# Proton spin-lattice relaxation in β-(BEDT-TTF)$_2$I$_3$

I. A. Heinmaa, M. A. Alla, A. M. Vaĭnrub, and E. T. Lippmaa

*Institute of Chemical and Biological Physics, Academy of Sciences, Estonian SSR*

(Submitted 20 September 1985)
Zh. Eksp. Teor. Fiz. **90**, 1748–1754 (May 1986)

The temperature dependence of the proton spin-lattice relaxation rates in the metallic state of the organic superconductor $\beta$-(BEDT-TTF)$_2$I$_3$ is measured in magnetic fields from 6 to 117 kG. Two distinct relaxation pathways are found, and their relative contributions are determined. Since one of the mechanisms involves proton-proton dipole coupling, this indicates that low-frequency molecular motion must occur in BEDT-TTF; the motion is thermally activated with an energy of $E_0 = 2100$ K and has a characteristic frequency of $\sim 10^8$ Hz at $T = 300$ K. The other relaxation channel involves the conduction electrons and obeys the Korringa relation at low temperatures, but for $T > 150$ K it exhibits features typical for systems with two-dimensional spin diffusion.

## 1. INTRODUCTION

The various crystalline bis(ethylenedithiolo)tetrathiofulvalene (BEDT-TTF) iodides form a novel class of quasi-two-dimensional organic metals, many of whose members become superconducting at low temperatures.[1] The triclinic $\beta$-modification (BEDT-TTF)$_2$I$_3$ in particular is of great interest owing to its striking superconducting properties. $\beta$-(BEDT-TTF)$_2$I$_3$ was first prepared by electrochemical oxidation in Ref. 2 and was found to be a superconductor with $T_c = 1.4$–$1.5$ K at atmospheric pressure. Shortly thereafter it was discovered that $T_c$ is higher for $\beta$-(BEDT-TTF)$_2$I$_3$ crystals grown by other methods, and these materials currently have the highest temperatures $T_c = 6$–$7$ K yet reported for organic superconductors.[3] $T_c$ also increases markedly from 1.5 to 7 K when a hydrostatic pressure ($P = 1.2$ kbar) is applied,[4] and this high value persists even after the pressure is removed.[5]

The multilayered crystal structure of $\beta$-(BEDT-TTF)$_2$I$_3$ (Ref. 6) and the behavior of the anisotropy of the upper critical magnetic field for superconductivity[7] indicate that the electron motion is two-dimensional and confined to the *ab* crystallographic plane. The conductivity in this plane is $\sim 30\ \Omega^{-1}\cdot\text{cm}^{-1}$ at $T = 300$ K and increases steadily by a factor of 150–500 as $T$ drops to 4.2 K (Refs. 2,7). A structural transition to an incommensurate phase occurs near 200 K (Ref. 8). Although the thermal emf changes sign here, the temperature dependence of the paramagnetic susceptibility has only a weak peak,[9] indicating that the electron rearrangement during the phase transition is minimal.

Nuclear relaxation studies are a powerful tool for analyzing molecular motion in solids and hyperfine interactions in metals.[10] In the present work we measure the proton spin-lattice relaxation in metallic $\beta$-(BEDT-TTF)$_2$I$_3$ and obtain data on the molecular dynamics and electron system.

## 2. EXPERIMENTAL METHOD

The $\beta$-(BEDT-TTF)$_2$I$_3$ crystals were prepared at the Institute of Chemical Physics at the same time as the specimens used in Ref. 9, in which the growth technique and the properties of the crystals were described. To keep the intense rf pulses from heating the conducting crystals, the NMR specimens were prepared by mixing 21 mg of randomly oriented $\beta$-(BEDT-TTF)$_2$I$_3$ single crystals with a pre-dried glass-ceramic powder. An SKhR-200 NMR spectrometer (manufactured by the firm Bruker) was used in the measurements. The magnetic fields were generated by superconducting solenoids with fixed fields 47 kG (proton Larmor frequency $f = 200$ MHz) and 85 kG ($f = 360$ MHz) together with an electromagnet that produced a weaker field 6.1–9.6 kG ($f = 26$–$40$ MHz). The measurements at $H = 177$ kG (500 MHz) were made using an AM-500 high-resolution spectrometer, also made by Bruker.

