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Proton NMR Relaxation in the High-T_c Organic Superconductor β-(BEDT-TTF)$_2$I$_3$.

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Abstract. – We report the measurement of a striking enhancement of the proton spin-lattice relaxation rate occurring at the critical temperature in the high-T_c superconducting state of β-(BEDT-TTF)$_2$I$_3$. The T_1^{-1} behaviour is attributed to a logarithmic critical singularity whose amplitude is enhanced by the low-dimensional character of these conductors.

1. Introduction.

The new series of organic conductors based on the (BEDT-TTF) ([1]) molecule has provided a superconductor β-(BEDT-TTF)$_2$I$_3$ with a T_c significantly higher than values encountered in the Bechgaard series [1]. First, superconductivity has been observed at 7.4 K in this compound under a pressure of ~ 1.3 kbar [2, 3]. Recently, we have shown that the high-T_c phase (called β-H) can be stabilized at ambient pressure following a well-defined process [4]. At 1 bar, without any pressure-temperature cycling, the β-H phase transforms into the thermodynamically stable phase (β-L) which is not yet fully characterized, but is presumably related to the structural instability taking place below 200 K [5].

In this work, we have performed a ^{1}H NMR study in both superconducting and metallic states. Under a pressure of 1.6 kbar, a large field-dependent anomaly of the spin-lattice relaxation rate is observed at the superconducting transition temperature. At atmospheric pressure, the T_1 behaviour clearly depends on the nature of the phase stabilized at low temperature: β-H or β-L.

([1]) BEDT-TTF = Bis(ethylenedithio)tetrathiofulvalene

2. Experimental.

Details concerning the preparation of the β-(BEDT-TTF)$_2$I$_3$ crystals can be found elsewhere [6]. Because of the high conductivity in this compound even in the metallic state, we have used a powdered sample with small-size grains of total weight ~ 30 mg.

A pulsed NMR spectrometer was operated at frequencies 25.9 and 12.4 MHz corresponding, respectively, to a resonant magnetic field of 6.1 and 2.9 kG for proton. All measurements were performed with the single-coil geometry. The spin-lattice relaxation time was determined by observing the time recovery of the free induction after a saturation comb pulse over more than one decade. In the case of a nonexponential relaxation, the recovery curves can be described with two time constants, which do not differ by more than 20%. Thus, T_1 is defined as the weighted average ($\frac{1}{3}$-$\frac{2}{3}$) of these two values and the error bars in fig. 1 and 2 take this difference into account.

