

Superconductivity in Fluorinated $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$

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The $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ structures have been fluorinated by a gas phase exchange technique, and ^{19}F NMR was used to identify the structural fluorine. Magnetic susceptibility measurements showed that the fluorination turned a marginally nonsuperconducting sample into a 40 K superconductor, as well as that it raised the onset of the superconducting transition of the 60 K superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ to about 100 K.

1. Introduction

Since the report that fluorine substitution into the high T_c YBCO structure significantly raised the superconducting transition temperature (T_c), the effect of fluorine incorporation has been a subject of much interest [1-4]. However, few reliable evidences of reproducible fluorine incorporation into the structure have been reported, and there have been some ambiguities and contradictory reports on the effect of fluorination of this system. Aside from the effect on the superconductivity, fluorine in the YBCO structure would also provide a sensitive spin 1/2 NMR probe for the microscopic environments in this system. In this work, various samples of the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ ($0 < x < 1$) structures were fluorinated using a gas phase exchange technique and studied using various techniques to study the fluorinated samples.

2. Experiment

The starting YBCO samples were made using the standard solid state reaction method, and then fluorinated using a gas phase exchange technique with a flow of 10 % F_2 -90 % N_2 gas mixture at 165 °C for several hours [2]. This processing temperature was chosen as elevated temperatures led to significant decomposition of the sample, while lower temperatures led to no fluorination. AC magnetic susceptibilities were measured for the superconducting transition temperatures, and 45 MHz ^{19}F NMR, x-ray and neutron diffraction measurements were also made to confirm the fluorine incorporation and to study the ef-

fect of the fluorination.

3. Results and Discussion

Fluorinated samples of $\text{YBa}_2\text{Cu}_3\text{O}_7$ showed no changes in the T_c or in the lattice parameters, but only reduced superconducting volume fraction. This indicates that no significant amount of fluorine was introduced into the $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure, and that the fluorination process mostly produced decomposed impurity phases as verified by visible white traces in heavily fluorinated samples [2]. ^{19}F NMR yielded a relatively narrow line of about 30 kHz FWHM (full-width at half maximum) linewidth, which can be attributed to a BaF_2 impurity phase. In fact, a white powder sample fully decomposed at 400 °C yielded a resonance line with similar linewidth and similar non-exponential spin-lattice relaxation pattern. Thus the thermodynamically favored impurity phase formation process seems to hinder the fluorine incorporation into the oxygen-saturated $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure, which would require the replacement of structural oxygen by fluorine as no vacant oxygen sites are available in this structure.

As it was believed that the fluorine incorporation would be easier into the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ structures with $x < 1$ with vacant O (1) sites, samples of tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_6$ with the maximum oxygen vacancy sites were fluorinated and tested. In fact, noticeable changes were observed in the lattice parameters, and the fluorine incorporation was confirmed by the neutron diffraction measurements. In addition to a relatively small amount of the impurity phase, the ^{19}F NMR measurements showed a

broad line of 400 kHz linewidth attributed to the structural fluorine, which has a single-exponential spin-lattice relaxation time of about 60 ms, in contrast to the very short spin-lattice relaxation time of about 1 ms for the impurity phase component. Only minor changes were observed in the linewidth and the spin-lattice relaxation time at 5 K for the structural fluorine component. An estimate was also made for the amount of fluorine incorporated into the YBCO structure by calibrating the ^{19}F NMR intensities with known F standards such as YF_3 , which gave a y value of about 0.35, in good agreement with the neutron diffraction results.

While fluorine is not easily incorporated into the $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure with no vacant O (1) sites, the $\text{YBa}_2\text{Cu}_3\text{O}_6$ with vacant O (1) sites show noticeable fluorine incorporation. This indicates that fluorine cannot replace oxygens in the YBCO structure but can only be introduced into the vacant O (1) chain sites by this gas phase exchange technique. Thus more fluorine would be introduced into the structure with more vacant O (1) sites before surficial decomposition prevents further structural fluorine incorporation. Since the fluorine incorporation in the $\text{YBa}_2\text{Cu}_3\text{O}_6$ structure is believed to take place into the vacant O (1) sites, the linewidth of 400 kHz can be explained by assuming magnetic moments of $0.05 \mu_B$ at the Cu (1) sites, or $0.5 \mu_B$ at the Cu (2) sites with second moment calculations. These magnitudes appear to be in good agreement with those reported by other workers for unfluorinated samples [5-9].

In order to see if fluorine incorporation can induce superconductivity in a nonsuperconducting YBCO structure, a marginally nonsuperconducting sample of tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$ was fluorinated. A change in the x-ray diffraction pattern was noticed showing some orthorhombic peaks, and the ac magnetic susceptibility measurements showed a broad superconducting transition at around 40 K. NMR analysis yielded an estimated fluorine content of 0.2 per formula unit.

While the unfluorinated $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ sample superconducts at around 60 K, a fluorinated $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ sample, $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}\text{F}_y$, shows an onset of the superconducting transition at around 100 K in the ac magnetic susceptibility measurements, although full diamagnetism is observed at around 93 K. For comparison, the ac susceptibility measurements for the $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}\text{F}_y$ sample as well as for a fully oxidized $\text{YBa}_2\text{Cu}_3\text{O}_7$ sample are shown in Fig. 1. It also shows that the fluorinated sample has a relatively large paramagnetism presumably due to the impurity phases formed by the fluorination. It appears that the fluorination of the $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ has really raised the onset temperature of the superconducting transition significantly, to about 100 K. Direct measurement of the resistivity is hindered by the surficial decomposition of the fluorinated grains.

