

# The Mechanism of Charge Carrier Transport in Non-Stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at High Temperatures

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## Abstract

Non-stoichiometry, electrical conductivity and thermoelectric power of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  were measured at thermodynamic equilibrium conditions as a function of temperature (650-1150 K) and oxygen pressure ( $30\text{-}10^5$  Pa).

It was shown that in all the range of existence of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  phase, singly or doubly ionized oxygen vacancies are dominating defects. Within the composition range  $\delta < 0.7$ , the carrier transport occurred via electron holes in the effective energy band whose width decreases with an increase in the deviation from the stoichiometry. For a deviation  $\delta = 0.7$ , a transition metal-semiconductor was observed.

A qualitative scheme for the electron structure of non-stoichiometric  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is set forth.

## 1. Introduction

The high temperature superconductivity observed in the oxide materials opened up new possibilities for ceramic materials and its technologies.

Aiming at getting at still higher and higher temperatures of transition into superconductivity, the technological barrier of nitrogen boiling point was broken through while synthesizing the compound  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  whose critical point constitutes ca. 94 K for  $\delta \approx 0$  /1/.

A big number of compounds of M-Ba-Cu-O (M=La,Y)-type shows a rather significant deviation from stoichiometry, which influences the value of critical temperature and electronic properties of the materials.

The  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  oxide shows a wide range of non-stoichiometry connected with the presence of vacancies in the oxygen sublattice. With an increase in deviation from stoichiometry (the  $\delta$ -value increases), their concentration goes up and at  $\delta = 0.6$  a structural transformation takes place and in result thereof the orthorhombic structure passes into the tetragonal one. The value of  $\delta$  corresponding with a modification in the crystallographical structure may get changed within certain limits, e.g., during de-oxidation conducted at low temperatures the orthorhombic structure did still exist even

for  $\delta = 0.7$  /2/.

The investigations of the concentration of point defects and its structure are necessary for understanding of high-temperature superconductivity mechanism.

High-temperature thermogravimetric investigations and research on electrical properties have not been made in full for the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  although they have been a classic tool of solid state chemistry. The accessible data are rather fragmentary and limited to a small range of change in thermodynamic conditions in which there is no distinct correlation between the electrical properties and the deviation from the stoichiometric composition. Yet it is generally assumed that the electrical conductivity of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  decreases with an increase in  $\delta$  /3,4/. A discontinuity of the temperature dependence of electrical conductivity has been observed at the transition from the orthorhombic into the tetragonal structure /5,6/ and the transition metal-semiconductor /7,8/ and the  $p$ - $n$  transition within the semiconductor phase /9,10/. Many works have been devoted to the carrier transport mechanism. Among others, the polaron mechanism in the tetragonal phase /10,11/ as well as the adaptations of the narrow band model /12/ have been proposed. Nevertheless, based on the examinations hitherto performed it is hard to determine unequivocally the structure of electron defects and the transport properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  at high temperature.

This paper presents the results of thermogravimetric measurements and the investigations of electrical conductivity and thermoelectric power of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  as a function of temperature and oxygen pressure at thermodynamic equilibrium conditions in order to obtain further information on the structure of ionic and electronic defects in crystalline lattice of this superconductor.

## 2. Experimental

The  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  oxide was obtained by the standard method, i.e., by sintering stoichiometric quantities of  $\text{Y}_2\text{O}_3$ , CuO and  $\text{BaCO}_3$  (of 0.999 purity) at a temperature of 1220 K. The sintering and grinding was repeated three times. The material in the form of pellets was heated at 1200 K in oxygen for 48 h and next slowly cooled to 670 K for 5 h, at which it was kept for

10 h, and then cooled again to room temperature. X-ray examinations have shown that the obtained compound is an orthorhombic phase of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , and that at a temperature of about 90 K it passes into a superconductive state. The deviation from stoichiometry was measured by means of a continuous gravimetric method using spiral microbalance McBain type.

The investigations of electrical conductivity and of the thermoelectric power were performed simultaneously on the same sample. A sample,  $0.2 \times 0.4 \times 1.5 \text{ cm}^3$ , was placed in a special holder between two platinum plates. Two thermoelements Pt-PtRh10, which were used to measure the temperature at the ends of the sample and simultaneously as current-carrying wires to measure electrical conductivity, were attached to the plates. Two platinum wires were additionally wound around the sample to measure the voltage drop at the current flow when the electrical conductivity was being measured. The measurement of electrical conductivity was carried out by the alternating current method. The thermoelectric power was determined by simultaneous registration of potential and temperature changes at the ends of the sample, induced by means of an electric heater. The desired oxygen pressure was obtained by passing a He-O<sub>2</sub> gas mixture through the apparatus at a rate of 10 l/h. The gas mixtures were prepared in steel bottles under a pressure of  $10^7 \text{ Pa}$  and after a period of 1 month were used for the measurements. Oxygen pressure was determined by measuring the EMF of a zirconia cell at 1070 K.

The investigations were carried out in the temperature range of 650-1150 K and oxygen pressure of  $10^5$ -30 Pa.

