

## Proton spin–lattice relaxation in the organic superconductor (BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>. Evidence for relaxation by localized paramagnetic centres

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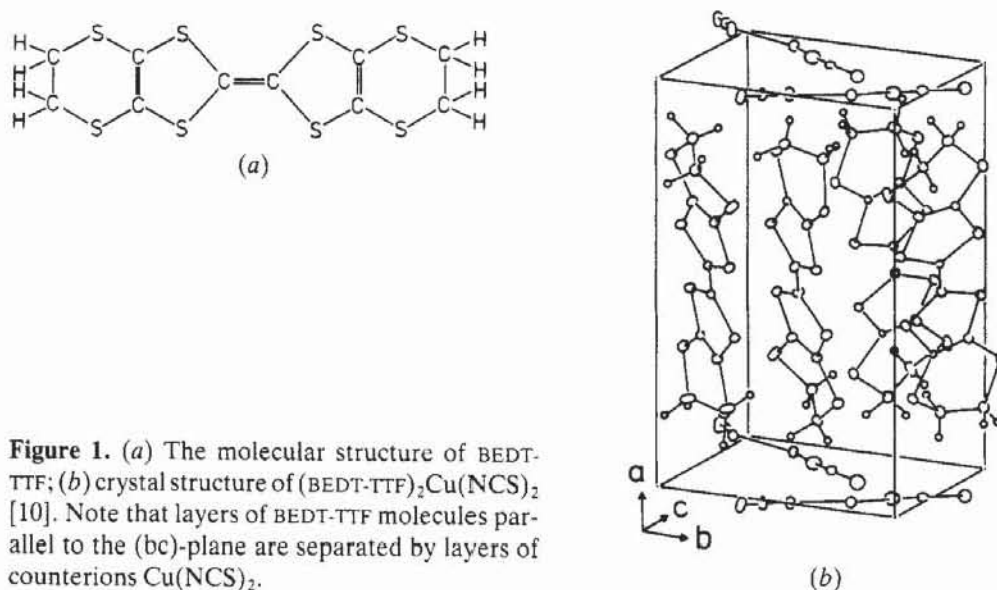
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**Abstract.** The spin–lattice relaxation of the protons in the title compound was investigated at  $\nu_L = 13.5$  MHz and 270 MHz for  $4.2 \text{ K} \leq T \leq 100 \text{ K}$ . The field corresponding to  $\nu_L = 13.5$  MHz,  $B_0 = 0.31 \text{ T}$ , is below the upper critical field and allows NMR measurements right in the superconducting state. Two kinds of samples were prepared: coarse grain crystals and finely powdered crystallites. In the finely powdered samples the proton relaxation at  $\nu_L = 13.5$  MHz follows an exponential-square-root law. This law is traced back to proton relaxation caused by localized paramagnetic centres. At  $\nu_L = 270$  MHz the relaxation follows a superposition of an exponential and an exponential-square-root law. The temperature dependence of the exponential contribution obeys the Korringa relation. This contribution is ascribed to conduction electrons. In coarse grain crystals the proton relaxation is exponential at  $\nu_L = 270$  MHz for  $T > 10 \text{ K}$  and becomes non-exponential for  $T < 10 \text{ K}$ . At  $\nu_L = 13.5$  MHz the transition from exponential to noticeably non-exponential relaxation occurs already at  $T \approx 25 \text{ K}$ . The cause for the non-exponential proton relaxation in the coarse grains is finite penetration of the RF-field (skin-effect) into the electrically conducting crystals. Powdering the crystals suppresses the skin-effect; this procedure, however, generates relaxation sinks in the form of localized paramagnetic centres. There is reason to believe that the skin-effect in coarse grains and generation of relaxation sinks by a powdering procedure complicate proton relaxation studies as well in other organic superconductors.

### 1. Introduction

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 [1–9].

To avoid exclusion of the RF-field from the conducting material nuclear magnetic resonance (NMR) and relaxation measurements are usually carried out on finely powdered samples, sometimes mixed with insulating material, e.g. finely powdered quartz. 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  $T \leq 100 \text{ K}$ . For such mechanisms exponential relaxation of the protons is expected. By contrast in essentially all published studies of



**Figure 1.** (a) The molecular structure of BEDT-TTF; (b) crystal structure of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  [10]. Note that layers of BEDT-TTF molecules parallel to the  $(bc)$ -plane are separated by layers of counterions  $\text{Cu}(\text{NCS})_2$ .

organic superconductors [1–9] a deviation from this behaviour is reported. Similar observations were reported on high- $T_c$  copper oxide superconductors. The non-exponential character of the build-up of the nuclear magnetization usually increases on lowering the temperature. Superconducting fluctuations have been offered in a highly speculative way as an explanation for the non-exponential spin relaxation [1, 3, 4]. The authors of references [2, 8, 9] frankly admit that they do not understand the non-exponential spin relaxation.

We made the same observations in our investigation of the proton spin relaxation in di(bisethyldithiotetrafulvalen)dithiocyanocuprate [ $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ ], which is an organic conductor at room temperature and becomes a superconductor at  $T_c = 10.4$  K. The molecular structure of BEDT-TTF is shown in figure 1(a), and the stacking of the BEDT-TTF molecules and the positions of the counterions  $\text{Cu}(\text{NCS})_2$  in figure 1(b). Electrical conductivity is high along both dimensions of the layers formed by the stacks of BEDT-TTF molecules, and low in the direction perpendicular to these layers.

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  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  of approximate size  $1 \times 0.5 \times 0.1$  mm<sup>3</sup>. The second was obtained by powdering the original crystals in a special agate mortar. This process resulted in a fine powder of microcrystallites of approximate size  $10 \times 10 \times 5$  μm<sup>3</sup>.

For both kinds of samples we measured the relaxation function

$$p(\Delta t) \equiv 1 - M_z(\Delta t)/M_0 \quad (1)$$

with  $M_0 = M_z(\Delta t \rightarrow \infty)$  and  $\Delta t$  being the delay after establishing the initial condition  $M_z(0) = 0$ . The Larmor frequencies and the fields were  $\nu_L = 270$  MHz  $\triangleq B_0 = 6.3$  T (this is the standard proton frequency in our laboratory) and, additionally,  $\nu_L = 13.5$  MHz  $\triangleq B_0 = 0.31$  T. For  $T \leq 8.3$  K the latter field is below  $B_{c2}$  of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  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 an exponential-square-root relaxation law

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

(see section 4.1). This relaxation law is clearly inconsistent with the assumption that proton–conduction electron coupling provides the dominant relaxation mechanism. On the other hand, such a relaxation law has been predicted theoretically by McHenry *et al* [11, 12] for a situation where the nuclei in a solid are relaxed by direct interaction with localized paramagnetic moments under conditions where spin diffusion plays a negligible role. No matter how large the influence of spin diffusion is, such a relaxation law may also be obtained if the nuclei are relaxed by direct interaction with localized paramagnetic centres and a distribution of  $1/T_1$  is assumed. The relaxation law, equation (2), then determines the shape of the distribution function  $f(1/T_1)$ . The main purpose of this paper is to convince the reader that direct dipole–dipole interaction of protons with localized electronic paramagnetic centres rather than dipole–dipole and contact interaction with conduction electrons provide the major source of proton spin relaxation in finely powdered samples of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  at ‘low’ frequencies (i.e., at 13.5 MHz) for  $T \leq 100$  K. We shall argue in section 5 that the description of the proton relaxation by a distribution function  $f(1/T_1)$  is appropriate. At ‘high’ frequencies, i.e.,  $\nu_L = 270$  MHz, we observe a superposition of proton relaxation by localized electronic moments and by conduction electrons.

If the sample consists of coarse grains of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ , we observe for  $\nu_L = 270$  MHz an exponential behaviour at all temperatures  $T$  in the range  $10 \text{ K} \leq T \leq 300 \text{ K}$  while for  $\nu_L = 13.5$  MHz an exponential relaxation behaviour is obtained only for  $T \geq 25$  K whereas for  $T \leq 25$  K the recovery of the magnetization becomes increasingly non-exponential on decreasing the temperature. Starting from essentially the same temperature ( $\approx 25$  K) the initial amplitude  $M_x(\Delta t \rightarrow \infty)$  of the free induction decay (FID) after a  $90^\circ$ -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  $M_x(\Delta t \rightarrow \infty)$  for the finely powdered sample 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 non-exponential if the RF-field penetrates only partially into the grains of the sample. This explains in a natural way why the nuclear magnetization observed in a pulsed NMR experiment recovers non-exponentially in the neighbourhood of  $T_c$ , and below  $T_c$ .

