# Magnetic correlations in the electron superconductor $Pr_2CuO_{4-x}F_x$ based on NMR data

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A reversible transition to an antiferromagnetically correlated state occurs in the normal phase of $Pr_2CuO_{4-x}F_x$. This transition increases the rate of nuclear spin relaxation by two orders of magnitude.

The superconducting metal oxides with an electron conductivity are distinguished from the hole-conductivity superconductors in that the suppression of magnetism by current carriers is far weaker. Just how this circumstance affects the interplay between the superconducting and magnetic properties of the $CuO_2$ layers of these compounds has yet to be resolved. We believe that a local method such as NMR may be exceedingly useful for resolving this question. Since a study of the magnetic properties of the $CuO_2$ planes in the electron superconductors is hindered by the magnetism of the rare-earth ions, there is particular interest in compounds in which these ions are in a singlet state, for which the magnetic fluctuations are typically frozen.

Our purpose in the present study was to use the NMR of $^{19}F$ in $Pr_2CuO_{4-x}F_x$ to study the dynamics of the magnetization of the $CuO_2$ layers in the normal and superconducting states. In this particular compound, the electron conductivity arises when oxygen is replaced by fluorine.[1] Most of the fluorine ions occupy oxygen sites in the $Pr_2O_2$ rare-earth layer; a much smaller number occupy sites in the $CuO_2$ plane.[1]

**1.** The ceramic $Pr_2CuO_{4-x}F_x$ ($x=0.26$) samples were prepared by the standard solid-phase synthesis procedure and then annealed in vacuum. The fluorine content ($x$) in a sample was set by the amount of PrOF in the starting material. An x-ray study of the as-synthesized compound verified that the compound had a tetragonal ($T'$) structure and that there were no traces of other phases. The superconducting transition temperature of the test samples was 22 K, according to ac susceptibility measurements.

**2.** The NMR was studied on a Bruker pulsed spectrometer at a frequency of 57 MHz in the temperature range 10–300 K. The NMR spectrum of $^{19}F$ consisted of two lines (high-field line $A$ and low-field line $B$), with negative Knight shifts which increase with decreasing temperature (Fig. 1). The two lines are identical in width. This width has a temperature dependence similar to that of the Knight shift of line $A$. The ratio of the intensities of these two lines varies with the temperature. For the series of samples which we studied, the intensities of the two lines are about the same at temperatures above $T^* \simeq 100$ K; below T*, the intensity of line $A$ falls off. At $T^{**} \simeq 30$ K it begins to rise again (correspondingly, line $B$ is predominant in the spectrum at temperatures 30–70 K).

At high temperatures, the spin-lattice relaxation rates $T_1^{-1}$ corresponding to the

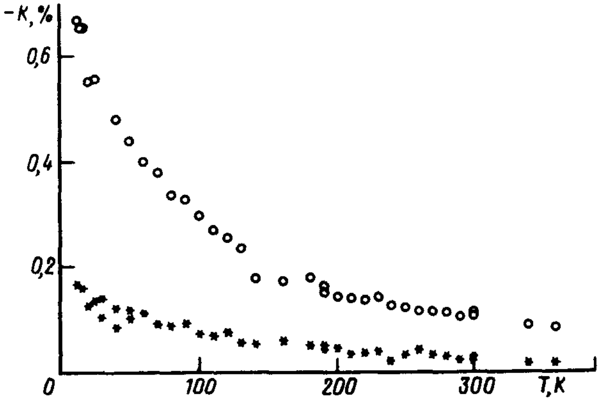

FIG. 1. Temperature dependence of the Knight shift K of $^{19}F$ nuclei in $Pr_2CuO_{3.74}F_{0.26}$ according to measurements at a frequency of 57 MHz. ○—Line *A*; *—line *B*.

two lines are identical (Fig. 2a); these rates fall off with decreasing temperature. Near $T^*$, they rise by more than an order of magnitude and then remain almost constant as the temperature is lowered further. At $T < T_c$, the relaxation rate $T_{1A}^{-1}$ falls off exponentially with decreasing temperature, while $T_{1B}^{-1}$ does not change at the superconducting transition (here and below, subscripts *A* and *B* specify properties corresponding to the two lines).