### 3. Results and Discussion

Structural research made on both the poly- and monocrystals /13-15/ shows that the crystalline structure is a derivative of that of perovskite (Fig. 1). The oxide having a stoichiometric composition ( $\text{YBa}_2\text{Cu}_3\text{O}_7$ ) crystallizes in the orthorhombic system (Pmmm space group) with the following parameters in the elementary cell:  $a=3.8198 \text{ \AA}$ ;  $b=3.8849 \text{ \AA}$ ,  $c=11.6762 \text{ \AA}$  /16/. The values of these parameters given by different authors are

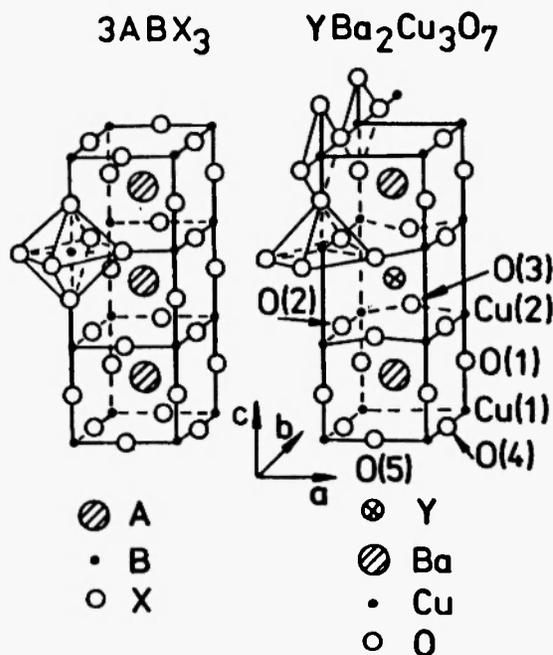


Fig. 1: Comparison of the crystalline structure of perovskite and the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  superconductor /6/.

slightly divergent one from another depending upon the conditions of sample preparation. In the stoichiometric compound ( $\delta=0$ ), all the O(4) positions are occupied, whereas the O(5) are empty. In turn, copper atoms occupy two non-equivalent positions: Cu(2) - with a coordination close to a tetragonal pyramid, and Cu(1) - in which copper has a flat, almost square coordination. The Cu-O squares, connected by their corners, constitute the copper-oxygen chains along the  $b$ -axis. The bond between Cu(2) copper and O(1) oxygen atoms is appreciably weaker than that between Cu(2) and O(2) or O(3) (the bond length being equal to 2.295 Å and 1.9299 Å or 1.9607 Å, respectively /16/. For this reason, in the crystalline structure, apart from the chains mentioned above, the copper-oxide planes placed perpendicularly to the  $c$ -axis are also distinguished.

The elementary cell of the tetragonal phase is described with a space group P4/mmm and has the following lattice constants:  $a=3.8570 \text{ \AA}$ ;  $c=11.8194 \text{ \AA}$  /17/. The investigations of neutron diffraction on  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  crystals show /18/ that the phase transition from an orthorhombic into tetragonal form is a

transformation of order-disorder type. A deviation from stoichiometry in the orthorhombic phase is related with oxygen vacancies exclusively in the 0(4) positions /16,18/; in the tetragonal phase the 0(4) and 0(5) positions are equivalent and the oxygen atoms occupy them randomly and thus they destroy the one-dimensional order along the  $b$ -axis. In the extreme case of the  $\text{YBa}_2\text{Cu}_3\text{O}_6$  compound, these positions remain unoccupied.

Figs. 2-7 present the results of high temperature investigations on the temperature and oxygen pressure dependence of the deviation from stoichiometry /19/, electrical conductivity and the thermoelectric power in terms of thermodynamic equilibrium.

As seen in Fig. 2, the deviation from stoichiometry is an exponential function of temperature:

$$\delta = \text{const} \cdot \exp\left(\frac{-\Delta H}{R \cdot T}\right) \quad (1)$$

where  $\Delta H$  is the enthalpy of defect formation. The  $\Delta H$  values found are of an order of 0.5 eV, and they are considerably lower than the values observed in simple oxide systems. It may be noted that for the orthorhombic phase the enthalpy of defect formation is higher (0.46 eV) than in the tetragonal one (0.22 eV).

The obtained character of the relation for a deviation from stoichiometry as a function of oxygen pressure (Fig. 3) may be reflected with the following equation:

$$\delta = \text{const} \cdot P_{\text{O}_2}^{-\frac{1}{n}} \quad (2)$$

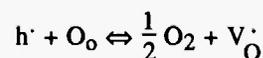
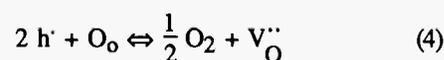
where  $n$  gets changed within the range 4 through 16. A negative exponent suggests that the dominating defects should be oxygen vacancies and electrons. However, the character of the oxygen pressure relation of the electrical conductivity (Fig. 5) expressed as follows:

$$\sigma = \text{const} \cdot P_{\text{O}_2}^{+\frac{1}{n}} \quad (3)$$

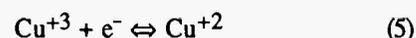
(where  $n$  changes within the range 2 through 7) indicates a positive type of carrier and a complex defect structure in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . The fall in electrical conductivity with temperature observed in Fig. 4 does not mean directly the metallic properties because with a change in temperature there occurs also a change of the concen-

tration of ionic and electron defects connected with non-stoichiometry (Eq. 1).

