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Nuclear Magnetic Relaxation in Fluorinated $YBa_2Cu_3O_{7-x}$

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The $YBa_2Cu_3O_{7-x}$ structure has been fluorinated by a gas phase exchange technique. The ^{19}F NMR (nuclear magnetic resonance) spin-lattice relaxation rate ($1/T_1$) measurements on a fluorinated sample gave a superconducting energy gap of $2\Delta = 4.6\,kT_c$.

1. Introduction

Since several groups reported 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 [1-3]. The ^{19}F nucleus is a spin 1/2 100 % abundant isotope and offers ease in interpretation, and would 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 when fluorination takes place, ^{19}F NMR would provide an effective local probe for the Cu planes.

While the solid state reaction method of fluorination is known to lack reproducibility, a sample of $YBa_2Cu_3O_{7-x}$ was reproducibly fluorinated using a gas phase exchange technique in this work and studied using ^{19}F NMR. Nuclear spin-lattice relaxation is a powerful local probe of quasiparticle dynamics in the superconducting state and can yield valuable information on the microscopic properties of superconductors, as first demonstrated by Hebel and Slichter in confirming the BCS theory. Thus, in this work the spin-lattice relaxation rate was measured in the superconducting state to throw some light onto the nature of the superconductivity in the YBCO structure as reflected by fluorine nucleus substituted into the structure. In fact, NMR has been playing a vital role in the effort to understand the high T_c superconductivity as the field penetration permitted by type-II superconductors allows NMR measurements in the mixed state.

2. 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 at 165 ℃ for several hours. This processing temperature was chosen as elevated temperatures led to significant decomposition of the sample, while lower temperatures led to no fluorination [4]. The ac magnetic susceptibility measurement showed that the fluorinated sample had a superconducting transition temperature (T_c) of about 95 K. The 45 MHz ^{19}F NMR measurements were made for the spin-lattice relaxation times (T_1) between 5 K and room temperature.

3. Results and discussion

Fig. 1 shows the room temperature spin-lattice relaxation pattern, which shows a nonexponential behavior. The initial magnetization decay is well fitted into the form of exp $[-(t/T_{1l})^{1/2}]$, and the long-time behavior is represented with a single-exponential decay. An identical form of the nonexponential decay was also observed in a fully decomposed white powder sample, which is easily attributed to the impurity phase [5]. Fig. 2 shows the temperature dependence of the time constant T_{1l} for the impurity relaxation, which is essentially temperature independent, supporting our assignment.

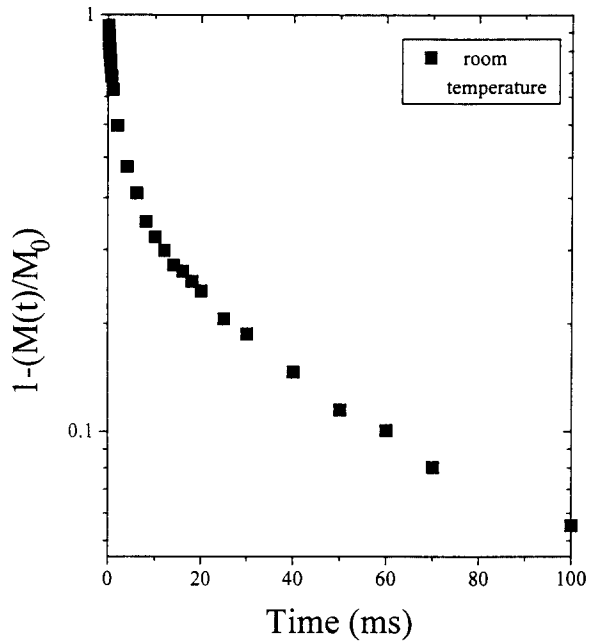

Fig. 1. The room temperature ^{19}F nuclear magnetization recovery pattern in the fluorinated $YBa_2Cu_3O_{7-x}$.

