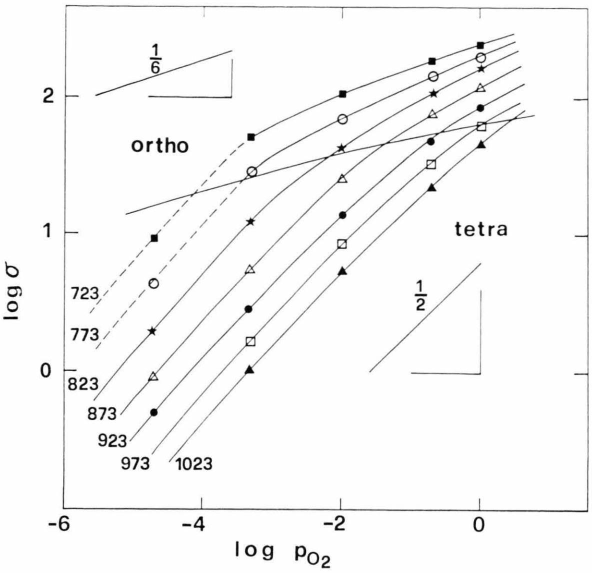

Fig. 3. Conductivity as a function of the oxygen partial pressure for the orthorhombic and tetragonal phases in the temperature range 723–1023 K (isotherms indicated in K).

In the following analysis we do not discuss the data obtained from samples equilibrated at the higher p_{O_2} ($2 \cdot 10^{-5}$ – 1 atm) in the temperature range 300–673 K because others authors [2] gave an exhaustive interpretation of the linear trends of $\log \sigma$ very close to the ones obtained in this work.

Let us first consider the results obtained in the temperature range 723–1023 K and the p_{O_2} range $2 \cdot 10^{-5}$ – 1 atm, by using the silver electrodes: in Fig. 3 $\log \sigma$ is plotted versus $\log p_{O_2}$ for seven isotherms. In the same figure the boundary line between the fields of existence of the orthorhombic and tetragonal phases is drawn. An important feature is that, on going from 723 K to 1023 K (at intervals of 50 K up to 1023 K) the slope gradually changes from about 1/6 to about 1/2.

For what concerns the orthorhombic phase, recent measurements by means of X-ray absorption [7], XPS and Auger spectroscopy [8–10] led to exclude the presence, in the ground state of this phase, of Cu^{3+} ions, as assumed by several authors [11] and pointed to the presence of the Cu^{+}, Cu^{2+} and O^{-} species. According to these results, the holes generated by the introduction of excess oxygen may reside only in the oxygen derived p-band forming the O^{1-} species (or, in

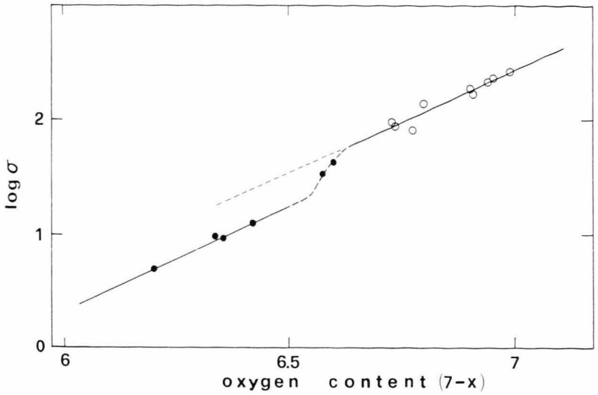

Fig. 4. Log σ as a function of oxygen content (7-x), for the tetragonal (filled circles) and the orthorhombic phase (open circles).

conformity with the Kröger [12] notation for the defects followed here, $O_O^{\cdot}$). These species, according to the most recent interpretation of the superconductivity mechanism in these compounds [13], assume a fundamental role when present as dimers, or as species formed with monovalent copper [14].

Now, assuming as reference the $YBa_2Cu_3O_{6.5}$ composition for which, formally, each ion has its "normal" valence, and taking into account that the gain and loss of oxygen concern only the basal plane of the orthorhombic structure, the corresponding equation for the defect formation is

$$1/2\,O_2 + O_O + V_O^{\cdot\cdot} \rightleftarrows 2O_O^{\cdot}, \qquad (1)$$

where $V_O^{\cdot\cdot}$ represents an oxygen vacancy in the $z = 0$ plane at (0, 1/2, 0) sites. If one analyzes the experimental data of x as a function of p_{O_2} for this phase, as given in the literature [4], it can easily be seen that the relationship is well interpreted by (1) for the whole T and p_{O_2} ranges where only the orthorhombic phase is present.