From the viewpoint of the electron structure of the solid state, the oxygen vacancies, generally accepted as dominating defects in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , constitute the donor centers. Their ionization should supply electrons for the conductivity band, whereas the measurements of electrical conductivity and those of the thermoelectric power as well as other independent experiments /20,21/ show that the electron holes are the dominating current carriers. They are related to the  $\text{Cu}^{3+}$  ions (formally in the stoichiometric phase of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  copper occurs at +2 and +3 oxidation numbers in the ratio 2:1); it is postulated that they exist also in the oxygen band /20,22/. With this in mind, a decrease in electrical conductivity with a fall in oxygen pressure (increase in the concentration of oxygen vacancies and thus an increase in the deviation from stoichiometry  $\delta$  (Fig. 8) should be associated with a fall in the concentration of effective carriers of current due to the recombination of electrons coming from the ionization of the donor centers (oxygen vacancies) with electron holes. The reactions of the formation of defects in the system considered may be expressed as follows:



where the first equation refers to the case of double ionization of oxygen vacancies whereas the second one is written for the single ionization. The compensation effect put forth may be also presented as



is corroborated by the results of XPS spectroscopic investigations /24/ in which a fall in the concentration of  $\text{Cu}^{3+}$  ions with increasing  $\delta$  has been found. It is also visible in the relation between the thermoelectric power and the deviations from stoichiometry (Fig. 9). With increasing  $\delta$  (decreasing concentration of electron holes), the thermoelectric power goes up (for  $\delta < 0.7$ ), and it points at an effective energy band existing in this range in which the charge transport takes place via carriers having energy close to that of Fermi. A stronger in-

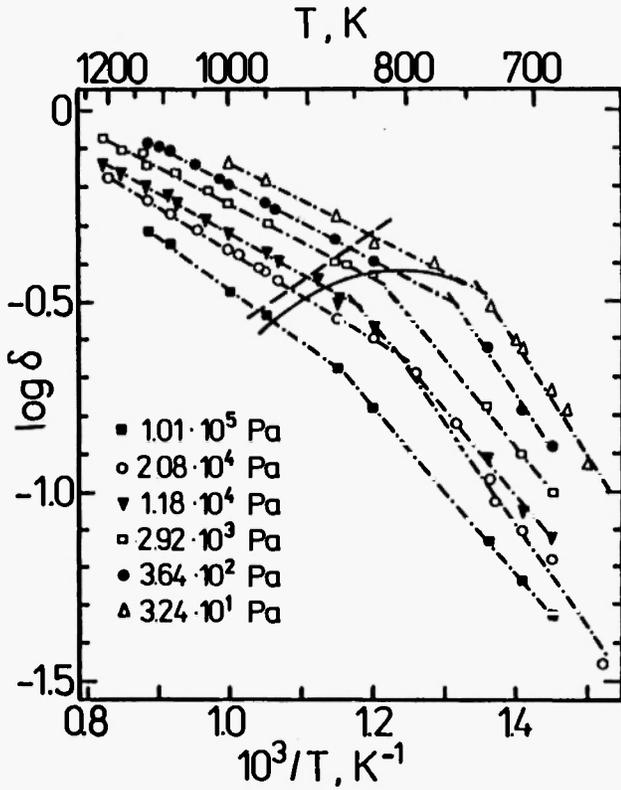


Fig. 2: Temperature relation of the deviation from stoichiometry in  $YBa_2Cu_3O_{7-\delta}$  at various oxygen pressures. The dashed line (---) stands for a transition temperature of the orthorhombic form into the tetragonal one obtained based on high temperature X-ray photography investigations /18/. The solid line corresponds to the temperatures at which breaks in the dependence of electrical conductivity vs. temperature were observed.

crease in the thermoelectric power in the tetragonal phase (for  $0.35 < \delta < 0.7$ ) suggests an increase in the effective mass of carriers caused by a narrowing of the band. In turn, a violent fall towards the negative values for  $\delta > 0.7$  points at a modification in the electron structure and at the occurrence of a gap in the density of states. A metal-insulator transition exists in the discussed system which, as said before, was also pointed out by other authors.

