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TITLE ON THE ISOTOPE EFFECT IN  $YBa_2Cu_3O_7$ : MEASUREMENTS FOR TWO METHODS OF SYNTHESIS

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ON THE ISOTOPE EFFECT IN  $\text{YBa}_2\text{Cu}_3\text{O}_7$ :

MEASUREMENTS FOR TWO METHODS OF SYNTHESIS

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Abstract

We prepared superconducting samples of  $\text{YBa}_2\text{Cu}_3(^{18}\text{O})_{7-x}$  and  $\text{YBa}_2\text{Cu}_3(^{16}\text{O})_{7-x}$  by two techniques: (a) burning powder of  $\text{YBa}_2\text{Cu}_3$  in  $^{18}\text{O}_2$  and  $^{16}\text{O}_2$  and (b) crystallizing amorphous powder of  $\text{YBa}_2\text{Cu}_3(^{16}\text{O})_{7.8}$  in flowing  $^{18}\text{O}_2$  and  $^{16}\text{O}_2$ . The percent of  $^{18}\text{O}$  in the  $\text{YBa}_2\text{Cu}_3(^{18}\text{O})_{7-x}$  samples was 96.5 at. % for method (a) and 92 at. % for method (b). The  $\text{YBa}_2\text{Cu}_3(^{16}\text{O})_{7-x}$  samples had 99.8 at. %  $^{16}\text{O}$ . Susceptibility measurements of the superconducting transition temperature show an oxygen isotope effect of 0.4 K for both methods.

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Paper to be published in "High Temperature Superconducting Oxides", edited by S. H. Whang and A. Dastgheib, (TMS, Warrendale, PA, 1989).

Various authors have measured the superconducting transition temperature  $T_c$  in oxide superconductors containing different oxygen isotopes with the goal of obtaining an insight into the mechanism of superconductivity (1-10). These measurements are summarized in Table 1. There is now a general agreement that the effect is small, close to 0.5 K. This shift is approximately one tenth of that which the BCS theory would predict if superconductivity were caused by a phonon-mediated pairing of electrons and the phonon frequency were mainly determined by the mass of the oxygen atoms. Although our initial motivation for this study was to measure the oxygen isotope effect in samples containing the highest possible concentration of  $^{18}\text{O}$ , we believe that isotope exchange can also be used as a tool to study oxygen mobility and phase transformations in these materials.

Ideally, one would like to measure the isotope effect in pairs of superconducting samples containing 100%  $^{18}\text{O}$  and  $^{16}\text{O}$  which are identical in all other aspects (microstructure, amount of second phase material, grain size, etc.). In the first experiments reported in the literature (1-6) the  $\text{YBa}_2\text{Cu}_3(^{18}\text{O})_{7-x}$  samples were prepared by annealing  $\text{YBa}_2\text{Cu}_3(^{16}\text{O})_{7-x}$  in  $^{18}\text{O}_2$ . Grimsditch et al. (11) raised the possibility that not all the  $^{16}\text{O}$  atoms were replaced by  $^{18}\text{O}$  during these annealings. If the oxygen atoms which were not replaced were playing an important role in the superconductivity, then the small measured effect could be explained in a natural way. The need for preparing samples with the highest possible  $^{18}\text{O}$  content prompted various investigators (8-10) to develop  $\text{YBa}_2\text{Cu}_3(^{18}\text{O})_{7-x}$  synthesis techniques not based on isotope substitution. In an earlier work (10) we reported the synthesis of  $\text{YBa}_2\text{Cu}_3(^{18}\text{O})_{7-x}$  with 96.5%  $^{18}\text{O}$  which had a  $T_c$  0.4 K lower than that of  $\text{YBa}_2\text{Cu}_3(^{16}\text{O})_{7-x}$ . It is thus clear that the oxygen isotope effect in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  is intrinsically small.

We report here  $T_c$  measurements in samples prepared by two disparate methods. The measurements for the first method were already described in an earlier publication (10) and are only summarized here.

TABLE 1. percentage of oxygen isotopes and  $T_c$  in  $YBa_2Cu_3O_7$  samples.

