NMR study of the ^{89}Y resonance in fluorinated YBa$_2$Cu$_3$O$_x$

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The line shape and Knight shift of the ^{89}Y NMR resonance was obtained for fully oxygenated ($x = 7$), oxygen deficient ($x=6.7$), and nonsuperconducting oxygen deficient ($x = 6$) fluorine-doped YBCO (Yba$_2$Cu$_3$O$_x$F$_y$). The results show that while fluorine can increase the onset superconducting transition temperature T_c in oxygen deficient material, the Knight shift is practically independent of the fluorine concentration. The consequences of this result as far as T_c is concerned are discussed.

I. INTRODUCTION

Fluorine has been inserted into the high-temperature superconducting compounds YBa$_2$Cu$_3$O$_x$ in order to modify the valence of the copper and study the resulting superconducting transition properties.[1-5] It was found that fluorine may have a restorative effect on the onset transition temperature. Thus an oxygen-deficient material YBa$_2$Cu$_3$O$_{6.7}$ having an onset T_c of 63 K, increases its T_c progressively upon fluorination to its final value of 91 K at a concentration of $y = 0.2$ (YBa$_2$Cu$_3$O$_x$F$_y$). Increasing the fluorine content beyond this concentration decreases the superconducting diamagnetic signal without further increasing T_c. Fluorination of a fully oxygenated material does not increase its T_c beyond 91 K, but has its diamagnetic signal decreased. This reduction is attributed to intergranular effects.[3,6] Neutron-diffraction studies performed on YBa$_2$Cu$_3$O$_{6.7}$F$_y$ indicate that at first the fluorine enters mostly the vacant chain oxygen sites, and then also the sites between the chain Cu along the a axis.[2,5]

The nuclear magnetic resonance of ^{89}Y is a convenient tool for probing changes in the electronic structure of these materials.[7-9] This is because ^{89}Y has a nuclear spin of $\frac{1}{2}$ and is thus free from complications due to quadrupole interactions. It has been found[7,8] that the ^{89}Y Knight shift steadily increases from negative to positive values as oxygen is removed and T_c decreases. Similarly, when the fully oxygenated material is doped with hydrogen, the Knight shift follows the same curve, i.e., the Knight shift becomes less negative with the introduction of hydrogen.[9] Also, the onset T_c remains constant until a concentration is reached where the material becomes a nonsuperconductor and the Cu(2) atoms in the plane align antiferromagnetically. Thus the Knight shift, which is a measure of the density of states at the Fermi level, is useful for following the electronic changes brought about by doping. We therefore used this method for investigating the effect of F doping on samples having three different values of the oxygen content, covering the fully oxygenated YBa$_2$Cu$_3$O$_7$ superconducting $T_c \approx 91$ K material, the partially oxygenated YBa$_2$Cu$_3$O$_{6.7}$ superconducting $T_c \approx 63$ K material, and the nonsuperconductor YBa$_2$Cu$_3$O$_6$.

II. EXPERIMENTAL TECHNIQUE

The three starting oxides YBa$_2$Cu$_3$O$_x$ ($x = 6$, 6.7, and 7) were prepared by solid-state reaction starting from the oxides and carbonates, following a procedure described in Ref. 3. These samples were then fluorinated by flowing diluted NF$_3$ gas (3% in N$_2$) at a temperature of about 300 °C for various reaction times.[3] The fluorine content was determined from the weight increase, the quality from x-ray diffraction, and T_c was determined by the mutual induction technique. The ^{89}Y resonance was measured at room temperature at a resonance frequency of 14.707 MHz using standard techniques described elsewhere.[9] Each spectrum represents an average of about 6000 echoes in the time domain, with a repetition time of 20 sec. This is of the order of the spin-lattice relaxation time T_1 for the superconducting material, and about half that value for the nonsuperconductor.[10] Hence if there are nuclei in different environments having different T_1's, the amplitudes of different spectral components may not fully reflect the absolute intensities, and the spectrum may be somewhat distorted.

III. EXPERIMENTAL RESULTS

We obtained the Knight shift, linewidth, and line shape of the ^{89}Y resonance in YBa$_2$Cu$_3$O$_7$F$_y$, where $y = 0$, 0.10, and 0.20; in YBa$_2$Cu$_3$O$_{6.7}$F$_y$, where $y = 0$, 0.10, 0.15, 0.25, 0.29, and 0.38; and in YBa$_2$Cu$_3$O$_6$F$_y$, where $y = 0$, 0.60, 0.98, and 1.50. The results of the measurements and the onset T_c of these samples (as obtained from the induction measurements) are summarized in Table I. The

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TABLE I. Line shift, linewidth, and onset T_c in $YBa_2CuO_xF_y$.

