PHYSICAL REVIEW B VOLUME 39, NUMBER 1 1 JANUARY 1989

Magnetic and structural properties of $YBa_2Cu_3O_{7-x}F_y$ as prepared by a NF_3 gas anneal

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(Received 31 May 1988; revised manuscript received 15 September 1988)

$YBa_2Cu_3O_{7-x}F_y$, $y=0.08$ to 1.11, has been prepared by annealing $YBa_2Cu_3O_{7-x}$ (1:2:3) in NF_3 gas. X-ray and neutron-diffraction studies show that the fluorine is structurally incorporated into the CuO chains, in the normally vacant O(5) sites along the a axis. Structurally, this results in a decrease in the orthorhombic strain $(b-a)/(b+a)$. This material exhibits significant increases in diamagnetic expulsion and exclusion as a function of fluorine content, but no increase in T_c. At sufficiently long anneal times (large y) the material undergoes an orthorhombic-to-tetragonal phase transition, and no longer superconducts. An amorphous phase also appears. These results tie together the various conflicting reports of fluorination of 1:2:3.

I. INTRODUCTION

The distinctive structural units in $YBa_2Cu_3O_{7-x}$ (1:2:3) superconducting system are the two-dimensional CuO_2 planes located adjacent to the yttrium sites and the ordered one-dimensional CuO chains situated between the barium sites. These chains and planes form a sublattice of repeating CuO_2-CuO-CuO_2 units along the c axis. Magnetic rare-earth substitution studies,[1] as well as the lack of copper-oxygen chains in the La-Ba-Cu-O superconducting system initially led some to believe that the CuO chains were responsible for the much higher transition temperatures in the new Y-Ba-Cu-O system. However, recent Zn and Ga substitution studies,[2] in addition to the discovery of the Bi-Sr-Ca-Cu-O superconductors,[3] which x-ray studies show possess the planes but not the chains, indicate that the CuO chains are not essential to high-temperature superconductivity. Their role is still not clear.

It has been proposed,[4] based on simple chemical and charge considerations, that two fluoride anions (F^-) could substitute for one oxide anion (O^{2-}) along the CuO chains. This would destroy the one-dimensional ordering of oxide anions and anion vacancies along the chains and replace them with two-dimensionally ordered CuF_2 planes. Double substitution of fluorine for oxygen would still maintain an average copper oxidation state of 2.33, which is thought to be the optimal state.[5] By observing the effects of preferential fluorine substitution on the structural and superconducting properties of the 1:2:3 system, we would be able to gain valuable insight into the role of the chains, and, perhaps, into the mechanism for superconductivity itself.

Since the first report of enhanced superconductivity in fluorine-doped 1:2:3,[6] many groups have attempted to synthesize these compounds, with mixed results.[7-10] Bansal, Sandkuhl, and Farrell[7] observed small systematic increases in T_c with increasing fluorine content, while Sumiyoshi, Hamada, and Kawabata[8] observed no increase in T_c, but a large increase in critical currents as estimated from magnetization curves near liquid-nitrogen temperatures. A majority[9,10] observed no enhanced superconducting properties in fluorine-doped materials prepared by a solid-state synthesis method. The conflicting data are probably due to inherent difficulties with the method employed: The solid fluoride starting material, whether BaF_2, CuF_2, or YF_3, is generally difficult to decompose and to incorporate into the perovskite structure. Fluorination of the 1:2:3 compound by other methods has resulted in reports of enhanced superconducting properties.[11-13] These methods include microwave plasma treatments,[11] sol-gel synthesis,[12] and ion implantation.[13]

Recently, attempts have been made to introduce fluorine into the structure via an F_2 gas anneal.[14] This produces an amorphous secondary phase, which appears to form as a surface layer and does not affect T_c significantly. Actual structural incorporation of the fluorine does not seem to take place readily, if at all, in this method. Here, we anneal 1:2:3 in NF_3 gas, producing fluorinated 1:2:3, $YBa_2Cu_3O_{7-x}F_y$, $y=0.08$ to 1.11. X-ray- and neutron-diffraction studies show that, at short anneal times, the fluorine is indeed incorporated into the perovskite structure, where it preferentially occupies the normally vacant O(5) sites along the a axis (see Fig. 1). Both diamagnetic expulsion and exclusion are enhanced by incorporation of fluorine, though T_c is not affected. At sufficiently long soak times in the fluoride gas, the material is driven tetragonal, and a significant amount of amorphous phase also appears. This material is not superconducting. These results tie together the various conflicting reports of fluorination of 1:2:3.

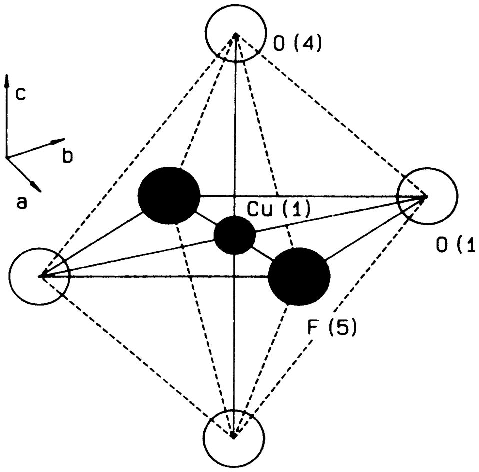

FIG. 1. A CuO_4F_2 octahedral unit. O(4) is the bridging oxygen site between the CuO chains and planes, O(1) the normally occupied oxygen site along the *b* axis in the chains, and O(5) [or F(5)] the normally vacant site along the *a* axis in the chains.

