MOBILE OXYGEN AND ISOTOPE EFFECT IN THE HIGH TEMPERATURE SUPERCONDUCTOR $YBa_2Cu_3O_{7-\delta}$

DONALD E. MORRIS[*†], U. M. SCHEVEN[†], L. C. BOURNE[*], MARVIN L. COHEN[*#], M. F. CROMMIE[*] and A. ZETTL[*]

[*] Department of Physics, University of California, Berkeley, CA 94720.
[†] Physics Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720.
[#] Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720.

ABSTRACT

We have studied the dependence of the superconducting properties of $YBa_2Cu_3O_{7-\delta}$ superconductors on the Oxygen content and thermal processing conditions. We find that the Oxygen content of this material decreases progressively on heating in O_2 above ~450°C, but this Oxygen loss is reversible upon slow cooling. Oxygen loss on heating in argon is larger, but still reversible upon annealing and slow cooling in O_2. The effect of thermal treatment in different atmospheres on the superconducting properties is described. The mobility of Oxygen is very high in this material, leading to a rapid approach to equilibrium Oxygen content after changes of temperature or Oxygen partial pressure in the space around the sample. Cooling rates are specified which optimize the final Oxygen content and are found to give good superconducting resistive transitions. The high Oxygen mobility permits replacement of the ordinary ^{16}O isotope in a sintered sample by exchange with $^{18}O_2$ gas placed in the surrounding space, by simple counter-diffusion at an elevated temperature. An isotope effect experiment was carried out. The T_c of the ^{18}O substituted material was found to be the same as a similar sample heated in ^{16}O, indicating the absence of an isotope effect in this material.

INTRODUCTION

Samples used in these experiments were broken from two pellets of sintered $YBa_2Cu_3O_{7-\delta}$. Both pellets were single phase according to X-ray diffraction measurements, and showed sharp superconducting transitions to the zero resistance state (see Fig. 2 (a) and Fig 3 (#R)). The first pellet had large grains (~50-100 μm), while the second pellet was fine grained (~1-2 μm). Most of the experiments were carried out on pieces of the first pellet, since the longer equilibration times of this material were easier to measure. Samples were heated in Oxygen or Argon and then cooled at various rates. All experiments were carried out at ambient pressure. The temperature dependence of equilibrium Oxygen content was determined using Thermo-gravimetric analysis (TGA). Pieces of the fine grained sample were used in the isotope effect counter-diffusion experiments because of the faster Oxygen diffusion in this material.

OXYGEN DIFFUSION TIME CONSTANTS

We find that Oxygen in this material is mobile at temperatures above 400-500°C, with very high diffusion rates. The equilibration time constant τ was measured at several temperatures by stepping the
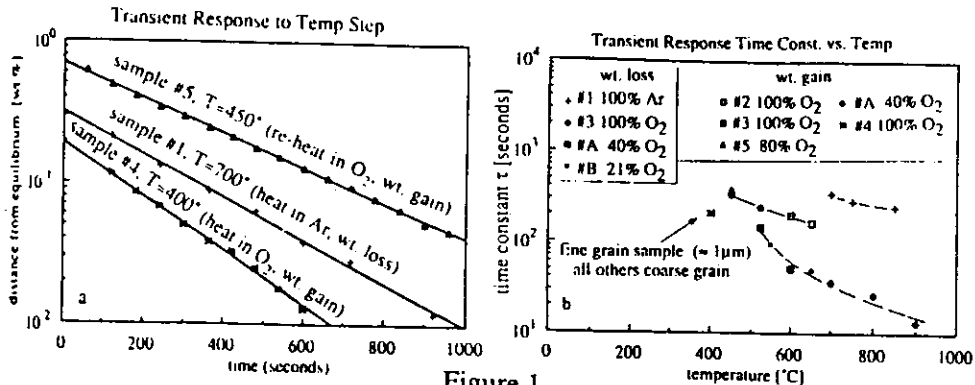

Figure 1

209

temperature by 25-50°, and observing the rate of approach to equilibrium weight. The sample weight change followed an exponential decay out to at least 3 τ. (See Figure 1(a).) In the temperature range 400°C - 1000°C, the time constant was surprisingly short. (See Figure 1(b).) Coarse grained samples (from the first pellet) had 15 < τ < 400 sec. The time constant depended on the atmosphere (Argon or Oxygen) and whether Oxygen was being gained or lost. A fine grained sample (~1-2 μm) had much shorter τ at temperatures ≤500° (<10 sec, our instrumental resolution), at 400°C we measured τ ~ 220 sec. The high diffusion rates may be a consequence of the large number of vacant Oxygen sites (~2 per formula unit), and the variable valence of the Cu which may permit local variations in Oxygen content without large changes in free energy.