Assuming that an energy effective band occurs for a composition of  $\delta < 0.7$  in  $YBa_2Cu_3O_{7-\delta}$ , we can evaluate

the effective concentration of electron holes based on the measurements of thermoelectric power. For a metallic orthorhombic phase ( $\delta < 0.35$ ), the thermoelectric power may be expressed with the following equation:

$$\alpha = \frac{2}{3} \left( \frac{\pi}{3} \right)^{2/3} \frac{m^* k^2 T}{eh^2} [h]^{-2/3} \quad (6)$$

where  $[h^*]$  is a concentration of electron holes, and the free electron mass was taken as the effective one. For the tetragonal phase, within the range of the occurrence of a narrow band ( $0.35 < \delta < 0.7$ ) the relation between the thermoelectric power and the concentration of holes is in turn described by /25/:

$$\alpha = \frac{k}{e} \cdot \ln \frac{1 - [h^*]}{[h^*]} \quad (7)$$

The results of calculation performed based on the two said equations are presented in Fig. 10. One may note that the concentration of electron holes (effective

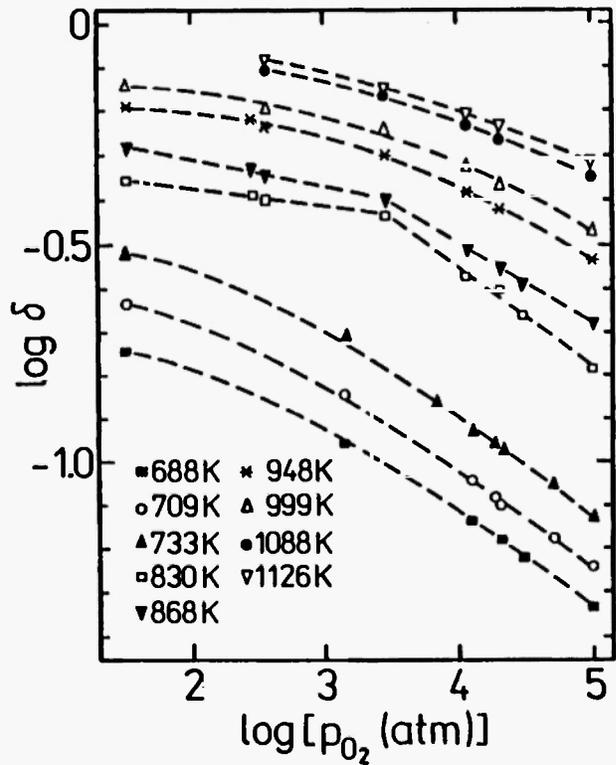


Fig. 3: The dependence of deviation from stoichiometry of  $YBa_2Cu_3O_{7-\delta}$  on oxygen pressure at different temperatures.

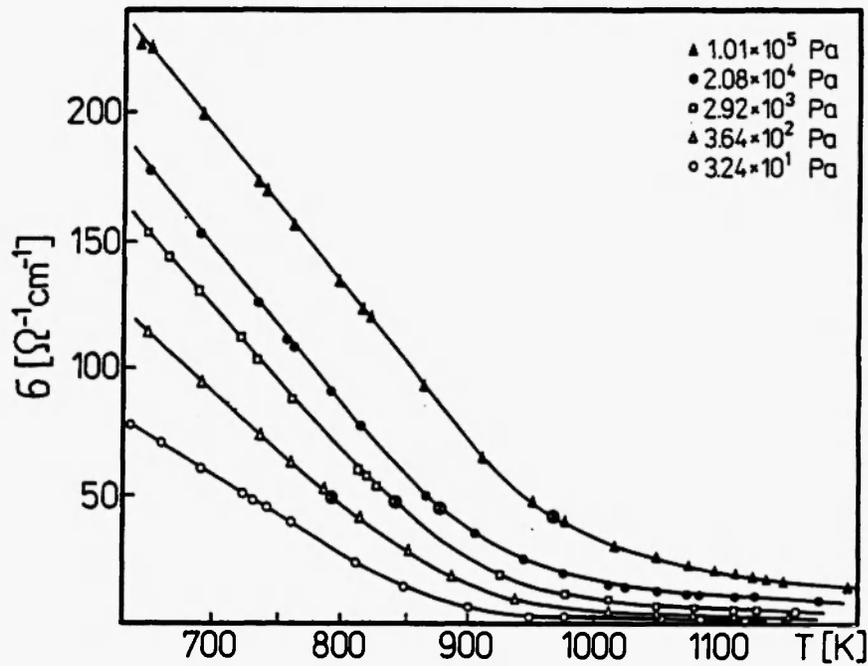


Fig. 4: Temperature dependence of electrical conductivity of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  at different oxygen pressures.  $\otimes$  shows the phase transition (orthorhombic-tetragonal phase).

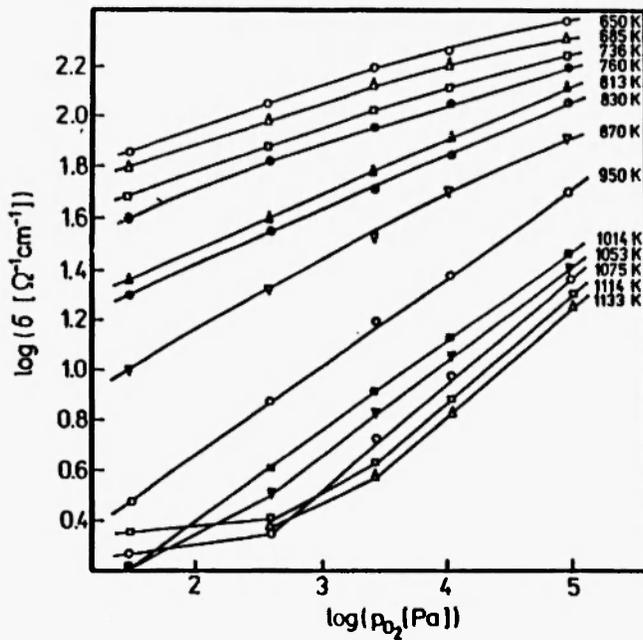


Fig. 5: The dependence of electrical conductivity of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  on oxygen pressure at different temperatures.