II. EXPERIMENTAL PROCEDURE

A single large master batch of $YBa_2Cu_3O_{7-x}$ was prepared by a standard calcination procedure.[9] This provided material for all of the fluorination studies, serving as a well-characterized reference with which to compare the fluorinated samples. X-ray diffraction showed that the master composition was phase pure. Thermogravimetric analysis (TGA) gave an oxygen content for the master composition of $x \simeq 0.35$, which provides ample oxygen vacancies for fluorine incorporation.

A series of fluorinated 1:2:3 samples ($YBa_2Cu_3O_{7-x}F_y$, $y=0.08$ to 0.68) was prepared in the TGA by soaking the orthorhombic master composition at a constant temperature 300 °C) for 5–300 min in the NF_3 gas, followed by a furnace cool in N_2. Thermogravimetric analysis was conducted using a Cahn 2000 microbalance which provided readings to the nearest microgram. Oxygen was used as a backing gas in order to assure that the reactive fluoride gas did not reach the balance mechanism while also keeping the mechanism cool. Powdered samples (mean particle size, 10 μm) of the master composition were used in order to maximize the surface area for reaction, and to provide short diffusion paths for the intercalation of fluorine ions. The exit gas was scrubbed with Sodasorb (W. R. Grace and Company) and bubbled through a $CaCl_2$ solution to remove any unreacted F^- or HF species. The entire apparatus was mounted under a hood to minimize the possibility of any leaks. Nominal fluorine content *y* was calculated directly from the weight gain of the samples.

Tetragonal samples of varying oxygen concentrations ($x=0.92$–0.60) were prepared from the nitrogen-annealed master composition. These were also fluorinated in NF_3 gas, at 300 °C.

X-ray powder diffraction for microphase identification and least-squares refinement was collected on a Siemens diffractometer utilizing Cu $K\alpha$ radiation. The powdered sample was mounted on a zero-background holder and measurements were taken every 0.02° utilizing a 10-s count time. A copper and fluorophlogophite internal standard was used for the least-squares refinement in order to correct the pattern for instrumental deviations.

Magnetic measurements of the powdered samples were conducted on a SHE system 330 superconducting quantum interference device (SQUID) magnetometer. Approximately 20 mg of powder was enclosed in a quartz tube and all measurements were taken under a constant applied field of 100 G. Magnetization measurements were conducted for both the zero-field-cooled (ZFC) branch and the field-cooled (FC) branch in order to obtain the diamagnetic shielding, M_D, and the Meissner state, M_M, magnetizations, respectively. The percent Meissner effect is defined as the ratio of the Meissner magnetization to the diamagnetic magnetization (M_M/M_D) at 4.5 K.

For neutron-diffraction measurements another series, of larger samples (~ 10 g), was made using the same procedure. The diffraction data were collected using the special environment powder diffractometer (SEPD) at the Intense Pulsed Neutron Source (IPNS) at the Argonne National Laboratory.[15] Data were collected over a 4-h period using the time-of-flight method to measure the incident neutron energies. The $2\theta = \pm 150°$ data were analyzed to obtain structural information via the time-of-flight Rietveld method.[16] Data from all of the samples could be indexed assuming *Pmmm* orthorhombic space-group symmetry. However, data from the nonsuperconducting semiamorphous sample were indexed with a *P4/mmm* tetragonal lattice; the amorphous component was fit and removed from the raw data by a Fourier-filtering technique[17] during structural refinement. The orthorhombic refinements included 796 Bragg reflections over a *d* range of 0.53–3.31 Å and 31 structural parameters were varied. There were slight discrepancies between the calculated and observed patterns (see Fig. 2) for a few of the peaks. Since the discrepancies were consistent and of the same magnitude throughout data from all samples, they could not be a result of the fluorination procedure. We attempted to index these discrepancies with all known impurity phases in the 1:2:3 system; they were found to be attributable to the presence of a CuO impurity phase. For the final refinement, site occupancies for the O(1), O(4), and O(5) sites[18] were allowed to refine while holding all other occupancies at their stoichiometric ratios. Since the scattering lengths for oxygen and fluorine are 0.5803 and 0.5654×10^{-12} cm, respectively, these were treated as identical throughout the refinement.

Magnetic measurements below T_c were also done on these samples. The master composition was used to determine the maximum diamagnetic magnetization $M_{\max}$ at temperatures of 4.5 and 78 K. At $T=4.5$ K, $M_{\max}$ is 3.02 emu/g and the applied field *H* is 2280 G. At a temperature of 78 K, $M_{\max}$ is 0.077 emu/g and *H* is 800 G. These two applied fields were used to measure the maximum Meissner magnetizations for all of the fluorinated materials at 4.5 and 78 K. Bean's model[19] was used to estimate the critical current density j_c. These values should be taken only qualitatively, as this model applies to bulk, not powder, samples.