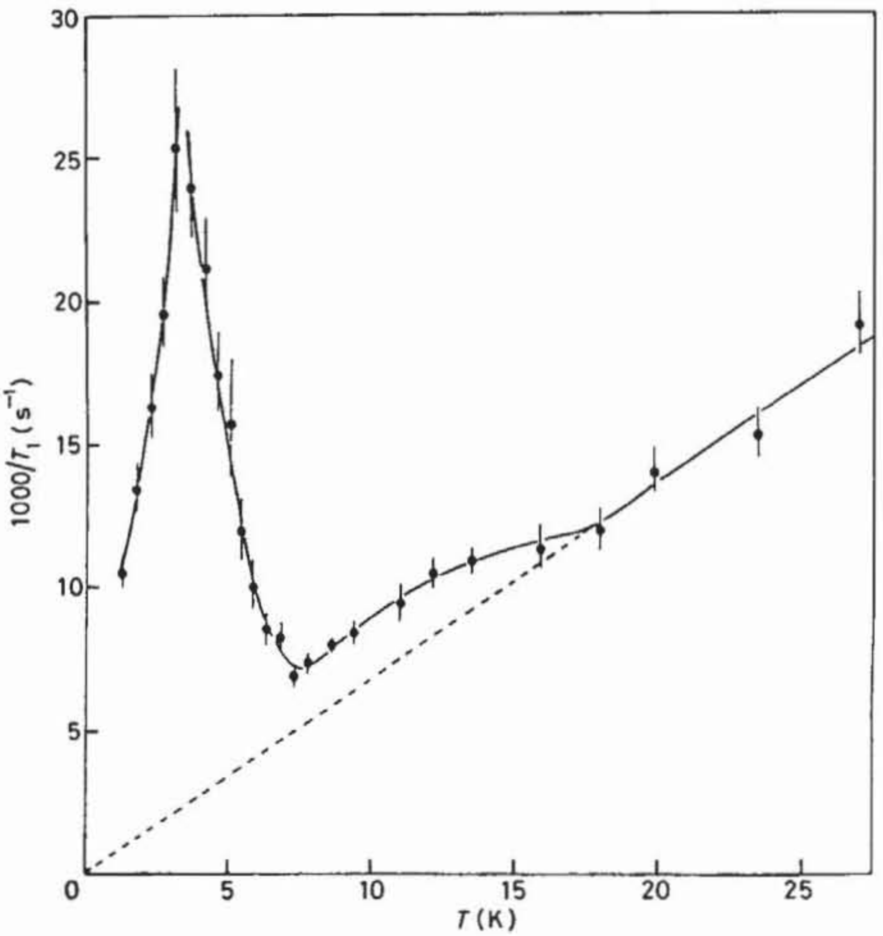

Fig. 1. – ^{1}H spin-lattice relaxation rate in β-(BEDT-TTF)$_2$I$_3$ under a pressure of 1.6 kbar at 6.08 kG.

3. Results.

The superconducting character of the transitions reported here was checked by the AC susceptibility technique reported in details in ref. [5].

$P = 1.6$ kbar. The results of the spin-lattice relaxation rate *vs*. temperature displayed in fig. 1 for a magnetic field of 6.1 kG can be devided into four parts. At high temperature, say above 18 K, a Korringa-like law $(T_1 T) = \text{const}$ is verified. Below 18 K, a slight enhancement of the spin-lattice relaxation rate compared to the expected Korringa behaviour takes place. Note that it is not possible to consider the whole temperature domain

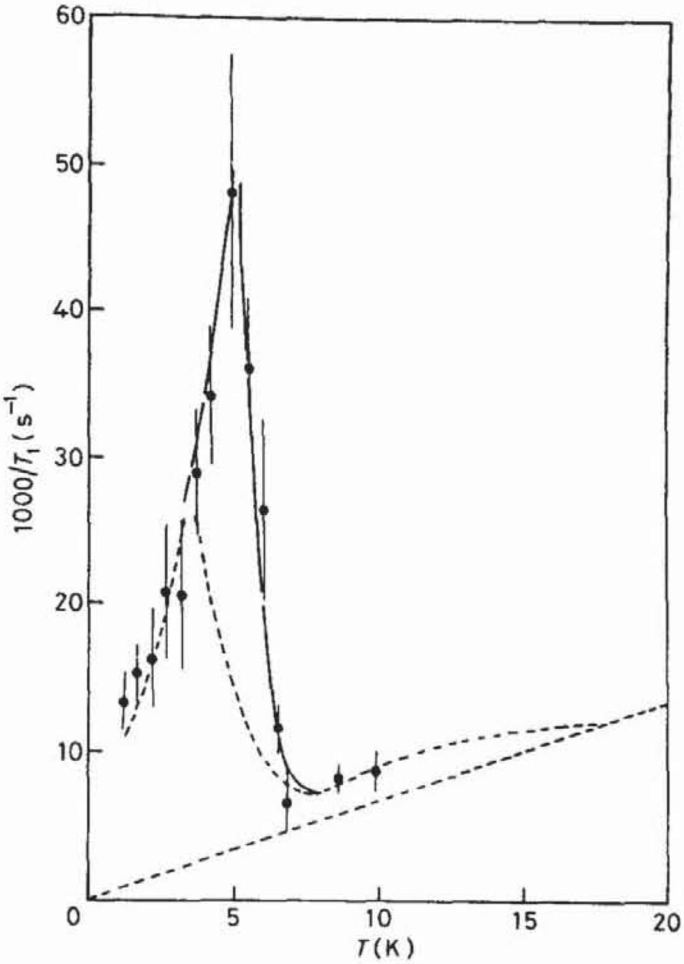

Fig. 2. – ^{1}H spin-lattice relaxation rate in β-(BEDT-TTF)$_2$I$_3$ under a pressure of 1.6 kbar at 2.91 kG. The dashed line represents the 6.08 kG data.

$(8 \div 27)$ K as a Korringa behaviour limited by an additional constant relaxation mechanism due to impurities, since the ambient pressure data do reveal a significantly longer $T_1(1000/T_1 = 1.8\,s^{-1})$ at 1.2 K. At 7.5 K, a rapid enhancement of the spin-lattice relaxation rate is observed, while decreasing the temperature down to 3.5 K. Furthermore, in this temperature region the relaxation was found slightly nonexponential. The anisotropy of the upper critical field H_{c2} in these materials [7] indicates that the lowest value of H_{c2} is obtained along c^*, which corresponds to 3.5 K at the considered field. This implies that in the temperature domain $(3.5 \div 7.5)$ K, the powdered sample becomes gradually superconducting, depending on the orientation of the individual crystallites with respect to the applied magnetic field. At low temperature ($T < 3.5$ K), the spin-lattice relaxation rate decreases, but does not tend towards zero. This is presumably not an impurity effect as already pointed out on account of the low value for T_1^{-1} obtained under atmospheric pressure at the same field. We have noticed that the comb pulse was less efficient to saturate the magnetization in this temperature domain [2] and that the relaxation was still nonexponential.