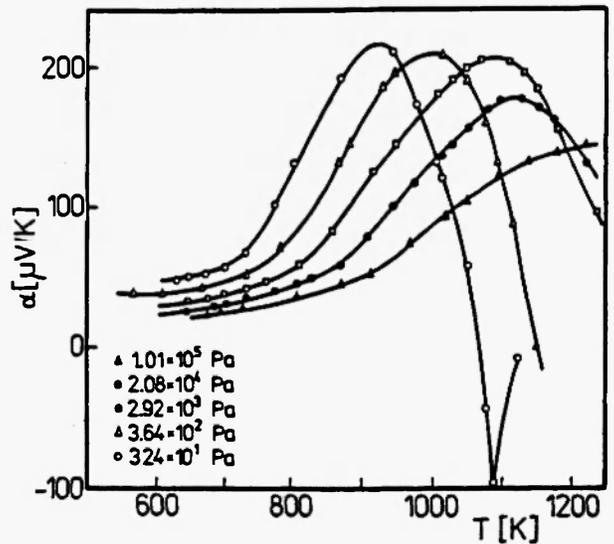


Fig. 6: Temperature dependence of thermoelectric power of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  for different oxygen pressures.

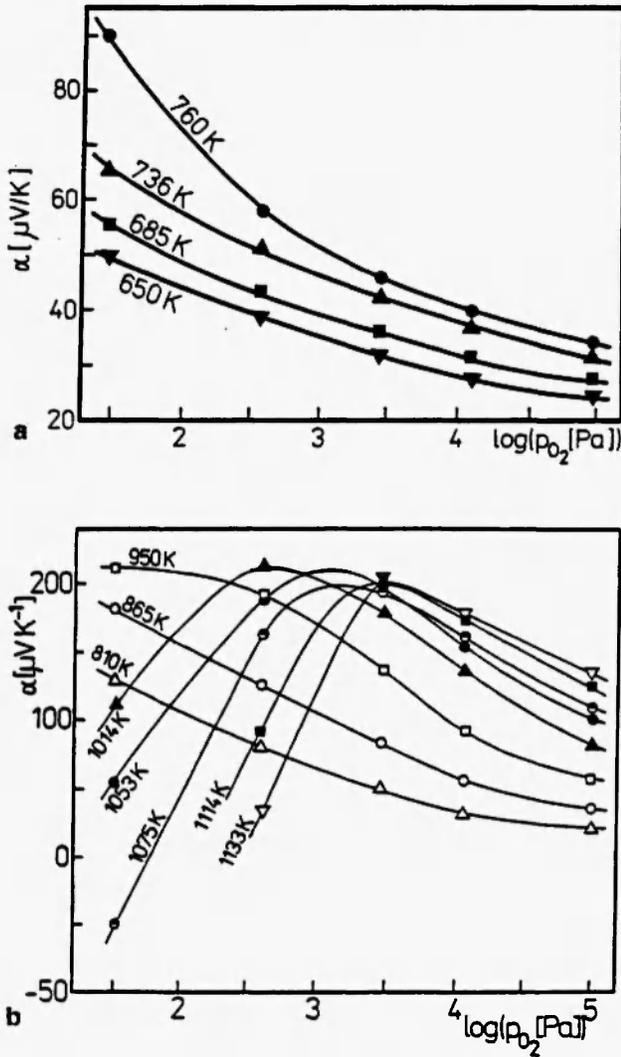


Fig. 7: (a and b) The dependence of thermoelectric power of  $YBa_2Cu_3O_{7-\delta}$  on oxygen pressure for different temperatures.

carriers) decreases linearly with an increasing deviation from stoichiometry  $\delta$ :

$$[h^{\cdot}] = a_h - r \cdot \delta \quad (8)$$

The coefficient of proportionality,  $r$ , amounts to 1 in the range of existence of the tetragonal phase, and it attests to the single ionization degree of oxygen vacancies. Respectively, in the orthorhombic phase the ionization degree of vacancies is higher. The  $a_h$  parameter in Eq. 8 has a determined physical sense, namely it stands for the concentration of intrinsic electron holes in the