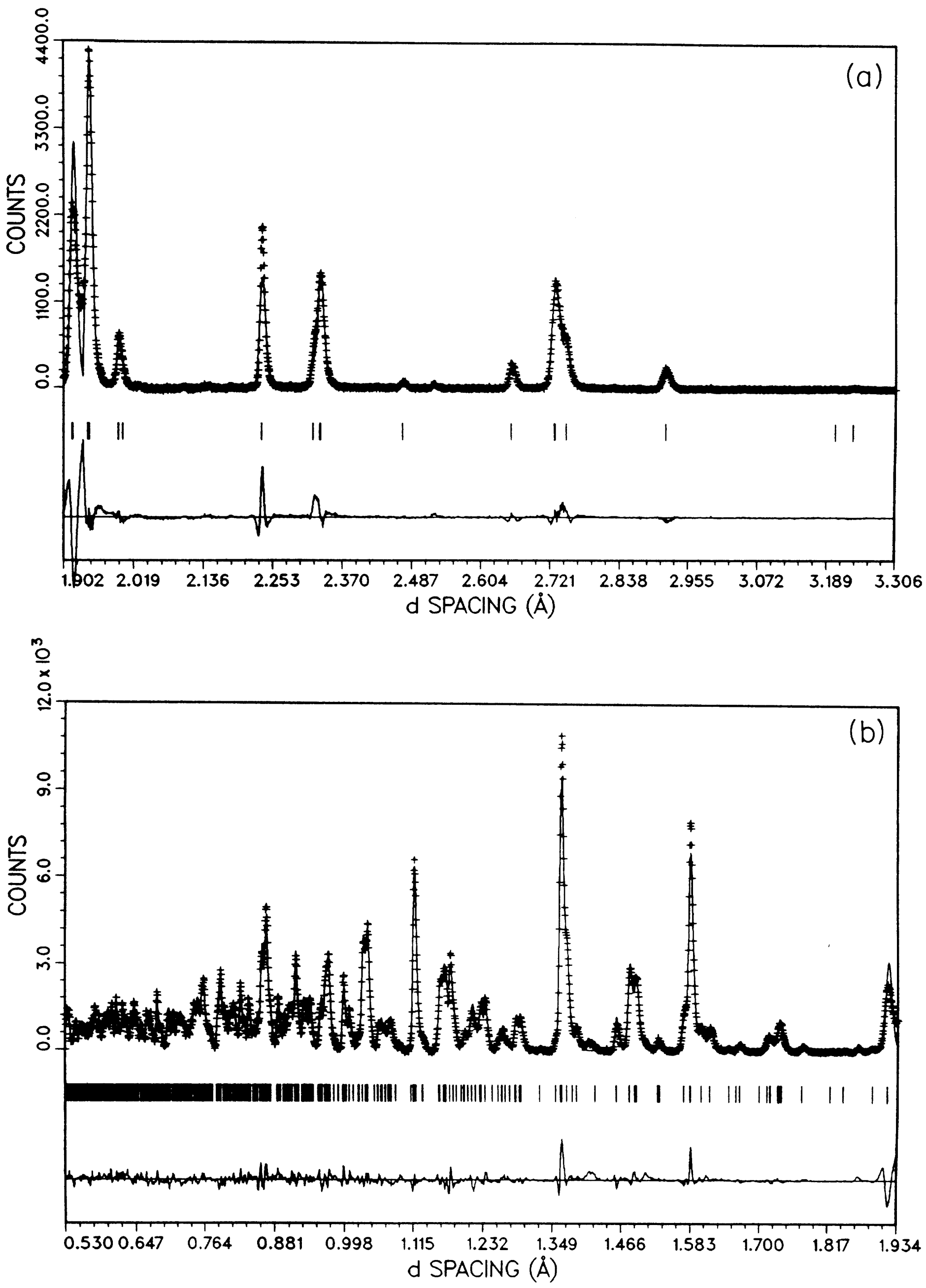

FIG. 2. Rietveld refinement profile for the master batch of 1:2:3 at room temperature. Plus marks (+) indicate the observed neutron-powder diffraction data, and the continuous line is the calculated profile; background has been removed prior to plotting. Tick marks below the profile indicate the positions of the Bragg reflections included in the calculation. A difference (observed−calculated) curve appears at the bottom of the figure. The systematic misfits in the difference curve are due to the presence of a CuO impurity in the sample, which was not considered in the analysis (see text).

III. RESULTS

In order to determine the reactivity of the NF_3 gas with the 1:2:3 system, two preliminary runs were done to monitor fluorine uptake in the orthorhombic and tetragonal samples as a function of temperature. Both materials appeared to begin reacting with the fluoride gas at approximately the same temperature (250 °C), though the tetragonal sample initially incorporated fluorine more readily than the orthorhombic material (Fig. 3). From these two runs a temperature (300 °C) was selected at which to anneal the samples. This temperature allowed sufficient reactivity with the fluoride gas while maintaining the system below those temperatures at which oxygen uptake is

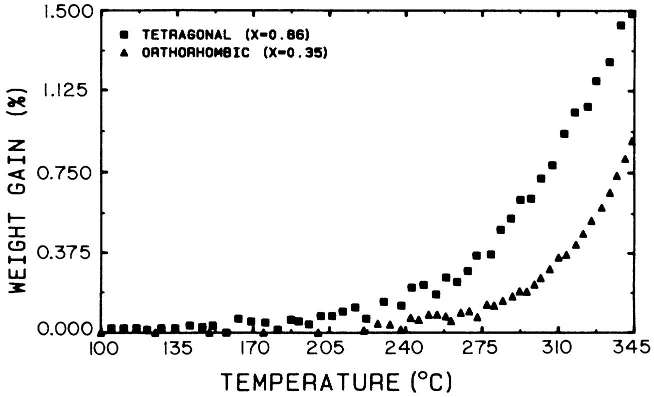

FIG. 3. Percent weight gain of orthorhombic and tetragonal 1:2:3 as a function of temperature in ambient NF_3, at a constant heating rate of 5 °C/min. At low temperatures, NF_3 reacts with the tetragonal material to form a passivation layer which keeps the material from being destroyed as observed when the tetragonal material is soaked with NF_3 at elevated temperatures (see Fig. 8). The error in weight gain is smaller than the symbols used for each data point.

