Oxygen Ordering and Superconducting Phases in Ceramics.

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Abstract. – The superconducting transition temperature and the orthorhombic distortion in $YBa_2Cu_3O_{7-\delta}$ are found to be determined mainly by the oxygen occupancy of the Cu-O chains and may explain the discrepancies between experiments with equal *total* oxygen stoichiometry. These results are obtained from simultaneous gas evolution, superconductivity and X-ray diffraction experiments geared towards understanding the role of the oxygen ordering in ceramic superconductors. The evolution kinetics is found to proceed by an initial large change followed by a constant chain occupancy. The superconducting transition temperature follows the change in chain occupancy and clear evidence is presented for the occasional presence of two distinct superconducting oxygen phases which are difficult to uniquely establish from scattering experiments. The presence of these phases is critically dependent on details of the preparation condition.

The effect of oxygen doping has been shown very early on, to be of crucial importance for the superconducting properties of ceramic superconductors. In particular, changes in the oxygen stoichiometry of $YBa_2Cu_3O_{7-\delta}$ produce an orthorhombic-to-tetragonal phase transition, together with a depression of the superconducting transition temperature T_c and an increase of the normal state resistivity ρ [1-7]. The exact oxygen stoichiometry dependence of these properties has not been clarified yet, probably due to mixed phase behavior. Whether the structural phase transition occurs exactly at an oxygen stoichiometry of 6.5 (only Cu^{+2} present) and whether the disappearance of superconductivity coincides exactly with this phase transition has not yet been uniquely established [2]. This is an important issue which allows to shed light on the phenomenology of high-temperature superconductors and its connection to structural and electronic features. We present here gas evolution studies from $YBa_2Cu_3O_{7-\delta}$ which show that the superconductivity is mostly determined by the oxygen concentration in the Cu-O layers containing the chains («Cu-O

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chains»). Moreover we report evidence for the existence of a «low»-T_c (~ 60 K) and a «high»-T_c (~ 90 K) phase, which are triggered by a well-defined oxygen stoichiometry, and which form an interconnected percolating network. If the role of the additional oxygen in the chains is to continuously dope the CuO_2 planes with more holes [8] (mobile or localized), it is not clear how it can explain the existence of *magic* oxygen concentrations responsible for the two superconducting phases. However, the possibility that the geometric arrangement of the Cu-O chains is crucial for superconductivity, cannot be ruled out.

Gas evolution is a technique which can determine the binding energy of a gaseous species (oxygen or hydrogen for instance) in a solid [9, 10]. The sample being investigated is placed in a vacuum vessel and heated at a constant rate, while the overall pressure is measured with high accuracy. A time derivative of the pressure in this experiment gives directly the number of oxygen atoms being evolved per unit time from the various inequivalent sites [11]. We have shown earlier [12], by comparing a large number of samples together with temperature-dependent neutron scattering studies [1, 13], that all the evolution experiments can be summarized as follows. The number of oxygen atoms desorbed from the sample consist of a peak centered at 600 °C corresponding to evolution from the Cu-O chains (where present) and a desorption centered around 800 °C corresponding to evolution from other oxygen containing planes or from impurity phases.

All the results presented here were obtained from samples prepared using standard powder metallurgical techniques [14]. In the present experiments the oxygen was evolved from the samples by annealing in vacuum ($P \simeq 10^{-6}$ Torr) for fixed amounts of time at 400 °C and in all cases the evolved gases were analyzed using a mass spectrometer to avoid any spurious results. Two independent sets of experiments were performed. In one, a single sample was repeatedly heated for a fixed time at 400 °C, slowly cooled and the superconducting properties were determined; in the other set a large number of samples were prepared from the same batch which were then consequently annealed at 400 °C for various lengths of time. Both sets gave consistent results. Moreover, the data were corrected for measured evolution from the wall of the quartz container which was at most 5% of the total amount of evolved gas.

The superconducting measurements were performed at a very small magnetic field (30 Gauss) using the frequency shift of an RLC circuit (oscillating at $\simeq 30$ MHz), which is directly proportional to the susceptibility variation. In this fashion, the superconducting phases present and their volume fraction are clearly detectable.

The inset of fig. 1 shows a typical evolution curve obtained from an $YBa_2Cu_3O_{7-\delta}$ sample heated at a rate of 10 °C/min. The first peak centered around 600 °C corresponds to oxygen evolved from the Cu-O chains (*i.e.* O1 and O5 sites) [1], whereas a second peak (a doublet) is centered around 850 °C.