The fluorination of the $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ sample was also checked by NMR. The room temperature ^{19}F NMR lineshape for the fluorinated sample also showed a broad line of about 200 kHz FWHM linewidth attributed to the structural fluorine. Figure 2 shows the spectra obtained by sweeping the frequency

at room temperature and at 5 K. The room temperature spin-lattice relaxation time (T_1) of the structural fluorine was about 80 ms. Together with the much different linewidths, this allowed us to easily separate the two distinct lineshape components. Since the fluorine incorporation in the $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ structure is also believed to take place into the vacant O (1) sites, the linewidth of 200 kHz can be explained by assuming magnetic moments of $0.025 \mu_B$ at the Cu (1) sites. This appears to be in good agreement with those reported by other workers for unfluorinated samples [9].

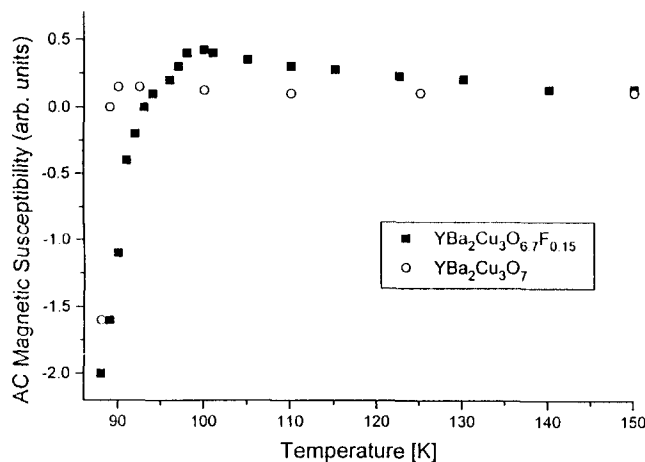


Fig. 1. Ac magnetic susceptibility measurements for the $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}\text{F}_y$ and for a fully oxidized $\text{YBa}_2\text{Cu}_3\text{O}_7$ sample.

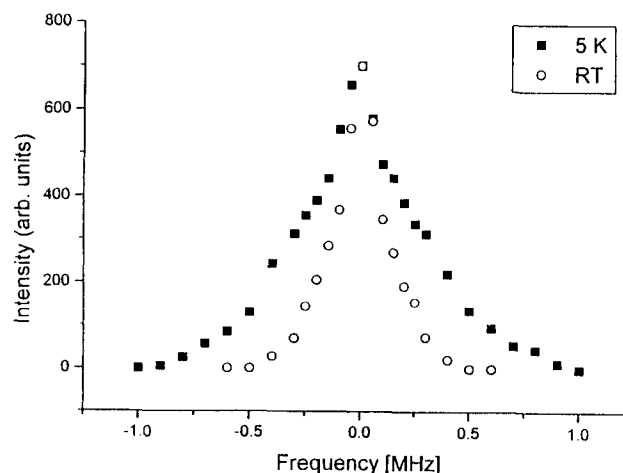


Fig. 2. The ^{19}F NMR lineshapes for the structural fluorine in $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ obtained point-by-point at room temperature and at 5 K.

An effort was also made to determine the amount of fluorine incorporated into the $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ structure by calibrating the ^{19}F NMR intensities, which gave an estimate for a y value of about 0.15. This indicates that the fluorine can in fact act favorably in raising the T_c in the YBCO structure. In compari-

son, the electron type high T_c superconductor $\text{Nd}_2\text{CuO}_{4-x}\text{F}_y$, gives slightly higher T_c than that of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ [4].

Our results using the gas phase exchange technique appear to provide a concrete and reproducible evidence of the fluorine incorporation into the YBCO structures and of its role on the superconductivity. While extended fluorination incorporating more structural fluorine would seem attractive, attempts to incorporate more fluorine into the YBCO structures by extending the fluorination time resulted in more decomposition, showing more impurity phases in the NMR measurements. This indicates that the structural fluorine incorporation is a process competed by the formation of the impurity phases such as BaF_2 . Thus with extended fluorination of the sample the impurity phases surrounding the YBCO grains appear to prevent the fluorine gas from further reaching the YBCO grains. The fluorine incorporation is believed to be a diffusion process. The fact that it takes place into the YBCO structures with low oxygen contents, but not into the oxygen-saturated $\text{YBa}_2\text{Cu}_3\text{O}_7$, indicates that the processing temperature is high enough for the fluorines to migrate into the vacant chain oxygen O (1) sites, but not high enough for the structural oxygens to migrate or for the fluorines to replace them. Higher processing temperatures produce noticeable impurity phase formation before the fluorine incorporation takes place.

In summary, a gas phase exchange technique has been employed to reproducibly introduce fluorine into the YBCO structure. Fluorine appears to occupy the vacant O (1) sites, and was shown to change the crystal structure and to have a favorable effect on the T_c .

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