The organization of the paper is as follows. Because of its importance to this work we briefly review in section 2 the current understanding of nuclear relaxation by localized paramagnetic centres. In the short experimental section 3 we describe the growth of the  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  crystals and the NMR techniques applied in this work. The central section 4 (results and discussion) begins with a careful study of the functional form of the recovery of the proton magnetization in a finely powdered sample at  $\nu_L = 13.5$  MHz and  $T = 21$  K (4.1). Here the validity of the  $\exp(-\sqrt{t/\tau_1})$  law is established. We continue with a discussion of the temperature dependence of  $\tau_1$  (4.2). Section 4.3 deals with the proton relaxation at  $\nu_L = 270$  MHz in the finely powdered sample. The data analysis yields the contribution  $1/T_{1K}$  of the conduction electrons to the spin relaxation, and estimates of the concentration of the postulated localized paramagnetic centres, and of their correlation time. In section 4.4 we turn to measurements of the relaxation and of

the initial amplitude of the FID as a function of the temperature on the coarse grain samples and introduce the two-reservoir model.

## 2. Nuclear relaxation in solids caused by localized paramagnetic centres

McHenry *et al* [11, 12] studied both theoretically and experimentally nuclear spin relaxation in solids containing rare paramagnetic ions which are naturally localized. The rare paramagnetic centres (concentration  $N_c$ ) occupy at random a large number (concentration  $N_s \gg N_c$ ) of available sites which are uniformly dispersed in the crystal. The nuclei under study are coupled to the centres via the dipole–dipole interaction. This interaction is time dependent because the spin orientations of the paramagnetic centres fluctuate in time due to spin–spin interactions between the centres. These are, at least in part, mediated by the conduction electrons. The time dependent electron–nucleus interaction causes transitions between the nuclear spin states. Assuming for the time being absence of nuclear spin diffusion and absence of other nuclear relaxation mechanisms the relaxation rate of a nucleus at a distance  $r$  from a paramagnetic centre will be (see equation (3) of reference [13])

$$1/T_1 = 9(\gamma_n \gamma_i \hbar)^2 S^2 [\partial B_s(x)/\partial x] r^{-6} \sin^2 \Theta \cos^2 \Theta (\tau_i / (1 + \omega_L^2 \tau_i^2)) \quad (3)$$

where  $\gamma_n$ ,  $\gamma_i$ ,  $\hbar$ ,  $S$ ,  $\Theta$ ,  $B_s(x)$  and  $\tau_i$  are, respectively, the gyromagnetic ratio of the nucleus and of the paramagnetic ion, Planck's constant, the spin of the paramagnetic centre, the angle between the applied field  $B_0$  and the distance vector  $r$ , the Brillouin function with  $x = g\mu_B S B_0 / k_B T$  and the spin correlation time of the paramagnetic centre. Since  $T_1$  is a function of the site of the nucleus,  $1/T_1(r) \propto r^{-6}$ , there will be a distribution of relaxation rates over the crystal. The macroscopic magnetization  $M_z(\Delta t)$  which we measure in a relaxation experiment is a spatial ensemble average. A detailed calculation of the relaxation function  $p(\Delta t)$  of the ensemble can be found in Appendix A of reference [12], and the result is

$$p(\Delta t) = \exp(-\sqrt{\Delta t / \tau_1}) \quad (4)$$

The characteristic time  $\tau_1$  is given by

$$1/\tau_1 = \frac{16}{9} \pi^3 N_c^2 (\gamma_n \gamma_i \hbar)^2 S^2 [\partial B_s(x)/\partial x] \tau_i / (1 + \omega_L^2 \tau_i^2). \quad (5)$$

As an application of their theory McHenry *et al* [11, 12] studied the field and temperature dependence of the Gd contribution to the spin–lattice relaxation of the  $\text{La}^{139}$  and  $\text{Al}^{27}$  nuclei in the intermetallic compound  $\text{La}_{1-c}\text{Gd}_c\text{Al}_2$  for different values of the concentration  $N_c$  of the Gd impurities. They found that the relaxation of  $\text{La}^{139}$  and  $\text{Al}^{27}$  can be described as a superposition of relaxation by conduction electrons and interactions to the impurities:

$$p(\Delta t) = \exp(-\Delta t / T_{1K} - \sqrt{\Delta t / \tau_1}) \quad (6)$$

where  $T_{1K}^{-1}$  is the conduction electron contribution.

In addition they concluded that the fluctuations of the Gd moments which modulate the nucleus–impurity interactions result from spin–spin interaction between the impurities. The analysis of the experimental data indicates that a Ruderman–Kittel–Kasuya–Yosida (RKKY) [14] coupling is the source of this interaction.

The decay rate  $1/\tau_i$  of the impurity correlation arising from the RKKY interaction between the impurities is independent of temperature and in the case of a three-dimensional free electron gas

$$1/\tau_i \propto [D(E_F)^2 E_F/k_F^3] J^2 N_c \quad (7)$$

where  $D(E_F)$  is the density of states of the conduction electrons at the Fermi surface and  $J$  is the average conduction electron–paramagnetic centre exchange energy.

The physical situation which McHenry *et al* describe consists of a uniform crystal lattice. Statistics are introduced by assuming a random occupation of  $N_s$  available sites by  $N_c$  centres with  $N_c \ll N_s$ . This results in a distribution of relaxation rates  $1/T_1$  for the nuclei.

Considering the treatment of our finely powdered samples we must also take into consideration the possibility that the very process of powdering the coarse grains resulted in non-uniform microcrystallites in which the concentration of paramagnetic centres differs from crystallite to crystallite. Even if spin diffusion is sufficiently fast to ensure uniform nuclear relaxation in each individual crystallite we may still observe a distribution of relaxation rates. The observable relaxation function  $p(\Delta t)$  will assume the form

$$p(\Delta t) = \int_0^\infty f(1/T_1) \exp(-\Delta t/T_1) d(1/T_1) \quad (8)$$

where  $f(1/T_1)$  is the distribution function of the relaxation rates. If this case applies to our finely powdered samples we may obtain  $f(1/T_1)$  from a measurement of  $p(\Delta t)$  and an inverse Laplace-transformation.

If the nuclear relaxation is influenced by spin diffusion to paramagnetic centres, two limits must be distinguished [13, 15, 16]: diffusion limited relaxation and rapid diffusion. In the first limit the relaxation process is determined by the rate at which spin magnetization can diffuse to the paramagnetic centres. For a crystallite with concentration  $N_c$  of paramagnetic centres  $1/T_1$  is given in this limit by

$$1/T_1 = \frac{8}{3} \pi N_c D^{3/4} \left[ \frac{6}{5} (\gamma_n \gamma_i \hbar)^2 S^2 [\partial B_s(x)/\partial x] \tau_i / (1 + \omega_L^2 \tau_i^2) \right]^{1/4} \quad (9)$$

where  $D$  is the spin diffusion constant. In the second limit  $1/T_1$  is determined by the rate at which the impurity can equilibrate spins in its immediate neighbourhood.  $1/T_1$  is given by:

$$1/T_1 = \frac{4}{3} \pi N_c \frac{6}{5} (\gamma_n \gamma_i \hbar)^2 S^2 [\partial B_s(x)/\partial x] (\tau_i / 1 + \omega_L^2 \tau_i^2) b^{-3} \quad (10)$$

where  $b$  is the radius of the so-called diffusion barrier, which actually is a poorly defined distance. Rather than taking the estimate for  $b$  suggested by Rohrschach [13] we shall follow the view of Richards [17] and simply choose

$$b^3 = (aad) \approx (4 \cdot 4 \cdot 15) \text{\AA}^3 \quad (11)$$

where  $a$  is the distance between the BEDT-TTF molecules and  $d$  is the distance between the BEDT-TTF layers.