The first peak, however, is quite broad in comparison with the other ones, and appears to hide an additional peak at the right. This large shoulder suggests the presence of another desorption site hidden in the background. The origin of this shoulder has been uncertain for a time. There are reports of high-temperature oxygen vacancies of the site in the Ba-O plane (O4 site) [13, 14], starting around 600 °C. The second peak (doublet) was originally attributed to other oxygen-containing planes. However, a systematic study of the impurity phases, together with the analysis of very pure samples from other sources (Philips Research Laboratories, Eindhoven; Federal Polytechnical School, Lausanne) indicates that the peaks centered around 850 °C most probably arise from impurity phases. The third peak (above 900 °C) corresponds to a decomposition of the material, and is associated with the evolution from the O2-O3 sites. *We should stress that the identification of the peaks with a particular oxygen site is based on neutron scattering results* [1, 13] and therefore any changes in their interpretation may also affect the interpretation presented here.
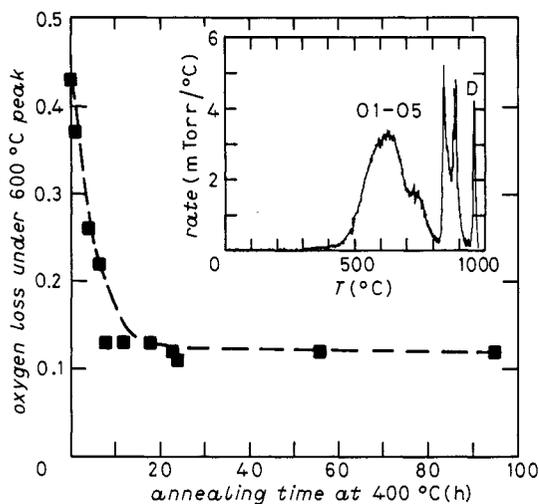
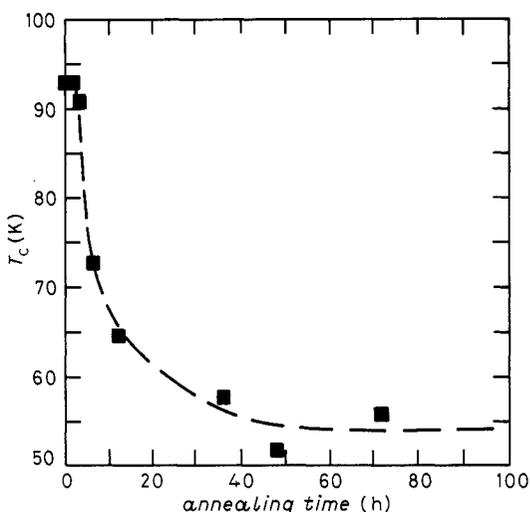Fig. 1.   Fig. 2.

Fig. 1. – Evolution of the O1 and O5 («chains») occupancy *vs.* annealing time at 400 °C. Note the fast decrease in this occupancy during the first 10 hours of annealing. The inset shows a typical oxygen evolution rate curve as described in the text (D = Decomposition). The site identification of the O1/O5 evolution peak is based on neutron diffraction results ref. [1, 13] and a comparison of a variety of systems ref. [12].

Fig. 2. – Evolution of the transition temperature T_c *vs.* annealing time at 400 °C.

The samples were annealed for a time at 400 °C and a subsequent evolution experiment was performed in order to determine the amount of oxygen lost during the annealing. The integrated intensity under the 600 °C peak is shown in fig. 1 as a function of annealing time. Up to 10 hours of annealing, a rapid decrease is observed in the intensity of this peak followed by a shallow plateau up to 90 hours of annealing, the longest annealing time in this experiment. These data show that for a 400 °C annealing the O1-O5 oxygens are mainly evolved in the first 10 hours and the evolved oxygen amount saturates for a value of 0.12. X-ray diffraction measurements show that a sample in this saturation regime still has a fixed orthorhombic distortion. It is not clear whether the residual concentration of 0.12 is or is not a «magic» number (see discussion below) [15].

