PROTON RELAXATION IN THE ORGANIC SUPERCONDUCTOR $(BEDT\text{-}TTF)_2Cu(NCS)_2$

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The origin of the nonexponentiallity of the proton spin-lattice relaxation in the organic superconductor $(BEDT\text{-}TTF)_2Cu(NCS)_2$ is clarified. In fine powders the nonexponentiallity results from localized paramagnetic centers whose concentration is nonuniform over the powder sample. In coarse grains at low temperatures it is due to finite penetration of the rf-field into the conducting grains.

The study of organic conductors and superconductors by proton relaxation has by now become an almost standard technique to get information about the distribution of the spin density of the conduction electrons and about the nature of the transition to the superconducting state [see, e.g.,1]. The raw data are always assuming that the dipole-dipole and the contact interaction of the conduction electrons with the protons is the dominant relaxation mechanism at $T \leq 100K$. For such mechanisms exponential relaxation of the protons is expected. By contrast in essentially all published relaxation studies of organic superconductors a deviation from this behavior is reported. The nonexponential character of the build-up of the nuclear magnetization usually increases on lowering the temperature.

We made the same observations in an investigation of the proton spin relaxation in $(BEDT\text{-}TTF)_2Cu(NCS)_2$ which is an organic conductor at room temperature and becomes a superconductor at T_c=10.4 K.

As we noticed during preliminary measurements that the degree of deviation from exponential relaxation depends on the sample under study we decided to do experiments under controlled conditions of sample preparation. Two kinds of samples were prepared. The first consists of coarse grains of crystals of

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$(BEDT-TTF)_2Cu(NCS)_2$ of approximate size $1*0.5*0.1$ mm^3. The second was obtained by powdering the original crystals. This process resulted in a fine powder of microcrystallites of approximate size $10*10*5$ μm^3. For both kinds of samples we measured the relaxation function

$$p(\Delta t) \equiv 1 - M_z(\Delta t)/M_o \qquad (1)$$

with $M_o = M_z(\Delta t \to \infty)$ and Δt=delay after establishing the initial condition $M_z(0)=0$. The Larmor frequencies (fields) were ν_L = 270 MHz (B_o = 6.3T) and ν_L = 13.5 MHz (B_o= 0.31T). For T $\le$ 8.3K the latter field is below B_{c2} of $(BEDT-TTF)_2$ $Cu(NCS)_2$ and allows NMR and relaxation experiments right in the superconducting state.

The key result on the finely powdered samples at ν_L= 13.5 MHz and T $\le$ 100K is the establishment of an *exponential-square-root* relaxation law

$$p(\Delta t) = \exp(-\sqrt{\Delta t/\tau_1}). \qquad (2)$$

This law is clearly inconsistent with the assumption that proton-conduction electron coupling provides for the dominant relaxation mechanism. Nonexponential relaxation may be obtained if the sample is inhomogeneous and a distribution of relaxation rates exists. $p(\Delta t)$ is then given by

$$p(\Delta t) = \int_0^\infty f(1/T_1)\exp(-\Delta t/T_1)d(1/T_1) \qquad (3)$$

where $f(1/T_1)$ is the distribution function. The relaxation law, equation 2, then determines the shape of $f(1/T_1)$.

If the sample consists of coarse grains of $(BEDT-TTF)_2Cu(NCS)_2$, we observe at ν_L= 13.5 MHz exponential relaxation for T>25K and nonexponential relaxation for T<25K.

Figure 1 shows the return to thermal equilibrium of the proton magnetization in coarse grains (△) and in a finely powdered sample (□) at T = 30K and ν_L= 13.5 MHz. The full curve through the squares (□) is $M_x(\Delta t)/M_x(\infty)$ = $(1-\exp(-\sqrt{\Delta t/\tau_1}))$ with $1/\tau_1$ = 0.133 s^{-1} while the full curve through the triangles (△) is $M_x(\Delta t)/M_x(\infty)$ = $(1-\exp(-\Delta t/T_1))$ with $1/T_1$ = 0.028 s^{-1}. This figure thus demonstrates (i) that the relaxation in the *coarse grains* of $(BEDT-TTF)_2Cu(NCS)_2$ is *exponential* at T= 30K while it obeys the *exponential-square-root* law in the *finely powdered* sample and (ii) that the over-all relaxation is much faster in the finely powdered sample than in coarse grains. The conclusion, we think, is inevitable that the process of powdering the coarse grains introduced relaxation sinks into the resulting microcrystallites. $1/\tau_1$ is found to be independent of T for 8K<T<100K. This is taken as evidence that the relaxation sinks introduced by the powdering procedure are localized paramagnetic centers. Their concentration is estimated at $\approx 10^{17}cm^{-3}$ or $\approx 10^{-4}$ per BEDT-TTF molecule.