OXYGEN ISOTOPE SUBSTITUTION BY COUNTER-DIFFUSION AND THE ISOTOPE EFFECT

The very rapid Oxygen diffusion in $YBa_2Cu_3O_{7-\delta}$ suggests that simple counter-diffusion at elevated temperature would be an effective method to replace the ^{16}O in a sintered sample by ^{18}O, from $^{18}O_2$ gas placed in the surrounding space. A fine grained pellet was used in this experiment. The untreated pellet had a sharp resistive transition to the superconducting state at 90 K (transition midpoint). Several pieces of the pellet were heated to 950°C in an atmosphere of $^{18}O_2$, held at that temperature for 10 hours, and cooled in 6 hours. This temperature and reaction time were chosen to insure maximal ^{18}O exchange with ^{16}O at both weakly bound and tightly bound sites.

Temperature programmed desorption (TPD) measurements were carried out using a quadrupole mass spectrometer. First, the sample was heated in flowing He to 830°C, and desorbed 1300 μmole of O atoms per gram. Of this, 900 μmole was in the form of 450 μmoles of O_2, with an ^{18}O fraction of 91%, the rest was mainly H_2O with small amounts of CO_2 and CO, with an ^{18}O fraction of 32%. (The counter-diffused sample was exposed to ambient air before the TPD measurements and may have adsorbed H_2O and CO_2.) The Oxygen removed in flowing He corresponds to the weakly bound Oxygen which came out of samples heated in argon, discussed in a subsequent section. The sample was then heated in flowing H_2, which destructively reduced the specimen to Y_2O_3, BaO, and Cu. An additional 4100 μmole of O atoms per gram evolved in the form of H_2O, with an ^{18}O isotope fraction of 90%. Of the total Oxygen removed from the sample (50% of total specimen content), 88% was ^{18}O.

Oxygen isotope substitution could have been done by repeated cycles of heating the sample in a vacuum or inert gas atmosphere to remove the weakly bound Oxygen followed by backfilling with $^{18}O_2$ gas. However, the repeated oxidation and reduction can adversely affect the superconducting transition, as shown later in this paper. This problem is avoided by using counter-diffusion, since exchange of isotopes of the same element leaves the oxidation state of the material unchanged.