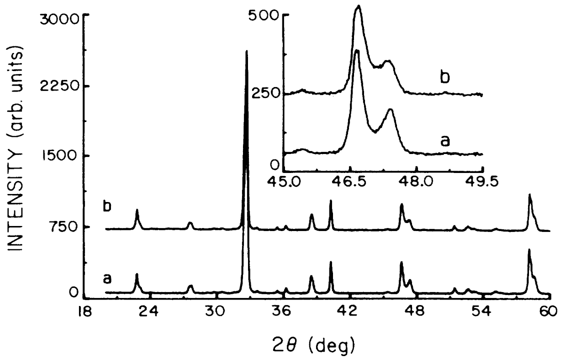

FIG. 4. X-ray diffraction patterns of (a) normal and (b) fluorinated 1:2:3. Note the broadening and shifting of the (006/200) and the (002) reflections near 47° 2θ of the fluorinated material.

observed first to take place in the normal 1:2:3 system.[20]

Fluorine incorporation, as measured by the weight gain in the TGA, was observed to increase with time of fluoride gas soak, as expected. All of these samples were superconducting, but there were no significant changes in their critical temperatures (Table I). All of the samples maintained *Pmmm* symmetry after fluorination and no growth of secondary phases was detected. The x-ray powder patterns were essentially identical for the master and fluorinated 1:2:3 samples (Fig. 4), except for the doublets associated with the CuO chains near 47° and 58°. The (060/200) peaks at 46.64° and the (002) peak at 47.32° were observed to broaden and shift with increased nominal fluorine content. The a axis expanded, and the b and c axes contracted, with increasing fluorine content, producing a systematic decrease in orthorhombic distortion, $(b-a)/(b+a)$ (Fig. 5).

Magnetic measurements show a substantial increase in the diamagnetic and Meissner magnetizations with increased nominal fluorine content in the orthorhombic samples (Figs. 6 and 7). The magnetization near liquid-nitrogen temperatures of sample 7 ($y \simeq 0.68$) for both flux exclusion and expulsion were two to three times greater than in the starting material (sample 1) or in the fully oxygenated material (sample 2). Annealing the master composition ($x \simeq 0.35$) in oxygen to oxygenate it fully ($x \simeq 0.0$) resulted in only a slight increase in the magnetic properties of the original material as compared to annealing the master composition in NF_3.

The rate of fluorine absorption was only slightly greater in the tetragonal material than in the orthorhombic material when both the materials were heated under a continuous flow of NF_3 gas. However, when the NF_3 gas was introduced into the tetragonal samples at 300 °C, the gas reacted quite vigorously resulting in the complete destruc-

TABLE I. Summary of sample data, initial series of samples.

Sample	Nominal fluorine content $(y)^a$	T_c	Magnetization[b] (−emu/g) M_D	M_M	Meissner effect[c]
1[d]	none	90	0.30	0.11	37%
2[e]	none	91	0.28	0.12	43%
3	0.08	90	0.31	0.13	43%
4	0.11	90	0.31	0.16	52%
5	0.18	90	0.33	0.16	49%
6	0.32	90	0.32	0.16	50%
7	0.68	91	0.30	0.16	58%

[a] Assumes oxygen content is unaffected by NF_3 anneal.
[b] At 4.5 K in applied field of 100 G.
[c] M_M/M_D at 4.5 K.
[d] $x = 0.35$ (master composition).
[e] $x = 0.00$ (fully oxygenated master composition).

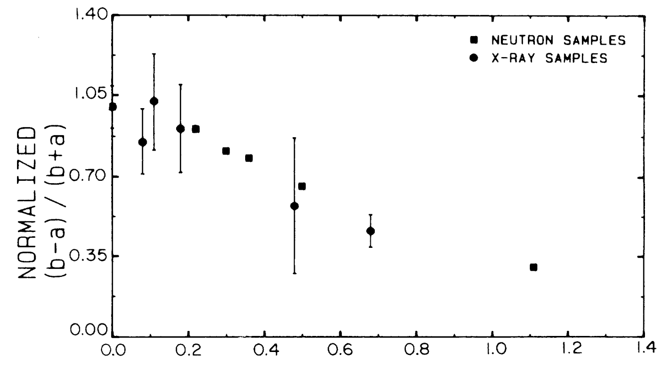

FIG. 5. Orthorhombic distortion $(b-a)/(b+a)$ as a function of nominal fluorine content, for the initial set of samples (as determined by x-ray diffraction), and the second set (as determined by neutron diffraction). Each set is normalized by the value for the unfluorinated (master) composition. The error bars on the second set of data are smaller than the symbols used.

