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An ^{17}O NMR Study on Oxygen Exchange in $YBa_2Cu_3O_{7-x}$

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This study evaluated the effect of reaction conditions on the extent and uniformity of ^{17}O-labeled $YBa_2Cu_3O_{7-x}$. It was shown by ^{17}O NMR spectroscopy and high-resolution SIMS that statistical ^{17}O-enrichment is achieved at high temperatures by synthesis from oxides under an $^{17}O_2$ atmosphere, or by direct $^{17}O_2$ exchange of preformed $YBa_2Cu_3O_{7-x}$. Nonuniform enrichment can be achieved at low temperatures and with the use of short reaction times. An $^{17}O_2$ circulator is described which proved useful for handling, purifying, and recovering the labeled oxygen.

Introduction

$YBa_2Cu_3O_{7-x}$ has two very distinctive properties. Most importantly, it is the first superconductor with T_c greater than the boiling point of nitrogen (*1*). Chemically this material is interesting because its oxygen content can be varied over the range $0 < x < 1$ while preserving the perovskite structure (*2*). These two distinctive properties are interdependent insofar as T_c varies from 92 K with $x \approx 0$, to 60 K for $x \approx 0.4$, to 30 K for $x \approx 0.7$ (*3*). The normal state resistivity of the material is also very sensitive to the value of x (*4*).

At least some of the oxygen sites in $YBa_2Cu_3O_{7-x}$ are directly involved in the superconducting pathway, while other oxygen sites appear to play a more indirect if not spectator role (*5*). Consequently, there is great interest in the development of ^{17}O NMR spectroscopy as an atomic level probe of the magnetic character of the various oxygen sites, both as a function of stoichiometry and temperature. Practical ^{17}O NMR spectroscopy requires enrichment since the natural abundance of the isotope is only 0.037%, and recent ^{17}O NMR studies have exploited the oxygen lability of $YBa_2Cu_3O_{7-x}$ to prepare isotopically enriched samples (*6, 7*). Similar techniques have been employed to prepare ^{18}O-enriched samples for study of the isotope effect on T_c (*8*). The reliability of these procedures has been debated with regard to the uniformity of the enrichment (*9*), and as a result newer procedures were developed; in these procedures Y, Ba, and Cu metals in a 1:2:3 ratio were burned in $^{18}O_2$ gas (*10–12*). Questions of uniform isotope enrichment hinge on the fact that there are four crystallographically different oxygen sites in the $x = 0$ compound, each of which can be expected to be differently labile.

In this report we describe experiments designed to test the uniformity of isotopic enrichment of $YBa_2Cu_3O_{7-x}$. The progress of this enrichment is evaluated by ^{17}O NMR

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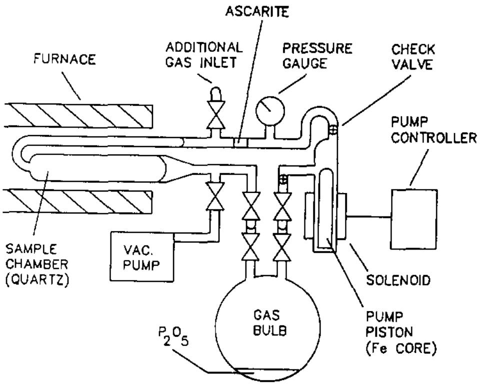

FIG. 1. Schematic diagram of $^{17}O_2$ gas circulator.

spectroscopy. We have recently shown that this technique, as applied to magnetically oriented crystallites of $YBa_2Cu_3O_{7-x}$, can resolve 19 of the 20 possible NMR transitions for the four crystallographically independent oxygen sites (*13*). Our ^{17}O NMR results reported herein show that uniform isotopic enrichment is easily achieved. We also show that under very mild conditions selective enrichment is also possible.

Results

Preparation of ^{17}O*-labeled* $YBa_2Cu_3O_{7-x}$. Our initial attempts to prepare ^{17}O-labeled $YBa_2Cu_3O_{7-x}$ focused on synthesis from individual metal oxides under a static $^{17}O_2$ atmosphere. We reasoned that this method of synthesis would probably guarantee ^{17}O labeling at each of the four oxygen sites. X-ray powder diffraction analysis showed, however, that samples produced in this way were heavily contaminated with $Y_2Ba CuO_5$ and $BaCuO_2$. The reason that these phases form in the static atmosphere is not obvious, although we propose that flowing gas may serve to drive off volatile impurities, like CO_2 and H_2O. In any case, these problems induced us to design an apparatus which would simulate flowing gas conditions without wasting precious $^{17}O_2$.

