

19 F NMR in the La-Sr-Cu-O(F) system

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The effects of the substitution of fluorine for oxygen in a lanthanum-strontium superconductor have been studied. The fluorine nuclei undergo a relaxation through current carriers. The size of the superconducting gap is determined.

The replacement of oxygen by other anions yields important information about the role and properties of oxygen holes in high- T_c superconductivity and makes it possible to bring new research methods into the effort.¹⁻³ In this regard, the replacement of oxygen by fluorine, as in the present experiments, has two important distinguishing features. First, from the standpoint of electronic structure, the fluorine ion F^{-1} and the oxygen ion O^{-2} have an identical outer shell, with the p^6 configuration. Second, among the halogens only the ^{19}F nucleus, with a spin $I = 1/2$, does not have a quadrupole moment and does have a large gyromagnetic ratio. This circumstance, which facilitates the observation of NMR at fluorine, has made it possible to carry out the study which we are reporting here, of the spin relaxation of fluorine nuclei in a superconducting lanthanum-strontium ceramic, and to obtain information about the nature of the current carriers. The test samples were prepared by two types of solid-phase synthesis. In the first method, lanthanum fluoride and cupric oxide were added to the original $La_{1.8}Sr_{0.2}CuO_4$ sample, and the synthesis was repeated (annealing at 1050 °C for 10 h). In the second method, a sample of $La_{1.8}Sr_{0.2}CuO_{4-x}F_x$ was prepared at the outset by solid-phase synthesis. Some of the La_2O_3 in the starting material was replaced by LaF_3 . The synthesis conditions were an annealing of the starting composition at 1000 °C for 10 h, regrinding, pressing, and repeated annealing at 1050 °C for 10 h. An x-ray method was used to determine the extent to which the samples were of a single phase.

To determine the superconducting transition temperatures in the samples with the various fluorine concentrations, we studied the behavior of the magnetic susceptibility; the slope changes on these curves correspond to the onset of the superconducting transition, T_{∞} (Fig. 1). Nearly all the samples underwent phase transitions at two temperatures: a first one at 38 K and a second at 28 K. This behavior can be interpreted as resulting from the presence of two phases with different fluorine arrangements, which are not manifested in the x-ray data. Since the ionic radii of F^{-1} and O^{-2} are the same, we would expect that the fluorine would assume oxygen positions. There are two possibilities here: a replacement of oxygen at the vertices of a CuO_6 octahedron and a replacement of oxygen in a CuO_2 plane.

The NMR was studied on a Bruker CXP-100 spectrometer at a frequency of 57 MHz over the temperature range 12-300 K. Figure 2 shows the evolution of the NMR signal, with a gyromagnetic ratio $\gamma_n = 2.52 \times 10^4 G^{-1} \cdot s^{-1}$, which is characteristic of the fluorine nucleus ^{19}F . We see that the temperature dependence of the linewidth is

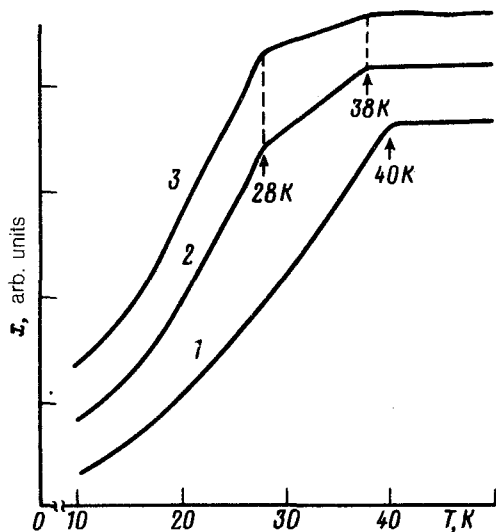


FIG. 1. Temperature dependence of the magnetic susceptibility χ_{ac} of $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{2-x}\text{F}_x$ samples with various fluorine concentrations x : 1— $x=0$; 2— $x=0.26$; 3— $x=0.52$.

weak: Lowering the temperature from 150 K to 20 K reduces the linewidth at half-maximum from 31 kHz to 29 kHz. At 10 K, the lines broaden again, to 31 kHz. The center of the NMR line is shifted with respect to the marker (an aqueous solution of KF) by $\Delta f = +5$ kHz. Measurements of the nuclear spin echo, carried out in a magnetic field gradient, yielded a transverse relaxation time $T_2 = 1.6 \times 10^{-5}$ s. From a

