^{19}F NMR study of superconductive and nonsuperconductive $Nd_2CuO_{4-x}F_y$

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We have synthesized superconductive and nonsuperconductive samples of the n-type high-T_c superconducting system $Nd_2CuO_{4-x}F_y$ from the same batch. They give very similar normal state ^{19}F NMR results, with decreasing spin-lattice relaxation time (T_1) and the spin-spin relaxation time (T_{2E}) and increasing negative line shift on decreasing temperature. Our results seem to indicate that the fluorine is more likely to be substituted into the O(2) sites between the Nd planes in this system.

I. INTRODUCTION

In 1989 a new high-T_c superconductor $Nd_{1.85}Ce_{0.15}CuO_4$ was synthesized (T_c=24 K) by the cation doping of the mother compound Nd_2CuO_4.[1] Subsequently the anion-doped n-type high-T_c superconductor $Nd_2CuO_{4-x}F_y$ was discovered (T_c=27 K).[2] In contrast to the previously reported p-type high-T_c superconductors, the charge carriers are not holes but electrons, and the doped elecrons have a Cu $3d$ character. The fact that CuO_2 planes in the high-T_c superconductors can have both types of charge carriers was believed to provide a test of the proposed theories for the conduction mechanism of the high-T_c superconductors.

$Nd_2CuO_{4-x}F_y$ has a tetragonal structure with a crystal symmetry $I4/mmm$ (T' phase) and the lattice parameters are $a=b=3.96$ Å and $c=12.13$ Å.[2] A unit cell has two oxygen sites O(1) and O(2). O(1) is in the CuO_2 planes whereas O(2) is between the Nd planes as shown in Fig. 1. The TEM (transmission electron microscope) and neutron scattering gave no significant results as to the F^- ion substitution site, and x-ray photoelectron spectroscopy gave opposite results.[3–6]

NMR (nuclear magnetic resonance) has been an important probe for superconductivity.[7–13] The ^{19}F nucleus has a spin 1/2, large gyromagnetic ratio, isotope abundance of 100%, and no quadrupole moment. Thus ^{19}F NMR can be a very sensitive and effective probe for the electronic and magnetic environments of $Nd_2CuO_{4-x}F_y$.[14,15]

II. EXPERIMENT

The samples were prepared by the solid-state reaction from stoichiometric mixtures of Nd_2O_3, CuO, and NdF_3. A DTA (differential thermal analysis) heat absorption peak at 916 °C, attributed to the sample decomposition, limited the processing temperature below 910 °C. The stoichiometric mixtures were calclined at 900 °C for 14 h in air, using a Pt crucible. After regrinding, they were pressed into cylindrical pellets and annealed at 890 °C for 14 h in flowing N_2. The pellets were furnace cooled to room temperatue with a cooling rate of 3 °C/min (sample I). A second annealing was performed successively for a part of sample I in the same condition for 10 h (sample II). The x-ray diffraction patterns for the prepared samples were in good agreement with known results. The SEM (scanning electron microscope) and SQUID (superconducting quantum interference device) measurements were also made on the samples. ^{19}F NMR measurements at 45 MHz were made for the superconductive sample I and the nonsuperconductive sample II well above the superconducting transition temperature, between 100 and 300 K, employing a home-built pulsed NMR spectrometer. The spin-lattice relaxation time (T_1) and the spin-spin relaxation time (T_{2E}), the resonance frequency shift, and the line shape were measured employing solid echo sequences using C_6F_6 as the ^{19}F NMR reference. The T_1 was measured by the saturation recovery method.

III. RESULTS AND DISCUSSION

Figure 2 is the SEM picture of the sample I, which shows that the samples consist of small grains of several μm. The sample II showed a similar microstructure. The temperature dependence of the SQUID magnetization measurements for the two samples is shown in Fig. 3. For an applied magnetic field of 10 G after zero field cooling, only sample I showed superconductivity. The onset temperature of the superconducting transition is 22 K and the Meissner effect is observed

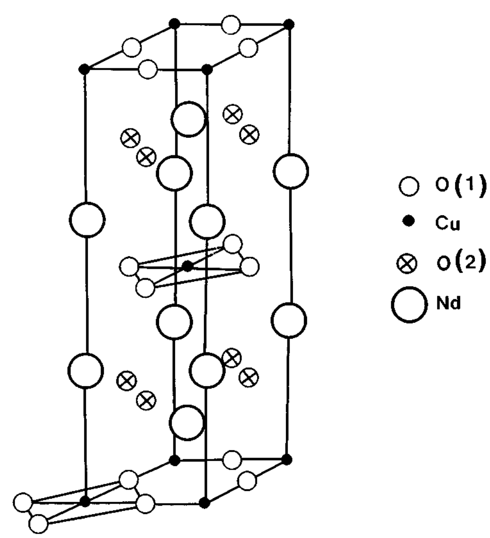

FIG. 1. Crystal structure of $Nd_2CuO_{4-x}F_y$.