### 3. Experimental

Crystals of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  were grown by electrochemical methods [18, 19] at 20 °C under constant voltage conditions with a current density of about  $1 \mu\text{A cm}^{-2}$  in

about eight days. Elongated hexagon-shaped crystals of typical size  $6 \times 2 \times 0.1 \text{ mm}^3$  were obtained.

As stated in the introduction, samples consisting either of coarse grains or of a fine powder of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  were prepared for the NMR measurements.

The proton spin–lattice relaxation was measured by the saturation-recovery technique. The broad NMR line was saturated by applying a string of 20  $90^\circ$ -RF-pulses of length  $2 \mu\text{s}$  separated by 2 ms. After a variable delay  $\Delta t$  a  $90^\circ$ -read-pulse was applied and the FID recorded. As a measure of the magnetization  $M_z(\Delta t)$  existing immediately before the read-pulse we took the area under the Fourier transform of the FID following the read-pulse. This area is proportional to  $M_z(\Delta t)$  provided the RF of the pulse penetrates unattenuated the volume of the entire sample.

## 4. Results and discussion

### 4.1. The functional form of the proton relaxation in finely powdered samples of $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ at $\nu_L = 13.5 \text{ MHz}$

The recovery of the proton magnetization in finely powdered samples at  $\nu_L = 13.5 \text{ MHz}$  was found to be non-exponential in the whole temperature range  $4.2 \text{ K} \leq T \leq 100 \text{ K}$ . To determine the functional form of the relaxation function  $p(\Delta t)$  we measured  $M_z(\Delta t)$  at  $T = 21 \text{ K}$  for 42 time delays  $\Delta t$  with  $\Delta t$  ranging from 10 ms to 300 s. We present the experimental data in the following form. We assume

$$p(\Delta t) = \exp(-(\Delta t/\tau_1)^a) \quad (12)$$

where  $a$  is an adjustable parameter. For exponential relaxation  $a = 1$ , for relaxation by uniformly dispersed localized centres in the absence of spin diffusion  $a = \frac{1}{2}$ . By taking the logarithm of equation (12) twice, we get:

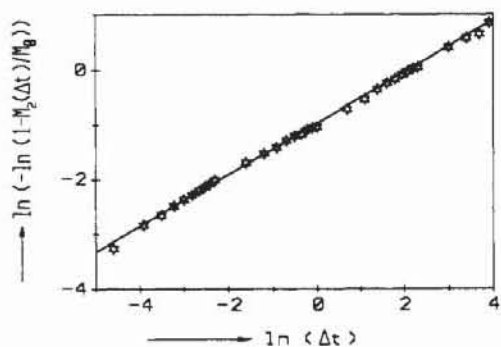
$$\ln(-\ln(p(\Delta t))) = a \ln(\Delta t) - a \ln(\tau_1). \quad (13)$$

In figure 2 we show a plot of  $\ln(-\ln(p(\Delta t)))$  versus  $\ln(\Delta t)$ . As can be seen, over the entire range of  $\Delta t$  the data can be well represented by a straight line. The full line in figure 2 was obtained by linear regression. Its slope is  $a = 0.50$  with a calculated uncertainty of  $\pm 0.01$ . This means that the proton relaxation in finely powdered samples of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  follows the  $\exp(-\sqrt{\Delta t/\tau_1})$  law at  $\nu_L = 13.5 \text{ MHz}$ . This is the relaxation law derived by McHenry *et al* for macroscopically uniform crystals in which the nuclei are relaxed by rare, localized paramagnetic centres and where spin diffusion plays no role, see equation (4). The data shown in figure 2 therefore seem to suggest that this mechanism dominates at  $\nu_L = 13.5 \text{ MHz}$  for the proton relaxation in finely powdered  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ .

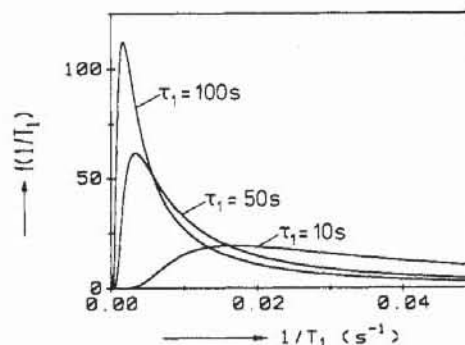
As stated in section 2 another possibility is, however, that the very process of powdering the original crystals resulted in non-uniform microcrystallites with varying concentrations of paramagnetic centres and, hence, in a distribution  $f(1/T_1)$  of relaxation rates regardless whether or not spin diffusion plays a role. Given  $p(\Delta t) = \exp(-\sqrt{\Delta t/\tau_1})$  the inverse Laplace transformation required to obtain  $f(1/T_1)$  can be carried out analytically. The result is

$$f(1/T_1) = 1/(2\sqrt{\pi})\tau_1^{-1/2}(1/T_1)^{-3/2} \exp(-T_1/4\tau_1). \quad (14)$$

This distribution function is shown in figure 3 for a set of parameters  $\tau_1$ . The maximum of  $f(1/T_1)$  occurs at  $1/T_1 = 1/6\tau_1$ .



**Figure 2.** The functional form of the relaxation law  $p(\Delta t) \equiv 1 - M_z(\Delta t)/M_0$  in finely powdered (BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> for  $T = 21$  K and  $\nu_L = 13.5$  MHz. The full line is obtained by a linear regression. Its slope is  $a = 0.50 \pm 0.01$ .



**Figure 3.** The distribution function  $f(1/T_1)$  for three values of  $\tau_1$ , cf. equation (14).

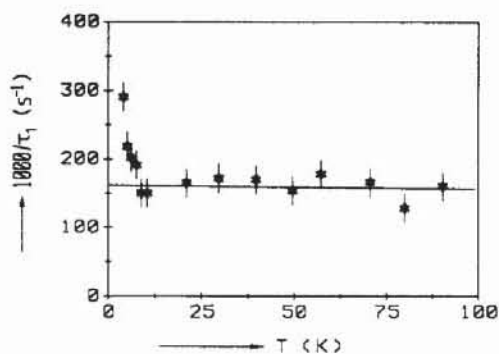
While the distribution function  $f(1/T_1)$ , equation (14), formally extends to infinity is obviously must have a finite upper limit since there cannot be microcrystallites in which the concentration of paramagnetic centres, and hence  $1/T_1$ , is arbitrarily large. This means that the exponential-square-root law cannot hold exactly for  $p(\Delta t)$ , but is only an approximation which is also implied in the work of McHenry *et al.* For the observed relaxation it does not make a noticeable difference whether  $f(1/T_1)$  extends to a large finite or to an infinite upper limit. The upper limit of  $f(1/T_1)$ , however, plays a crucial role in any attempt to estimate the total number of postulated paramagnetic centres in the actual sample of microcrystallites, see section 4.3.

A discussion of whether our samples of finely powdered (BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> fits the picture of McHenry *et al* or should be described by a distribution of relaxation rates resulting from non-uniform microcrystallites requires, among other things, estimates of the density of paramagnetic centres, the spin diffusion constant and the temperature dependence of  $\tau_1$ . We therefore postpone such a discussion to section 5 and turn now to the experimental determination of the temperature dependence of  $\tau_1$  and to an estimate of the density of the postulated localized paramagnetic centres.

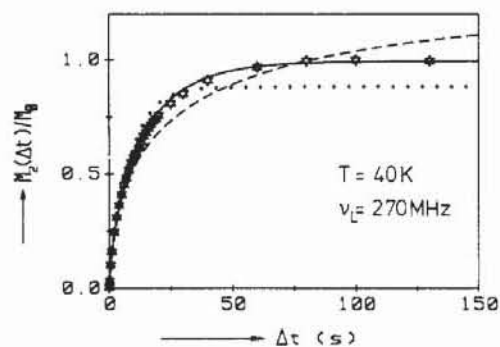
#### 4.2. The temperature dependence of $\tau_1$

To determine the temperature dependence of  $\tau_1$  we measured the proton relaxation in a finely powdered sample of (BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> at  $\nu_L = 13.5$  MHz in the temperature range  $4.2 \text{ K} \leq T \leq 100 \text{ K}$ . The data were analysed with the  $\exp(-\sqrt{t/\tau_1})$  law. In the entire range of  $T$  this law always describes well the functional form of  $p(\Delta t)$ . Figure 4 shows some results. In the range  $8 \text{ K} \leq T \leq 100 \text{ K}$  the rate  $1/\tau_1$  is nearly independent of  $T$  with  $1/\tau_1 = (0.16 \pm 0.01) \text{ s}^{-1}$ . For  $8 \text{ K} > T > 4.2 \text{ K}$  it increases:  $[1/\tau_1(4.2 \text{ K})]/[1/\tau_1(8 \text{ K})] \approx 2$ .