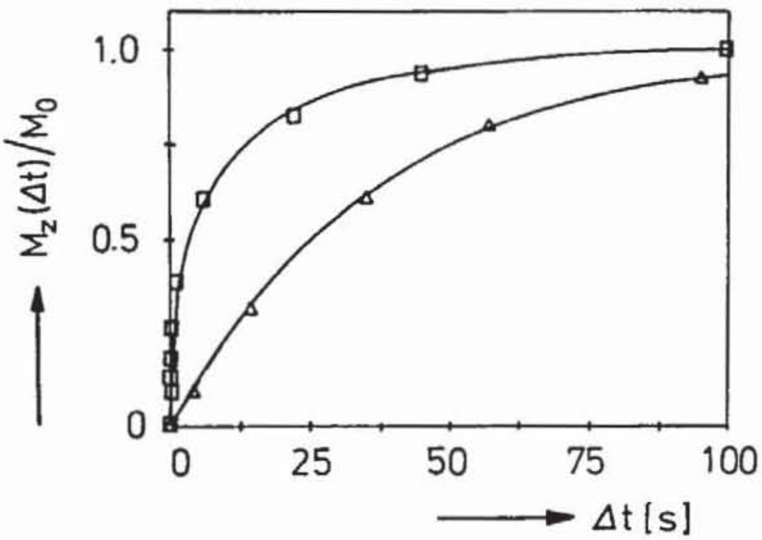

Fig.1: Comparison of the recovery of the proton relaxation in coarse grains (Δ) and in finely powdered $(BEDT\text{-}TTF)_2Cu(NCS)_2$ (□) at ν_L=13.5MHz and T=30K. Full curve through squares (□): $\exp(-\sqrt{\Delta t/\tau_1})$ with $1/\tau_1=0.133s^{-1}$, full curve through triangles (Δ): $\exp(-\Delta t/T_1)$ with $1/T_1=0.028s^{-1}$.

In the coarse grains the recovery of the magnetization becomes increasingly nonexponential on decreasing T for T≤25K. Starting from essentially the same temperature the initial amplitude $M_x(\Delta t\to\infty)$ of the FID after a 90^o-pulse, which should be proportional to M_o, deviates from the Curie law, see figure 2. This is clearly a result of finite penetration of the rf-field into the conducting grains. Indeed for the finely powdered sample $M_x(\Delta t\to\infty)$ follows the Curie law down to 4.2 K, see figure 2. Figure 2 shows another remarkable feature namely that the skin-effect is much smaller at 270 than at 13.5 MHz. This is evidence that the electrical conductivity σ is a *decreasing* function of the frequency ν.

A simple two-reservoir model which devides the proton spins in the coarse grains into two groups, the first of which is accessed by the rf-field while the second is not, shows that the observed relaxation behavior must indeed be nonexponential if the rf-field penetrates only partially into the grains. This explains in a natural way why the nuclear magnetization observed in a pulsed NMR experiment recovers nonexponentially in the neighbourhood of T_c, and below T_c.

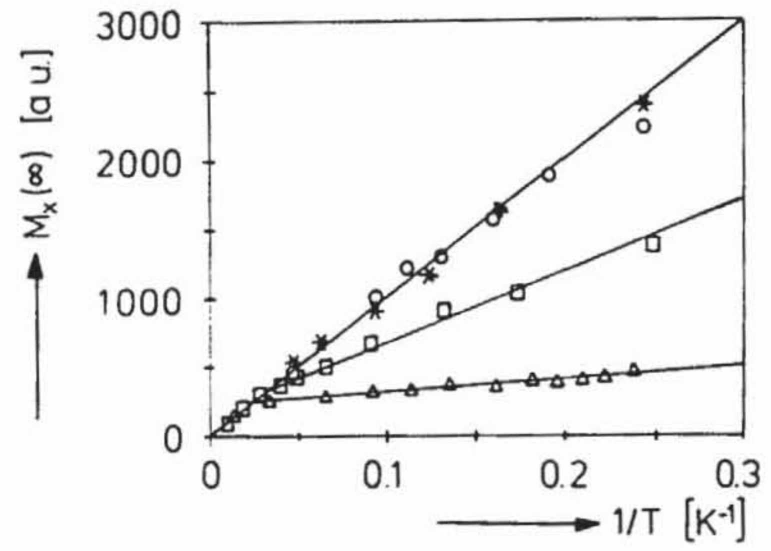

Fig.2: Initial amplitude $M_x(\infty)$ of the FID for coarse grains measured at ν_L=13.5MHz (△) and ν_L=270MHz (□) and for finely powdered $(BEDT\text{-}TTF)_2Cu(NCS)_2$ at ν_L=13.5MHz (O) and ν_L=270MHz (*). For $1/T \leq 0.05\ K^{-1}$ only a few representative data points are shown.

The study of organic conductors and superconductors by nuclear spin relaxation is usually motivated by interest in the nuclear spin-conduction electron interaction. This was also the starting point of this work on $(BEDT\text{-}TTF)_2$ $Cu(NCS)_2$. The results presented here pinpoint the dilemma we face when we adopt this point of view: If we study coarse grains we inevitably run into the skin effect problem. It prevents us from "seeing" the spins in the bulk and causes, at low temperatures, the relaxation to become nonexponential. Powdering the grains circumvents the skin effect but extra relaxation paths are automatically created which prevent us from accessing what we initially set out to study, i.e., the conduction electron contribution to the nuclear relaxation. We believe that the results obtained here for $(BEDT\text{-}TTF)_2Cu(NCS)_2$ apply to other organic conductors and superconductors as well.

Reference

1 I.A. Heinmaa, M.A. Alla, A.M. Vainrub, E.T. Lippmaa
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