Author	Synthesis technique	at. % $^{18}O$	$T_c$ shift (K)
Batlogg et al. (1)	$^{16}O \rightarrow ^{18}O$ Gas exchange	75	0
Bourne et al. (2)	$^{16}O \rightarrow ^{18}O$ Gas exchange	90	0
Leary et al. (3)	$^{16}O \rightarrow ^{18}O$ Gas exchange	90	0.40
Benitez et al. (4)	$^{16}O \rightarrow ^{18}O$ Gas exchange	90	0.16
Morris et al. (5)	$^{16}O \rightarrow ^{18}O$ Gas exchange	88	0.20
Katayama et al. (6)	$^{16}O \rightarrow ^{18}O$ Gas exchange	?	0.40
Ott et al. (7)	nitrites of $^{18}O$	95	30
Garcia et al. (8)	oxidation of metals in $^{18}O$	90	< 1.0
Mattausch et al. (9)	oxidation of metals in $^{18}O$	?	0.40
Yvon et al. (10)	oxidation of $YBa_2Cu_3$ in $^{18}O$	96.3	0.4
Present work	$^{16}O \rightarrow ^{18}O$ Gas exchange	92	0.40

### Experimental

#### Synthesis of the Superconducting Samples

We prepared superconducting powder samples of  $YBa_2Cu_3(^{16}O)_{7-x}$  and  $YBa_2Cu_3(^{18}O)_{7-x}$  by two methods (a) burning an alloy powder of  $YBa_2Cu_3$  in  $^{16}O_2$  and  $^{18}O_2$  and (b) annealing and crystallizing an amorphous powder of  $YBa_2Cu_3(^{16}O)_{8.5}$  in  $^{16}O_2$  and  $^{18}O_2$ .

Method A. Burning of  $YBa_2Cu_3$  powder in  $^{16}O_2$  and  $^{18}O_2$  The  $YBa_2Cu_3$  powder was prepared by ball milling a 2:1 molar mixture of BaCu and YCu powders. Details on the synthesis of the  $YBa_2Cu_3$  powder have been published (10). We used a differential scanning calorimeter (DSC) (1) to oxidize the  $YBa_2Cu_3$  powder in  $^{16}O_2$  and  $^{18}O_2$ . In order to control the oxidation rate, oxygen was initially allowed into the DSC at a slow rate while the sample was being heated to  $300^\circ C$  at  $2 K min^{-1}$ . Most of the oxidation occurred below  $300^\circ C$ . Figure 1 shows the DSC traces for  $YBa_2Cu_3$  powder heated at  $10^\circ C min^{-1}$  in  $^{16}O_2$  and  $^{18}O_2$  flowing at  $15 cm^3 min^{-1}$ . Additional oxidation of the powder occurs during subsequent heating from  $300^\circ C$  to  $400^\circ C$ . Between  $650^\circ C$  and  $900^\circ C$  the DSC traces show several small

to the formation of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . These reactions will not be studied here. At  $940^\circ\text{C}$  the DSC traces show a sharp exothermic peak corresponding to the reaction (13)



where L(pl) is a liquid phase of composition close to  $\text{YBa}_2\text{Cu}_5\text{O}_y$ . In a related work (14) we found that the preparation of superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_7$  requires heating the oxide to a temperature above that for the peritectic reaction in Eq. (1). After annealing the samples at  $975^\circ\text{C}$  for 2 h, we cooled them in flowing  $^{16}\text{O}_2$  (or  $^{18}\text{O}_2$ ) at  $2^\circ\text{C min}^{-1}$ .

Method B: Crystallization of amorphous  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$  Inside an argon-filled glovebox we mixed high-purity  $\text{Y}_2\text{O}_3$ ,  $\text{BaO}_2$ , and  $\text{CuO}$  powders in the proportions necessary to form the alloy  $\text{YBa}_2\text{Cu}_3\text{O}_{8.5}$ . We used mechanical alloying (MA), a high-energy form of ball milling, to alloy these powders. The MA was done using a hardened-steel milling vial and balls. Energy-dispersive x-ray analysis of the milled powder revealed traces ( $<1$  at.%) of iron. We monitored the degree of alloying as a function of milling time by taking x-ray diffraction patterns on small powder samples removed from the milling vial at 2h intervals. Thorough mixing of the powders, down to the atomic level, was apparent after eight hours of MA. At this stage the x-ray diffraction pattern showed a broad diffraction band corresponding to an amorphous oxide and weak Bragg peaks corresponding to crystalline  $\text{Y}_2\text{O}_3$  and  $\text{BaCuO}_2$ . Most of the powder was in the amorphous state. During MA the powder loses oxygen and, from the change in weight of the milling vial, we calculate that at the end of MA the powder had a composition close to  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ .

We used the same DSC of method A to anneal the amorphous  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$  powder in  $^{16}\text{O}_2$  (or  $^{18}\text{O}_2$ ) flowing at  $15 \text{ cm}^3 \text{ min}^{-1}$ . The annealing treatment consisted of heating the samples at the rate of  $10^\circ\text{C min}^{-1}$ , holding them at  $940^\circ\text{C}$  for 2 h, and cooling them at the rate of  $2^\circ\text{C min}^{-1}$ . The DSC traces in Fig. 2, obtained during the initial heating of the powder, show four distinct peaks labeled A to D. Peaks A to C are not observed during the cooling step, nor during subsequent heatings, and thus correspond to irreversible reactions. We identified these reactions through x-ray diffraction patterns taken on powder samples that were heated to temperatures just below and above each of the peaks (14). Peak A

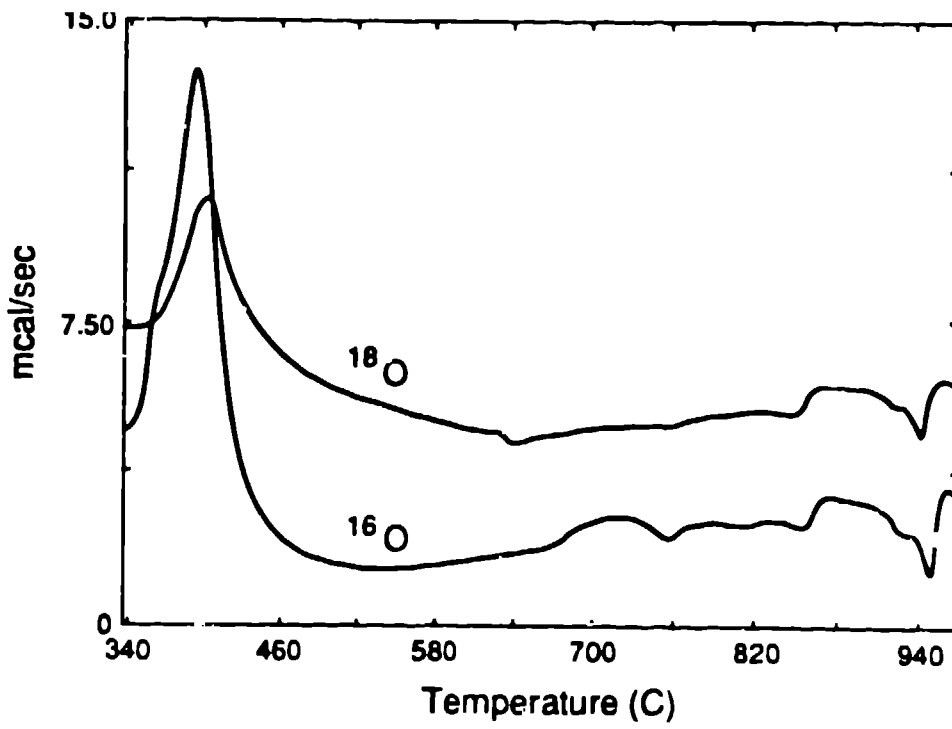


Figure 1 - Differential scanning calorimeter traces for YBa<sub>2</sub>Cu<sub>3</sub> powder oxidized in <sup>16</sup>O<sub>2</sub> and <sup>18</sup>O<sub>2</sub>.