The quartz/Pyrex apparatus shown in Fig. 1 allows for the closed system circulation of $^{17}O_2$ gas, which is pumped with a water-cooled solenoid piston. The pump has the capability of adjustable flow rates. The circulating gas is continuously scrubbed, at room temperature, with P_4O_{10} (for H_2O) and Ascarite, a CO_2-absorbing reagent containing NaOH, and the $^{17}O_2$ is then reheated before contact with the sample. At the end of an experiment the $^{17}O_2$ is recovered into a storage bulb by condensing it with liquid nitrogen. The pressure in the apparatus was monitored with a vacuum/pressure gauge; in our experiments the pressure varied from 0.8 atm (at 100°C) to 1 atm (at 970°C).

Sample *A* (Table I) was prepared from a pellet of Y_2O_3, BaO_2, and Cu_2O in the aforementioned circulator at 970°C. After two such preparations we observed that part of the dessicant which was originally a free-flowing powder, had become a viscous liquid, indicating that it had partially hydrolyzed. X-ray powder diffraction demonstrated that all $YBa_2Cu_3O_{7-x}$ samples were highly pure (Fig. 2). Magnetic susceptibility measurements on magnetically aligned polycrystals (see below) showed that the samples have sharp diamagnetic transitions (Fig. 2, inset).

^{17}O *NMR characterization*. The ^{17}O-NMR spectrum of Sample *A* was obtained at 11.7 *T*, using a spin echo pulse sequence on magnetically aligned crystallites embedded in Duro-TM epoxy resin (*6*). The spec-

TABLE 1

SAMPLE PREPARATION SUMMARY

Samples	Precursors	Reaction duration
A	Cu_2O, BaO_2, Y_2O_3	36 hr at 970°C and 24 hr at 490°C
B	$YBa_2Cu_3O_{7-x}$	168 hr at 400°C
C	$YBa_2Cu_3O_{7-x}$	24 hr at 400°C
D	$YBa_2Cu_3O_{7-x}$	4 hr at 400°C

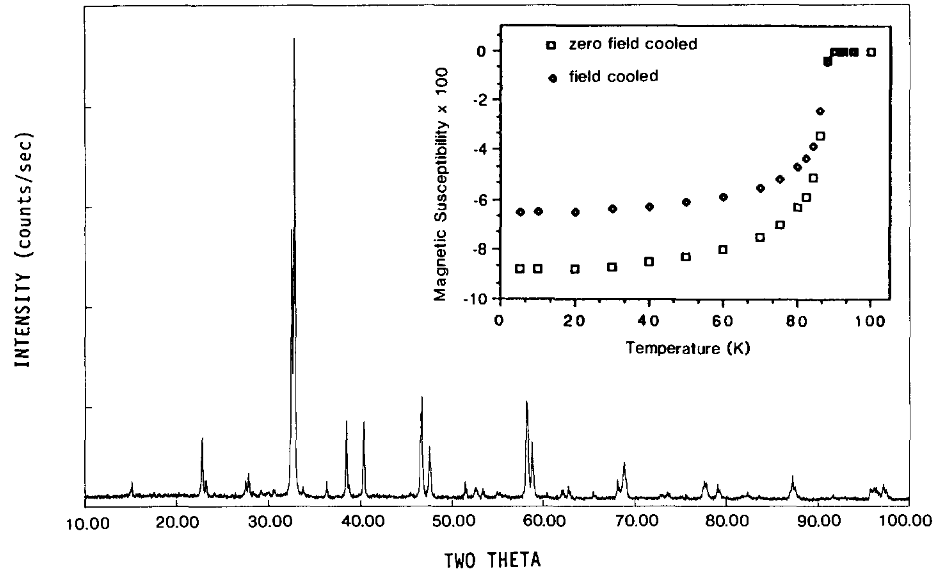

FIG. 2. X-ray powder patterns for Sample *A* (see Table I). Inset: Magnetic susceptibility data on polycrystals of Sample *A* in an epoxy matrix.