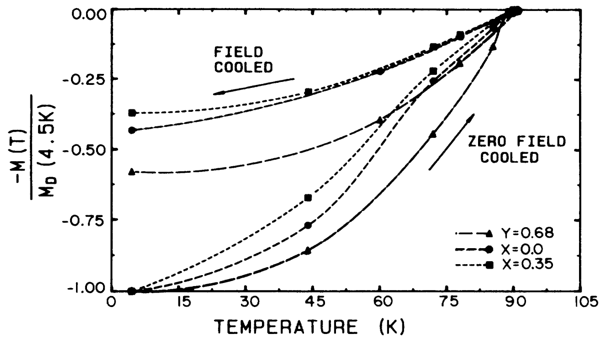

FIG. 6. Magnetization induced by an applied field of 100 G, normalized to the diamagnetic signal at 4.5 K, for (a) 1:2:3 (sample 1), (b) oxygenated 1:2:3 (sample 2), and (c) fluorinated 1:2:3 (sample 7).

tion of the 1:2:3 phase. Most of the weight gain occurred in the initial 2 min of exposure to the NF$_3$ gas, after which the weight stayed essentially constant for the duration of the soak (Fig. 8). The weight gained in the destruction of the tetragonal material was observed to depend directly upon the concentration of oxygen vacancies: $x \simeq 0.60$ material gained 9.88%; $x \simeq 0.86$ material, 13.2%; and $x \simeq 0.92$ material, 13.7%. The x-ray-diffraction patterns were essentially identical for all of the fluoride gas annealed tetragonal samples regardless of soak time and revealed numerous unknown phases, none of which resembled the 1:2:3 structure.

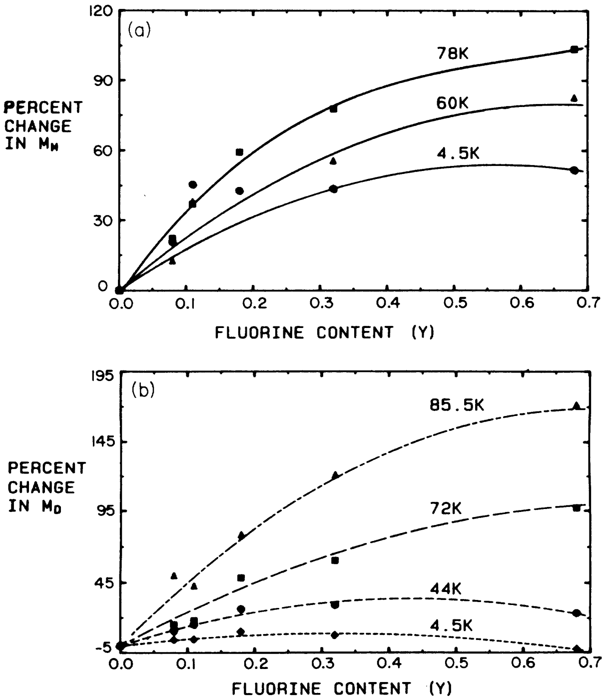

FIG. 7 Percent change in (a) diamagnetic (M_D) and (b) Meissner (M_M) magnetization as a function of temperature at different nominal fluorine contents. All measurements were made under a constant applied field of 100 G. The error in magnetization is less than the size of the symbols used for each data point.

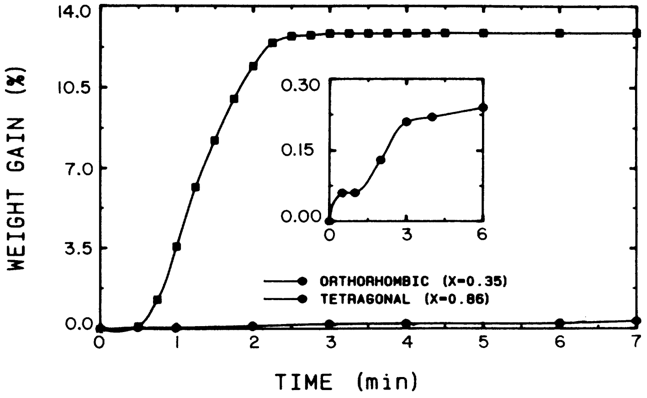

FIG. 8. Percent weight gain in orthorhombic and tetragonal 1:2:3 during a NF$_3$ gas soak at 300° as a function of time. The tetragonal material was always destroyed within 3 min of exposure to the NF$_3$ gas. The error in percent weight gain is smaller than the size of the symbols used for each data point.

Neutron diffraction also shows no growth of secondary phases with increased fluorine content. The orthorhombic distortion of the lattice was again seen to decrease systematically with increasing fluorine content (Fig. 5). The effect on the lattice parameters is shown in Fig. 9. The fractional O(5) site occupancy increases with increased nominal fluorine content, ranging from 0.09 in the starting unfluorinated 1:2:3 material to 0.34 in the fluorinated 1:2:3 material (Table II). The fractional O(1) and O(4) site occupancies remained essentially constant at 0.75 ± 0.03 and 1.01 ± 0.01, respectively (Fig. 10). The effect of fluorine doping on the copper-oxygen bond lengths is shown in Fig. 11. The Cu(1)–O(4) bond length increases by 0.009 ± 0.003 Å from nominal F stoichiometry 0 to 1.11, while over this same range, Cu(2)–O(4) decreases by 0.019 ± 0.004 Å. (Here, of course, "oxygen" refers to the occupant of the oxygen site.)