	y^a	K Shift (ppm)	Width (kHz)	T_c (K)
$x=7$	0.00	-88 ± 7	1.5 ± 0.1	91.0
	0.10	-94 ± 7	1.5 ± 0.1	91.0
	0.20	-93 ± 7	1.6 ± 0.1	91.0
$x=6.7$	0.00	-39 ± 7	1.6 ± 0.1	62.5
	0.10	-36 ± 7	1.5 ± 0.1	71.0
	0.15	-47 ± 7	1.6 ± 0.1	89.5
	0.25	-44 ± 7	1.5 ± 0.1	91.0
	0.29	-50 ± 7	1.9 ± 0.1	91.0
	0.38	-50 ± 7	1.7 ± 0.1	91.0
$x=6$	0.00	12 ± 20	4 ± 0.5	Non
	0.60	-14 ± 20	8 ± 2	Non
	0.98	19 ± 20	4 ± 1	Non
	1.50	20 ± 15	2.5 ± 0.5	50^b

^{a}Determined from weight increase with an estimated error of ±0.02.
^{b}Measured on another sample with the same composition.

Knight shift was measured relative to ^{89}Y in an aqueous solution of YCl_3. The onset T_c of the last entry in the table ($YBa_2Cu_3O_6F_{1.5}$) was not measured since its value was less than 54 K, the lower limit of the temperature range of our measurements. However, it was seen that the sample contains some superconducting volume at 4 K. A previous sample having the same composition had an onset T_c of 50 K.[3] The accuracy of the K shift and linewidth of the nonsuperconducting samples was much more difficult to determine, since the lines are considerably wider due to the antiferromagnetic interaction.

The linewidth of ^{89}Y in undoped $YBa_2Cu_3O_x$ is of the

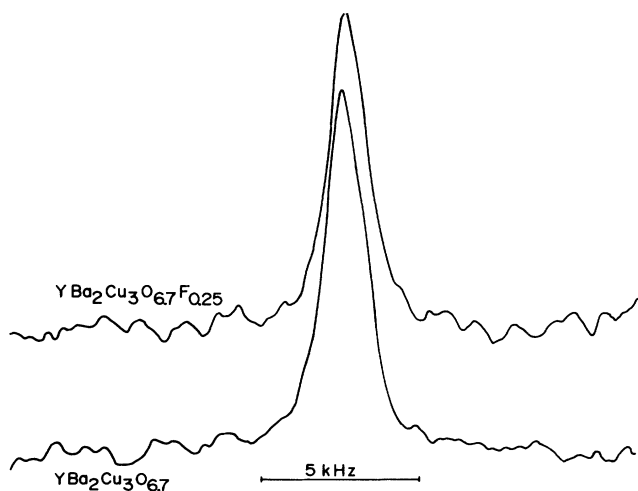FIG. 1. Comparison of the ^{89}Y NMR line shape for fluorine-free ($YBa_2Cu_3O_{6.7}$) and fluorine-doped ($YBa_2Cu_3O_{6.7}F_{0.25}$) YBCO showing that doping with F in the superconducting material has no effect on the line shape.

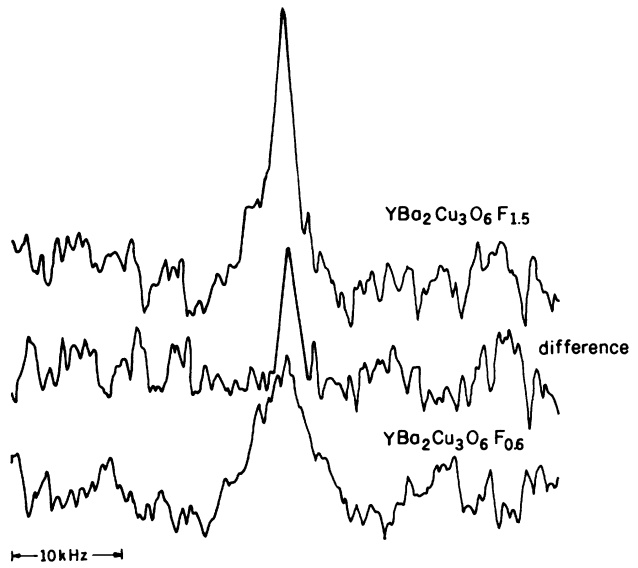FIG. 2. Comparison of the ^{89}Y line shape for nonsuperconducting $YBa_2Cu_3O_{6.0}F_{0.6}$ with that for $YBa_2Cu_3O_{6.0}F_{1.5}$, which has its high-T_c superconducting property partially restored. The line of the F free material is wide due to the antiferromagnetic interaction. The F-doped material shows a narrower line superimposed on the wide line. This is emphasized in the middle trace, which is obtained by taking the difference between the top and bottom spectra. The wide line cancels, leaving only the narrow component. The narrow component is attributed to the existence of nonantiferromagnetic superconducting material.