tra were referenced with respect to water at 0 ppm, positive values corresponding to high-frequency shifts (IUPAC δ scale). The absorptions at ~2700, ~1800, and ~900 ppm downfield from H_2O were assigned to the chain (O4), the plane (O2, O3), and the column (O1) oxygens, respectively (Fig. 3) and are due to $\frac{1}{2}$, $-\frac{1}{2}$ transitions (*13*). The carrier frequency was set between the O1 and O2, O3 resonances. The chemical shifts are in agreement with those obtained in previous studies by ourselves and Takigawa *et al.*, in which the samples were prepared differently (*6*, *7*). Synthesis of $YBa_2Cu_3O_{7-x}$ from its oxide precursors under flowing $^{17}O_2$ gas ensures a high probability of homogeneous ^{17}O atom distribution among the four oxygen sites.

Selective ^{17}O enrichment. The availability of statistically enriched (as determined from integrated intensities of spectra recorded on resonance) $YBa_2Cu_3O_{7-x}$ encouraged us to attempt selective ^{17}O-labeling. Samples *B–D*, derived from a single batch of $YBa_2Cu_3O_{7-x}$, $x \sim 0$, were exposed to flowing $^{17}O_2$ at 400°C for 7 days, 1 day and 4 hr, respectively.

In recording the ^{17}O NMR spectra of these three samples, the spectrometer frequency was first centered on the O1 resonance, to compare the (O2, O3)/(O1) intensity ratio, and then on the O4 resonance, to compare the (O2, O3)/(O4) intensity ratio. Since Sample *D* was only exposed to $^{17}O_2$ for 4 hr, the level of enrichment is low, and the signal-to-noise ratio of its NMR spectrum was not as good as those of the other samples.

Figure 4 shows the ^{17}O NMR spectra of the three samples when the spectrometer frequency was centered on the O1 resonance. As can be seen from these spectra, the (O2, O3)/(O1) intensity ratio decreases on going from Samples *B* to *D*. Figure 5 shows the ^{17}O NMR spectra of Samples *C* and *D* when the spectrometer frequency was on the O4 resonance. These results show that the (O2, O3)/(O4) ratio of Sample *C* is greater than that of Sample *D*; Sample *B* has a similar (O2, O3)/(O4) ratio as Sam-

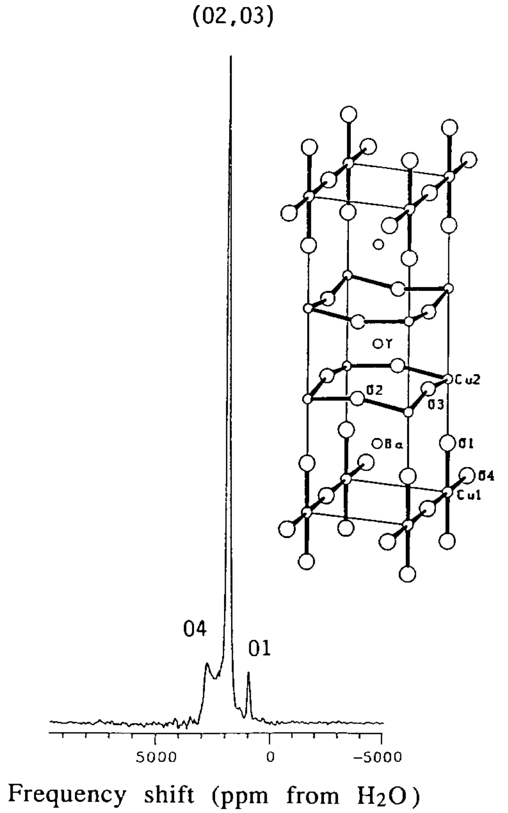

FIG. 3. ^{17}O NMR spectrum for Sample *A* (spectrometer frequency was offset between the resonant frequencies of the chain and the plane oxygens. Inset: Structure of $YBa_2Cu_3O_{7-x}$, showing the labeling scheme for chain (O4), column (O1), and plane (O2, O3) oxygens.