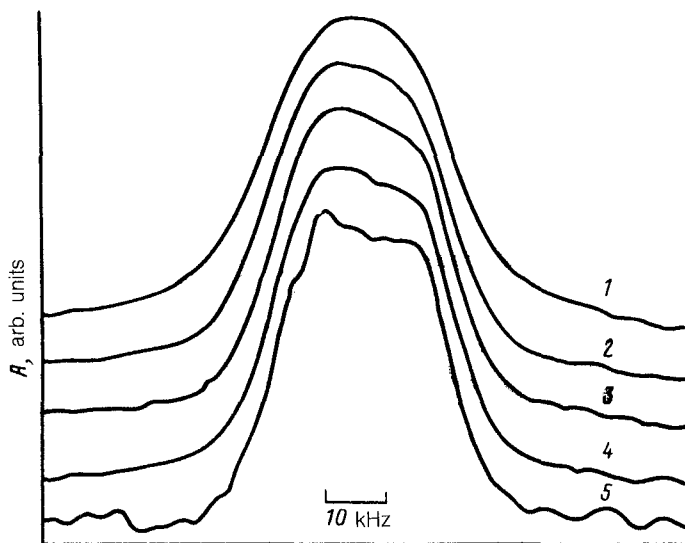


FIG. 2. NMR spectrum of ^{19}F nuclei in an $\text{La}_{1.83}\text{Sr}_{0.17}\text{CuO}_{2.96}\text{F}_{1.04}$ sample at various temperatures T : 1— $T=10$ K; 2— $T=20$ K; 3— $T=30$ K; 4— $T=40$ K; 5— $T=120$ K.

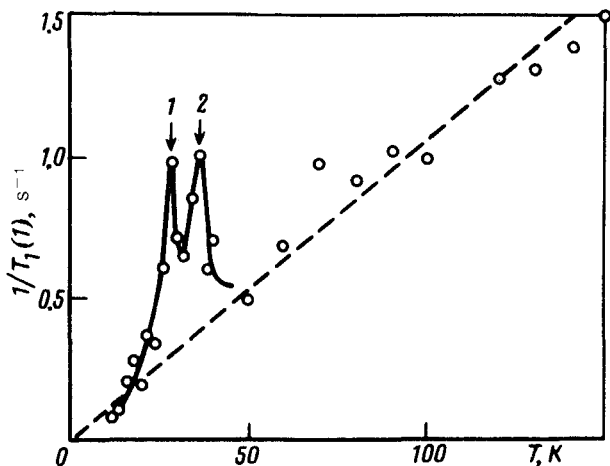


FIG. 3. Temperature dependence of the rate of spin-lattice relaxation of ^{19}F nuclei in the F(1) position of an $\text{La}_{1.83}\text{Sr}_{0.17}\text{CuO}_{2.96}\text{F}_{1.04}$ sample. 1— $T=28$ K; 2— $T=38$ K. The slope of the dashed line is $B = 1.1 \times 10^{-2} \text{ s}^{-1} \cdot \text{K}^{-1}$.

comparison of T_2^{-1} with the linewidth we conclude that the contributions of homogeneous and inhomogeneous broadening are comparable in magnitude.

In addition to these measurements, we studied the longitudinal nuclear relaxation by a saturation method with the help of a train of 90° pulses. The saturation of the longitudinal magnetization is described well by the sum of two exponential functions of the time. This result appears to be a consequence of the presence of two nonequivalent positions of fluorine atoms, F(1) and F(2). We denote the corresponding longitudinal relaxational times by $T_1(1)$ and $T_1(2)$; $T_1(2)$ is shorter than $T_1(1)$ and depends only weakly on the temperature at high temperatures. The relaxation rate $1/T_1(1)$ (Fig. 3) is described at $T > T_c$ by the Korringa law,⁴ which is customary for a relaxation through current carriers:

$$[1/T_1(1)]_n = (16/9)\pi^3 \hbar^3 \gamma_e^2 \gamma_n^2 u_f^2 \rho^2(E_f) \cdot kT = B \cdot T, \quad (1)$$