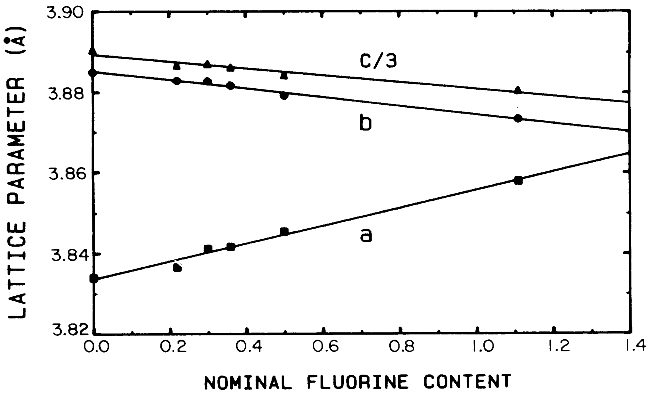

FIG. 9. Lattice parameters as functions of nominal fluorine content for YBa$_2$Cu$_3$O$_{7-x}$F$_y$ as determined from neutron-powder diffraction. The error bars are smaller than the symbols used.

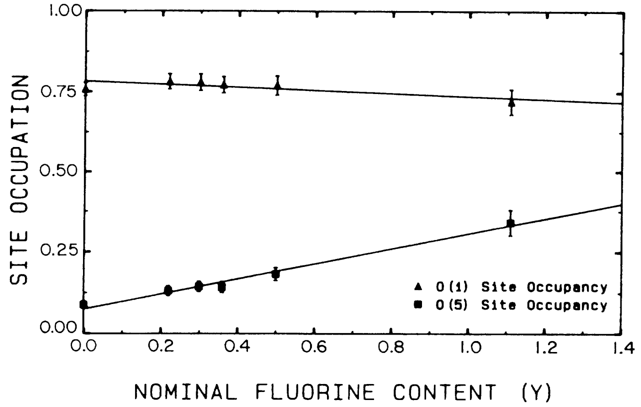

FIG. 10. O(1) and O(5) site occupancies as determined from refinement of the neutron powder data. The O(4) site (not shown) changes little (1.01 ± 0.01) with fluorination.

At sufficiently long fluoride anneals, the material was driven tetragonal. The lattice parameters were indexed as $a=3.8659$ and $c=11.6340$ Å. Both x-ray and neutron powder patterns revealed a significant amount of an amorphous phase also present (Fig. 12). The material was not superconducting. The combined oxygen site occupancy is significantly greater than the 6–6.5 observed in the normal tetragonal 1:2:3 material. The fractional O(1) site occupancy was 0.68 as compared to a normal occupancy of 0–0.25 in the tetragonal 1:2:3 system (Table III).

IV. DISCUSSION

The x-ray data clearly establish that structural changes take place as a result of the NF_3 anneal. There may be secondary phases forming as seen by others,[14] even at short soak times though our data do place an upper limit on the amounts that there could be; however, this effect, if present, must be in addition to the alterations in the 1:2:3 structure itself. The neutron site occupancy data show that the major change taking place in the structure is a dramatic increase in the O(5) site occupancy, an increase that is not seen in standard oxygen anneals.[21] In fact, though the similarity in the scattering lengths of oxygen and fluorine prevent our being able to distinguish between them on the basis of the neutron data alone, it is unlikely that the increase in occupancy observed on the O(5) sites could be due to oxygen incorporation, for two reasons. First, the fluoride anneal was conducted at temperatures far below those at which oxygen incorporation in 1:2:3 is first observed to take place.[20] As a check, a sample of the master composition was annealed in oxygen up to the

TABLE II. Summary of data, second series of samples. Note that j_c does not behave monotonically with increasing fluorine content: for large y, j_c appears to decrease. This is because the material is close to the phase transition to the tetragonal (nonsuperconducting) structure.

Nominal fluorine content (y)	T_c (K)	O(5)[a]	Critical current density (A/cm^2) j_c (4.5 K)	j_c (78 K)
0.00	90	0.09(1)	690(34)	110(5)
0.22	90	0.13(1)	1010(50)	190(9)
0.30	90	0.14(2)	1020(50)	200(10)
0.36	90	0.14(2)	990(49)	220(11)
0.50	90	0.18(2)	1310(65)	310(15)
1.11	90	0.34(4)	920(46)	210(10)

[a] O(1) = 0.75 ± 0.03.