Since the carriers, as known, are holes travelling through the p-band, in order to interpret the conductivity data, (1) must be rewritten as

$$1/2\,O_2 + V_O^{\cdot\cdot} \rightleftarrows O_O + 2h^{\cdot}, \qquad (2)$$

from which

$$K_1 = \frac{[h^{\cdot}]^2}{p_{O_2}^{1/2}\,[V_O^{\cdot\cdot}]}\,.$$

Taking into account the electronegativity condition $2[V_O^{\cdot\cdot}] = K/[h^{\cdot}]$, one obtains

$$[h^{\cdot}] = K'\,p_{O_2}^{1/6}\,.$$

The total conductivity of this phase is completely due to hole migration, so that we can write $\sigma \propto p_{O_2}^{1/6}$ in accordance with the trend observed experimentally.

Let us now consider the tetragonal phase ($x > 0.4$). The oxygen gain process in terms of holes and interstitial oxygen formation may be written

$$1/2\,O_2 + V_i \rightleftarrows O_i'' + 2h^{\cdot}, \qquad (3)$$

where V_i is the interstitial vacancy in the basal plane sites at (0, 1/2, 0) and (1/2, 0, 0) available for oxygen. The trend of x vs. p_{O_2} [4, 14] is well interpreted by (3). On the contrary, if the present conductivity data are considered (obviously neglecting those obtained with $p_{O_2} = 5 \cdot 10^{-7}$ atm and anyhow all the data relevant to the predominant oxygen-ion transport), one observes, as already seen, a dependence of σ on p_{O_2} (expressed by the slope $d\log\sigma/d\log p_{O_2}$) of about 1/2. Therefore, not all the holes estimated by (3) are available for conductivity. One might think that, in this phase, the holes probably associated with monovalent copper, $Cu'_{Cu} + h^{\cdot} \rightleftarrows Cu_{Cu}$, are, in part, localized.

This localization becomes evident on observing the trend of the σ values, corrected for the temperature dependence and used independently of the oxygen partial pressure, as a function of x [15] (Figure 4). It appears clearly that, outside the x region involved in the transition, the σ values for the tetragonal phase are lower than those obtained by extrapolating to lower x values the straight line which interpolates the orthorhombic phase data ($0.02 \le x \le 0.4$). Taking into account that the carrier concentration and the scattering mechanism are determined by the oxygen vacancy concentration [16], the lower σ values observed for the tetragonal phase may be only due to a lower concentration of free holes.

If it is possible to extend to lower temperatures the coincidence observed for $p_{O_2} = 5 \cdot 10^{-7}$ atm in the range 873–1023 K between the σ values measured with silver and those with blocking electrodes, then the activation energy, $E^* = 0.65$ eV (see above) represents the sum of the activation enthalpies for the oxygen migration and for the oxygen defect formation. In the present case, however, the change in x is very small; actually, for p_{O_2} values lower than 1 ppm and in this temperature range it was found [17] that $x > 0.9$, and we have to do with the pure tetragonal phase (Figure 1 b). The negligible x variation explains why the conductivity is not appreciably affected by the p_{O_2} variation. The above E^* value for the oxygen transport may appear small; it should, however, be noted that the basal plane of the tetragonal cell presents more than 95% of the available sites (O_1 and O_5) vacant, and therefore the activation energy determined can almost completely be attributed to the oxygen-ion hopping in the vacant sites along the directions (1, 1, 0) and (1, $\bar{1}$, 0) of the $z = 0$ plane.

Recently other authors [18] measured the oxygen-ion conductivity for the pure orthorhombic phase ($0.05 \leq x \leq 0.09$) in the temperature range 663–773 K, obtaining an activation energy four times higher ($E^* = 2.5 \pm 0.1$ eV) than the present value. Such a large difference obviously involves a different transport mechanism; very reasonably it might be for this phase as the one proposed by Alario-Franco et al. [19] to interpret the process of oxygen loss from $YBa_2Cu_3O_7$. According to this mechanism, the O_1 oxygen is able to migrate along a tunnel with direction (1/2, 0, 0) and limited by the Cu, Ba ions and by the oxygen located at (0, 1/2, 0) sites.

Finally, as regards the kinetic results, they can tentatively be explained by considering the oxygen gain and loss processes nearly instantaneous in the pure orthorhombic phase ($p_{O_2} = 1$ or 0.2 atm) while, the larger x becomes (i.e., the more the tetragonal phase is involved, the more they slow down. The rate becomes again high for $x > 0.9$, when practically there is no exchange of oxygen with the atmosphere.

In order to reach a deeper insight in this particular problem, an extension of the research is in progress. It will provide an integration of the conductivity data with thermogravimetric and X-ray diffraction measurements, and a consequent structural investigation on the modifications of the oxygen distribution in the O_1 and O_5 sites of the basal planes.

In conclusion, this work, besides confirming some results already known, i) analyses the defect structure of the orthorhombic and tetragonal phases, ii) states the importance of the oxygen migration contribution to the total conductivity, and iii) puts into evidence the influence of the structure of $YBa_2Cu_3O_{7-x}$ on the oxygen gain and loss process.

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