Since at  $\nu_L = 13.5 \text{ MHz}$   $\partial B_s(x)/\partial x \approx 1$  for  $T \geq 4.2 \text{ K}$  and, as we shall argue in section 4.3,  $\omega_L \tau_i \ll 1$ , the rate  $1/\tau_1$  is proportional to  $\tau_i$ , cf. equation (5). This is also true of  $1/T_1$  in each crystallite if a distribution of relaxation rates applies. We therefore conclude that the electronic correlation time  $\tau_i$  is constant for  $100 \text{ K} \geq T \geq 8 \text{ K}$  and increases below  $T = 8 \text{ K}$ , which is the temperature where the sample becomes superconducting.  $T_c = 8.3 \text{ K}$  is the temperature where for  $B_0 = 0.31 \text{ T}$  all crystallites of the sample, regardless of their orientation, have become superconducting [20].



**Figure 4.** The temperature dependence of  $1/\tau_1$  for  $\nu_L = 13.5$  MHz.



**Figure 5.** The recovery of the proton magnetization in finely powdered  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  at  $\nu_L = 270$  MHz. For  $\Delta t \leq 1$  s only a few representative data points are shown. Dotted curve indicates best fit to exponential relaxation law; broken curve indicates best fit to exponential-square-root relaxation law; full curve indicates fit to  $\exp(-\sqrt{\Delta t/\tau_1} - \Delta t/T_{1K})$ .

A plausible interpretation of the increase of  $\tau_1$  for  $T \leq T_c$  is as follows. According to equation (7) the correlation rate  $1/\tau_1$  of the postulated localized paramagnetic centres is proportional to  $D(E_F)^2 E_F/k_F^3$ . For a 3d free electron gas  $D(E_F)^2 E_F/k_F^3 \propto C^{1/3}$  where  $C$  is the concentration of the conduction electrons. While it is true that the conduction electrons of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  cannot be considered as a 3d free electron gas the interaction between the localized paramagnetic centres by the RKKY coupling still depends on the concentration  $C$  of the conduction electrons and will decrease when  $C$  decreases. As below  $T_c = 8.3$  K the number of unpaired conduction electrons drops due to the formation of Cooper pairs, the correlation rate  $1/\tau_1$  of the localized paramagnetic centres will decrease as well. This is what we inferred from the observed increase of  $1/\tau_1$  on lowering the temperature through  $T = 8$  K.

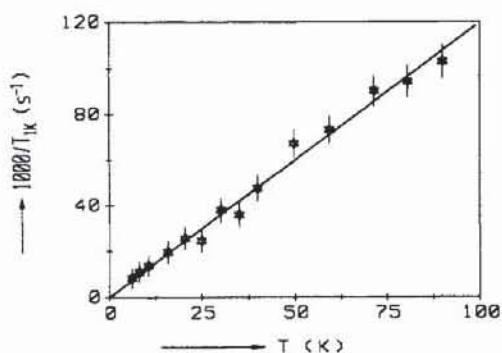
#### 4.3. The proton relaxation in finely powdered samples at $\nu_L = 270$ MHz. The conduction electron contribution $1/T_{1K}$ , estimates for $\tau_1$ and the concentration $N_c$ of paramagnetic centres

In finely powdered samples of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  the recovery of the proton spin magnetization after complete saturation is non-exponential as well at  $\nu_L = 270$  MHz. However, in contrast to its behaviour at  $\nu_L = 13.5$  MHz the relaxation function  $p(\Delta t)$  now becomes exponential for 'long' delays  $\Delta t$ . In figure 5 we show the results of a careful measurement of  $M_2(\Delta t)$  at  $\nu_L = 270$  MHz and  $T = 40$  K. The dotted and broken curves are, respectively, the best fits of the data to a purely exponential and a purely exponential-square-root relaxation law. It is evident that neither of these laws actually fits the data. The full curve in figure 5 is a fit with the superposition  $p(\Delta t) = \exp(-\sqrt{\Delta t/\tau_1} - \Delta t/T_{1K})$ . It describes well both the short and the long term behaviour of the relaxation. From the fit we obtain:

$$\left. \begin{aligned} 1/\tau_1 &= (0.017 \pm 0.004) \text{ s}^{-1} \\ 1/T_{1K} &= (0.046 \pm 0.006) \text{ s}^{-1} \end{aligned} \right\} \nu_L = 270 \text{ MHz}, T = 40 \text{ K.}$$

While the  $\sqrt{\Delta t/\tau_1}$  part of the relaxation is still thought to arise from localized paramagnetic centres, the  $\Delta t/T_{1K}$  part is ascribed to the conduction electrons.





**Figure 6.** The temperature dependence of the conduction electron contribution  $1/T_{1K}$  to the proton relaxation for  $\nu_L = 270$  MHz.

As stated at the end of section 4.2 the rate  $1/\tau_1$  measured at  $\nu_L = 13.5$  MHz increases for  $T \leq T_c$ . This increase should be suppressed at  $\nu_L = 270$  MHz  $\triangleq B_0 = 6.3$  T which is larger than the upper critical field  $B_{c2}$ . Indeed our 270 MHz data do not indicate any rise of  $1/\tau_1$  at very low temperatures.

We now turn to the question of why the relaxation caused by the conduction electrons is comparable with that of the localized centres at  $\nu_L = 270$  MHz but not at 13.5 MHz. The point is that  $1/T_{1K}$  is independent of the Larmor frequency [4, 21] while  $1/\tau_1$  is found to be almost 10 times smaller at 270 MHz than at 13.5 MHz. It is, in fact, comparable to  $1/T_{1K}$  at  $\nu_L = 270$  MHz. According to equation (5) the field- and frequency-dependence of  $1/\tau_1$  has two sources, (i) the derivative of the Brillouin function and (ii) the factor  $\tau_i/(1 + \omega_L^2 \tau_i^2)$ .  $\partial B_s(x)/\partial x \approx 1$  at 40 K even for  $B_0 = 6.3$  T, therefore the frequency dependence of  $1/\tau_1$  arises predominantly from the factor  $\tau_i/(1 + \omega_L^2 \tau_i^2)$ . The measured ratio

$$[1/\tau_1(\nu_L = 270 \text{ MHz})]/[1/\tau_1(\nu_L = 13.5 \text{ MHz})] = 0.017/0.16$$

allows us to obtain the estimate  $\tau_i \approx 1.7 \times 10^{-9}$  s for the correlation time of the localized paramagnetic centres.

The temperature dependence of  $1/\tau_1$  is known from the measurements at  $\nu_L = 13.5$  MHz:  $1/\tau_1$  is nearly independent of  $T$  for  $8 \text{ K} \leq T \leq 100 \text{ K}$ . At  $\nu_L = 270$  MHz, i.e. in a twentyfold higher field  $B_0$ , the temperature dependence of  $1/\tau_1$  through the derivative of the Brillouin function (see equation (5)) can no longer be neglected. This dependence is, however, well known, and therefore we can use the value of  $1/\tau_1 = (0.017 \pm 0.004) \text{ s}^{-1}$  measured carefully, i.e., with as many as 49 delays  $\Delta t$  at  $T = 40$  K to infer the temperature dependence of  $1/\tau_1$  at  $\nu_L = 270$  MHz. This allows us to analyse our 270 MHz relaxation data at temperatures other than 40 K, which were collected with only eight to ten delays  $\Delta t$ , with  $T_{1K}$  as the only fit parameter. This procedure results in much more stable fits than attempts to analyse the data with fits where both  $\tau_1$  and  $T_{1K}$  are kept as adjustable parameters.