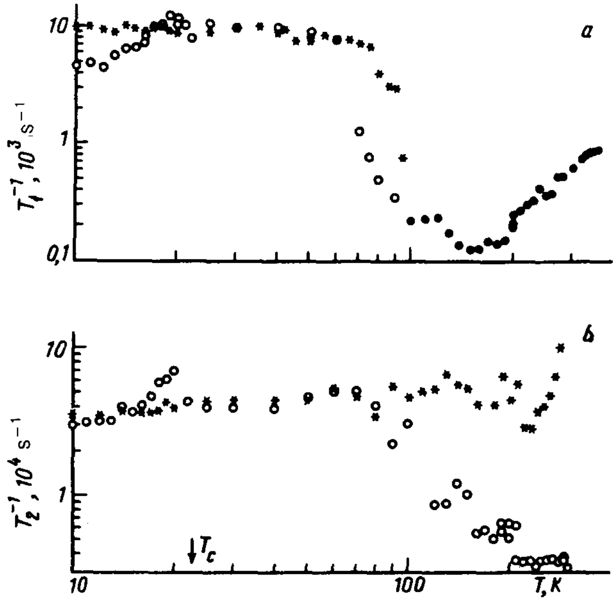

FIG. 2. Temperature dependence of the relaxation rates of $^{19}F$ nuclei in $Pr_2CuO_{3.74}F_{0.26}$ according to measurements at 57 MHz. ○—Line *A*; *—line *B*. a) Spin-lattice relaxation $T_1^{-1}$ [at high temperatures $T > T^* \sim 100$ K, the rates $T_1^{-1}$ for the two lines are equal (●)]; b) transverse relaxation rate $T_2^{-1}$.

The transverse relaxation rate $T_{2B}^{-1}$ is a weak function of the temperature, while $T_{2A}^{-1}$ increases $\propto 1/T$ as the temperature is lowered to $T^*$ (Fig. 2b). Below $T^*$, the rate $T_{2A}^{-1}$ varies slowly, but near $T_c$ its increase gives way to an sharp decrease.

3. The temperature dependence of the Knight shift of line $A$ at $T > 30$ K reproduces the behavior of the transverse susceptibility of praseodymium, $\chi_{\mathrm{Pr}}$. We can thus assume that it is due to a hyperfine interaction with $\mathrm{Pr}^{+3}$ ions. Working from the known values[2] of $\chi_{\mathrm{Pr}}$, we can determine the hyperfine coupling constant of the $^{19}$F nucleus with the $\mathrm{Pr}^{+3}$ magnetic moment: $A_{\mathrm{sf}} = KN_a\mu_{\mathrm{B}}/\chi_{\mathrm{Pr}}$, where $K$ is the Knight shift, $N_a$ is Avogadro's number, and $\mu_{\mathrm{B}}$ is the Bohr magneton. For line $A$ we find $A_{\mathrm{sf}} = 2970\ \mathrm{Oe}/\mu_{\mathrm{B}}$. Since the temperature dependence of the width of each line and that of the Knight shift of line $A$ are identical, we conclude that the broadening is due to a scatter in the static local fields, which is the same for all the $^{19}$F nuclei.

The reason for the appearance of line $B$ is that some of the nuclei are subjected to an additional internal field due to the magnetic moments of electrons localized near structural defects associated with deviations from stoichiometry. According to our estimates, this field varies from 10 to 70 Oe as the temperature is lowered from 300 to 10 K. [Since there are no quadrupole effects, the particular features of the NMR associated with the existence of different sites for $^{19}$F nuclei ($I = 1/2$) are not manifested.]

Near a localized electron, a region with developed antiferromagnetic correlations forms. These correlations make the transverse relaxation rate $T_{2B}^{-1}$ large in comparison with $T_{2A}^{-1}$. The field shift between the $A$ and $B$ lines at $T > T^*$ has a Curie-like temperature dependence $\propto (T+\theta)^{-1}$ with $\theta = -40$ K. This temperature dependence implies that the effective internal field is antiferromagnetic. The distribution of this field along the sample determines the relative intensities of the $A$ and $B$ signals. While this field acts in only a relatively small volume at high temperatures, as the temperature is lowered, the number of localized moments increases, as does the total volume of antiferromagnetically correlated regions. As a result, there is a significant intensification of line $B$, and a magnetic ordering occurs at $T^*$ in the external field (at least in the $\mathrm{CuO_2}$ planes). This tendency toward an antiferromagnetism can explain why $T_{2A}^{-1}$ increases with decreasing temperature, reaching $T_{2B}^{-1}$ at temperatures on the order of $T^*$.

As the temperature is lowered further, the long-range interaction between magnetic defects causes these defects to begin to freeze in random orientations at $T \sim T^{**}$. This effect causes variations in the internal field; on the other hand, the frustrating effect of the randomly oriented moments disrupts the magnetic order.[3] As a result, signal $A$ intensifies, while $B$ weakens. In the former case, the signal comes from $^{19}$F nuclei in regions in which the long-range order has been disrupted, and a superconductivity has arisen; in the latter case, it comes from nuclei in regions which have not gone superconducting.

4. We might expect that, like the Knight shift, the relaxation of the fluorine nuclei would be governed by the magnetism of praseodymium and would depend on the population of its excited magnetic levels. However, it has not been found possible to describe the temperature dependence of $T_1^{-1}$ (Fig. 2a) on the basis of the energy-

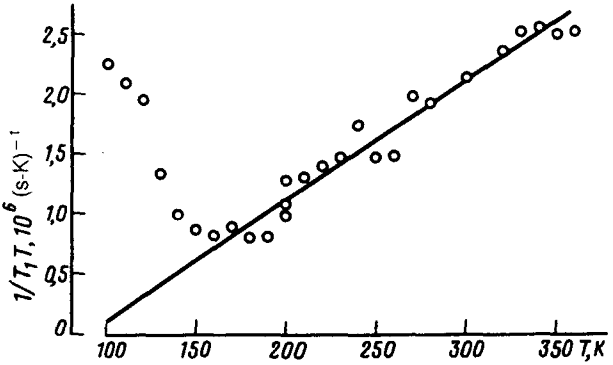

FIG. 3. Temperature dependence of the susceptibility of a $CuO_2$ plane, $\chi/\Gamma \propto (T_1T)^{-1}$, demonstrating the linear decay at high temperatures: $(T_1T)^{-1}=C(T+\theta)$, where $C=10^4\ s^{-1}\cdot K^{-2}$ and $\theta=-90$ K.