The measurements at 200 and 360 MHz were carried out at temperatures $4 \leqslant T \leqslant 300$ K in a helium cryostat (diam 75 mm) which we built ourselves. The capacitors used to tune the NMR sensor were located outside the cryostat at room temperature and were connected to the NMR coil by a matched coaxial line of length equal to a multiple of $\lambda/2$. This arrangement made it easy to tune the NMR frequency over a wide range and enabled us to use the narrow $^{79}$Br resonance ($f = 50.1$ kG, $H = 47$ kG) in polycrystalline KBr as a low-temperature reference for measuring the NMR shifts. At the other frequencies the distance between the magnet poles was too small to accommodate the cryostat, and the crystals were therefore cooled by a stream of liquid nitrogen vapor.

The spin-lattice relaxation time was measured by the saturation-recovery technique. The broad NMR line was saturated by applying a sequence of 100 rf pulses of length 5 $\mu$s, where each pulse was separated by 5 ms. After a suitable delay $\tau$, a $\pi/2$-pulse was applied and the drop in the free induction was recorded. The rf field intensities for the various sensors ranged from 50 to 80 kG. The recovery of the magnetization was nearly exponential in all of the measurements above 40 K. Below 40 K, the recovery was better approximated as a sum of two exponentials. The reason for this behavior remains unclear, and in any case we continued to use a single-exponential approximation to calculate the relaxation time for $T < 40$ K.

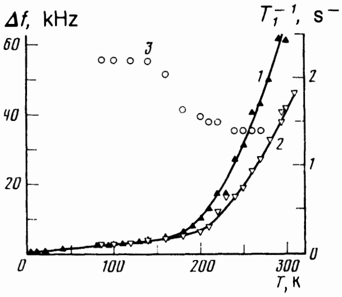

FIG. 1. Temperature dependence of the spin-lattice relaxation rate $T_1^{-1}$ (NMR frequency $f = 200$ MHz and 360 MHz, curves 1, 2, respectively) and NMR linewidth $\Delta f$ (curve 3, $f = 360$ MHz).

## 3. EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependence of the spin-lattice relaxation rate $T_1^{-1}$ at the NMR frequencies $f = 200$ and 360 MHz, along with the measured NMR linewidths $\Delta f$ at half-maximum. We see that $T_1^{-1}$ was proportional to $T$ and was independent of the NMR frequency $f$ for $T \leqslant 150$ K. $T_1^{-1}$ increased more rapidly as $T$ rose above 150 K, and the faster growth rate commenced sooner for $f = 200$ MHz than for $f = 360$ MHz. This change in $T_1^{-1}(T)$ was preceded by a narrowing of the NMR line from $\Delta f = 55$ kHz at $T = 140$ K to $\Delta f = 38$ kHz at $T \geqslant 220$ K. Figure 1 shows the dependence $\Delta f(T)$ for $f = 360$ MHz; the linewidth and temperature behavior were similar for $f = 200$ MHz.

Figure 2 shows that for $T > 200$ K, $T_1^{-1}$ increased as $f$ decreased, and the curves $T_1^{-1}(T)$ also differed at high and low frequencies. At the high frequencies $f = 200$, 360, and 500 MHz, $T_1^{-1}$ increased monotonically upon heating to room temperature, while at the low frequencies $f = 30$ and 40 MHz, $T_1^{-1}$ had peaks near 260 and 275 K, respectively.