Figure 2 shows the main feature of the ^{1}H spin-lattice relaxation rate properties at the superconducting transition. The dashed line draw the previous measurement at 6.1 kG. The new data obtained at lower field (2.9 kG) do not deviate from this line, except in the

[2] Quantitatively, the residual magnetization just after the comb pulse was less than 10% of the total magnetization; this may be due to a modification of the RF penetration depth in the superconducting state.

temperature interval $(3.5 \div 7.5)$ K (solid line). The larger enhancement occurs in a reduced temperature window ($(5 \div 7.5)$ K) in good agreement with the reduction of the H_{c2} anisotropy, and $1/T_1$ peaks at a much higher value. At 5 K the spin-lattice relaxation rate decreases and meets the higher-field data at 3.5 K. It is easy to imagine that, at zero field, the typical behaviour of the spin-lattice relaxation rate without anisotropy would be a very sharp increase at 7.6 K followed by a smoother decrease at lower temperature which resembles very closely a lamba-like anomaly.

$P = 1$ bar. The work of ref. [4] and [5] has already shown that it is possible to prepare β-(BEDT-TTF)$_2$I$_3$ at ambient pressure in either β-H or β-L phases, exhibiting superconductivity at high T_c or low T_c, respectively. First, using the Orsay process [4], we have stabilized the β-H phase at 1 bar. Figure 3 shows that there is essentially no significant deviation of the NMR relaxation properties from those obtained at 1.6 kbar. Secondly, by annealing at 250 K, the sample was prepared in the β-L phase at low temperature. The corresponding results displayed in fig. 3 do not reveal any anomaly around 8 K. At high temperature, a reduction of the Korringa constant is clearly observed and amounts to about 25%.

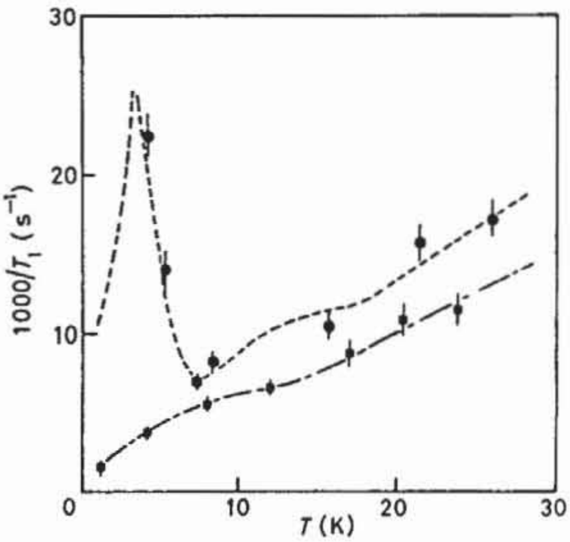

Fig. 3. – ^{1}H spin-lattice relaxation rate in β-(BEDT-TTF)$_2$I$_3$ at ambient pressure in both states β-L (■) and β-H (•).

4. Discussion.

In the following, we shall discuss in more details the origin of the divergence of the nuclear relaxation in the very vicinity of T_c, since the effect of local field inhomogeneities does not allow a simple interpretation of the data far below T_c [8]. By looking at the data of fig. 2, it is interesting to notice that the field dependence of the temperature which corresponds to the peak of the relaxation is essentially the same as that for the superconducting transition temperature when $H \| c^*$ [3]. This feature indicates that the divergence of the spin-lattice relaxation rate is connected to the appearance of superconducting long-range order. It is also clear from this figure that the amplitude of the enhancement increases at smaller fields. This fact contrasts, however, with the temperature for the onset of the enhancement which is apparently field independent and located near the zero field value of $T_c \sim 7.5$ K. This shows that the true critical width in the limit of zero applied field must be very small. In fact, the apparent large and symmetrical critical width observed at $H = 6$ kG seems to be extrinsic and probably comes from a powder effect on T_c

vs. H. In the zero field limit, the powder exhibits a unique value of $T_c \sim 7.5$ K and we expect, as supported clearly by the 3 kG data, a singularity of the spin lattice relaxation rate taking place within a very small critical width. Such a critical profile of T_1^{-1} is reminiscent of logarithmic or lambdalike singularities where the critical width is exponentially small.