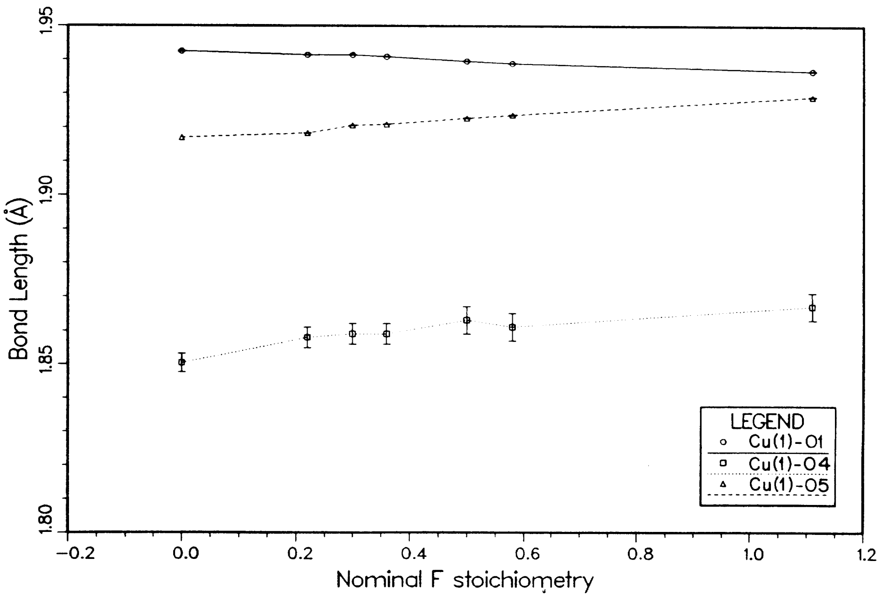

FIG. 11. Copper-oxygen bond lengths as a function of y. From top to bottom, the data represent: Cu(1)—O(1), Cu(1)—O(5), and Cu(1)—O(4). The Cu(2)—O bond length, over the same range of y, changes from 2.308 Å at $y=0$ to 2.283 Å at $y=1.1$, a difference of 0.025 Å which is $\simeq 3-4\sigma$.

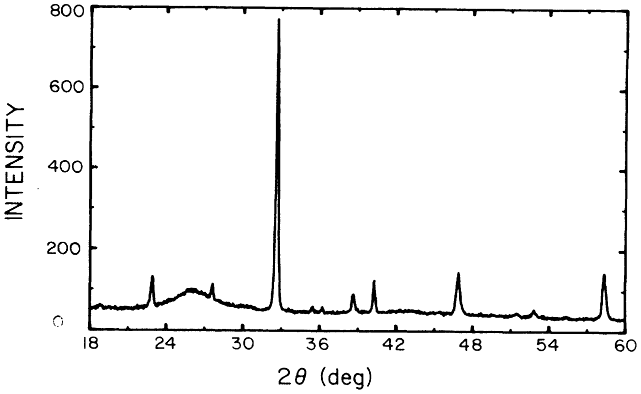

FIG. 12. X-ray powder diffraction of the amorphous-tetragonal fluorinated sample which is nonsuperconducting.

same temperature (300 °C) at which the NF_3 anneal was done. No weight gain was observed. Second, standard annealing of 1:2:3 in oxygen results in incorporation of oxygen onto the vacant O(1) sites and little, if any, onto the O(5) sites.[21] Oxygen normally only goes into the O(5) site if the sample is rapidly quenched and/or driven through the orthorhombic-to-tetragonal structural phase transition, both of which result in partial occupancy of the O(5) site at the expense of the O(1). When this occurs, the c axis expands; this is because the decrease in the chain site oxygen occupancies reduces the electrostatic screening of the Ba^{2+}-Ba^{2+} ion repulsion. Our data show a *contraction* of the c axis, the obvious explanation for which is that fluorine atoms on the O(5) site are *increasing* this electrostatic screening. It must, however, be pointed out that the bond-length data are ambiguous: while they are certainly consistent with this picture, they would also be consistent with a picture in which the fluorine substituted into the O(1) or O(4) sites, with the displaced oxygen moving into the O(5) sites. It is also possible that there may be charge transfer between Cu(1) and Cu(2) taking place: The changes in the bond lengths are in the right direction.

The behavior of the tetragonal material under fluorination is especially interesting. While it reacted similarly to the orthorhombic material if heated under a constant flow of gas, it was quickly destroyed if the NF_3 gas was first introduced into the system after the anneal temperature (300 °C) was reached. At lower temperatures, it appears that the fluoride gas reacts with the tetragonal material to form a passivation layer of fluorinated 1:2:3 or fluoride impurity phase which limits the uptake of fluorine into the system once higher temperatures are reached. However, if NF_3 gas is first introduced at these higher temperatures, the gas is far too reactive to allow a passivation layer to be formed and the tetragonal material is quickly destroyed. This dramatic reaction was not observed, however, in the oxygen deficient ($x = 0.35$) orthorhombic material (Fig. 8). Thus, it seems that oxygen vacancies, especially in the tetragonal material, serve as active sites for the incorporation of fluorine and so determine the rate at which the NF_3 gas reacts with the 1:2:3 structure.

This interesting result indicates that the NF_3 gas is reacting along the basal CuO chains, resulting in the incorporation of fluorine anions onto the oxygen vacancies. This is also supported by the changes observed in the x-ray powder patterns. Removal of oxygen from these chains in the tetragonal material increased the reactivity of the material with the NF_3 gas at elevated temperatures. It seems that oxygen vacancies in the orthorhombic material have much less effect on the reactivity of the NF_3 gas with the 1:2:3 material, at least in comparison to the tetragonal material.

The properties of the nonsuperconducting semiamorphous material provide further evidence for structural incorporation of fluorine along the CuO chains. The combined oxygen and fluorine stoichiometry as determined from the site occupancies is greater than 7 which is atypical of the normal 1:2:3 tetragonal material in which the occupancy is always 6.0–6.5. Since the O(1) site occupancy in the orthorhombic material appears to vary little with increasing fluorine content, it is most likely that fluorine occupied the O(5) site until both sites are equally occupied, resulting in a tetragonal phase transition. The trend of the lattice parameters and of the chain site oxygen occupancies in the orthorhombic material support this observation. The O(1) and O(5) sites are structurally symmetric in the tetragonal material with a fractional occupancy of 0.68. This is significantly greater than the occupancy of 0–0.25 in the normal 1:2:3 tetragonal material (Table III). Note also the contraction of the c axis as shown in Table III. The c axis of the amorphous-tetragonal material is smaller even than that of the orthorhombic 1:2:3; this is because of the increased screening due to chain site occupancy.