## 4. DISCUSSION

Two mechanisms must be considered in order to explain the proton spin-lattice relaxation in $\beta$-(BEDT-TTF)$_2$I$_3$. The first mechanism is typical for metals and can be described by the relaxation rate $T_{1e}^{-1}$; it is due to the hyperfine coupling with the conduction electrons. According to this mechanism, in conductors with little carrier scattering (mean free path much greater than the lattice constant), $T_{1e}^{-1}$ is independent of the external magnetic field (equivalently, the nuclear Larmor frequency) and obeys the Korringa relation $T_{1e}TK^2 = \text{const}$, where $K$ is the Knight NMR shift.[10] Studies using TCNQ complexes[11] have shown that diffusion of the electron spins determines the relaxation in conductors with strong carrier scattering (mean free path comparable to the lattice constant). The field (frequency) dependence depends on whether the diffusion is one-, two-, or three-dimensional, $T_{1e}^{-1}$ being proportional to $\omega^{-1/2}$, $\ln(1/\omega)$, and independent of $\omega$, respectively. The temperature dependence of $T_{1e}^{-1}$ is determined by the temperature dependence of the diffusion coefficients.

For a model two-dimensional gas of nearly free electrons, we can use the formula

$$l = \hbar\sigma k_F/e^2 n, \quad k_F = (4\pi p/ab)^{1/2}$$

to estimate the mean-free carrier path in $\beta$-(BEDT-TTF)$_2$I$_3$, which gives $l = 3800$ and $l = 3$ Å at $T = 4.2$ and 150 K, respectively. Here $k_F$ is the Fermi wave vector, $n = 5.9 \cdot 10^{20}$ cm$^{-3}$ is the density of the conduction electrons, $a = 6.6$ Å and $b = 9.1$ Å are the lattice constants in a crystal layer of conductivity $\sigma$ (Ref. 6), where $\sigma \approx 1.5 \cdot 10^5$ and 100 $\Omega^{-1} \cdot$cm$^{-1}$ at $T = 4.2$ and 150 K, respectively,[2,7] and $p = 0.5$ is the fill-factor for the conduction band. We see that the mean free path $l$ is much greater than $a$, $b$ at low temperatures but becomes smaller than the lattice parameters as $T$ increases.

The other relaxation mechanism is described by the rate $T_{1n}^{-1}$ and is due to dipole-dipole coupling between the nuclear spins.[10] This mechanism is important only if the nuclear spins move in such a way that the dipole coupling is modulated at a frequency comparable to the nuclear Larmor frequency. We will show below that our data imply that such a modulation occurs in $\beta$-(BEDT-TTF)$_2$I$_3$, and the properties of the corresponding nuclear motion will be determined. The two relaxation mechanisms may be taken to be independent, so that the total relaxation rate is the sum

$$T_1^{-1} = T_{1e}^{-1} + T_{1n}^{-1}.$$

We first consider the measurement results at low frequencies. The fact that $T_1^{-1}$ is proportional to $T$ and independent of $H$ (Fig. 1), and the long mean-free path at these temperatures both indicate that the Korringa relaxation mechanism is dominant here. With the data in Fig. 1, the Korringa relation gives an upper bound $K = 1.5 \cdot 10^{-5}$ for the Knight shift. Such a value is typical for situations when the hyperfine interaction is dominated by an isotropic contact contribution, but it is too high if anisotropic dipole-dipole coupling is also important. The relative magnitudes of these two components of the hyperfine interaction are not known for the protons in $\beta$-(BEDT-TTF)$_2$I$_3$; however, because the Knight shift is less than 3 kHz at a Larmor frequency $f = 200$ MHz, $K$ cannot be determined for the experimentally observed linewidths $\Delta f = 55$ kHz.