where $B = (1.1 \pm 0.1) \times 10^{-2} \text{ s}^{-1} \cdot \text{K}^{-1}$, and $\rho(E_f)$ is the density of states (per atom) at the Fermi level. The relaxation rate of the fluorine nuclei is lower by nearly an order of magnitude than that of ^{17}O nuclei in the CuO_2 plane of the Y-Ba-Cu-O compound (in which we have⁵ $B = 6 \times 10^{-2} \text{ s}^{-1} \cdot \text{K}^{-1}$), despite the fact that the electron densities at the nucleus, u_f , should be comparable in magnitude in view of the similarity of the electronic structures of F^{-1} and O^{-2} , while the gyromagnetic ratio for oxygen is significantly smaller, $\gamma_n = 0.36 \times 10^7 \text{ G}^{-1} \cdot \text{s}^{-1}$. The reason for the slowing of the relaxation is that the local carrier density at the fluorine position is extremely low. Working from the known values of the carrier density of states (per unit cell) in the yttrium-barium and lanthanum-strontium ceramics [6.3 eV^{-1} (Ref. 6) and 2.7 eV^{-1} (Ref. 7), respectively], we can estimate the ratio of the densities of states at fluorine and oxygen in the system under study here: $\rho_F(E_f) \rho_O(E_f) \approx 0.1$. The apparent reason

for this decrease in the local density of holes at fluorine is the greater electronegativity of fluorine.

After the transition to the superconducting state (at 28 and 38 K), the relaxation rate $[1/T_1(1)]_S$ increases sharply, undergoing the characteristic jump which is linked with an increase in the density of states upon the formation of a gap near the Fermi level.⁸ The fact that there are two jumps, at different temperatures, correlates with the two slope changes on the curve of the diamagnetic susceptibility (Fig. 1). The apparent reason for these two jumps is the existence of two regions, with typical dimensions greater than the coherence length $\xi \approx 2 \times 10^{-7}$ cm, which differ in fluorine concentration. The relaxation occurs at different rates in these two regions. Experimentally, on the other hand, as a result of spin diffusion, we observe a magnetization averaged over the diffusion length $L_S = (DT_1)^{1/2}$, in whose relaxation both jumps are manifested. Here the sizes of the regions with the different values of T_c would have to be smaller than L_S . Since the spin diffusion coefficient is $D_S \approx a^2/T_2$, by using the value $a = 3.7 \times 10^{-8}$ cm and the measured values $T_2 = 1.6 \times 10^{-5}$ s and $T_1 = 1$ s we find $L_S \approx 8 \times 10^{-6}$ cm. The relative change in relaxation rate upon the superconducting transition is $[1/T_1(1)]_S/[1/T_1(1)]_n = 2.5$, where $[1/T_1(1)]_n = BT_{co}$ (the rate of spin-lattice relaxation in the normal state). At temperatures below $T_{co} = 28$ K, the relaxation rate $[1/T_1(1)]_S$ falls off as $\exp(-\Delta/kT)$, and we find the value $2\Delta/kT_{co} = 3.0 \pm 0.5$.

The presence of a Korringa relaxation and the jump in the relaxation rate $[1/T_1(1)]_S$ near the superconducting transition both point to a direct contact of fluorine in the F(1) position with current carriers. We can thus conclude that F(1) replaces oxygen in CuO_2 planes. Correspondingly, F(2) replaces oxygen at the vertices of the octahedron. Below $T_{co} = 28$ K the relaxation rate $[1/T_1(2)]_S$ decreases and acquires a temperature dependence which can be described by $[1/T_1(2)]_S = AT^3$. One way to explain this dependence is in terms of a relaxation through magnetic fluctuations at d electrons of copper.⁹

We should point out that the compound is unstable just after the synthesis. A superconducting transition and a jump in the relaxation rate (a greater jump) are observed only at a single temperature (28 K). As time elapses, however, the system goes into a two-phase state, and a month after the synthesis or after several cycles between liquid-helium temperature and room temperature the stable pattern described above is established.

In summary, the jumps in the relaxation rate of the fluorine nuclei are evidence that the superconducting gap is isotropic, i.e., that the pairing of the current carriers is an s pairing. These carriers are *p* holes, which, by virtue of the low local density of states at fluorine nuclei, lead to a slow spin-lattice relaxation.

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