The superconducting resistive transition remained sharp after the isotope substitution. A piece broken from the same pellet was given almost identical counter-diffusion treatment, but in ^{16}O, and was used as a control. The T_c of the ^{18}O substituted material was compared to the control (see Fig. 2), and to a fragment of the untreated pellet. They were found to be the same within 0.3 K, the experimental uncertainty, taking into account possible temperature variation across the measurement probe and variations in T_c in different portions of the parent pellet. The expected isotope shift in basic BCS theory is $T_c \propto M^{-1/2}$. This would correspond to a reduction in T_c of ~4.6 K on substitution of 90% of the ^{16}O by ^{18}O, if T_c is determined by motion of the O ions. We find that the oxygen isotope effect is absent in this material.
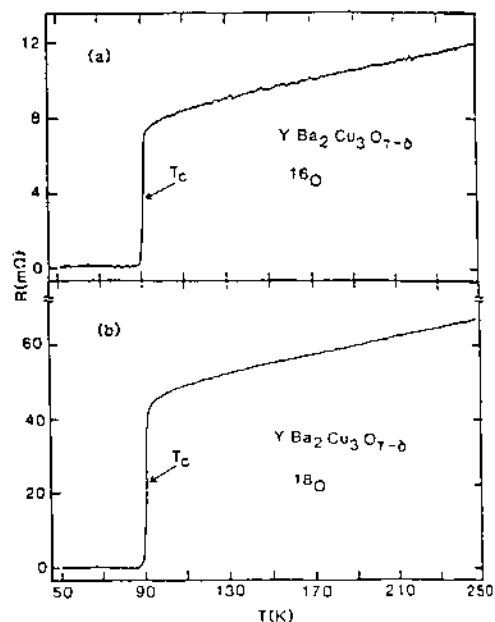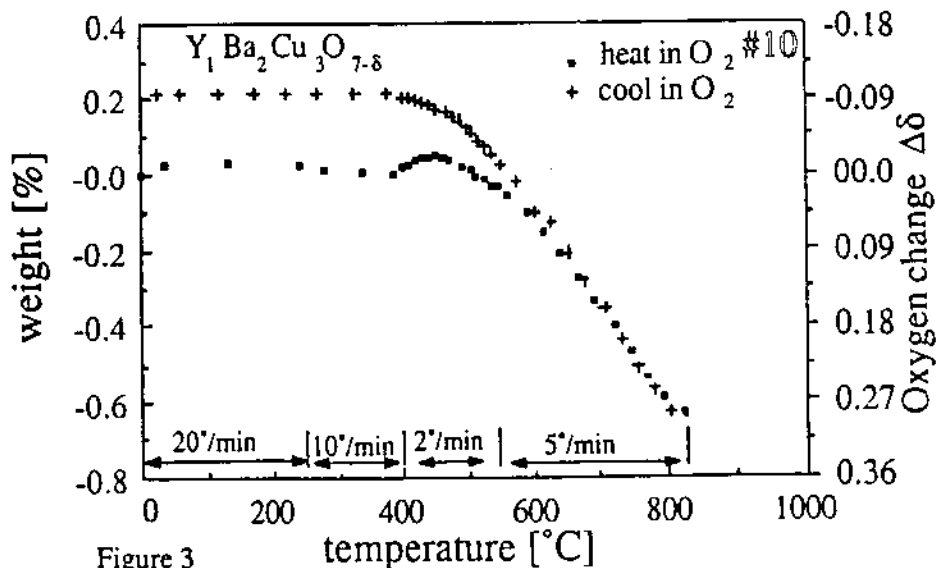
Figure 2

Figure 3

along with the R vs T curve for the treated sample. The final weight was slightly greater than the initial weight (+0.037%), indicating that the source pellet had not been fully oxygenated. The resistance above T_c and the sharpness of the resistive transition are nearly as good as before the heating and cooling.

Sample #3 was heated to the same temperature, but the cooling was too rapid for the sample to reach equilibrium at 500°. (The TGA indicated that the weight had not reached a constant value before the temperature was further reduced.) The final weight was less than the initial weight by 0.11%. The result (Fig 3 (#3)) was a high residual resistance below T_c.

Sample #4, made from a fine grained pellet, was also heated to 900°, where the weight loss was 1.0%. Rapid cooling resulted in a severely broadened resistive transition. The final sample weight was 0.16% higher than initially, but this sample had gained as much as 0.24% weight on initial heating to 400°, so the source pellet was apparently not fully oxygenated.

Sample #10 was carefully heated and cooled at rates which permitted nearly equilibrium weight (and Oxygen content) to be maintained throughout the process. The sample weight vs temperature data from TGA is shown in Fig 3, in which the heating and cooling rates are indicated near the lower edge. The appropriate rates were determined from the data on other samples shown in Fig 1(b), which gives the response time to a temperature step, at various temperatures. The initial weight increase between 400° and 450° indicates that the source pellet was not saturated with Oxygen. After heating to 825° the weight loss was reversible down to 600°. The weight continued to increase upon further cooling, apparently beyond the maximum that could be achieved by heating the cold pellet to 400 - 450°. The final weight gain was 0.21%, corresponding to an decrease in the Oxygen deficit ($\Delta\delta \approx -0.09$ per formula unit). Nevertheless, the sample had increased resistance and a negative temperature coefficient above T_c, and also showed substantial residual resistance below T_c. It appears that simply replacing the Oxygen which had been driven out by heating is not sufficient to fully restore the superconducting properties, and longer annealing or slower cooling is needed.

EFFECTS OF HEATING IN ARGON AND COOLING IN ARGON OR OXYGEN

Experiments were carried out in which samples were heated in Argon, and quenched. This left large Oxygen deficits. One sample (#6) was heated to 1000°C in Argon and quenched. The weight loss was 2.0%, corresponding to a loss of ~0.9 O per formula unit. There was no weight gain after quenching to below 50°C. The sample showed very high resistance, over $10^5 \Omega$ at ambient temperature; low temperature measurements were not made.

