Proton Relaxation in the Superconducting Organic Solid $(BEDT-TTF)_2Cu(NCS)_2$: Evidence for Relaxation by Localized Paramagnetic Centers.

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The study of organic conductors and superconductors by proton relaxation has by now become almost a standard technique to get information about the distribitution of the spin density of the conduction electrons and the nature of the transition to the superconducting state [1-7].

To avoid exclusion of the rf-field from the conducting material nuclear magnetic resonance and relaxation measurements are usually carried out on finely powdered samples. In the analysis of the raw relaxation data it is always assumed that the dipole-dipole and the contact interaction of the conduction electrons with the protons is the dominant relaxation mechanism at $T \leq 100\,K$. For such mechanisms an exponential relaxation of the protons is expected. By contrast in essentially all reported studies of organic superconductors [1-7] a deviation from this behaviour is reported. The nonexponential character of the build-up of the nuclear magnetization usually increases on lowering the temperature. Superconducting fluctuations have been offered in a speculative way as an explanation for the nonexponential spin relaxation [1].

We have observed the same relaxation behaviour in our investigation of the proton spin relaxation in $(BEDT-TTF)_2Cu(NCS)_2$ which is an organic conductor at room temperature and becomes a superconductor at $T_c = 10.4\,K$ at ambient pressure. 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 $(BEDT-TTF)_2Cu(NCS)_2$ of approximate size $1 \times 0.5 \times 0.1\,mm^3$. The second was obtained by powderizing the original crystals in a special agate mortar. This process resulted in a fine powder of microcrystallites of approximate size $10 \times 10 \times 5\,\mu m^3$.

For these samples we measured the relaxation function $\rho(\Delta t) = 1 - M_z(\Delta t)/M_0$ with $M_0 = M_z(\Delta t \to \infty)$ and Δt = the time delay after establishing the initial condition $M_z(0) = 0$. The Larmor frequencies and fields were $\nu_L = 270\,MHz \mathrel{\hat{=}} B_0 = 6.3\,Tesla$ and additionally $\nu_L = 13.5\,MHz \mathrel{\hat{=}} B_0 = 0.31\,Tesla$. The latter field is below B_{c2} of $(BEDT-TTF)_2Cu(NCS)_2$ and allows NMR and relaxation experiments right in the superconducting phase.

The key result of our measurements on the finely powdered samples at $\nu_L = 13.5\,MHz$ and $T \leq 100\,K$ is the establishment of a relaxation law $\rho(\Delta t) = \exp - (\sqrt{\Delta t / \tau_1})$. Such a relaxation law has been predicted theoretically by McHenry et al [8] for a situation where the nuclei in a solid are relaxed by direct interactions with localized paramagnetic moments under conditions where spin diffusion plays a negligible role. We conclude therefore that direct dipole-dipole interaction of protons with localized electronic paramagnetic centers rather than dipole-dipole and contact interaction with conduction electrons provide for the major source of proton spin relaxation in finely powdered samples of $(BEDT\text{-}TTF)_2Cu(NCS)_2$ at "low" frequencies (i.e., 13.5 MHz) for $T \leq 100$ K. The postulated localized electronic centers must have been introduced into the microcrystallites by the very process of powderizing the original crystals.

At "high" frequencies i.e., $\nu_L = 270$ MHz, we observed a superposition of proton relaxation by localized electronic moments and by conduction electrons. If the sample consists of coarse grains of $(BEDT\text{-}TTF)_2Cu(NCS)_2$ we observed for $\nu_L = 270$ MHz an exponential behaviour at all temperatures T in the range $10\,K \leq T \leq 300\,K$ while for $\nu_L = 13.5$ MHz an exponential behaviour is obtained only for $T \geq 25$ K whereas for $T \leq 25$ K the recovery of the magnetization becomes increasingly nonexponential on decreasing the temperature. Starting from essentially the same temperature (≈ 25 K) the initial amplitude of the free induction decay (FID) after a 90^0-pulse, which should be proportional to M_0, deviates from the Curie law. This is clearly a result of finite penetration of the rf-field into the conducting grains. Indeed $M_z(\Delta t \rightarrow \infty)$ for the finely powdered samples follows the Curie law down to 4.2 K. A calculation for a simple two-reservoir model shows that the observed relaxation behaviour must be indeed nonexponential if the rf-field penetrates only partially into the grains of the sample. This explains in a natural way why the observed nuclear magnetization recovers nonexponentially in the neighbourhood of T_c and below T_c.

References

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