ple *C* (spectrum not shown). The comparison of CuO_2 plane/nonplane oxygen intensity ratios strongly suggests that ^{17}O atoms in Sample *D* are not distributed between sites in the same way as those in Samples *B* or *C*: ^{17}O has replaced the column and chain sites more than plane positions, in Sample *D*. We thus conclude that ^{17}O atoms first exchange into nonplane sites. However, as the enrichment proceeds, site exchange occurs between the nonplane and plane positions. We did not investigate anneal times shorter than 4 hr since such poorly labeled samples would require extremely long data acquisition times. We did anneal $YBa_2Cu_3O_{7-x}$ in $^{17}O_2$ gas at 300°C for 24 hr, and the ^{17}O NMR spectrum of that sample (data not shown) again had a very poor *S*/*N* ratio, but showed a weak signal, due to the plane oxygens (O2, O3).

Our observation of ^{17}O labeling of the plane (O2, O3), column (O1), and chain (O4) sites at low anneal temperatures is consistent with a recent Raman study on ^{18}O selective enrichment of $YBa_2Cu_3O_{7-x}$ (*14*).

$^{16}O:{}^{17}O:{}^{18}O$ ratios for enriched samples. Using high-resolution secondary ion mass spectrometry (SIMS), we examined the $^{16}O:{}^{17}O:{}^{18}O$ isotope ratio of Samples *A* and *B*. This technique is capable of distinguishing ^{17}O from $^{1}H^{16}O$, $\Delta M \cong 0.005$ amu. The intensity *vs* time plots obtained from this analysis are shown in Fig. 6. The $^{16}O:{}^{17}O:{}^{18}O$ ratio and the ^{17}O level in both of these samples were virtually the same. This implies that ^{17}O-labeling of $YBa_2Cu_3O_{7-x}$ at 400°C for 1 week produces the same results as ^{17}O-labeling done at 970°C for 36 hr.

Conclusions

The primary result of this study is that the four oxygen sites in $YBa_2Cu_3O_{7-x}$ can be statistically enriched. Our arguments rest on the fact that the ^{17}O NMR and SIMS data are unaffected by the method of synthesis, be it synthesis from oxides under $^{17}O_2$ or gas exchange of preformed $YBa_2Cu_3O_{7-x}$. The study permits more confident interpretation of recently published ^{17}O NMR spectra (*13*), at least with regard to relative peak intensities. Under very mild conditions we could effect selective enrichment into nonplane sites: this selectivity was, however, achieved at the cost of a rather low net enrichment.

Experimental Section

Chemicals. $^{17}O_2$ gas was prepared by electrolysis of $H_2{}^{17}O$ by Dr. J. Fitzpatrick,

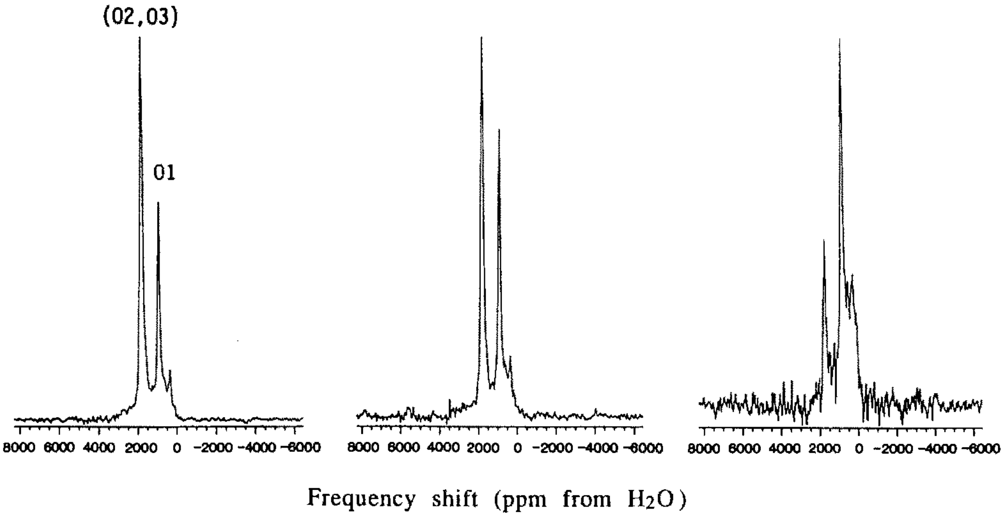

FIG. 4. ^{17}O NMR spectra for Samples *B* (left), *C* (middle), and *D* (right); the spectrometer frequency was centered on the column oxygen signal at ≈900 ppm. These spectra show the effect of oxygen exchange times (168, 24, and 4 hr, respectively) on the relative intensity of the column oxygen signal.

