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^{19}F NMR Study of Fluorinated $YBa_2Cu_3O_{7-x}$

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A sample of $YBa_2Cu_3O_{7-x}$ fluorinated by a high temperature (400 °C) gas exchange technique has been investigated by means of ^{19}F NMR (nuclear magnetic resonance) measurements in both superconducting and normal state. As a result, behaviors characteristic of the superconductor, including a peculiarity in the spin-lattice relaxation rate (1/*T1*) around 250 K, were observed.

I. Introduction

Fluorine incorporation into the high T_c YBCO structure has been a subject of much interest since several groups reported that fluorine substitution significantly raised the superconducting transition temperature (T_c) [1-3]. The ^{19}F nucleus is a spin 1/2 100% abundant isotope, which would offer ease in interpretation and provide a sensitive spin 1/2 NMR probe for the microscopic environments in the YBCO structure. Since fluorine is expected to take the oxygen sites in the perovskite structure, ^{19}F NMR can be an effective local probe for the Cu planes. In fact, some workers have made spin 5/2 ^{17}O NMR measurements to probe the superconductivity in $YBa_2Cu_3O_7$ [4].

A sample of $YBa_2Cu_3O_{7-x}$ was reproducibly fluorinated using a gas phase exchange technique at an especially high temperature for maximal fluorination and studied using ^{19}F NMR [5,6]. Nuclear spin-lattice resonance has been employed as a powerful local probe of quasiparticle dynamics in the high T_c superconductors yielding much valuable information on the microscopic properties. Thus, in this work ^{19}F NMR measurements were made in the normal and superconducting states to throw some additional light onto the nature of the superconductivity in the YBCO structure as reflected by fluorine nucleus substituted into the structure.

II. Experiment

The starting $YBa_2Cu_3O_{7-x}$ sample was 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 [5] at an elevated temperature of 400 °C for several hours. For χ close to zero, relatively low temperature fluorination showed little change in the superconducting transition temperature (T_c) or sign of structural incorporation of fluorine as probed by ^{19}F NMR or by x-ray or neutron diffraction. However, this high temperature process decomposed surface layer and produced an outer nonsuperconducting white impurity phase [5,6].

A black superconducting phase well inside the fluorinated pellet was separated for analysis. While the starting sample showed a T_c of 90 K, the fluorinated black phase showed a superconducting transition at 95 K. According to previous observations, the fluorine is most likely to take the chain O(1) sites [5]. The 45 MHz ^{19}F NMR measurements were made between 5 K and room temperature.

III. Results and discussion

Figures 1 and 2 show the temperature dependences of the inverse nuclear magnetization and the ^{19}F NMR linewidth. In Fig. 1, the Meissner effect is apparent as the magnetization shows a decrease below the superconducting transition temperature. In other words, since the YBCO is a type II superconductor, the magnetic field is expelled from some regions of the sample, from which no NMR signal will be detected. As the temperature is lowered, the sample will be more superconducting, and there will be more deviation from the simple Curie law of the nuclear magnetization due to the Meissner effect as is evidenced in Fig. 1. The deviation from Curie law thus reflects the degree of superconductivity. Figure 2 also shows an inhomogeneous line broadening arising from magnetic field gradients below T_c due to a finite penetration depth and the resulting vortex lattice structure [7]. In NMR the linewidth is indicative of the magnetic field distribution, and the linewidth in the superconducting state signifies the field distribution broadened by superconductivity.

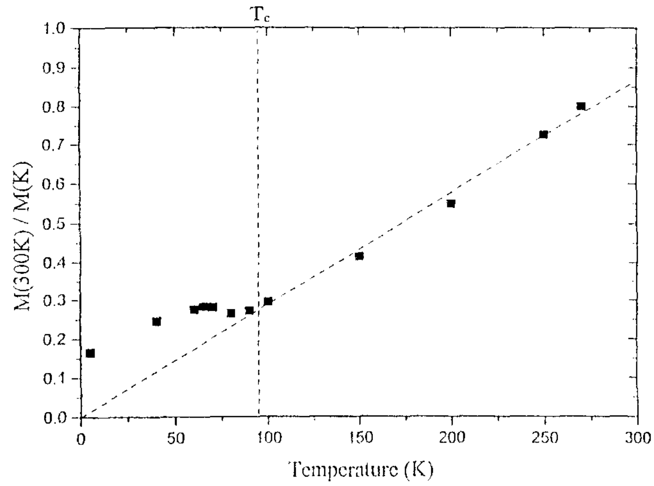

Figure 1. Temperature dependence of the inverse nuclear magnetization.

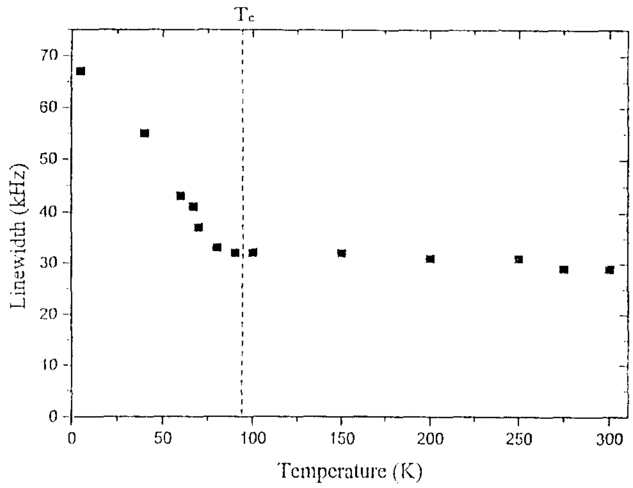

Figure 2. Temperature dependence of the ^{19}F NMR linewidth.