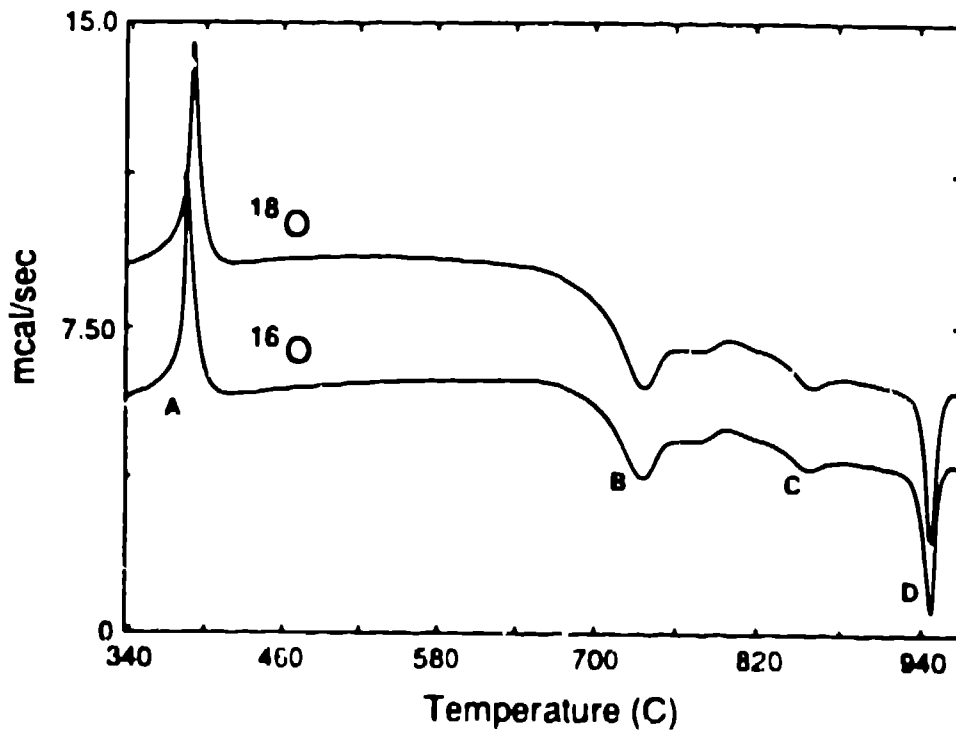


Figure 2 - Differential scanning calorimeter traces for YBa<sub>2</sub>Cu<sub>3</sub> powder annealed in <sup>16</sup>O<sub>2</sub> and <sup>18</sup>O<sub>2</sub>.

... has an onset of 500°C and corresponds to the crystallization of the amorphous oxide powder forming  $Y_2O_3$  and  $BaCuO_2$ . Peak B (endothermic) has an onset near 700°C and corresponds to the formation of tetragonal  $YBa_2Cu_3O_{7-x}$  by an irreversible solid-state reaction. In general, such reactions are exothermic. The DSC curve shows an endothermic event because the reaction also involves the evolution of  $O_2$ , as clearly detected by thermogravimetry. Peak C (endothermic) has an onset temperature of 840°C. This reaction is still under investigation. Peak D (endothermic), with onset of 940°C, corresponds to the peritectic reaction in Eq. (1).

During the annealing of the amorphous  $YBa_2Cu_3(^{16}O)_{7.8}$  powder in the DSC, the powder loses oxygen irreversibly, ending at a composition close to  $YBa_2Cu_3O_{7.0}$ . We used a thermogravimetric balance (15) to measure the changes in powder weight during a heating and cooling cycle in flowing  $^{16}O_2$ , and the results are shown in Fig. 3. The heating rate, dwell time at 975°C, and cooling rate were the same as those used in the DSC runs for methods A and B. Once the powder has been heated to 975°C, the weight change is reversible and weight-temperature data taken on further heating or cooling superimposes onto the lower (cooling) curve in Fig. 3. The irreversible weight changes during the first heating of the powder are therefore given by the difference between the two curves in the figure. It is apparent that the largest oxygen loss occurs above 730°C, following the nucleation and growth of the tetragonal phase of  $YBa_2Cu_3O_7$ .

