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EFFECT OF THE OXYGEN DISTRIBUTION ON HIGH Tc SUPERCONDUCTIVITY.

Y. BRUYNSERAEDE, J.-P. LOCQUET(°), J. VANACKEN, B. WUYTS, C. VAN HAESENDONCK and Ivan K. SCHULLER *

Laboratorium voor Vaste Stof-Fysika en Magnetisme, Katholieke Universiteit Leuven, 3030 Leuven, Belgium;
* Physics Department - B019, University of California - San Diego, La Jolla, California 92093, USA.

We have performed extensive gas evolution, x-ray diffraction and superconducting measurements on $YBa_2Cu_3O_7$ as a function of oxygen content. Gas evolution studies at a constant heating rate allow an identification of the oxygens evolving from the various inequivalent sites. Vacuum annealing of $YBa_2Cu_3O_{7-\delta}$ at 400°C during various lengths of time induces a large change in chain occupancy. Susceptibility measurements indicate the presence of two superconducting phases whose relative fraction changes with varying chain occupancy.

1. INTRODUCTION

It is by now clearly established that changes in oxygen content can strongly affect the properties of high temperature ceramic superconductors. However, to date no clear cut picture has emerged which establishes uniquely the role of oxygen ordering, orthorhombicity, oxygen stoichiometry and their relationship to the superconducting properties.[1]

For the past two years we have embarked on a program dedicated to answer some of these questions. In this program, we have applied powder metallurgy techniques to prepare samples, x-ray and neutron diffraction together with gas evolution to establish the structure and stoichiometry, and resistivity, magnetisation and high-frequency susceptibility measurements to study the superconducting properties.[2,3] In order to address these problems we have restricted our attention to $YBa_2Cu_3O_7$.

2. DETERMINATION OF OXYGEN CONTENT

We have applied a gas evolution technique, previously used to study hydrogen kinetics in amorphous silicon, to study oxygen bonding in high temperature superconducting ceramics. These type of measurements allow a quantitative determination of oxygens in sites which have distinct binding energies.

The sample (10 - 30 mg) is placed in an evacuated quartz tube. The temperature is then raised at a constant rate (typically 10°C/min), the pressure is measured and the evolved gases are analysed using a mass spectrometer. The number of evolved oxygen atoms is directly related to the time derivative of the pressure provided a constant heating rate is applied.

By using this technique we have found[3] that the oxygen escapes from the Cu-O chains at approximately 600°C by annealing in vacuum. The other oxygen sites have a higher binding energy.

The oxygen desorption kinetics can be studied very conveniently using this method. In order to allow proper ordering of the oxygens, long annealing times (up to 100 hrs) were used in a vacuum ($P = 10^{-6}$ Torr) at a low temperature (T=400°C).

After each annealing cycle the sample was slowly (100°C/hr) cooled to room temperature. Then the reversible magnetic susceptibility was measured between 300 K and 20 K. Once the superconducting properties were measured gas evolutions as described earlier were performed up to 950°C.

Figure 1 shows the oxygen loss in $YBa_2Cu_3O_7$ from the Cu-O chains as a function of anneal time at 400°C. The evolution is characterized by a fast decrease in oxygen concentration in the first few hours of annealing followed by a plateau which is constant up to 100 hrs.

The difference in the oxygen kinetics at 400°C can be explained in terms of the oxygen thermodynamics. The heat of solution of oxygen has a very strong dependence on the overall oxygen concentration.[3]

(°) Present address : IBM Research Division, Säumerstrasse 4, 8803 Rüschlikon, Switzerland.

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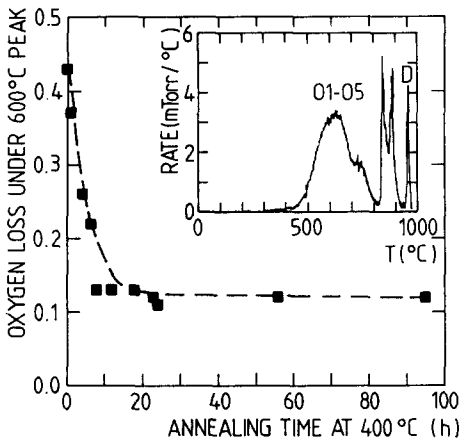

Figure 1
Evolution of the O1 and O5 ("chains") occupancy versus annealing time at 400°C. The inset shows a typical oxygen evolution curve.

3. SUPERCONDUCTIVITY

The correlation of the superconducting properties with the gas evolution has been established by measuring the frequency shift of an RLC circuit, oscillating at 32 MHz, which is directly proportional to the susceptibility variation. In this way, the superconducting phases and their volume fraction are clearly detectable. The superconductivity is signaled by a sharp peak starting at 92 K for the samples annealed less than 1 h at 400°C. From 2-8 hrs anneal time, their is a clear evidence for the presence of two phases: one at 90 K and another at 60 K. In a resistive measurement, the percolation between the two superconducting phases will prevent an observation of the individual phases.The coexistence of the two superconducting phases is probably due to grain size inhomogeneity in the sample. Small grains will produce the 60 K phase, because they are quickly depleted from oxygen; larger grains will continuously change T_c from 90 K to 60 K. In more homogeneous samples only one phase is observed. The evolution of the various phases is consistent with models wich predict spinodal decomposition into two ore more distinct oxygen phases[4].
Longer annealing times yield a progressive decrease in the volume fraction of the 60 K phase, although the total oxygen content does not change (see Fig.1). Therefore, the decrease of the 60 K superconducting phase must be due to ordering of the remaining oxygens.

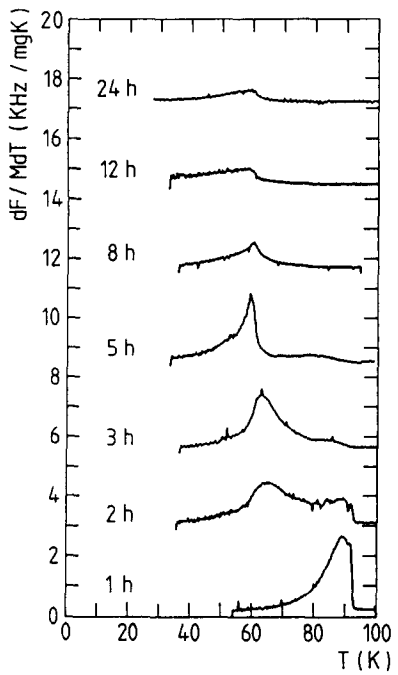

Figure 2
Normalized (with respect to mass) change in the oscillator frequency versus temperature for a set of samples with different annealing times at 400°C. Curves are shifted upwards for clarity.

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