The growth of the amorphous component in the tetragonal material also explains the discrepancy in the fluorine content of the samples as measured from both the O(5) site occupancy and the weight gain. The ratio of the O(5) site occupancy to the nominal fluorine content is approximately 1:5 except for the $y = 0.22$ sample (2:5). X-ray powder diffraction did not detect any growth of secondary phases in the orthorhombic materials; therefore, the unaccounted weight gain must be attributed to the growth of an amorphous component which x-ray powder diffraction would not be able to detect easily at low concentrations.

TABLE III. Comparison of orthorhombic and tetragonal 1:2:3 with fluorinated amorphous-tetragonal 1:2:3. Here, O(1) and O(5) are the fractional site occupancies. Note the contraction of the c axis upon fluorination, orthorhombic to amorphous tetragonal.

	Master composition	Normal tetragonal[a]	NF_3 annealed tetragonal
T_c (K)	90	. . .	. . .
a (Å)	3.8340(1)	3.857	3.8659(1)
b (Å)	3.8851(1)	. . .	. . .
c (Å)	11.6718(3)	11.819	11.6340(5)
O(1)	0.76(2)	0–0.25	0.68(2)
O(5)	0.09(1)	. . .	. . .

[a] A. Santoro *et al.*, Mater. Res. Bull. **22**, 1007 (1987).

The preferential substitution of fluorine onto the CuO chains is, of course, to be expected from the behavior of 1:2:3 with oxygen,[20] and was, in fact, predicted from electronic structure studies[22] as being the configuration most likely to raise T_c. However, although the diamagnetism and critical current of the fluorinated material are enhanced, there is no observable effect on the critical temperature. If both chains and planes are directly involved in the superconducting mechanism, with, perhaps, different energy gaps and transition temperatures,[23] one would expect T_c to vary with fluorine concentration; the fact that it does not seems to constitute further evidence that the long-range order in these systems is primarily a two-dimensional phenomenon. The chains may in some way mediate the interplanar coupling, by facilitating direct hopping of recombined holon-spinons[24] or through some more complicated mechanism.[25]

V. CONCLUSIONS

Doping the 1:2:3 system with fluorine via a solid-state synthesis route results in multiphasic, unreliable, and irreproducible material, and has given rise to a multiplicity of results concerning the superconducting properties. Some[6,7] have seen enhancements of T_c, some[8,9] have not; some[8,26] have seen enhancements of critical-current density, some[9,10] have not. Because of the nature of the material synthesized it is difficult to isolate the variables involved. For example, a recent study on sintered pellets[26] appears to show that the addition of fluorine causes grain growth, and this mechanism is proposed to explain the observed enhancement of j_c. However, since we see the same types of effects on fluorinated powders, this is unlikely to be a complete explanation. Moreover, it cannot account for the changes we observe in the lattice parameters.

We have shown that fluorination by NF_3 gas anneal suffers from none of the problems that have plagued solid-state synthesis attempts. We have been able to synthesize $YBa_2Cu_3O_{7-x}F_y$ material reproducibly using this procedure. Diffraction unambiguously demonstrates systematic structural changes with fluorination. Fluorine ions are preferentially incorporated onto the vacant O(5) sites located along the *a* direction, which reduces the orthorhombic strain in the unit cell. Sufficient NF_3 annealing induces an orthorhombic-to-tetragonal phase transition which renders the 1:2:3 material nonsuperconducting. This tetragonal material also contained a substantial amorphous component, in agreement with results by other researchers.[14] The introduction of fluorine onto the O(5) chain sites resulted in enhanced diamagnetism and critical-current densities, with no concurrent change in T_c. These results are consistent with the idea that the CuO chains are not directly involved in the superconductivity mechanism. Incorporation of fluorine along the CuO chains has no effect on T_c as long as the material remains orthorhombic, though if enough vacant sites are occupied that the material is driven tetragonal, superconductivity is destroyed. Exactly why is not clear.

While our data establish that fluorine is indeed structurally incorporated into the 1:2:3 structure by an NF_3 anneal, and that diamagnetism is increased in samples so treated, we have not conclusively established that the two are causally related to each other. It is possible, for example, that fluorine may also be being introduced into the grain boundaries, and that it is this component which is responsible for the observed magnetic behavior. Studies are currently underway to expand our knowledge in all directions.[27]

ACKNOWLEDGMENTS

We are grateful to Air Products and Chemicals, Inc., for funding this project, and especially to Carole Gressler and David Taschler for their technical support. This work was also supported by the New York Science and Technology Foundation. In addition, we wish to thank Professor Hagai Shaked for helpful discussions concerning 1:2:3 impurity phases. This work has benefited from the use of the Intense Pulsed Neutron Source at Argonne National Laboratory, which is funded by the U.S. Department of Energy, Office of Basic Energy Sciences—Materials Science, under Contract No. W-31-109-ENG-38.

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