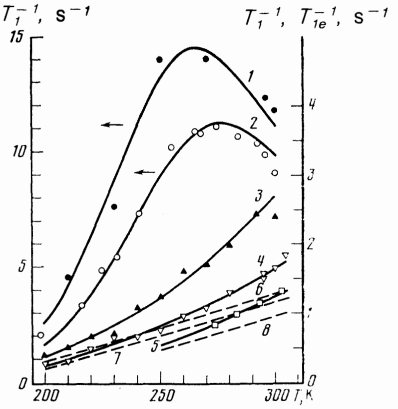

FIG. 2. Temperature dependence of the total spin-lattice relaxation rate $T_1^{-1}$ (curves 1–5) and its electron component $T_{1e}^{-1}$ (curves 6–8): 1) $f = 30$ MHz; 2) 40 MHz; 3) 200 MHz; 4, 7) 360 MHz; 5, 8) 500 MHz; 6) 30, 40, and 200 MHz. Points give experimental data, curves plot calculated values.

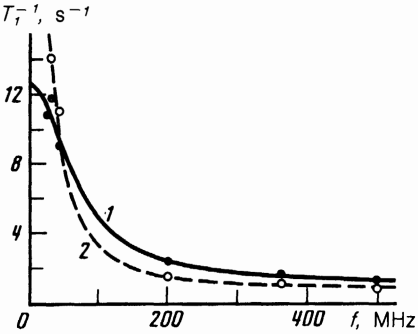

FIG. 3. Spin-lattice relaxation rate vs NMR frequency: 1) $T = 300$ K; 2) 267 K. The points give experimental values, the curves show the approximation obtained using Eq. (1).

We now discuss the measurements for $T > 100$ K. At low temperatures, the width of the NMR line is determined by the dipole-dipole coupling of the protons in a rigid lattice. Indeed, for an isolated methylene group ($-CH_2-$), the splitting in a Peik doublet in equal to 37 kHz. The observed width $\Delta f = 55$ kHz is in full agreement with the dipole width if we correct for the additional broadening due to the inter- and intramolecular interactions of the ($-CH_2-$) groups. Due to the anisotropy of the chemical bonds and the spatial variations of the demagnetizing field in the polycrystalline specimen, any broadening proportional to the external magnetic field was negligible and too small to be observed experimentally. The narrowing of the line above $T = 140$ K reflects the "unfreezing" of the motions of the BEDT-TTF molecule, which tend to average-out the dipole-dipole interaction. As pointed out above, these motions permit relaxation via the dipole channel, and the relaxation rate is given by[10]

$$T_{1n}^{-1} = 4\pi^2 A^2 [\tau_c (1+\omega^2\tau_c^2)^{-1} + 4\tau_c (1+4\omega^2\tau_c^2)^{-1}], \qquad (1)$$

where $A^2$ is the mean-square amplitude ($A$ is modulated by the motion of some of the interacting dipoles); $\tau_c$ is the correlation time; $\omega = 2\pi f$ is the Larmor frequency. We note that by (1), the relaxation is fastest when $\tau_c$ satisfies $\omega\tau_c = 0.616$.

Figure 3 shows the frequency dependence $T_1^{-1}(f) = T_{1e}^{-1} + T_{1n}^{-1}$ calculated using (1) together with experimental results for $T = 300$ and 267 K deduced from the data in Fig. 2, supplemented by data for $f = 26$ MHz. The agreement is seen to be good if we take $A = 6.66$ kHz, $\tau_c = 1.34 \cdot 10^{-9}$ and $3.07 \cdot 10^{-9}$ s, and $T_{1e}^{-1} = 1$ and 0.8 s$^{-1}$ for $T = 300$ and 267 K, respectively. We note that $A$ remains unchanged but $\tau_c$ increases as $T$ drops. In comparing the experimental and calculated values, we assumed that $T_{1e}^{-1}$ is independent of $f$; this will be justified below, where we see that $T_{1e}^{-1}$ is much less sensitive than $T_1^{-1}$ to the Larmor frequency, so that $A$ and $\tau_s$ remain virtually unchanged if the dependence $T_{1e}^{-1}(\omega)$ is included.