EFFECTS OF HEATING AND COOLING IN OXYGEN

At temperatures above about 450°C, Oxygen is lost, but the process is reversible up to at least 1000°C, where the weight loss in O_2 at one atmosphere pressure reaches about 1.3%. This corresponds to about 9% of the total Oxygen content or a change of ~0.5 Oxygen per formula unit. The change of Oxygen per formula unit is denoted by $\Delta\delta$ in Figs. 3-5. When samples were cooled slowly in O_2 (see below), the Oxygen content increased until a maximum was reached at 400-450°C. Below this temperature range Oxygen uptake becomes very slow. The permissible cooling rates throughout the temperature range were determined from the measured response times for temperature steps. (see below) , and are indicated along the lower margin of Fig. 4. Heating in Argon (discussed in the following section) yielded nearly twice as much weight loss at each temperature; this loss was only reversible when the sample was annealed in O_2 and then cooled slowly.

Samples #2, #3, #4 and #10 were heated and cooled in Oxygen. During initial heating, a very slight weight loss (0.02-0.07%) took place below 400° due to outgassing of H_2O and CO_2 from the samples. (The outgassing molecules were identified by temperature programmed desorption (TPD) measurements using a quadrupole mass spectrometer.) Sample #2, was heated to 900°, where the weight loss was 0.83% (corresponding to an increase in the Oxygen deficit $\Delta\delta$ ~0.37 per formula unit), and then annealed and cooled slowly (in about one hour). The cooling schedule is given in Fig 4 (#2),
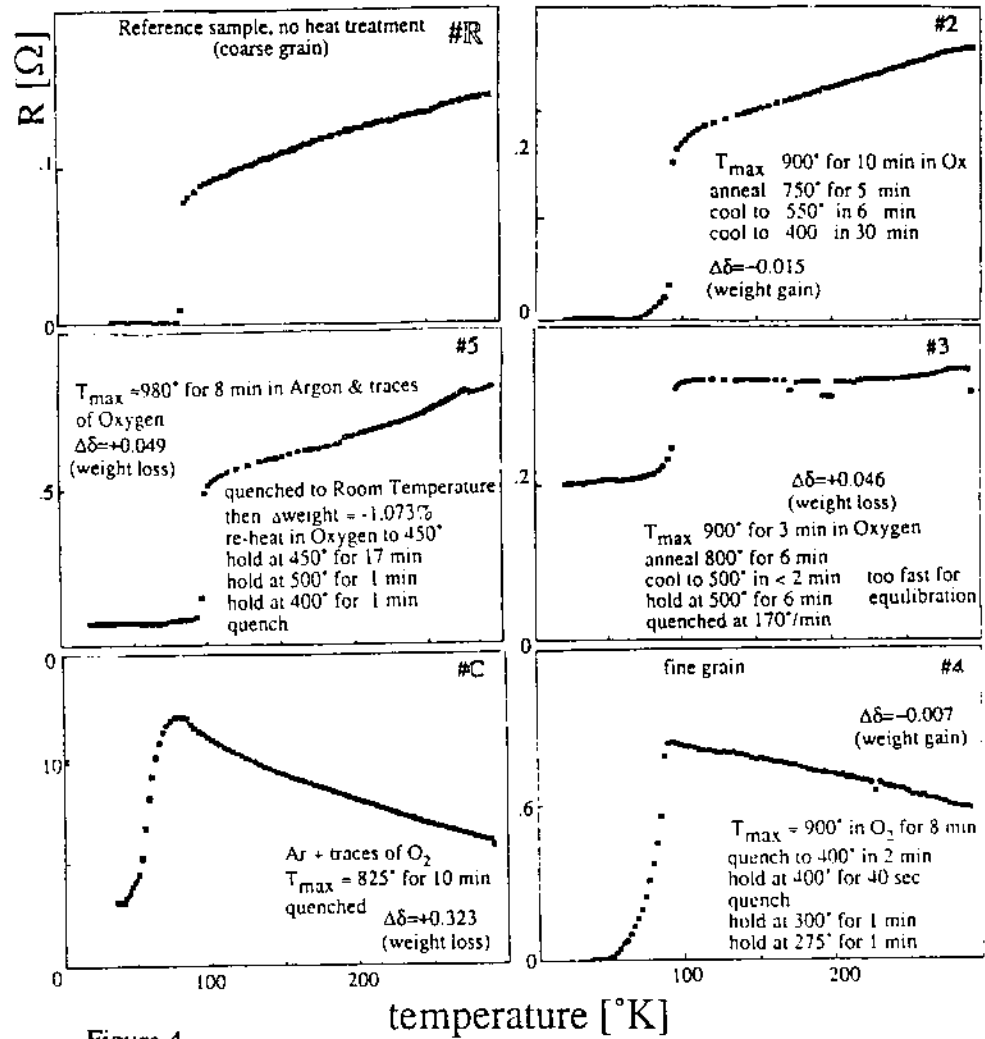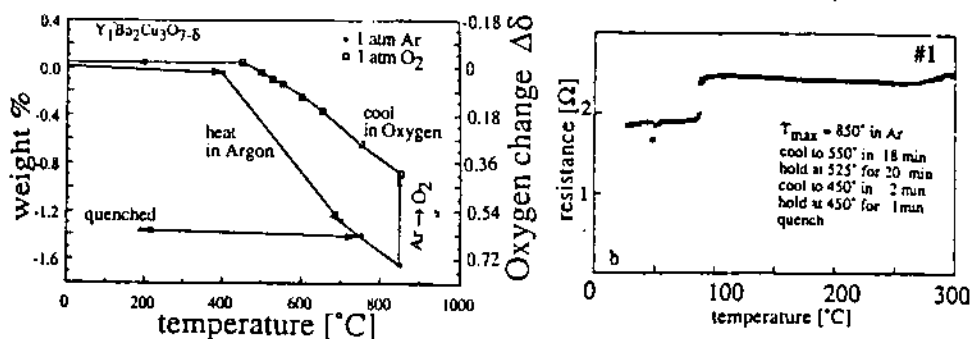