at the Los Alamos National Laboratory. Its isotopic composition was 23.2% (^{16}O), 47.2% (^{17}O), and 29.6% (^{18}O); this gas was used throughout this study. The following chemicals were used as purchased: BaO_2 (99.99%, Anderson Physics, Urbana, IL), Y_2O_3 (99.99%, Aldrich, Milwaukee, WI), Cu_2O (99.95%, Alfa, Danvers, MA), As-

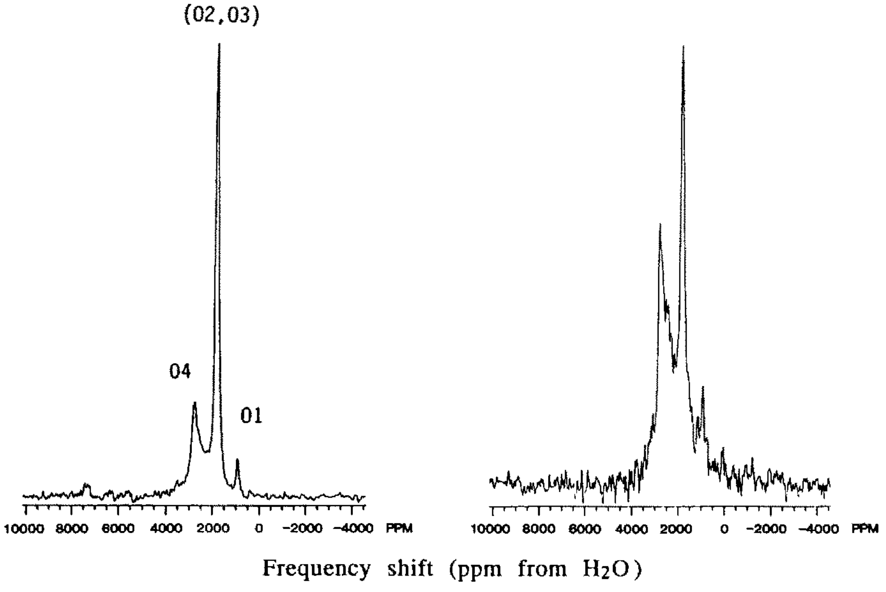

FIG. 5. ^{17}O NMR spectra for Samples *C* (left) and *D* (right) (the spectrometer frequency was centered on the chain oxygen signal at ≈2700 ppm). These spectra show the effect of oxygen exchange times (24 and 4 hr, respectively) on the relative intensity of the chain oxygen signal.