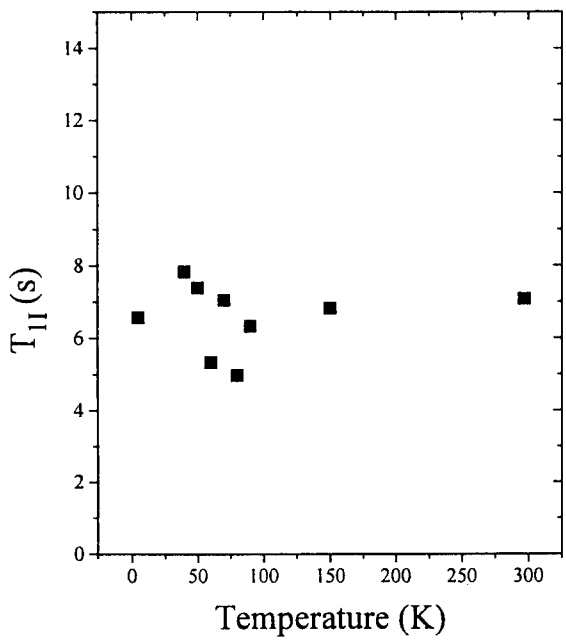

Fig. 2. Temperature dependence of the relaxation time constant T_{1l} for the fluorinated $YBa_2Cu_3O_{7-x}$.

The single-exponential relaxation part, which is absent in the fully decomposed sample, can be attributed to the structural fluorines. The temperature dependence of the corresponding spin-lattice relaxation time T_1 is shown in Fig. 3, which shows some fluctuations around the superconducting transition temperature. These fluctuations around the T_c have not been observed in other NMR or NQR (nuclear quadrupole resonance) measurements in unfluorinated YBCO, and may arise from the presence of the nonsuperconducting impurity phases in this fluorinated sample.

The low temperature behavior is quite well fitted into the BCS spin-lattice relaxation form of $\exp(-\Delta/kT)$, which gives the corresponding superconducting energy gap of $2\Delta = 4.6\ kT_c$. This value is somewhat greater than the BCS value of $3.5\ kT_c$ as generally reported in the high T_c measurements [6-9]. It is actually close to the values obtained for the Cu (1) chain sites by Cu NQR or NMR, but much smaller than those for the Cu (2) plane sites. This is quite reasonable and consistent with our observation that fluorine takes the vacant O (1) chain sites by this gas exchange technique, since fluorination takes place more readily into the perovskite structures with more vacant chain oxygen sites. The value of $2\Delta = 3.5\ kT_c$ arises from the BCS model based on the isotropic s-wave superconductivity. Thus, the greater energy gaps observed in the high T_c systems are indicative of the anisotropic d-wave nature of the wavefunctions, and the greater values for the plane sites would indicate the wavefunctions have more overlaps at those sites than at the chain sites.

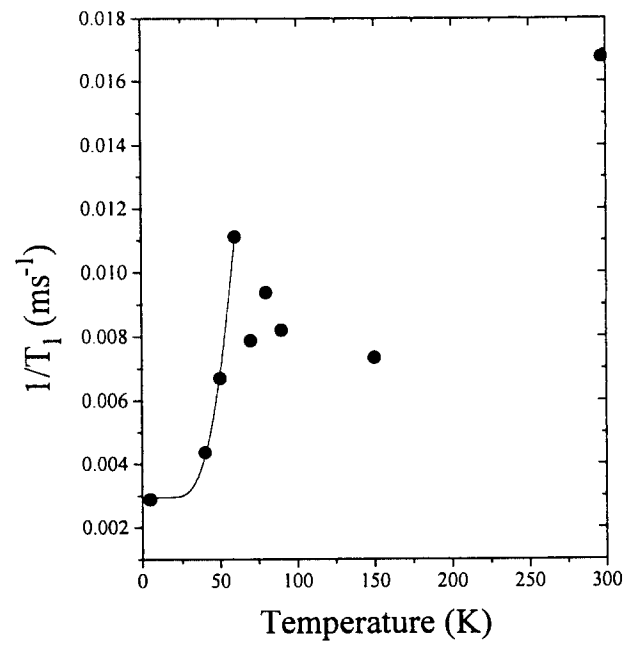

Fig. 3. Temperature dependence of the spin-lattice relaxation rate $(1/T_1)$ as obtained by ^{19}F NMR in the fluorinated $YBa_2Cu_3O_{7-x}$. The curve in the low temperature region represents a fit to the form of $\exp(-\Delta/kT)$ as described in the text.

Fig. 3 also shows that the zero-temperature spin-lattice relaxation rate is finite, about 0.03/s. This residual relaxation is believed to arise from the contribution of local magnetic moments as observed in other works [9-12].

In summary, a gas phase exchange technique has been employed to reproducibly introduce fluorine into the YBCO structure. ^{19}F NMR spin-lattice relaxation measurements on a fluorinated $YBa_2Cu_3O_{7-x}$ sample in the superconducting state

showed some characteristic behaviors and yielded a superconducting energy gap comparable to those reported in revous works.

Acknowledgments

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