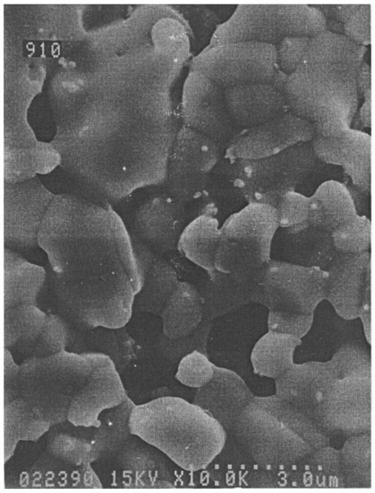

FIG. 2. SEM (scanning electron microscope) picture of the superconductive $Nd_2CuO_{4-x}F_y$.

at 16 K. Both samples were paramagnetic at all temperatures in 5000 G.

The ^{19}F NMR intensities indicated that the two samples contain comparable F contents. The two samples gave nearly identical Gaussian line shapes as shown in Fig. 4. The single Gaussian line shape seems to indicate that the substituted F^- ions are located at only one oxygen site at least for the most part.

As shown in Fig. 5, the two samples gave very similar line shift in the whole temperature range. The negative line

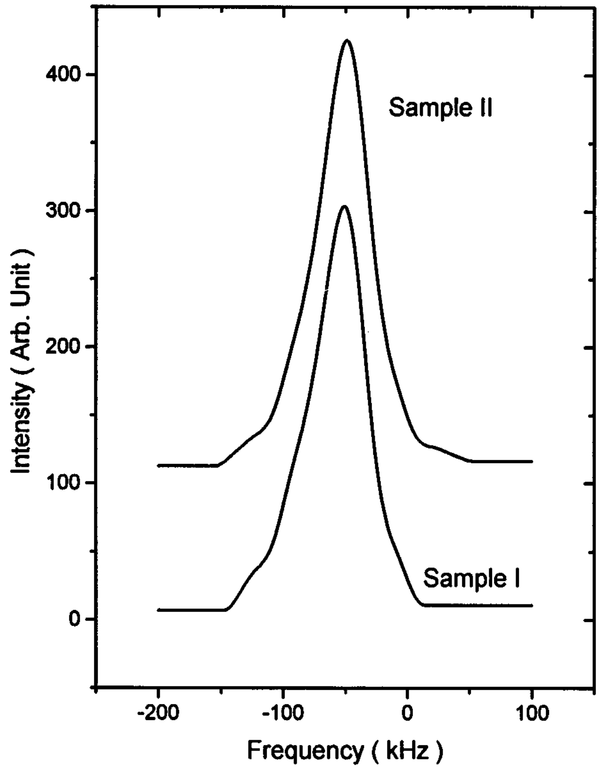

FIG. 4. Room temperature line shapes of the superconductive and the nonsuperconductive $Nd_2CuO_{4-x}F_y$. The zero frequency corresponds to the C_6F_6.