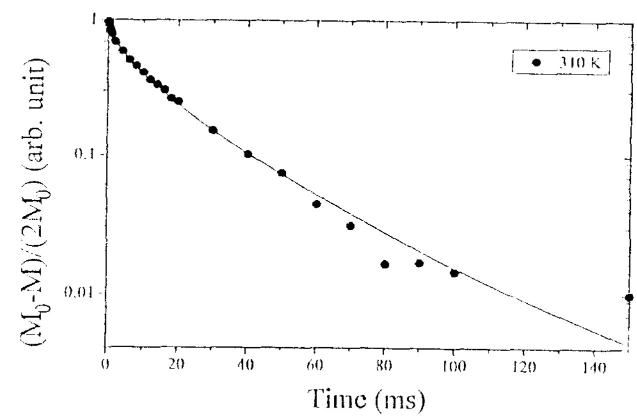

Figure 3. The ^{19}F nuclear magnetization recovery pattern at 310 K in the fluorinated $YBa_2Cu_3O_{7-x}$.

Figure 3 shows the NMR spin-lattice relaxation pattern, which is clearly nonexponential. In fact, it is well fitted by the so-called stretched-exponential type, $M(t) = M_0\{1 - \exp[-(t/T_1)^{1-n}]\}$. The nonexponential relaxation pattern can arise from a distribution of the microscopic correlation time, and thus inhomogeneous local environments. It is also known to take place in the presence of paramagnetic impurities. The value of $n = 0$ corresponds to the usual single-exponential type, and greater values of n correspond to greater degree of inhomogeneity of the local environment as probed by ^{19}F nuclei, or greater amount of local paramagnetic moments which are known to arise from the copper ions in the structure. In our case, the inhomogeneous fluorine substitution can also give rise to the inhomogeneous local environments, and the degree of nonexponentiality, or the value of n, can reflect the degree of inhomogeneous fluorine substitution, or the amount of paramagnetic moments created in the structure. The spin-lattice relaxation is well fitted into the stretched-exponential form, with $n = 1/3$, at all temperatures. Figure 4 shows the temperature dependence of the spin-lattice relaxation rate ($1/T_1$) thus obtained.

In Fig. 4, no particular anomaly, such as a coherence peak, is observed at the superconducting transition temperature. However, a slight fluctuation is noticed below the transition temperature, which is believed to arise from the presence of nonsuperconducting impurity phases in this fluorinated sample. The low temperature behavior of $1/T_1$ in Fig. 4 can be fitted into the BCS spin-lattice relaxation form of $\exp(-\Delta/kT)$, which gives a relatively small value for the corresponding superconducting energy gap, $2\Delta = 1.4\ kT_c$ [7-10]. Figure 4 also shows that the zero-temperature spin-lattice relaxation rate is finite, about 0.027/s. This residual relaxation is believed to arise from the contribution of local magnetic moments as observed in other works [10-13].

The high temperature behavior of $1/T_1$ is particularly interesting. In Fig. 4, it is shown that the slope undergoes an obvious change around the temperature of 250 K. While the

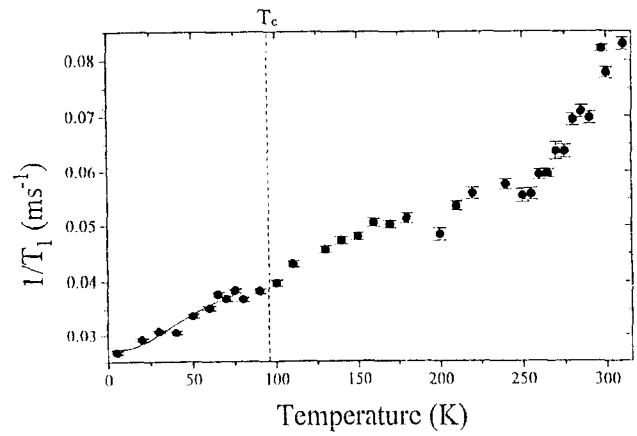

Figure 4. Temperature dependence of the spin-lattice relaxation rate ($1/T_1$) as obtained by ^{19}F NMR in the fluorinated $YBa_2Cu_3O_{7-x}$. The curve in the low temperature region represents a fit to the form of exp($-\Delta/kT$) as described in the text.

normal state spin-lattice relaxation mechanism in the $YBa_2Cu_3O_{7-x}$ system has not been unambiguously established, the MMP (Millis, Monien, Pines) model of the antiferromagnetic correlation has been proposed as a plausible candidate [14]. In that model, the change in the slope is indicative of that in the antiferromagnetic correlation. It should be mentioned that this peculriarity has not previously been observed in $YBa_2Cu_3O_{7-x}$ samples with small x values fluorinated at lower temperatures of about 165°C. We believe that this is an indication that high temperature fluorination is more effective in incorporating fluorines into the structure. Although no definite evidence can be offered at this point, it may also be related to the unreproduced and unconfirmed reports of extraordinary high superconducting transition temperatures in the $YBa_2Cu_3O_{7-x}$ systems [1-3].

In summary, a fluorinated sample of $YBa_2Cu_3O_{7-x}$ was made using a gas phase exchange technique at a relatively high temperature for maximal fluorine incorporation. As a result, some characteristic behaviors were observed from the ^{19}F NMR measurements of the fluorinated sample.

Acknowledgments

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