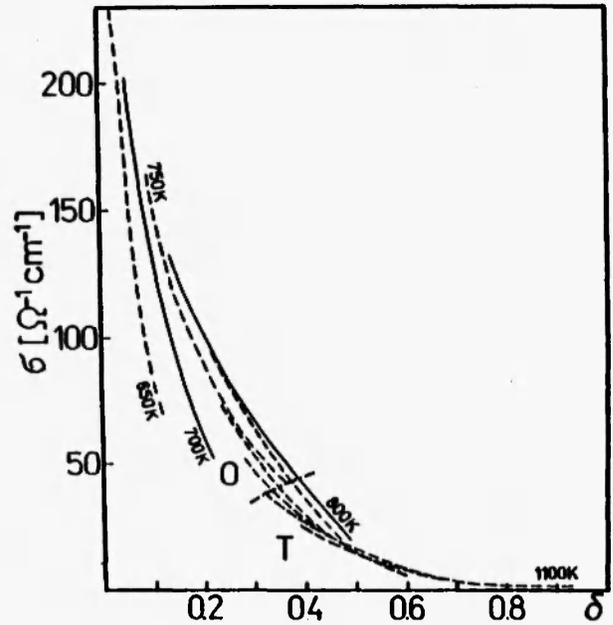


Fig. 8: The dependence of electrical conductivity of  $YBa_2Cu_3O_{7-\delta}$  on deviation from stoichiometry for different temperatures. Line (-.-.-) stands for phase transition.

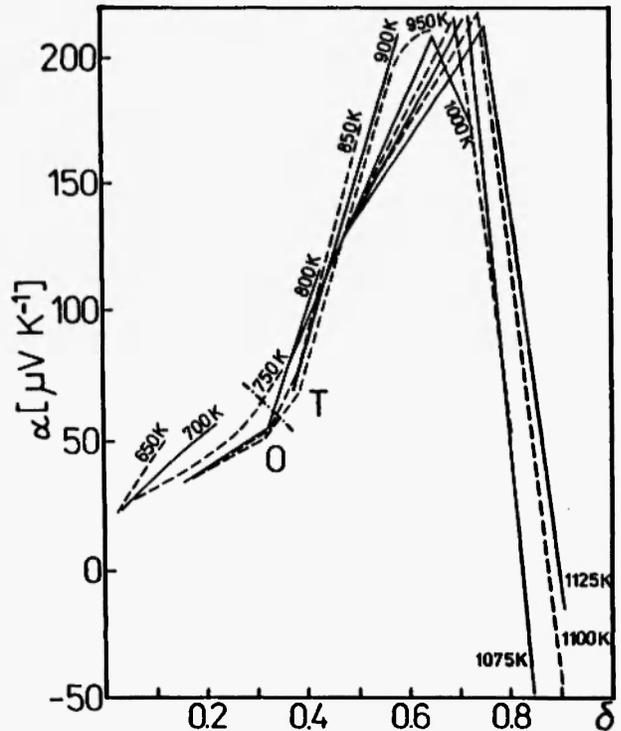


Fig. 9: The dependence of thermoelectric power of  $YBa_2Cu_3O_{7-\delta}$  on deviation from stoichiometry for different temperatures. Line (-.-.-) stands for phase transition.

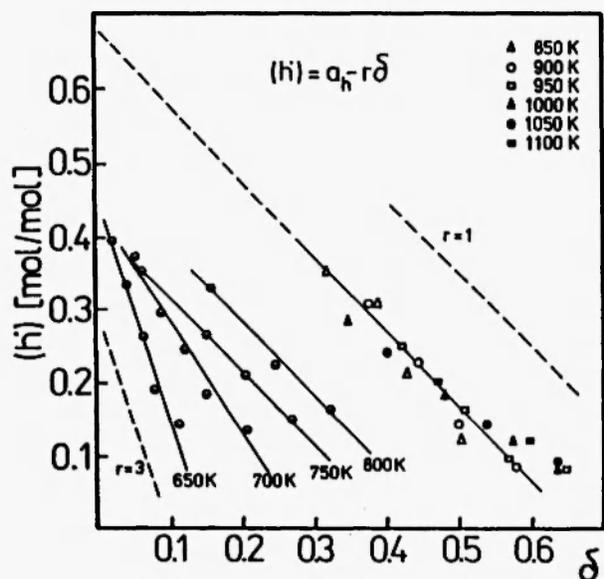


Fig. 10: The dependence of concentration of electron holes in  $YBa_2Cu_3O_{7-\delta}$  on deviation from stoichiometry. (●) values calculated by Eq. 6 (orthorhombic phase); other points calculated by Eq. 7 (tetragonal phase).

compound having the stoichiometric composition  $YBa_2Cu_3O_7$  and this value should theoretically be equal to 1 mole/mole (1 mole/mole of  $Cu^{+3}$  ions). The determined lower concentration of the intrinsic holes (0.4 mole/mole in the orthorhombic phase and 0.7 mole/mole in the tetragonal one) corroborates the opinion of a low, for the metallic phase, concentration of carriers being of an order of  $10^{20} \text{ cm}^{-3}$  [5,21,24], and it suggests the possibility of interaction of some electron holes on other hitherto not noted defects which have a negative effective charge. The role of such defects might be played by cation vacancies in the form of crystallographic vacancies in the copper-oxygen planes [19]. The electroneutral complexes coming to exist because of the hypothetical reaction mentioned would have no contribution to the charge transport.