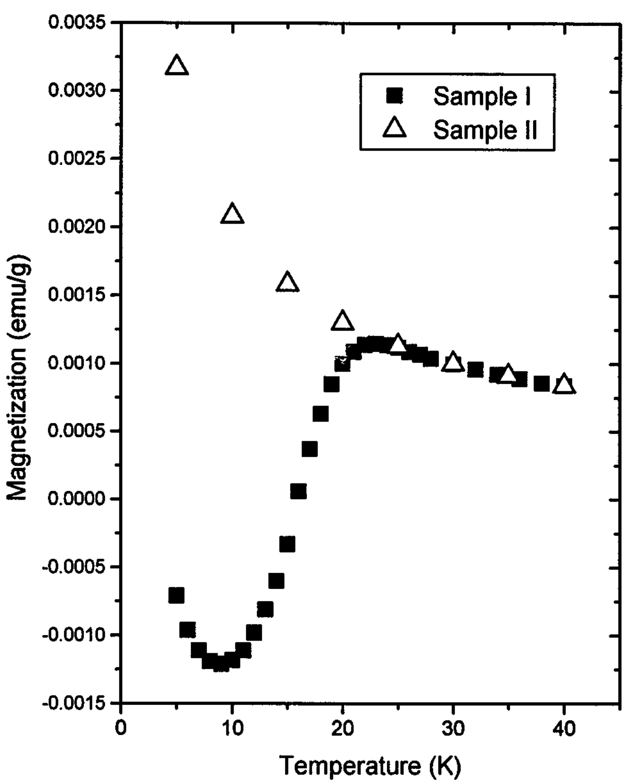

FIG. 3. Temperature dependence of magnetization for the superconductive and nonsuperconductive $Nd_2CuO_{4-x}F_y$.

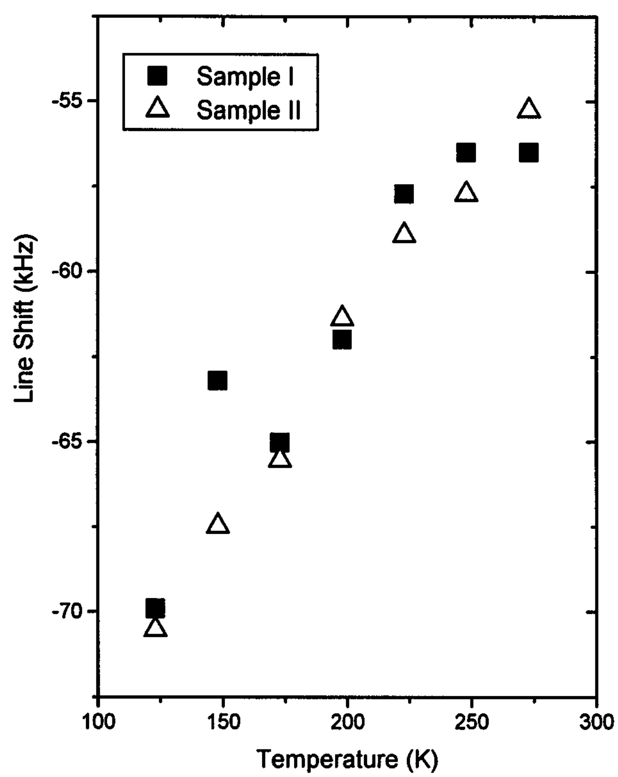

FIG. 5. Temperature dependence of the negative line shift for the superconductive and the nonsuperconductive $Nd_2CuO_{4-x}F_y$.

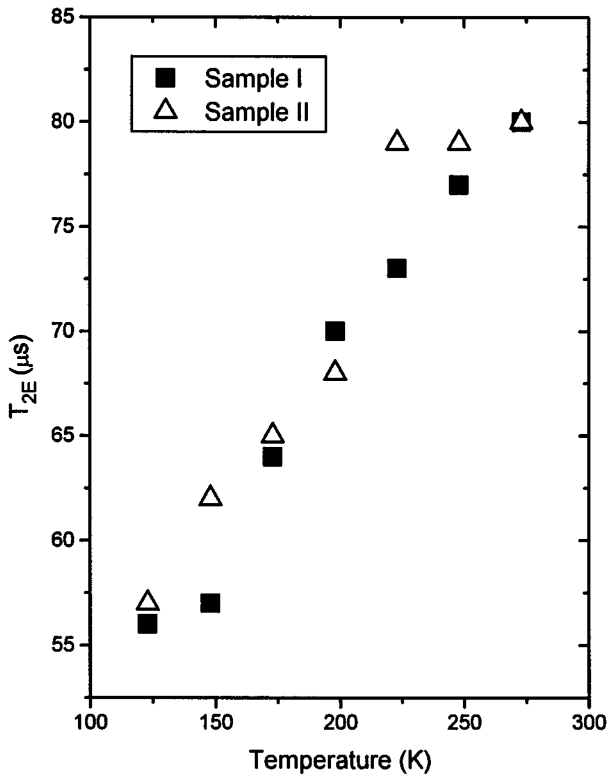

FIG. 6. Temperature dependence of spin-spin relaxation time (T_{2E}) for the superconductive and the nonsuperconductive $Nd_2CuO_{4-x}F_y$.