Figure 4

Figure 5

Another sample (#C) was heated to 825°C in Argon, which gave a weight loss of 1.08%. The sample was quenched, but apparently traces of Oxygen were present, since the weight increased during cooling, leaving a weight deficit of only 0.77%. The resistance vs. temperature behavior of this sample is shown in Fig 3 (#C). The resistance increased as the sample was cooled toward T_c, possibly indicating the presence of the tetragonal phase. The superconducting transition was broad and the resistance below T_c remained above zero, indicating the presence of a large non-superconducting fraction.

A third sample (#5) was heated to 980° in Argon + traces of Oxygen, and quenched. The weight deficit at ambient temperature was 1.07%, even larger than for sample #C. However, after the sample was reheated in O_2 to about 450° and annealed for 18 minutes and quenched, the low resistance above T_c and the sharp superconducting resistive transition were nearly restored (see Fig. 3 (#5), except for some residual resistance below T_c.

In contrast, sample #1 (Fig.5) was heated to 750°C in argon and then quenched (cooled at about 150°/min). The weight deficit was nearly 1.4%. The sample was reheated in Argon to 850°, then held in Argon for 7 minutes and annealed in O_2 for 6 minutes. This was followed by stepwise cooling in which the sample was allowed to reach equilibrium weight at each temperature step. The final weight was +0.04% greater than the starting weight. The resistive transition was sharp and there was no negative temperature coefficient above T_c, but the residual resistance below T_c was large. The only obvious difference between sample #C and sample #1 was the different annealing temperature.

CONCLUSIONS

The Oxygen content of the Oxygen deficit perovskite $YBa_2Cu_3O_{7-\delta}$ decreases progressively on heating in O_2 above ~450°C, but this Oxygen loss is reversible upon slow cooling. Oxygen diffusion in this material is very rapid, but if the sample is cooled too rapidly, not all the Oxygen is regained. The resistance of such material is very high above T_c and shows a negative temperature coefficient. With somewhat slower cooling, all the Oxygen is regained. However, residual resistance below T_c is found in some samples, indicating presence of a non-superconducting phase. A phase change or ordering, with a longer time constant than for Oxygen diffusion, may be necessary to fully restore the superconductivity.

Oxygen isotope substitution was successfully carried out by counter-diffusion. The T_c of the ^{18}O substituted material was compared to the control and to a fragment of the untreated pellet. The T_c was found to be unchanged. We conclude that the isotope effect is absent in this material.

213