The concentration of electron holes (for  $d < 0.7$ ) calculated from the experimental results of the thermoelectric power has served for the presentation of electrical conductivity as a function of the concentration of effective carriers (Fig. 11). In this case, the electrical conductivity increases linearly with this parameter (see

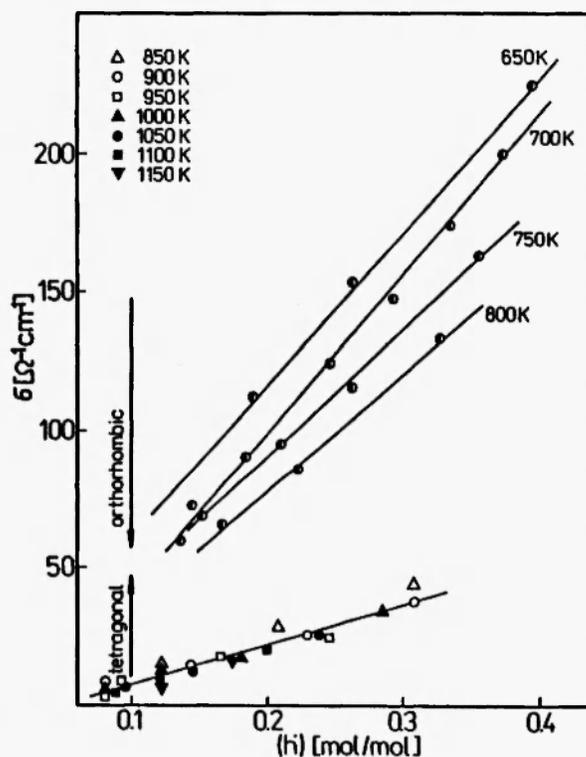


Fig. 11: The dependence of electrical conductivity of  $YBa_2Cu_3O_{7-\delta}$  on concentration of electron holes for several temperatures, calculated by Eq. 6 (points ●) and Eq. 7.

Fig. 8). One may notice that the conductivity is higher in the orthorhombic phase than in the tetragonal one. Moreover, for the orthorhombic phase in the case of a constant concentration of electron holes,  $\sigma$  comes down with increasing temperature, and it points at a metallic character of this phase. The temperature relation of electrical conductivity in the tetragonal phase is very weak at the constant concentration of the holes. Using the equation:

$$\mu = \frac{\sigma}{e \cdot [h]} \quad (9)$$

the mobility of holes in both phases was assessed (Fig. 12). It is higher in the orthorhombic form. In conjunction with its temperature dependence, the thesis on the metallic character of this phase is supported. Also the observed linear increase of the thermoelectric power with an increase of temperature at fixed concentration of holes (Fig. 13; Eq. 6) confirms the assumption on the metallic

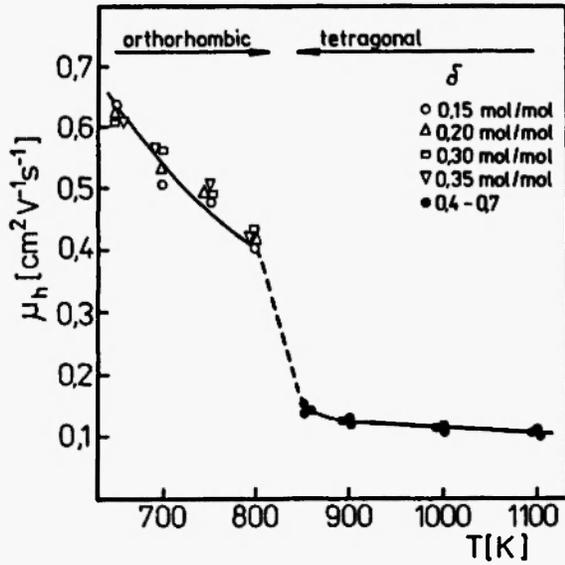


Fig. 12: Temperature dependence of holes mobility in  $YBa_2Cu_3O_{7-\delta}$  at fixed deviation from stoichiometry.

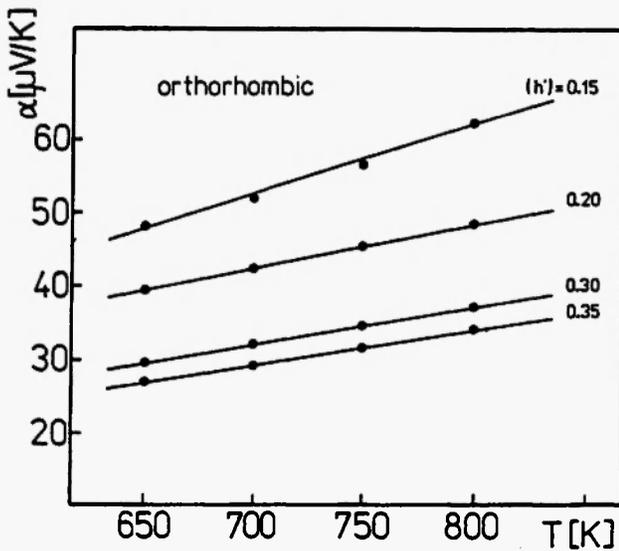


Fig. 13: Temperature dependence of thermoelectric power of  $YBa_2Cu_3O_{7-\delta}$  at fixed concentration of electron holes (Eq. 6).

character of this phase. The appreciably lower values of  $\mu$  in the tetragonal phase are connected with an increase in the effective mass of holes caused by narrowing of energy band.