Figure 6 shows the temperature dependence of  $1/T_{1K}$  obtained in this way.  $1/T_{1K}$  increases linearly with  $T$  for  $T \leq 100$  K as predicted by the Korringa law [21]. The slope is  $m = 1.2 \times 10^{-3} \text{ K}^{-1} \text{ s}^{-1}$  and can be expressed by [22]

$$m \propto K_c^2(1 + 2\langle d^2 \rangle / \langle a^2 \rangle)$$

where  $\langle d^2 \rangle$  and  $\langle a^2 \rangle$  are, respectively, the averaged squared anisotropic (dipole–dipole interaction) and the averaged squared isotropic (Fermi contact interaction) parts of the proton–electron interaction. We have obtained an estimate of 5 ppm for the upper limit of the Knight shift  $K_c$  of the protons from the frequency dependence of the resolution

in proton decoupled magic angle sample spinning  $^{13}\text{C}$  spectra [23]. Inserting  $m$  and this upper limit for  $K_c$  in equation (15) we may conclude that the dominant part of the conduction electron contribution to the proton relaxation in  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  is due to dipolar and not to contact interaction. Remember that contact interaction is the dominant nucleus–conduction electron interaction in ordinary metals.

Concentration  $N_c$  of localized paramagnetic centres. If the microcrystallites are uniform and equation (5) applies an estimate for the concentration  $N_c$  of the localized paramagnetic centres may be obtained by inserting the measured values of  $1/\tau_1$  and the value of  $\tau_i$  inferred from the frequency dependence of  $1/\tau_1$  into equation (5) and solving for  $N_c$ . For  $S$  and  $\gamma_i$  free electron values are used. In this way we obtain  $N_c \approx 5 \times 10^{18} \text{ cm}^{-3}$ . As the number of BEDT-TTF molecules in a cubic centimetre is  $N_B = 2.37 \times 10^{21}$  this estimate for  $N_c$  implies  $N_c/N_B \approx 2 \times 10^{-3}$ .

If, on the other hand, the microcrystallites are non-uniform (as we think they are, see below) and a distribution of relaxation rates exists we must consider the two limiting cases mentioned in section 2. We can immediately rule out diffusion limited relaxation (case i) for the microcrystallites of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  since the frequency dependence predicted by the relevant equation (9) is much too weak to account for the observed data of  $1/\tau_1$  at  $\nu_L = 13.5$  and 270 MHz. In the second limit the relaxation rate in a given crystallite is determined by the rate at which impurities can equilibrate spins in their immediate neighbourhood and equation (10) applies. As explained in section 4.1. it is not possible to derive an overall concentration of paramagnetic centres for the entire sample of non-uniform microcrystallites since the distribution function  $f(1/T_1)$ , equation (14), leads to a diverging result. The divergence is avoided by truncating  $f(1/T_1)$  at some upper limit. While it is obvious that there must be a finite upper limit it is not clear which value should be chosen. We therefore refrain from trying to estimate the overall concentration  $\bar{N}_c$  of the paramagnetic centres and confine ourselves to considering a ‘representative’ crystallite. Somewhat arbitrarily we choose for this purpose a crystallite with  $1/T_1 = 1/\tau_1$ . By numerical integration for various values of  $\tau_1$  we find

$$\int_0^{1/\tau_1} f(1/T_1) d(1/T_1) \approx 1/2$$

i. e., in one half of the crystallites (by volume) the relaxation rate  $1/T_1$ , and hence  $N_c$ , is smaller, in the other half it is larger than in the representative crystallite. Inserting again free electron values for  $S$  and  $\gamma_i$  and the measured value of  $1/\tau_1$  for  $1/T_1$  on the left-hand side of equation (10), and  $\tau_i = 1.7 \times 10^{-9} \text{ s}$  and  $b^3 = 240 \text{ \AA}^3$  (see equation (11)) on the right-hand side we may solve for  $N_c$  and obtain  $N_c \approx 10^{17} \text{ cm}^{-3}$ . In this case the ratio  $N_c/N_B$  is  $4.2 \times 10^{-5}$ . Note that due to the asymmetric shape of the distribution function  $f(1/T_1)$  the overall-concentration  $\bar{N}_c$  is higher than  $N_c$  in the representative crystallite.

Proton relaxation is certainly an indirect method for estimating  $N_c$  or  $\bar{N}_c$ . It is natural to ask whether the postulated localized paramagnetic centres can be detected by some direct method such as EPR or by measuring the temperature dependence of the static susceptibility. The difficulty is to discriminate the signal from the localized paramagnetic centres against that from the conduction electrons. The number of conduction electrons per  $\text{cm}^3$  contributing, e. g., to the EPR signal is  $n_F \approx n \cdot T/T_F$  where  $n = 1.18 \times 10^{21} \text{ cm}^{-3}$  is the total number of conduction electrons per  $\text{cm}^3$  (we assume a charge transfer of 1/2 electron per BEDT-TTF molecule, cf. reference [24]) and  $T_F$  is the Fermi temperature which, according to reference [25], is  $T_F = 1510 \text{ K}$ . For  $T = 10 \text{ K}$ , e. g.,

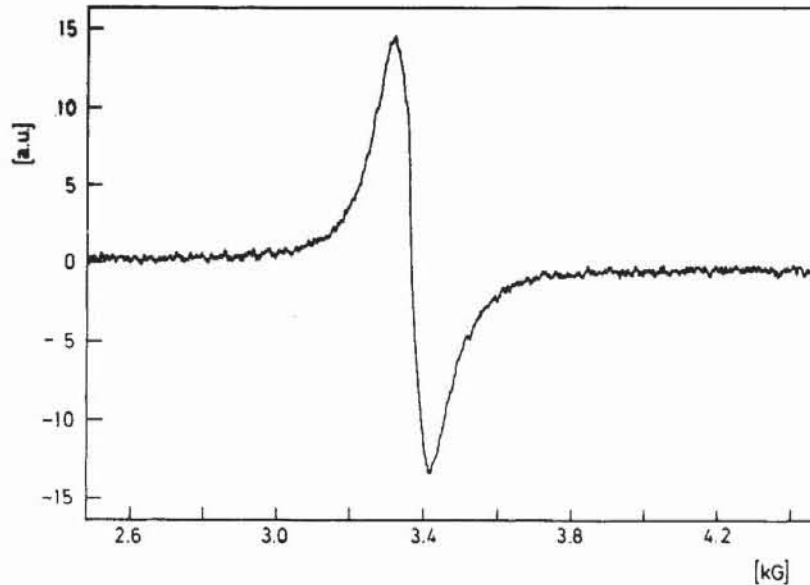


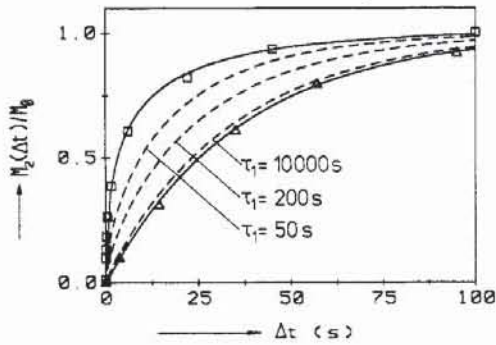
Figure 7. X-band EPR spectrum of a grain of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  at  $T = 10$  K.

$n_F \approx 7.8 \times 10^{18} \text{ cm}^{-3}$ . Note that the intensity of the EPR from the conduction electrons should be independent of  $T$ . For uniform microcrystallites our estimate for  $N_c$  is  $5 \times 10^{18} \text{ cm}^{-3}$ . That means it should be possible to detect the localized paramagnetic centres by an increase of the EPR intensity for  $T \leq 10$  K. If the microcrystallites are, on the other hand, non-uniform and the respective estimate  $N_c \approx 10^{17} \text{ cm}^{-3}$  applies the EPR signal from the centres is much weaker than that from the conduction electrons for all  $T > T_c$  and it will be very hard to detect it. It is true that  $n_F$  should be compared with  $\bar{N}_c$  rather than with  $N_c$  but unless  $\bar{N}_c$  is very much larger than  $N_c$  the conclusion is the same.