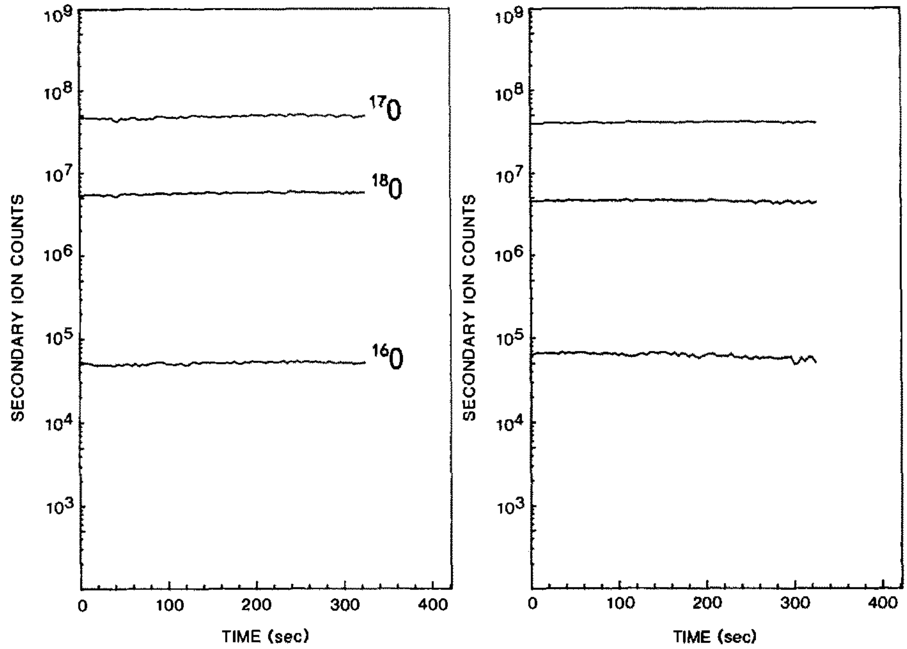

FIG. 6. SIMS ion intensity *vs* sputter time profiles of Samples *A* (left) and *B* (right).

carite II (Thomas Scientific, Swedesboro, NJ).

Apparatus. The schematic diagram of the $^{17}O_2$ gas circulator is shown in Fig. 1. It consists of four detachable parts: the solenoid driven piston pump, the $^{17}O_2$ gas bulb, the quartz sample chamber, and a right-angled connector which connects the gas bulb to the sample chamber. The four parts are interconnected by greased (Dow Corning, Midland, MI) ground-glass ball-joints.

The piston of the pump is a glass tube packed with iron powder. The pump controller consists of a Signetics NE 555 integrated circuit timer which has a variable pulse rate, adjusted by a potentiometer. The timer drives a Magnecraft solid-state relay which in turn switches the 117-V AC line to the solenoid coil. The solenoid coil (number 20 formvar insulated copper wire) is wound on a nylon bobbin with a center hole. Gas pressure inside the apparatus, as indicated by the vacuum/pressure gauge (H. O. Trerice Co., Detroit, MI), is 0.8 atm at 100°C and 1 atm at a sample temperature of 970°C.

Instrumentation. Powder X-ray diffraction patterns were recorded using a Rigaku Geigerflex D/max-B diffractometer. Magnetic susceptibility measurements were carried out using a SQUID magnetometer (SHE Corporation, San Diego, CA). A MnF_2 standard (National Bureau of Standards, Washington, DC) was used to measure the actual applied field. No demagnetizing corrections were used. ^{17}O NMR measurements were performed on a 500 MHz (11.7 T) spectrometer using a "home-built" probe (*13*). $^{16}O : ^{17}O : ^{18}O$ ratios were obtained using a CAMECA secondary ion mass spectrometer (SIMS) by Dr. C. Hitzman (Charles Evans and Associates, Redwood City, CA). Syntheses were done using a prelinearized two-zone horizontal furnace (Marshall, Scott Valley, CA).

Preparation of Sample A. A mixture of

4.768 g of Y_2O_3, BaO_2, and Cu_2O in the metal atom ratio of 1 : 2 : 3 was ground using an agate mortar and pestle under an N_2 atmosphere, then pressed into five pellets, each 8 mm in diameter and 2 mm thick. The pellets were oriented in a platinum boat so as to minimize their contact with the Pt surface. The apparatus was evacuated for 4 h with the sample chamber set at 100°C. At the end of the evacuation time, $^{17}O_2$ was released from the storage bulb and the pump was started at a flow rate of 5 cm^3/s. The sample was heated at 970°C for 24 hr. A small amount of green material, probably Y_2BaCuO_5 and $Ba_3Y_2PtCu_2O_{10}$ (*15*) was scraped from where the pellets had contacted the boat. The pellets were then ground, repelleted, and subjected to a second heat treatment at 970°C for 12 hr followed by annealing at 490°C for 24 hr. Throughout this and the other syntheses the heating rate was always 100°C/hr and the cooling rate was 50°C/hr.

Preparation of Samples B–D. A mother batch of unenriched $YBa_2Cu_3O_{7-x}$, $x \sim 0$, was prepared using a standard procedure (*6*). The batch was divided into three portions. The first portion was annealed in a flowing $^{17}O_2$ gas at 400°C for 168 hr (Sample *B*). The second and third portions were annealed at the same temperature but for 24 hr (Sample *C*) and 4 hr (Sample *D*), respectively.

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