The dependence of T_c on the annealing time at 400 °C is quite revealing. The T_c decreases rapidly to $(55 \div 60)$ K and then levels off (see fig. 2). A comparison of fig. 1 and 2 shows that the change in superconducting transition temperature is primarily determined by the «chain» occupancy (sites O1-O5). The origin of the plateau is associated with the plateau in the occupancy of the oxygen chain (fig. 1). It is interesting to note that most experiments to date seem to observe a T_c plateau between $(55 \div 60)$ K [16]. This could be interpreted as an indication for the existence of a distinct superconducting phase with a $T_c \simeq (55 \div 60)$ K.

A detailed study of the high-frequency signal clearly reveals the signature of the two different phases. Figure 3 shows a graph of the normalized (with respect to the mass) change in oscillator frequency *vs.* temperature for a set of samples (prepared from the same batch) for various annealing times at 400 °C. The superconductivity is signaled by a sharp peak starting at 92 K for samples annealed less than 1 hour at 400 °C. From 2-6 hours anneal time a clear cut signal emerges showing the presence of two phases; one at high-temperature («90 K phase») and another at lower temperatures («60 K phase»). As the annealing time increases the 60 K signal becomes stronger and the 90 K signal becomes
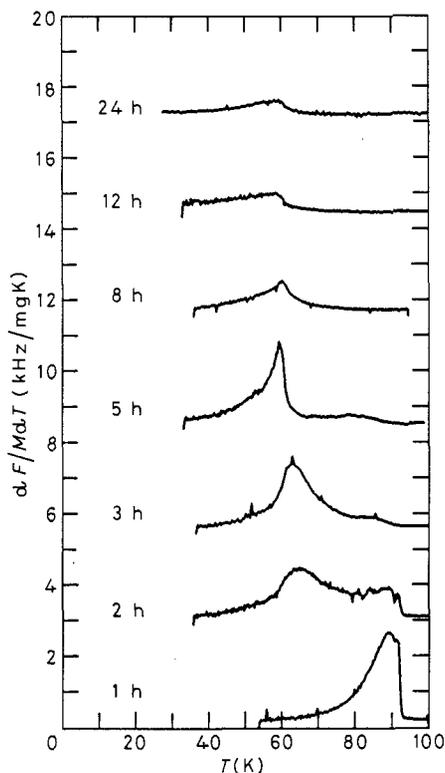
Fig. 3. – Frequency change of the RLC oscillator circuit (proportional to the susceptibility change) vs. temperature for samples with different annealing times at 400 °C. Curves are shifted upwards for clarity.

progressively weaker and disappears. Ultimately, longer annealing yields also a decrease of the superconducting 60 K fraction.

The interpretation is straightforward. As the sample is annealed for longer times the 90 K phase is transformed progressively into the 60 K phase. Consequently, when the fraction of the 90 K phase has become lower than the percolation limit, the T_c is given by a percolating network of the 60 K phase. This phase is slowly depleted of oxygen and eventually the transition temperature drops to zero.

The evolution of the various phases is thus consistent with thermodynamic theories which predict spinodal decomposition into two or more distinct oxygen phases [17-20]. The interesting additional information implied by the present experiments is that the two phases are both superconducting. The details of the oxygen kinetics together with sample microstructure give origin to the presence of the plateau [3] in the transition temperature vs. oxygen content graph.

At this point, two possible viewpoints can be taken. If the superconductivity is caused by a geometrical ordering of the chains [21-24] or orthorhombicity [25], then clearly the oxygen occupancy will be the main factor determining T_c. As more and more oxygen atoms are added in the not superconducting sample, locally the geometrical ordering starts inducing superconductivity, until 100% of that ordering is obtained. From there on another geometrical ordering leads to the 90 K phase in an analogous way. Several superstructures have been found in these materials, but it is not clear which of these are specific to the superconducting phases.

If the presently more commonly accepted viewpoint is adopted, which claims that the role of the chains is to provide holes to the conduction CuO_2 planes [8], the results presented here imply that the changes in T_c are due to a continuous change in hole concentration on the CuO_2 planes for T_c's between 60 K and 90 K. This may give rise to the presence of two distinct superconducting percolating networks, one at high temperature ~ 90 K and one at lower temperature ~ 60 K.

The present results bring into agreement a variety of seemingly contradictory results in which only the total oxygen stoichiometry is determined. Conclusions based on total oxygen stoichiometry can therefore be misleading and could depend on the particular sample preparation method. In addition the presence of two superconducting phases which form an intermixed percolating network should be taken into account for the interpretation of the results.

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