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## Synthesis and superconducting critical temperature of $\text{YBa}_2\text{Cu}_3^{18}\text{O}_{7-\delta}$

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$\text{YBa}_2\text{Cu}_3^{18}\text{O}_{7-\delta}$  (90%  $^{18}\text{O}$ , 44%  $^{18}\text{O}$ ) has been synthesized from the elements in order to minimize the possibility of preferential substitution at different crystallographic sites. Magnetic-flux exclusion measurements show that the  $T_c$  of the substituted material shifts by no more than  $\sim 0.2$  K from the material synthesized with natural-abundance  $\text{O}_2$ .

The discovery of superconductivity above 90 K in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Refs. 1 and 2) has sparked debate about whether Bardeen-Cooper-Schrieffer (BCS) theory<sup>3</sup> and phonon-mediated superconductivity is applicable. To test this, several groups have carried out experiments in which  $^{18}\text{O}$  has been substituted for  $^{16}\text{O}$  through gas exchange at elevated temperatures.<sup>4-7</sup> In  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , a maximum of  $\sim 5$  K decrease of  $T_c$  would be predicted if complete exchange of  $^{18}\text{O}$  for  $^{16}\text{O}$  is achieved, and if the important phonon mode depends only on the oxygen mass.

Published accounts report a decrease of, at most, a few tenths of a degree.<sup>4-7</sup> These studies imply that vibrational modes which involve oxygen atoms do not play an important role in the mechanistic aspects of superconductivity in this class of compounds. Since  $^{18}\text{O}$  enrichment of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  was accomplished in those studies through exchange between gaseous  $^{18}\text{O}$  and  $^{16}\text{O}$  in the solid and complete substitution was not achieved, and because there are four crystallographically independent oxygen lattice sites that might be expected to exchange oxygen at different kinetic rates, the question of preferential substitution must be addressed. This brings into question whether previous experiments are unambiguous evidence for the absence of an isotope effect. It is possible that under the experimental conditions of previous investigations one of the oxygen sites, which might be of critical importance in affecting  $T_c$ , was left relatively unsubstituted. This concern has also recently been raised<sup>8</sup> and addressed by others.<sup>9</sup> In light of this uncertainty, we felt it important to synthesize  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  from the elements (using  $^{18}\text{O}_2$ ) in a manner that presumably results in uniform substitution of the heavier isotope in all oxygen sites.

The synthetic procedure produced three samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  containing an isotopic concentration of  $^{18}\text{O}$  at natural abundance, 44% and 96% levels. In order to accomplish this, the oxides of yttrium, copper, and barium were prepared by heating the metals (Y, Aldrich 99.9% pure; Ba, Strem 99.5% pure; and Cu, Fisher electrolytically purified) under an atmosphere of oxygen with the desired  $^{18}\text{O}$  level. The metals were placed in alumina boats in a dry-box and quickly ( $\sim 10$  sec) transferred to a fused silica tube. The glass container was evacuated and placed in a tube furnace and backfilled with 1 atm of  $^{18}\text{O}$  containing oxygen gas. Copper and yttrium were heated

for 18 h at 850°C and 1 atm of oxygen, and barium was heated for 18 h at 600°C. In the case of barium, the temperature was raised slowly (6 h), and the oxygen was diluted with 20% high-purity nitrogen in order to prevent too vigorous a reaction, i.e., burning barium metal. Each oxide was prepared three times using an appropriately isotopically enriched oxygen gas to give the three isotopically enriched oxides at the desired levels.

Once the oxides were synthesized, they were ground together, placed in alumina boats, and fired under an atmosphere of the correspondingly  $^{18}\text{O}$ -enriched oxygen for 48 h at 930°C. The material was reground after the first 24 h. Subsequently, the temperature was lowered to 550°C and the sample was maintained at that temperature for 24 h with the oxygen pressure at 1 atm. Finally, the furnace power was turned off and the reaction product was kept in the furnace until room temperature was reached ( $\sim 4$  h). The sample was not pressed into a pellet since it was felt that firing as a ground powder rather than as a pressed pellet would ensure full occupation of the oxygen sites and avoid complications arising from the well-known oxygen substoichiometry in these superconductors. As a loose powder there would be poor contact between the grains that would most likely result in incomplete reaction, but this was deemed acceptable in order to assure a short diffusion path length for oxygen and prevent oxygen substoichiometry in the superconductor.

The reaction products were characterized by powder x-ray diffraction. Diffraction patterns were obtained with a Siemens D500 diffractometer using  $\text{Cu } K\alpha$  radiation and a graphite diffracted-beam monochromator. The diffraction region of  $2\theta$  from 5° to 90° was examined with a step scan of 0.02° and a counting time of 2 sec per step.

Superconducting properties were characterized with a superconducting quantum interference device (SQUID)

TABLE I. Lattice parameters for  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

$^{18}\text{O}$ Composition	$a$ (Å)	$b$ (Å)	$c$ (Å)
Natural abundance	3.8160(7)	3.8843(5)	11.679(1)
44%	3.815(2)	3.887(2)	11.667(3)
90%	3.818(1)	3.884(2)	11.664(3)