#### Determination of the Oxygen Isotope Content

We used laser-ionization mass spectroscopy (LIMS) to obtain accurate measurements of the  $^{16}O$ ,  $^{17}O$ , and  $^{18}O$  concentrations in the samples. The  $YBa_2Cu_3(^{18}O)_7$  samples prepared by method (a) had 96.5 at%  $^{18}O$ , close to the concentration 97.2%  $^{18}O$  in the enriched gas used to prepare them. During the LIMS measurements on the samples prepared by method (b) we noticed that the  $^{18}O$  concentration increases with increasing depth. Below a depth of several microns the  $^{18}O$  reaches a steady value of 92 at%. This indicates that during the sea-day shipment of the sample to Livermore for the LIMS measurements, the sample lost  $^{18}O$  at the surface by exchanging it with atmospheric  $^{16}O$ . The  $YBa_2Cu_3(^{16}O)_7$  samples had 99.8 at%  $^{16}O$ .

#### Measurements of $T_c$

We derived the  $T_c$  of the compacts from dc magnetic moment measurements. Figures 4 and 5 show the magnetic moments of  $YBa_2Cu_3(^{16}O)_{7.2}$

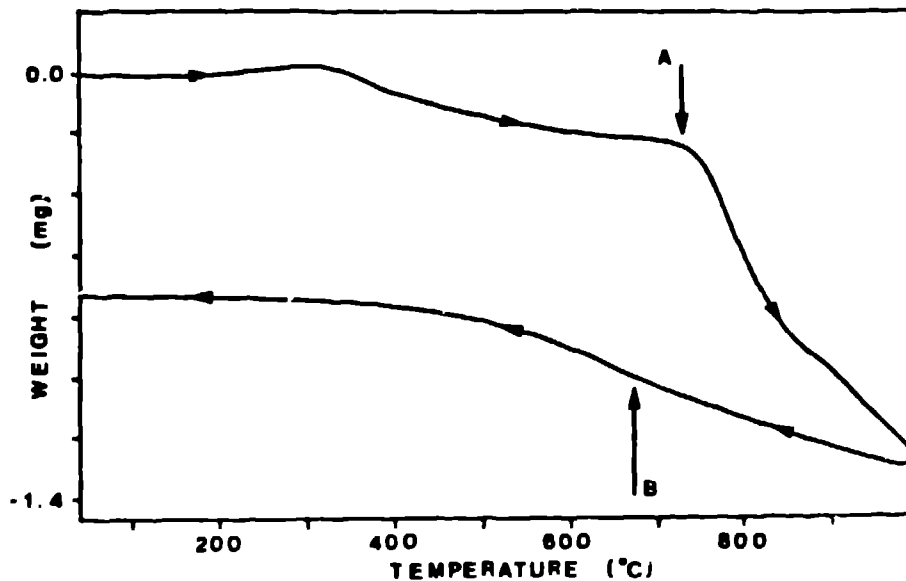


Figure 3 - Weight change of a 39.2 - mg  $\text{YBa}_2\text{Cu}_3(^{16}\text{O})_{7.8}$  sample during an anneal in  $^{16}\text{O}$ .

and  $\text{YBa}_2\text{Cu}_3(^{18}\text{O})_{7-x}$  measured at 1-K intervals while heating the samples from 7 K in a magnetic field of 100 G. The magnetic moment measurements have been plotted in units of  $4\pi\chi$ , where  $\chi$  is the magnetic susceptibility. To make the change of units we assumed that the sample has the demagnetizing factor of a homogeneous spheroid with principal axis equal to the major dimensions of our samples. In reality, our samples are cylindrical with one end spherical and the other flat, as shown in Fig. 1 in Ref. [10]. The inserts in Figs. 5 and 6 show  $\chi$  near  $T_c$ . Within this temperature regime the applied magnetic field is much larger than the sample's critical field  $H_{c1}$  and the  $\chi$  measurements are very sensitive to the overall change in the magnetic properties of the sample. With decreasing temperature, and as the volume fraction of superconducting phase increases, the sample changes from slightly paramagnetic above  $T_c$  to diamagnetic below  $T_c$ . From the figure inserts we deduce that for both methods of synthesis the onset of superconductivity is 0.4 K higher in  $\text{YBa}_2\text{Cu}_3(^{16}\text{O})_{7-x}$  than in  $\text{YBa}_2\text{Cu}_3(^{18}\text{O})_{7-x}$ .