An analysis of the properties of the tetragonal phase for  $\delta > 0.7$  points at its semiconductor character. From the viewpoint of electron structure, a deviation from stoichiometry of an order of 0.7 is the critical value. At this value splitting of the energy effective band takes place and a gap in state densities comes up. Within the composition of  $\delta > 0.7$ , the thermoelectric power changes its sign into negative (Fig. 9), whereas the electrical conductivity is of an activated character (Fig. 14). The evaluated activation energy of the conductivity of an order of 0.5 eV should refer to the thermic activation of carriers via the energy gap that appears. In such a case, the Fermi level is situated then in the gap in the state density and the transport of charge runs in more than one band. The existence of an energy gap of an order of 1 eV in  $YBa_2Cu_3O_{7-\delta}$  with  $\delta > 0.7$  is corroborated by spectroscopic investigations too [26].

#### 4. Summary

A summary of high temperature research on the  $YBa_2Cu_3O_{7-\delta}$  oxide may be proposed by a qualitative model of its electron structure (Fig. 15). In the ortho-

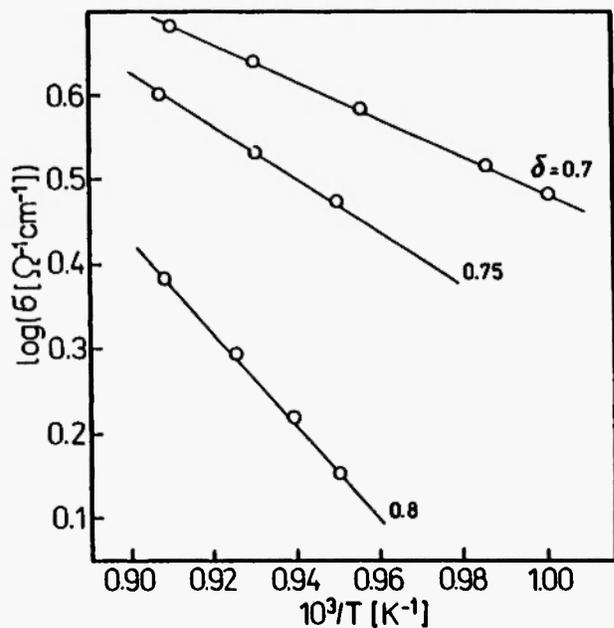


Fig. 14: Temperature dependence of electrical conductivity of  $YBa_2Cu_3O_{7-\delta}$  at fixed deviation from stoichiometry for  $\delta > 0.7$ .

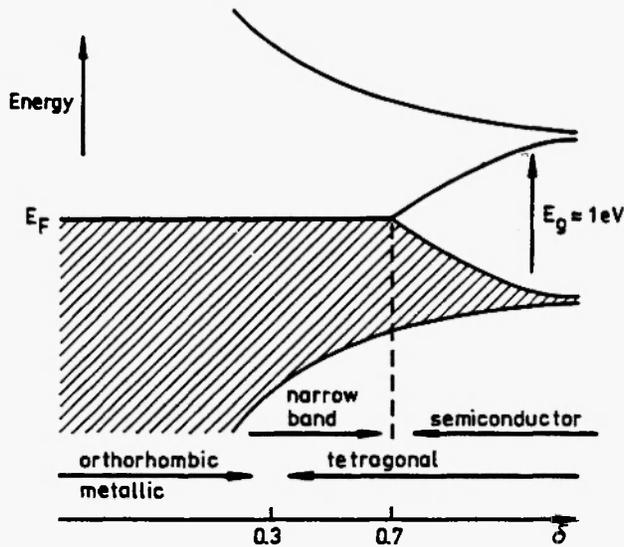


Fig. 15: Scheme of the electronic structure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .

rhombic phase ( $\delta < 0.35$ ), the Fermi level is situated inside the energy band having metallic properties. For the tetragonal phase within the range of stoichiometry deviation of  $0.35 < \delta < 0.7$ , we observe a gradual narrowing of this band; this narrowing can probably be connected to an increase in the disordered state of the system caused by increasing non-stoichiometry, and it increases its tendency for localization. Within the composition range of  $\delta < 0.7$ , an increase in the deviation from stoichiometry results in a fall in the effective concentration of electron holes due to the compensation effect.

At the critical deviation from the stoichiometric composition ( $\delta = 0.7$ ), there occurs a splitting in the effective energy band and a gap in the state density results. It corresponds with the semi-conductive properties in this composition range.

The investigations carried out on the electrical properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  at low temperatures point to the fact that the superconductor analyzed exhibits high applicable properties only in the case of freezing its orthorhombic structure which has metallic properties ( $\delta < 0.35$ ; Fig. 15).

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