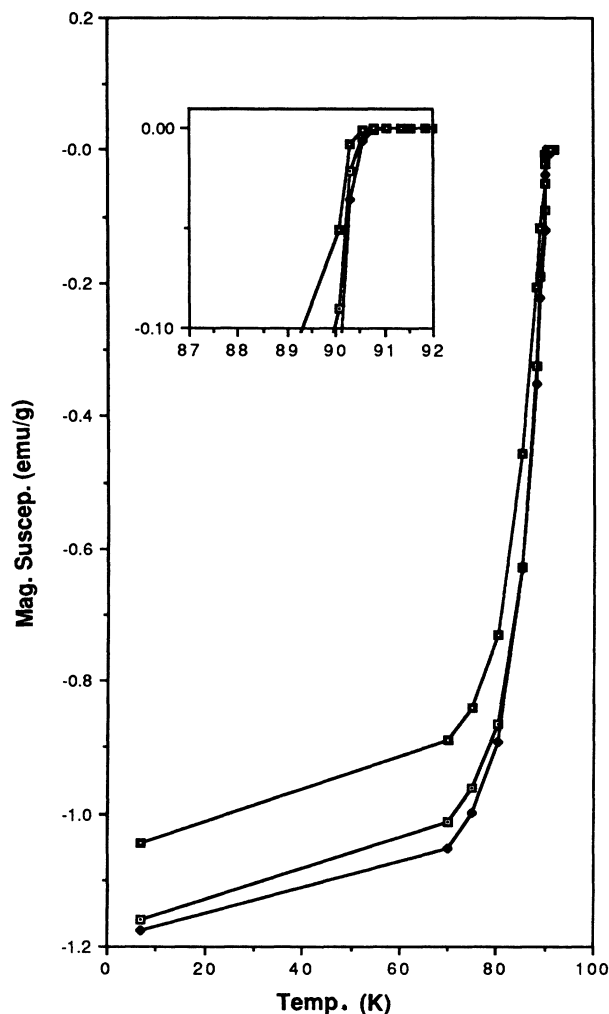


FIG. 1. SQUID magnetic susceptibility data.  $\square$ ,  $^{16}\text{O}$ ;  $\blacklozenge$ , 44%  $^{18}\text{O}$ ;  $\square$ , 90%  $^{18}\text{O}$ .

magnetometer. The susceptibility of the samples as powders was measured by zero-field cooling to 7 K followed by application of a magnetic field of 100 Oe and slowly raising the temperature. The superconducting volume fraction derived from the susceptibility of the powder samples at 7 K was calculated without correction for a demagnetization factor and as such are overestimated (Table II).

The products were also analyzed for  $^{18}\text{O}$  content by laser-ionization mass spectroscopy (Lawrence Livermore National Laboratory) and by high-energy  $\alpha$  backscattering (Los Alamos Ion Beam Laboratory). The total oxygen content was estimated by iodometric titrations.<sup>10</sup>

Powder x-ray diffraction of the reaction products shows that complete reaction of the oxides was not achieved. The phases adjacent to  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  in the ternary phase diagram ( $\text{Y}_2\text{BaCuO}_5$ ,  $\text{CuO}$ ,  $\text{BaCuO}_2$ ) are each present in approximately 2% level in all cases. However,

TABLE II. Magnetic characterization of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

$^{18}\text{O}$ Composition	$T_c$ (K)	$T_{1/2}$ (K)	Shielding (%)
Natural abundance	$90.85 \pm 0.05$	86	94
44%	$91.15 \pm 0.10$	86	95
90%	$90.60 \pm 0.05$	84	82

the  $a$  and  $b$  lattice parameters of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  phase (Table I) are the same, within experimental error with a  $5\sigma$  difference between the largest and smallest  $c$  parameter. We have observed this difference for other samples made using standard ceramic routes and commercially available oxides and carbonates. We do not feel that the small differences in the  $c$  axis can be attributed to some isotope effect. These parameters are also in agreement with those found for full occupation of the oxygen positions, i.e.,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .<sup>11</sup> The sample synthesized with 96%  $^{18}\text{O}$  was also analyzed for oxygen content by iodometric titrations, with the assumption of a 94% yield of the superconductor as found from the x-ray diffraction, an oxygen composition of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.95(5)}$  was determined. This material was examined with laser ionization mass spectroscopy to verify the amount of isotopic enrichment, and the following levels were found:  $^{18}\text{O}$ ,  $86.1 \pm 1.5\%$ ;  $^{17}\text{O}$ ,  $2.3 \pm 0.4\%$ ;  $^{16}\text{O}$ ,  $11.6 \pm 2.0\%$ . High-energy alpha backscattering indicated that the surface of a cold pressed and unsintered pellet of the nominal 96%  $^{18}\text{O}$  sample contained  $15 \pm 2\%$   $^{16}\text{O}$  at the surface ( $1 \mu\text{m}$ ) and  $7 \pm 1\%$   $^{16}\text{O}$  in the bulk. The two measurements, while not in complete agreement, indicate an  $^{18}\text{O}$  composition of  $\sim 90\%$ .

The magnetic susceptibility data for the three samples are plotted in Fig. 1. Some differences are evident in the width of the superconducting transition and in the susceptibility values at 7 K, but as stated above, the susceptibility values at 7 K have not been corrected and depend on the physical morphology of the sample. Nevertheless, the key observation derived from these data is that even with a high, presumably uniform,  $\text{O}^{18}$  substitution, only a  $\sim 0.2$  K shift of the superconducting critical temperatures is observed. Other values of interest obtained from the magnetic data are listed in Table II.

In conclusion, we have synthesized  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  in a manner that, we believe, assures uniform substitution of  $^{18}\text{O}$  in the oxygen sites of the unit cell. This has been done for natural abundance, intermediate (44%), and very high (90%) levels of the heavier isotope. Even at 90% substitution of  $^{18}\text{O}$  for  $^{16}\text{O}$ , no change of greater than  $\sim 0.2$ – $0.5$  K is evident.

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