Below 20 K,  $\chi$  becomes temperature-independent. At these low temperatures  $H_{c1}$  is much larger than 100 G (strength of the measured field) and the data gives the true magnetic moment of the sample. The fact that  $\chi$  does not reach  $-4\pi$  can be due to (a) a small mass fraction of the

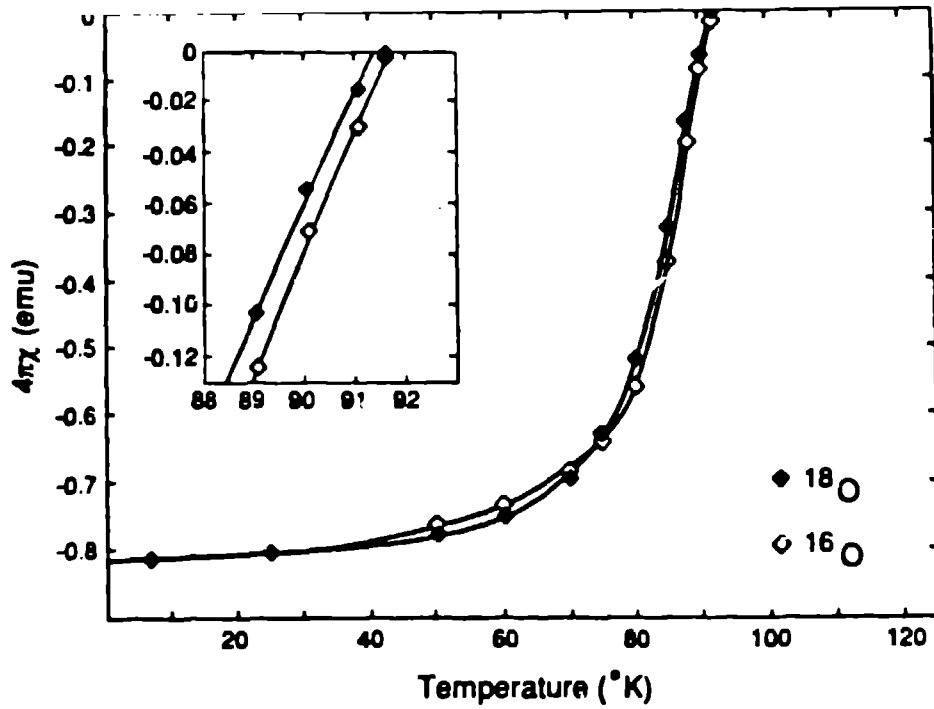


Figure 4. Magnetic susceptibility measurements in  $\text{YBa}_2\text{Cu}_3(^{16}\text{O})_7$  and  $\text{YBa}_2\text{Cu}_3(^{18}\text{O})_7$  powder prepared by method (a) during the heating of the samples in a magnetic field of 100 G. The insert shows the measurements near  $T_c$ .