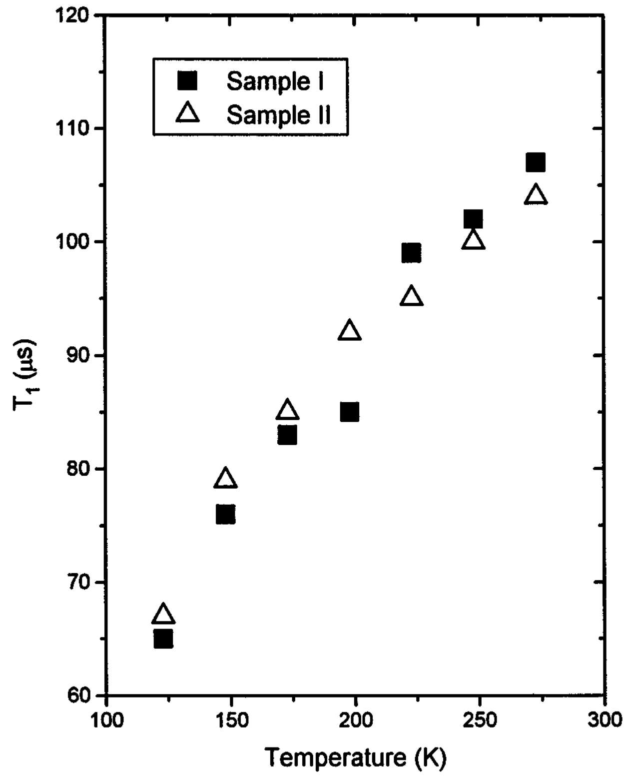

FIG. 7. Temperature dependence of spin-lattice relaxation time (T_1) for the superconductive and the nonsuperconductive $Nd_2CuO_{4-x}F_y$.

shift increases with decreasing temperature. The negative line shift indicates the presence of the core polarization.[8,16,17] The exchange interaction between non-*s* conduction electrons and local 1*s* core electrons can give rise to a contact hyperfine interaction between the local 1*s* core electrons and the nucleus, which is proportional to the spin polarization of the non-*s* band. The direction of the hyperfine field due to the core polarization is opposite to that of the applied field, causing a negative line shift. The non-*s* band Pauli susceptibility is temperature dependent, resulting in a temperature-dependent shift. A similar negative Knight shift would be found for the fluorine substituting into either of the oxygen sites.

Figure 6 shows the spin-spin relaxation time measurements. The T_{2E} also decreases with decreasing temperature for the two samples, which corresponds to a line broadening. In these samples both the T_1 and the T_{2E} are very short, with comparable values. The observed temperature dependence of the T_{2E} indicates that the fluorine nuclei are under the influence of the Nd^{3+} paramagnetic ions according to a resonant photoemission study. It shows the Nd $4f$–O $2p$ hybridization in $Nd_{1.85}Ce_{0.15}CuO_4$.[18] A Nd $4f$–F $2p$ hybridization would be possible if the doped F^- ions substitute for the O(2) sites between the Nd planes in $Nd_2CuO_{4-x}F_y$. By this hybridization, the F nucleus will be directly affected by the Nd $4f$ electrons. It should also be noted that the Cu $2d$–F $2p$ hybridization would yield a similar result.

Figure 7 shows the spin-lattice relaxation time measurements. While the T_1 increases with decreasing temperature in most solids, it decreases with decreasing temperature for both samples of $Nd_2CuO_{4-x}F_y$. This temperature dependence may be explained by the Kondo effect observed in this system. An electrical resistivity minimum at low temperatures, the Kondo effect, arises from the exchange interactions between the localized magnetic moments and the conduction electrons.[19–21] The rare earth $4f$ electrons are highly localized and the direct coupling between localized Nd^{3+} moments is negligibly small except at very low temperatures. Thus the rare earth metallic system $R_{2-x}Ce_xCuO_4$ can show the Kondo effect even in the nondilute case.[22,23] A Kondo effect was also observed in the $Nd_2CuO_{4-x}F_y$,[3] which may cause the magnetic fluctuation of the Nd $4f$ electrons to increase with decreasing temperature, leading to the greater spin-lattice relaxation rates. However, this argument can work only on the assumption that the conduction electrons are delocalized enough to influence the F site in any case.

The observed NMR behaviors (T_1, T_{2E}, and the negative line shift) of the superconductive and the nonsuperconductive $Nd_2CuO_{4-x}F_y$ are very similar in the whole temperature range. This seems to indicate that the microscopic environment at the substituted oxygen site is very similar in the two samples in the normal state, and that the fluorines are more likely to be substituted into the interplane O(2) sites, since the conductive CuO_2 plane environments are expected to be noticeably different in the two systems.