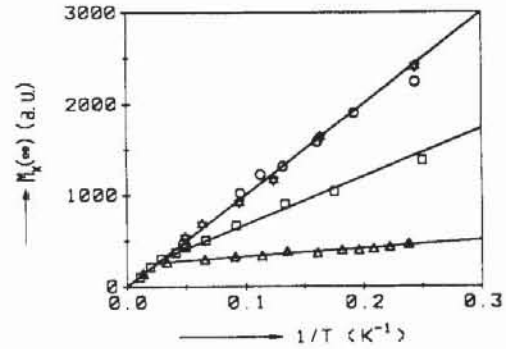
In a preliminary experiment we have applied X-band EPR in an effort to detect the localized paramagnetic centres. We first recorded for  $8 \text{ K} \leq T \leq 300 \text{ K}$  EPR spectra from a single coarse grain. The lower end of the temperature range was limited to 8 K to avoid complications arising from the onset of superconductivity. The spectrum recorded at  $T = 10$  K is shown in figure 7 and is further discussed in section 4.4 in the context of the question whether or not the microwave field penetrates fully into such conducting grains. As expected for coarse grains the intensity of the EPR was independent of  $T$  within the accuracy of the measurements. This confirms that the observed EPR results from conduction electrons. We then powdered this particular grain and recorded again EPR spectra in the same temperature range. The EPR intensity was essentially the same as before and again did not reveal any significant dependence on  $T$ . This negative result of the effort to detect localized paramagnetic centres by EPR suggests that our powdered samples represent a collection of non-uniform rather than uniform microcrystallites but unfortunately the quality of the EPR intensity measurements was not good enough in this preliminary experiment to reach a definitive conclusion. We are currently engaged in improving the capability of our EPR spectrometer to yield reliable EPR intensities at accurately known low temperatures and plan to repeat these measurements in the near future. We return to the question of uniform or non-uniform microcrystallites in the summary, section 5.

#### 4.4. The proton relaxation in coarse grains of $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$

The experimental results in coarse grains of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  are as follows. At  $\nu_L = 13.5 \text{ MHz}$  the recovery of the proton magnetization is exponential for  $T \geq 25 \text{ K}$ ,



**Figure 8.** Comparison of the recovery of the proton relaxation in coarse grains ( $\Delta$ ) and in finely powdered  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  ( $\square$ ) at  $\nu_L = 13.5$  MHz and  $T = 30$  K. Full curve through squares ( $\square$ ) indicates  $\exp(-\sqrt{\Delta t/\tau_1})$  with  $1/\tau_1 = 0.133$  s $^{-1}$ ; full curve through triangles ( $\Delta$ ) indicates  $\exp(-\Delta t/T_1)$  with  $1/T_1 = 0.028$  s $^{-1}$ ; broken curves indicate  $\exp(-\sqrt{\Delta t/\tau_1} - \Delta t/T_1)$  with  $1/T_1 = 0.028$  s $^{-1}$  and  $\tau_1$  as indicated.



**Figure 9.** Initial amplitude  $M_x(\infty)$  of the FID for coarse grains measured at  $\nu_L = 13.5$  MHz ( $\Delta$ ) and  $\nu_L = 270$  MHz ( $\square$ ) and for finely powdered  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  at  $\nu_L = 13.5$  MHz ( $\circ$ ) and  $\nu_L = 270$  MHz ( $\star$ ). For  $1/T \leq 0.05$  K $^{-1}$  only a few representative data points are shown.

whereas for  $T \leq 25$  K the relaxation becomes increasingly non-exponential. The same behaviour is observed at  $\nu_L = 270$  MHz: exponential relaxation for  $T \geq 10$  K and increasingly non-exponential relaxation for  $T \leq 10$  K. For a given temperature  $T < 10$  K the non-exponentiality is not as drastic at 270 MHz as it is at 13.5 MHz.

Figure 8 shows the return to thermal equilibrium of the proton magnetization in coarse grains ( $\Delta$ ) and, again, in a finely powdered sample ( $\square$ ) at  $T = 30$  K and  $\nu_L = 13.5$  MHz. The full curve through the squares ( $\square$ ) 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 ( $\Delta$ ) 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 proton relaxation in the coarse grains of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  is exponential at  $T = 30$  K while it obeys the exponential-square-root law in the finely powdered sample and (ii) that the overall relaxation is much faster in the finely powdered sample than in coarse grains. The conclusion, we think, is inevitable that the very process of powdering the coarse grains introduced relaxation sinks (localized paramagnetic centres) into the resulting microcrystallites.

The broken lines in figure 8 are theoretical curves for

$$M_x(\Delta t)/M_x(\infty) = 1 - \exp(-\Delta t/T_1 - \sqrt{\Delta t/\tau_1}) \quad (15)$$

with  $1/T_1 = 0.028$  s $^{-1}$  and various values of  $1/\tau_1$ . From figure 6 we conclude that in coarse grains  $1/\tau_1$  cannot be larger than  $10^{-4}$  s $^{-1}$ . This means

$$[1/\tau_1 (\text{fine powder})]/[1/\tau_1 (\text{coarse grains})] \geq 1300.$$

If we translate this ratio of  $1/\tau_1$  into concentrations  $N_c$  of localized paramagnetic centres we find that  $N_c$  must be at least 40 times smaller in the coarse grains than in the microcrystallites if we assume validity of the model of uniform crystallites, whereas this number is 250 for non-uniform crystallites and a distribution of relaxation rates. When deriving these numbers it must be remembered that  $\tau_i$  is also dependent on  $N_c$ .

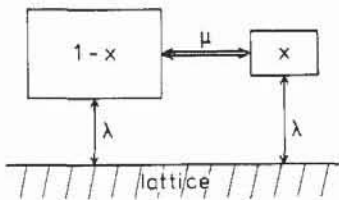
We now turn to the question why the proton relaxation in the coarse grains becomes (increasingly) non-exponential for  $T \approx 25$  K. We first argue that this behaviour cannot

be due to localized paramagnetic centres as in the case of the microcrystallites. From the measurements on the finely powdered samples we know that  $1/\tau_1$  is nearly independent of  $T$  for  $8\text{ K} \leq T \leq 100\text{ K}$  and  $\nu_L = 13.5\text{ MHz}$ , and that the temperature dependence of  $1/\tau_1$  at  $\nu_L = 270\text{ MHz}$  arises from the temperature dependence of the Brillouin function. According to equation (15) the relaxation becomes non-exponential for decreasing  $T$  if  $1/T_1$  becomes so small that it becomes comparable in size with  $1/\tau_1$ . If we identify  $1/T_1$  with the conduction electron contribution  $1/T_{1K}$  it indeed decreases in proportion to  $T$  but even at  $4.2\text{ K}$  (lowest temperature of these measurements) it remains much larger than the upper limit of  $1/\tau_1$  in the coarse grains of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ . Therefore the observed non-exponential relaxation in the coarse grains at  $T \leq 25\text{ K}$  cannot be traced back to localized paramagnetic centres.