level structure determined from neutron-scattering experiments[4] (the distance to the first magnetic excited level of the $Pr^{+3}$ ion is $\Delta=180$ K). The implication is that the relaxation of the $^{19}F$ nuclei stems from fluctuating fields induced by magnetic moments from $CuO_2$ planes. The spin-lattice relaxation rate would then be

$$T_1^{-1}=kT\sum_q A_q^2 \mathrm{Im}\chi(q,\omega_n)/\omega_n, \tag{1}$$

where $\chi(q,\ \omega_n)$ is the magnetic susceptibility transverse with respect to the external field, $q$ is the wave vector, $\omega_n$ is the NMR frequency, and $A_q$ is the hyperfine interaction constant[5-7]. In our case, the possible positions of fluorine (in the $Pr_2O_2$ and $CuO_2$ planes) are symmetric with respect to copper ions. Accordingly, if the magnetic moments of the latter are antiferromagnetically correlated, the contributions to the local field at fluorine corresponding to the wave vector $Q=(\pi/a,\ \pi/a)$ cancel out, and an antiferromagnetic acceleration of the relaxation does not occur. Consequently (at least at $T>T^*$), the rate $T_1^{-1}$ is dominated by the uniform susceptibility $\chi(0)$, and we have $(T_1T)^{-1}\propto\chi(0)\Gamma$ (Fig. 3), where $\Gamma$ is a characteristic rate of electron spin relaxation corresponding to a zero wave vector.

The high transverse relaxation rate $T_2^{-1}$ (Fig. 2b) and the nature of its temperature dependence indicate that this relaxation is related to an indirect interaction[8] of nuclear spins of fluorine through magnetic moments of copper ions of $CuO_2$ planes. The transverse relaxation is governed by the time scale of spin diffusion over a distance on the order of the size of the antiferromagnetically correlated regions ($l_{AF}$), which is related to the antiferromagnetic susceptibility $\chi_{AF}(Q)$. Here we have $T_2^{-1}\propto l_{AF}^2\propto\chi_{AF}(Q)$.

Comparison of these formulas with the experimental curves allows us to discuss the behavior of the susceptibilities $\chi(0)$ and $\chi_{AF}(Q)$. At $T>T^*$, these susceptibilities behave in the same way as in hole superconductors: $\chi(0)$ decreases with decreasing temperature ($\Gamma$ depends only weakly on the temperature). The increase in $(T_1T)^{-1}$ near $T^*$ (Fig. 3) stems from the onset of a long-range order in the orien-

TABLE I.

| | 1-2-3 ($O_7$) | 1-2-3 ($O_{6.63}$) | La-$Sr_{0,15}$ | $Pr_2CuO_{4-x}F_x$ |
|---|---|---|---|---|
| $T_c$(K) | 90 | 60 | 40 | 22 |
| $\theta$(K) | 113 | -30 | -38 | -90 |

tation of the antiferromagnetic regions in the external magnetic field. It follows from an analysis of Fig. 2b that at $T > T^*$ the antiferromagnetic susceptibility $\chi_{AF}(Q)$ increases with decreasing temperature $\propto (T+\theta)^{-1}$ with $\theta = -90$ K. This behavior of the susceptibility is also characteristic of hole superconductors. As $T_c$ is lowered, the temperature $\theta$ increases (Table I),[7] but for $Pr_2CuO_{4-x}F_x$, in contrast with other systems, we have $|\theta| > T_c$, and a magnetic ordering occurs at temperatures on the order of $\theta$. Admittedly, as was mentioned above, this ordering is reversible; the order is disrupted by long-range magnetic defects as the temperature is lowered further.[3] At the superconducting transition, the number of normal quasiparticles decreases, causing a decrease in the relaxation rates $T_{1A}^{-1}$ and $T_{2A}^{-1}$ (Fig. 2, a and b). In contrast with the case of hole superconductors, however, the relaxation rate decays to a level comparable to the rate in the normal state. It follows that even at $T < T_c$ the magnetic susceptibility is comparable to the corresponding quantity in the normal phase, possibly because of the presence of unfrozen spin degrees of freedom.

5. The fundamental distinction between $Pr_2CuO_{4-x}F_x$ and hole superconductors is thus the stronger manifestation of antiferromagnetic properties. In particular, a reversible transition to a state with a magnetic order in the $CuO_2$ plane can occur in the normal phase of compounds of superconducting composition in an external magnetic field, at temperatures $T \sim T^* \sim \theta$. This magnetically ordered state is disrupted at temperatures $T^{**} \geqslant T_c$.

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