order of 1 kHz for x in the superconducting range, and jumps by a factor of about 4 when x is such as to make it a nonsuperconductor.[7] This is because of the local magnetic field caused by the antiferromagnetic alignment. For our samples, adding fluorine has no noticeable effect on the line shape, provided the material remains a superconductor. This is illustrated in Fig. 1, where the spectra of ^{89}Y in $YBa_2Cu_3O_{6.7}$ and $YBa_2Cu_3O_{6.7}F_{0.25}$ are compared. The nonsuperconducting material gives a much larger linewidth. It is interesting to note that when a fluorine concentration of $y=1.5$ is added to $YBa_2Cu_3O_6$, superconductive behavior is restored. This is also reflected in the ^{89}Y line shape (Fig. 2), where a narrow line is seen to be superimposed on the wide line of the nonsuperconducting material. This shows that the $YBa_2Cu_3O_6F_{1.5}$ must be a mixture of a superconducting and nonsuperconducting phases. When the ^{89}Y line shape of the nonsuperconducting phase ($YBa_2Cu_3O_6F_{0.6}$) is subtracted, only the narrow line of the superconducting phase remains.

IV. DISCUSSION

When oxygen is added to oxygen-deficient $YBa_2Cu_3O_x$, the onset T_c increases, and is restored to its value of 92 K when x reaches 7. At the same time the ^{89}Y Knight shift decreases to more negative values with increasing x.[7] reflecting the increase of the hole concentration in the material. It was seen that adding F to oxygen-deficient $YBaCu_2O_x$ also has a T_c restoring effect on the material.
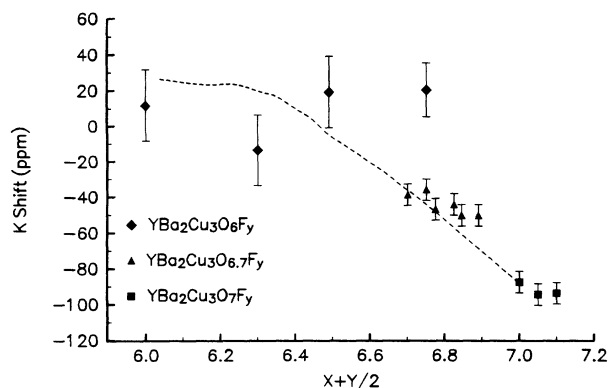
FIG. 3. The Knight shift of ^{89}Y in $YBa_2Cu_3O_xF_y$ as a function of $x + y/2$. The broken line gives the shift as a function of oxygen concentration for the fluorine-free material, and is taken from the results of Alloul et al. and Balakrishnan et al. (Refs. 7 and 8). It can be seen that F doping has very little (if any) effect on the K shift. Had fluorine contributed holes to the conduction band, the K shift points should have been on the broken line.

If the hole concentration were the only underlying criterion determining T_c, then this should be reflected in the change in the Knight shift in a manner similar to that of adding oxygen. Such a change in the Knight shift was obtained in the case of hydrogen addition, where the addition of two hydrogens was equivalent to the removal of one oxygen.[9] Since F has a valency of unity, one might expect that adding two F's, may shift the Knight shift by the same amount as adding one oxygen. Figure 3 is a plot of the Knight shift as a function of $x + y/2$, where x is the oxygen concentration per unit cell and y is the

fluorine concentration. The broken curve is the ^{89}Y K shift for the fluorine-free material. It is a smooth curve of a locally weighted regression through the experimental points obtained by Alloul et al.[7] and Balakrishnan et al.[8] One can see that (a) the Knight shift of the fluorine-free samples obtained in this study agrees with those of Alloul et al. and Balakrishnan et al.; and (b) rather than following the changes obtained by oxygen addition, F doping has very little if any effect on the Knight shift.

The fact that doping $YBa_2Cu_3O_{6.7}$ with F can raise T_c and restore superconductivity in $YBa_2Cu_3O_6$ without changing the Knight shift can be taken as evidence that the carrier concentration is not the sole factor in determining T_c. This can also be seen from the behavior of T_c as a function of oxygen concentration. While the Knight shift changes steadily with oxygen concentration, T_c exhibits a steplike change in that there are two plateaus above and below $x = 6.5$.[11] This has been attributed to an ordering of the chain oxygen into alternating full and empty chains.[12] Thus the local crystallographic environment is an important factor in the behavior of T_c. A similar effect was seen upon hydrogen doping. Although the Knight shift steadily changes as a function of H concentration,[9] the onset T_c remains constant at 92 K, until a hydrogen concentration is reached where antiferromagnetic order takes over[13,14] and the material becomes a nonsuperconductor.

ACKNOWLEDGMENT

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