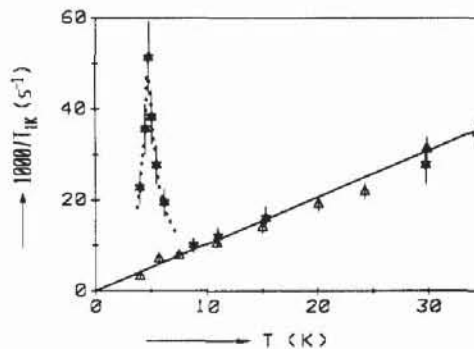
A key to the actual cause for the non-exponential proton relaxation in the coarse grains is provided by measurements of the initial amplitude  $M_x(\infty)$  of the FID after a  $90^\circ$ -pulse for  $\Delta t \rightarrow \infty$ . The experimental data at  $13.5\text{ MHz}$  and  $270\text{ MHz}$  for the finely powdered sample and for the coarse grains are presented in figure 9. Remember that the usual procedure of measuring  $T_1$  implies that  $M_x(\infty)$  is proportional to the thermal equilibrium magnetization  $M_0$ , i.e., obeys the Curie law. As figure 9 clearly shows  $M_x(\infty)$  samples do follow the Curie law at  $13.5\text{ MHz}$  and  $270\text{ MHz}$  in the finely powdered samples, whereas in the coarse grains  $M_x(\infty)$  deviates drastically from this law for  $1/T \geq 0.03\text{ K}^{-1}$ . This behaviour of  $M_x(\infty)$  in the coarse grains results from finite penetration of the RF-field (skin effect) into the conducting grains. It is remarkable that the skin effect seems to be much smaller at  $\nu_L = 270\text{ MHz}$  than at  $\nu_L = 13.5\text{ MHz}$ . This can only be understood if the electrical conductivity  $\sigma$  is a decreasing function of the frequency  $\nu$ . An independent observation of decreasing  $\sigma$  with increasing frequency is provided by the shape of X-band EPR spectra which we have recorded from the coarse grain of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ . In figure 7 we have shown the EPR spectrum obtained at  $T = 10\text{ K}$ . As shown theoretically by Dyson [26] and experimentally by Feher [27] the shape of the EPR of metallic samples becomes asymmetric if the microwave field does not penetrate fully into the sample. As figure 7 shows, the EPR of the coarse grain of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  is essentially symmetric, which demonstrates absence of skin effect and thus low electrical conductivity at X-band frequency. We point out that the shape of the EPR did not change appreciably on rotating the grain relative to the applied field. In view of the large anisotropy of the DC conductivity of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  this is additional evidence that the conductivity of this material decreases with increasing frequency.

To explain the non-exponentiality of the proton relaxation in the coarse grains of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  we now present a simple model which takes into account the skin effect. If the RF-field cannot penetrate into the bulk of the sample, the string of saturation pulses which is part of the  $T_1$ -measurement sequence creates a non-uniform saturation in the spin system of the protons. While the variation with depth of the saturation is certainly gradual we consider the following grossly simplified two-reservoir model (figure 10). The first reservoir contains the spins located in surface layers of the coarse grains. They are fully accessed by the RF-field. These spins generate, as well, the measurable NMR signal. The second reservoir represents the spins in the interior of the coarse grains. They are not accessed by the RF-field and do not contribute to the NMR signal. Both reservoirs of spins are assumed to relax towards thermal equilibrium with the same rate  $\lambda$  and are assumed to be coupled with the rate  $\mu$ . A natural coupling mechanism is provided by spin diffusion.

Let  $x$  be the fraction of the spin in the surface layers and  $M_{1z}$ ,  $M_{2z}$ , respectively, the  $z$ -magnetization in the surface layers and in the interior of the coarse grains.



**Figure 10.** The two-reservoir model. The box  $x$  contains the spins in the surface layer, the box  $(1-x)$  those in the interior of the grains.



**Figure 11.** The temperature dependence of the conduction electron contribution  $1/T_{1K}$  of the proton relaxation in coarse grains of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  at  $\nu_L = 13.5$  MHz (★) and  $\nu_L = 270$  MHz (Δ). Note the enhancement of  $1/T_{1K}$  at  $\nu_L = 13.5$  MHz, and its absence at  $\nu_L = 270$  MHz, for  $T \leq T_c$ .

The rate of change of  $M_{1z}$  and  $M_{2z}$  will be

$$\dot{M}_{1z} = \lambda \cdot (M_z(\infty) - M_{1z}) + \mu \cdot (M_{2z} - M_{1z}) \cdot (1-x) \quad (16a)$$

$$\dot{M}_{2z} = \lambda \cdot (M_z(\infty) - M_{2z}) + \mu \cdot (M_{1z} - M_{2z}) \cdot x. \quad (16b)$$

The factors  $(1-x)$  and  $x$  enter the right-hand side of equations (16a) and (16b) because  $M_{1z}$  and  $M_{2z}$  designate magnetization, i.e., magnetic moments per unit volume. Using equation (16) we get for

$$p(t) = \begin{bmatrix} p_1(t) \\ p_2(t) \end{bmatrix} = \begin{bmatrix} 1 - M_{1z}(t)/M_z(\infty) \\ 1 - M_{2z}(t)/M_z(\infty) \end{bmatrix}$$

the equation

$$\dot{p} = \begin{bmatrix} -\lambda - (1-x)\mu & (1-x)\mu \\ x\mu & -\lambda - x\mu \end{bmatrix} \cdot p. \quad (17)$$

We are interested in the solution of equation (17) for the initial condition

$$p(0) = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

which applies immediately after the saturation sequence taking into account the skin effect. The solution of equation (17) for this initial condition is

$$p_1(t) = x \cdot \exp(-\lambda \cdot t) + (1-x) \cdot \exp(-(\lambda + \mu) \cdot t) \quad (18a)$$

$$p_2(t) = x \cdot \exp(-\lambda \cdot t) - x \cdot \exp(-(\lambda + \mu) \cdot t). \quad (18b)$$

In the experiment we observe only the signal from the surface layers of the coarse grains, i.e.,  $x \cdot p_1(t)$ . For  $\mu \neq 0$ ,  $x \cdot p_1(t)$  decays exponentially to zero only for  $x \approx 1$  or  $x \ll 1$ . For intermediate values of  $x$  the decay of  $x \cdot p_1(t)$  will be a superposition of two exponentials. Clearly if we had considered continuous attenuation of the RF-field instead

of the two-reservoir model we would have obtained a continuous distribution of relaxation rates. For comparison with the experiment we return to the two-reservoir model: at high temperatures the conductivity  $\sigma$  of (BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> is low and the RF-field penetrates fully into the coarse grains. This means  $x \approx 1$ , the recovery  $x \cdot p_1(t)$  is exponential and  $\lambda = 1/T_{1K}$ . As the temperature is lowered  $\sigma$  increases [5], and, according to figure 6,  $x$  becomes significantly smaller than unity for  $T < 25$  K. This is the condition for the relaxation to become non-exponential provided  $\mu$  is comparable or larger than  $\lambda = 1/T_{1K}$ . Indeed it is a fast (and not a slow) relaxation component that appears at  $T < 25$  K.

The rate of the dipole–dipole-induced flip-flop-transitions of a pair of protons which are joined by a vector of length  $r$  subtending an angle  $\Theta$  with the external field  $B_0$  is given by

$$W = (\pi/2)\omega_1^2 f(\omega_0) \quad (19)$$

where  $\omega_1 = (\gamma_n^2 \hbar / 2r^3)(1 - 3 \cos^2 \Theta)$  and the NMR lineshape function  $f(\omega)$  is normalized to unity and has a maximum at  $\omega = \omega_0$  (reference [28], p 138). For Gaussian lines  $f(\omega_0)$  is given by  $1.67(2\pi\Delta f)^{-1}$ . Inserting  $r = 4 \text{ \AA} \approx$  distance of the CH<sub>2</sub>-groups of neighbouring BEDT-TTF molecules along the stack, and from stack to stack,  $\Delta f =$  width at half height of the proton NMR line which is about 50 kHz and  $\langle(1 - 3 \cos^2 \Theta)^2\rangle = 4/5$  (powder average) we obtain from equation (19)  $W \approx 230 \text{ s}^{-1}$ . The two-reservoir model is too coarse for directly identifying  $\mu$  and  $W$ . Nevertheless these considerations show that spin diffusion does provide for a coupling mechanism between the protons in crystals of (BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> which is fast on the time scale of  $T_{1K}$ .

From a material point of view we are interested in the conduction electron contribution  $1/T_{1K}$  to the relaxation of the protons. The two-reservoir model suggests fitting the experimental data for  $T < 25$  K with the superposition of two exponentials and identifying the smaller of the two rates  $\lambda$  with  $1/T_{1K}$ . This is the way we analysed our relaxation data from the coarse grains at  $T < 25$  K. In what follows we therefore concentrate on the smaller of the two rates, which we shall continue to call  $1/T_{1K}$ .