In summary, the normal state ^{19}F NMR behaviors of the superconductive and the nonsuperconductive $Nd_2CuO_{4-x}F_y$ were observed to be nearly identical. The temperature dependences of the spin-lattice relaxation time (T_1) and the spin-spin relaxation time (T_{2E}), and the negative line shift were also explained. Our results indicate that the fluorine substitution is more likely to occur in the O(2) sites between the Nd planes in the $Nd_2CuO_{4-x}F_y$ system.

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[1] H. Takagi, S. Uchida, and Y. Tokura, Phys. Rev. Lett. **62**, 1197 (1989).

[2] A. C. W. P. James, S. M. Zahurak, and D. W. Murphy, Nature **388**, 240 (1989).

[3] J. Sugiyama, Y. Ojima, T. Takata, K. Sakuyama, and H. Yamauchi, Physica C **173**, 103 (1991).

[4] M. Alexander, H. Romberg, N. Nücker, P. Adelmann, J. Fink, J. T. Markert, M. B. Maple, S. Uchida, H. Takagi, Y. Tokura, A. C. W. P. James, and D. W. Murphy, Phys. Rev. B **43**, 333 (1991).

[5] J. Sugiyama, R. Itti, H. Yamauchi, N. Koshizuka, and S. Tanaka, Phys. Rev. B **45**, 4952 (1992).

[6] S. M. Butorin, V. R. Galakhov, E. Z. Kurmaev, S. M. Cheshnitsky, S. A. Lebedev, and E. F. Kukovitzkii, Phys. Rev. B **47**, 9035 (1993).

[7] L. C. Hebel and C. P. Slichter, Phys. Rev. **133**, 1504 (1957).

[8] A. M. Clogstone, A. C. Gossard, V. Jaccarino, and Y. Yafet, Rev. Mod. Phys. **36**, 170 (1964).

[9] R. E. Walstedt, W. W. Warren, Jr., R. Tycko, R. F. Bell, G. F. Brennert, R. J. Cava, L. Schneemeyer, and J. Waszczak, Phys. Rev. B **38**, 9303 (1988).

[10] A. J. Vega, W. E. Farneth, E. M. McCarron, and R. K. Bordia, Phys. Rev. B **39**, 2322 (1988).

[11] A. J. Millis, H. Monien, and D. Pines, Phys. Rev. B **42**, 167 (1990).

[12] M. Takigawa, A. P. Reyes, P. C. Hammel, J. D. Thompson, R. H. Heffner, Z. Fisk, and K. C. Ott, Phys. Rev. B **43**, 247 (1991).

[13] F. Borsa, A. Rigamonti, M. Corti, J. Ziolo, O-B. Hyun, and D. R. Torgeson, Phys. Rev. Lett. **68**, 698 (1992).

[14] J. Sugiyama, T. Machi, I. Tomeno, H. Yamauchi, N. Koshizuka, and H. Yasuoka, Physica C **214**, 316 (1993).

[15] E. F. Kukovitzkii, R. G. Mustafin, and G. B. Teitelbaum, Physica C **169**, 643 (1990).

[16] D. E. MacLaughlin, *The Solid State Physics* (Academic Press, New York, 1976), Vol. 31, p. 13.

[17] R. M. White, *Quantum Theory of Magnetism* (McGraw-Hill, New York, 1970), p. 88.

[18] H. Namatame, A. Fujimori, Y. Tokura, M. Nakamura, K. Yamaguchi, A. Misu, H. Matsubara, S. Suga, H. Eisaki, T. Ito, H. Takagi, and S. Uchida, Phys. Rev. B **41**, 7205 (1990).

[19] C. Kittel, *Introduction to Solid State Physics*, 6th ed. (John Wiley and Sons, New York, 1988), p. 598.

[20] J. Kondo, *The Solid State Physics* (Academic Press, New York, 1969), Vol. 23, p. 183.

[21] A. J. Heeger, *The Solid State Physics* (Academic Press, New York, 1969), Vol. 23, p. 283.

[22] J. L. Peng, R. N. Shelton, and H. B. Radousky, Phys. Rev. B **41**, 187 (1990).

[23] B-H. O and J. T. Markert, Synth. Met. **71**, 1579 (1995).