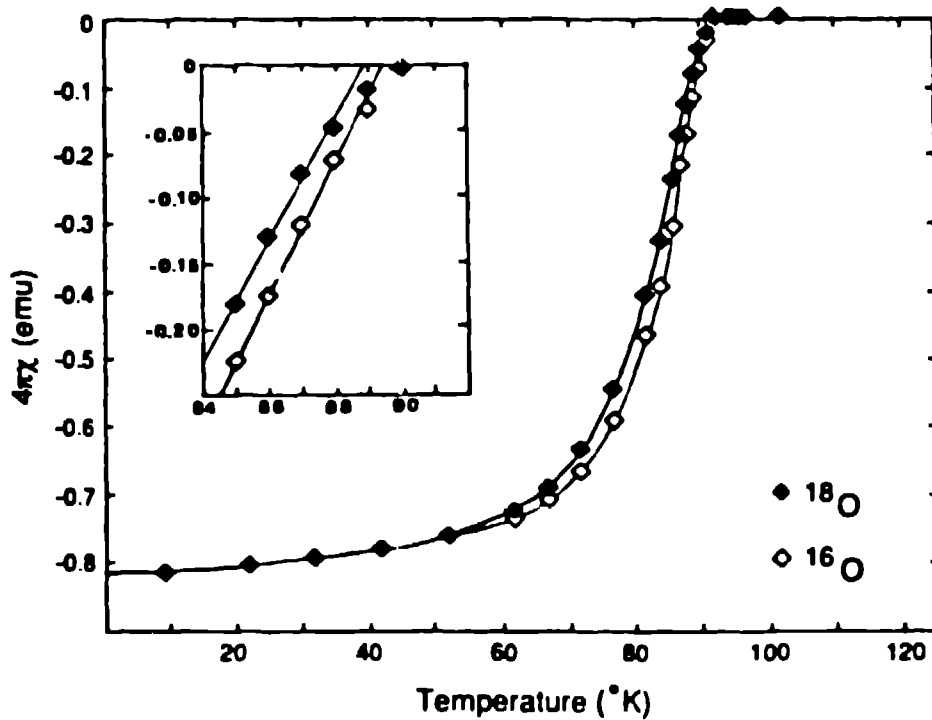


Figure 5. Magnetic susceptibility measurements in  $\text{YBa}_2\text{Cu}_3(^{16}\text{O})_7$  and  $\text{YBa}_2\text{Cu}_3(^{18}\text{O})_7$  powder prepared by method (b) during the heating of the samples in a magnetic field of 100 G. The insert shows the measurements near  $T_c$ .

... in the normal state and/or (b) an inaccurate value of the demagnetizing factor. The minimum value of  $\chi$  for each pair of samples is the same, and this suggests that the only difference between the samples is their oxygen isotope content.

### Discussion

It should not be surprising that the  $\text{YBa}_2\text{Cu}_3(^{18}\text{O})_{7-x}$  samples prepared by oxidizing  $\text{YBa}_2\text{Cu}_3$  powder in  $^{18}\text{O}_2$  have an  $^{18}\text{O}$  content almost identical to that of the enriched gas used to prepare them. The  $\text{YBa}_2\text{Cu}_3(^{18}\text{O})_{7-x}$  samples prepared by annealing and crystallizing amorphous  $\text{YBa}_2\text{Cu}_3^{16}\text{O}_{7.8}$  in  $^{18}\text{O}_2$  have 92 at.%  $^{18}\text{O}$ , which is 2 at% higher than the concentration of  $^{18}\text{O}$  achieved by previous investigators that used gas-exchange techniques (see Table I). The small difference, if real, could be attributed to the  $^{18}\text{O}$  contents in the enriched gases used by previous authors being lower than in ours. Another explanation is that in our experiments the starting amorphous  $\text{YBa}_2\text{Cu}_3^{16}\text{O}_{7.8}$  powder undergoes several structural phase transitions while in an atmosphere of enriched  $^{18}\text{O}$  before becoming a crystalline (tetragonal) phase of  $\text{YBa}_2\text{Cu}_3^{16}\text{O}_{7-x}$ . The atomic reshuffling during these structural transformations may help in the isotope substitution. In contrast, during the annealing of  $\text{YBa}_2\text{Cu}_3(^{16}\text{O})_{7-x}$  in  $^{18}\text{O}_2$  there is only a minor structural transformation near  $650^\circ\text{C}$ , when the structure changes from orthorhombic to tetragonal.

The orthorhombic-to-tetragonal transformation is absent during the first heating of the amorphous  $\text{YBa}_2\text{Cu}_3^{16}\text{O}_{7.8}$  powder because the tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_7$  phase nucleates at  $730^\circ\text{C}$ , above the transformation temperature. Certainly, the reverse tetragonal-to-orthorhombic transformation occurs on cooling and is indeed detected as a small change in the slope of the lower curve in Fig. 3. This transformation involves most likely only local atomic rearrangements of the oxygen ions.

The onset of superconductivity in  $\text{YBa}_2\text{Cu}_3(^{16}\text{O})_{7-x}$  is approximately 0.4 K higher than in  $\text{YBa}_2\text{Cu}_3(^{18}\text{O})_{7-x}$  and this effect must be attributed to the difference in the atomic masses of  $^{16}\text{O}$  and  $^{18}\text{O}$ . This shift is, however, smaller than that which can be explained by the BCS theory of superconductivity.

~~CONFIDENTIAL~~

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