Its temperature dependence for  $4.2 \text{ K} \leq T \leq 35 \text{ K}$  is shown in figure 11 for  $\nu_L = 13.5 \text{ MHz}$  (★) and  $270 \text{ MHz}$  (△). At  $\nu_L = 270 \text{ MHz}$   $1/T_{1K}$  is linear in  $T$  as predicted by the Korringa relation. Its slope is  $m = 10^{-3} \text{ K}^{-1} \text{ s}^{-1}$ . The same slope for  $1/T_{1K}$  we find at  $\nu_L = 13.5 \text{ MHz}$  for  $T \geq 9 \text{ K}$ . The value of  $m$  obtained for the coarse grains is thus essentially equal to that obtained from the finely powdered sample, see section 3.3, and indeed it should be so. The discussion of  $m$  in section 3.3 therefore applies as well to the coarse grains.

At  $\nu_L = 13.5 \text{ MHz}$ ,  $1/T_{1K}$  increases for  $5 \text{ K} \leq T \leq 9 \text{ K}$ , and at  $T = (5 \pm 0.5) \text{ K}$  a maximum is observed. Similar enhancements have been observed in other superconducting organic metals [1–9]. The enhancement in (BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> is about 10 times the rate  $1/T_{1K}$  expected by the Korringa law. Between  $T = 5 \text{ K}$  and  $T = 4.2 \text{ K}$ , which is the lowest temperature accessible with our cryostat,  $1/T_{1K}$  drops sharply. The maximum of  $1/T_{1K}$  caused by the so-called coherence effect [29, 30] in a BCS superconductor is expected for  $T \approx 0.8 T_c$ . The observed temperature  $T = 5 \text{ K}$  for the maximum of  $1/T_{1K}$  is in fair agreement with this expectation. Remember  $T_c \approx 8.3 \text{ K}$  for  $B_0 = 0.31 \text{ T}$ . The factor 10 of the enhancement points towards a ‘dirty’ superconductor defined by  $\xi > 1$  where  $\xi$  and  $l$  are, respectively, the coherence length of Cooper pairs and the mean free path of the conduction electrons [29]. Indeed measurements of the

upper critical field  $B_{c2}$  by Gogu [20] strongly suggest that superconductors with BEDT-TTF as a donor belong to the class of ‘dirty’ superconductors in the sense of reference [29]. Therefore we conclude that the relaxation rate  $1/T_{1K}$  due to the conduction electrons in  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  follows the Korringa relation in the normal state and shows an enhancement in the superconducting state as predicted by the BCS-theory for ‘dirty’ superconductors. Naturally no enhancement of  $1/T_{1K}$  is found at  $\nu_L = 270$  MHz since the 6.3 T field suppresses the superconductivity in  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ .

## 5. Summary and conclusion

The recovery of the proton magnetization of finely powdered samples of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  measured at  $\nu_L = 13.5$  MHz is non-exponential in the temperature range  $4.2 \text{ K} \leq T \leq 100 \text{ K}$ . It obeys the exponential-square-root relaxation law  $p(\Delta t) = \exp(-\sqrt{\Delta t}/\tau_1)$ . If the measurement frequency is increased to 270 MHz the relaxation law becomes  $p(\Delta t) = \exp(-\Delta t/T_{1K} - \sqrt{\Delta t}/\tau_1)$  with comparable values of  $\tau_1$  and  $T_{1K}$ .

The proton magnetization in coarse grains of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  recovers exponentially for  $\nu_L = 270$  MHz and  $T > 10$  K. For  $T < 10$  K it becomes non-exponential. The transition occurs for  $\nu_L = 13.5$  MHz already at  $T \approx 25$  K.

It is important to note that the origin of the non-exponential proton spin relaxation is different in fine powders and in coarse grains. In coarse grains it is the result of screening of the RF-field (skin effect) from the interior of the electrically conducting grains. In fine powders, by contrast, it is due to localized paramagnetic centres. Regardless of the details of the relaxation mechanism the very fact that the nuclear relaxation is speeded up by powdering the crystals, and that the relaxation law changes, is proof that relaxation sinks were created in the powdering process. The temperature dependence of the ‘new’ relaxation paths is accounted for only if the relaxation sinks are localized paramagnetic centres. The crystallites of the fine powder are still too large for paramagnetic centres created exclusively on the surfaces of the crystallites to be responsible for the observed relaxation behaviour. Spin diffusion is not able to cover distances of the order of  $1\text{--}5 \mu\text{m}$  within a time of roughly  $\tau_1 \approx 7$  s. We are thus led to the conclusion that localized paramagnetic centres must have been created by the powdering process not only on the surface but in the bulk of the microcrystallites as well.

The nature of these centres on the molecular level remains an open problem. We think they are related to defects and dislocations which disrupt intermolecular sulphur–sulphur contacts of the BEDT-TTF molecules. Such contacts are generally believed to be responsible for the electrical conductivity of the BEDT-TTF radical salts [25]. A charge transfer from a BEDT-TTF molecule to a  $\text{Cu}(\text{NCS})_2$  complex need not be inhibited by the disruption of its sulphur–sulphur contacts. The event of disruption of the sulphur–sulphur contacts of a BEDT-TTF molecule plus charge transfer thus creates a radical ion, i.e., a localized paramagnetic centre. If the charge transfer does not involve only one electron per  $(\text{BEDT-TTF})_2$ -dimer as in the undisturbed crystal a paramagnetic counterion is created as well. In view of the fact that BEDT-TTF has several closely spaced oxidation steps it seems not unlikely that the amount of the charge transfer of a BEDT-TTF molecule is affected by nearby defects or dislocations. Both types of localized paramagnetic centres envisaged here, BEDT-TTF radical cations and paramagnetic anions, will be effective in relaxing the proton spins.



### 5.1. Uniform crystallites, negligible spin diffusion or non-uniform crystallites with rapid spin diffusion?

The picture of McHenry *et al* [11, 12] implies uniform crystallites and negligible spin diffusion. The attractive feature of this picture is that it leads automatically to the observed functional form of  $p(\Delta t)$ , i.e.,  $p(\Delta t) = \exp(-\sqrt{\Delta t/\tau_1})$ . Moreover, the concentration  $N_c$  of localized paramagnetic centres is well defined. The weakness of this picture is that spin diffusion must be excluded. This requirement is hard to accept since we have demonstrated that spin diffusion in coarse grains of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  plays a crucial role for the relaxation to become non-exponential at low temperatures. There is no reason why spin diffusion should not be operative as well in small crystallites.

We therefore tend to conclude that our fine powder samples represent an ensemble of non-uniform crystallites and that within each crystallite rapid spin diffusion takes care of exponential relaxation, with the relaxation rate differing from crystallite to crystallite. Remember, this picture is also favoured by the results of our preliminary EPR measurements. Its drawback is that the introduction of a distribution function has always the touch of a stopgap, but we cannot avoid admitting that a distribution of relaxation rates appears to be a natural consequence of the powdering procedure.

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  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ . The results presented here pinpoint the dilemma we face when we adopt this point of view. If we study by NMR coarse grains as obtained directly by the electrochemical crystallization process we inevitably run into the skin effect problem. It prevents us from ‘seeing’ the spins in the bulk of the grains and causes, at low temperatures, the relaxation to become non-exponential. If, on the other hand, the coarse grains are finely powdered in order to circumvent the skin effect problem we automatically create extra relaxation paths which prevent us from accessing what we initially set out to study, i.e., the conduction electron contribution to the nuclear relaxation. The analysis of our relaxation and thermal equilibrium magnetization measurements suggests that the conduction electron contribution to the proton relaxation is measured with the least interference of perturbing effects (skin effect, localized paramagnetic centres) in coarse grains at high frequencies (e.g.,  $\nu_L = 270$  MHz) where the electrical conductivity is low. However, Larmor frequencies in applied fields  $B_0$  low enough such that superconductivity is not suppressed are, naturally, of particular interest. In such fields the skin effect becomes very pronounced even at temperatures well above  $T_c$ . We have shown that in this situation the ‘long’ component of the relaxation function is still a good measure for the conduction electron contribution to the nuclear relaxation.

It is worth pointing out that the enhancement of the relaxation rate in the coarse grains observed at  $\nu_L = 13.5$  MHz for  $T$  near and below  $T_c$  is a real effect and not an artifact of the treatment of the raw data.

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