For an isotropic singlet superconductor, MANIV and ALEXANDER (MA) [9] have shown that the first-order fluctuation contribution to the spin-lattice relaxation rate is logarithmically singular in H_0 as T_c is approached from above. As noted by MA, this critical contribution to T_1^{-1} has to be distinguished from the well-known Hebel-Slichter [10] effect which takes place only in the presence of a finite superconducting gap ($T < T_c$). For an organic superconductor, which is expected to show somewhat anisotropic properties, the result of MA for the spin-lattice relaxation rate critical enhancement $(T_1^{-1})_c$ over the normal metal or Korringa-like contribution $(T_1^{-1})_K$ becomes

$$\frac{(T_1^{-1})_c}{(T_1^{-1})_K} \simeq \left(\frac{\pi}{2k_F\xi_0}\right)^2 I \ln\left[\left(r + A\left(\frac{\omega_N}{T}\right)^2\right)^{-1}\right], \qquad A \approx 10^{-2}, \tag{1}$$

which is valid for a 3D anisotropic system. Here $(\pi/2k_F\xi_0)^2$ is the amplitude of the logarithmic singularity given by MA for the isotropic case with $\xi_0 = 7\zeta(3)/8\pi^2 T_c^2$ as the Ginzburg-Landau coherence length in the direction of highest conductivity ($\zeta(3) = 1.21\ldots$) and k_F is the Fermi wave vector. The nuclear Larmor frequency ω_N is proportional to the static magnetic field H_0 through the nuclear gyromagnetic ratio γ_N and $r = \ln(T/T_c) \approx ((T - T_c)/T_c)$. It is a numerical factor which depends on the anisotropy of the electronic spectrum and is given by

$$I = \frac{1}{2}\int_0^{\pi} \frac{d\varphi}{[\eta_x^2\cos^2\varphi + \eta_y^2\sin^2\varphi]^{\frac{1}{2}}} \qquad (\eta_x < 1,\ \eta_y < 1) \tag{2}$$

with $\eta_x = t_b/t_a$ and $\eta_y = t_c/t_a$. t_i is the electronic overlap integral in the i-direction ($i = a, b, c$). For the $(BEDT\text{-}TTF)_2X$ compounds, band calculations [11] predict a closed Fermi surface in the (a, b)-plane with $t_b \approx t_a/2 \approx 0.1$ eV. The anisotropy in the c direction, though much stronger, is not known so far, but it is expected to be similar to the one found in $(TMTSF)_2X$ compounds. From the experimental data of ref. [12], we will take for β-$(BEDT\text{-}TTF)_2I_3$, $t_a \sim 2t_b \sim 10^2 \ldots 10^3 t_c$, which gives with eqs. (1) and (2) $(\pi/2k_F\xi_0)^2 \sim 10^{-3}$ and $I \sim 10^2 \ldots 10^3$. It follows, from this order of magnitude analysis, that the amplitude of the logarithmic divergence is no longer a small number and the effect of superconducting fluctuations on the relaxation becomes dominant in the vicinity of the transition. At T_c, for example, the expression (1) gives an upper bound for the enhancement of the order of $\ln(T_c^2/A\omega_N^2) \sim 30$ with $A(\omega_N^2/T_c^2) \sim 10^{-11}$ and 10^{-12} at fields $H = 6.1$ kG, and 2.9 kG, respectively. These values account fairly well for observed enhancements of the order of 10 for both fields.

Finally, the ratio of Korringa constants in the β-L state and the β-H state stabilized at ambient pressure by the Orsay process is not large enough to explain the ratio of critical temperatures (by a density of states effect) within the BCS formalism, assuming a constant pairing interaction. Consequently, these results suggest different pairing interactions for the superconducting phases.

5. Conclusion.

The spectacular feature of the spin-lattice relaxation rate clearly demonstrates that organic superconductors are probably the best candidates to make critical fluctuation effects observable. In this respect, it is of interest to estimate the amplitude of the enhancement for $(TMTSF)_2X$ superconductors. For these compounds, $T_c = 1$ K and this gives $(\pi/2k_F\xi_0)^2 \sim 10^{-4}$ for the isotropic part. The electronic spectrum is very anisotropic, however, giving rise to an open Fermi surface characterized by $t_a \sim 0.25$ eV $\sim 15t_b \sim 500t_c$ and leading to $I \sim 10^2$. Therefore, the amplitude of the logarithmic singularity has an upper bound of 10^{-1} or so. Fluctuation effects on the spin-lattice relaxation rate should then be detectable at low enough fields.

Furthermore, this work has shown that the metastable β-H phase at ambient pressure cannot be distinguished from the same phase stabilized under pressure.

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