Our analysis of the dipole relaxation also yields a qualitative explanation for the observed temperature dependence $T_1^{-1}(T)$ in various magnetic fields $H$ (Fig. 2). Indeed, since $A(T) = \text{const}$ and $\tau_c$ increases with $1/T$, the maxima at $f = 30$ and 40 MHz reflect the fact that $\tau_c$ is smallest here (i.e., the condition $\omega\tau_c = 0.616$ for fastest relaxation is satisfied); we thus get $\tau_c = 3.27 \cdot 10^{-9}$ and $2.45 \cdot 10^{-9}$ s for $T = 260$ and 275 K, respectively. For $f \geqslant 200$ MHz, $\omega\tau_c$ was greater than 0.616 at all temperatures and $T_1^{-1}$ did not pass through a maximum. One must know the dependence $\tau_c(T)$ explicitly before (1) can be used to describe $T_{1n}^{-1}(T)$ quantitatively. If we assume that the correlation times obeys the Arrhenius law $\tau_c = t_0 \exp(E_0/kT)$ (the physical significance of this is discussed below), the above values $\tau_c$ give $\tau_0 = 1.2 \cdot 10^{-12}$ s and a thermal activation energy $E_0 = 2100$ K. We estimated $T_{1e}^{-1}$ by subtracting the calculated rate $T_{1n}^{-1}$ from the experimentally measured $T_1^{-1}$. Figure 2 shows the resulting dependence $T_{1e}^{-1}(T)$ (dashed curves 6–8) and $T_1^{-1} = T_{1e}^{-1} + T_{1n}^{-1}(T)$ (solid curves 1–5) for several magnetic fields. We see that the estimate for $T_{1e}^{-1}(T)$ is quite inaccurate for $f = 30$ and 40 MHz, because $T_{1e}^{-1}$ is $\ll T_1^{-1}$ and coincides with $T_{1e}^{-1}(T)$ for $f = 200$ MHz to within the experimental error. For $f \geqslant 200$ MHz, $T_{1e}^{-1}$ increases with $T$ or with $1/H$, as predicted by the relation

$$T_{1e}^{-1} \propto (T/D)[\ln(D/ab\omega) + C],$$

for the relaxation rate in the two-dimensional spin diffusion model; here $D$ is the diffusion coefficient, and the constant $C$ depends on the parameters of the hyperfine interaction.[11] The observed departure from the proportionality $T_{1e}^{-1} \propto T$ probably reflects a decrease in $\sigma$ (and hence also in $D$) with increasing $T$.

The results yield several conclusions about the nature of the molecular motion in $\beta$-(BEDT-TTF)$_2$I$_3$. The interaction within the methylene group at ~40 kHz is substantially stronger than the other proton-proton interactions and is therefore presumably responsible for the component of the dipole-dipole interaction modulated by the molecular motion ($A = 6.66$ kHz). This motion reorients the proton-proton vector in the ($-CH_2-$) group relative to the external magnetic field, so that dipole relaxation takes place due to fluctuations in the dipole-dipole coupling strength. The most likely candidates are thermally activated transitions between two nonplanar conformations of the BEDT-TTF molecule. If the geometry of the conformations is independent of temperature, then $A(T) = \text{const}$ and the transition frequency (which determines the inverse correlation time) obeys the Arrhenius law, which justifies the assumptions made in describing the experimental results. This molecular motion is consistent with the results of structural studies at $T = 300$ K, which reveal that the position of one of the two ethylene groups in BEDT-TTF is slightly distorted whereas the other is not.[6] According to these results, the transition between the two conformations should affect only one-half of the BEDT-TTF molecule, and spin diffusion determines the relaxation time, which is the same for all the protons in the molecule.

Indeed, consider a pair of protons which are joined by a vector of length $r$ making an angle $\theta$ with the external field; then the frequency of the dipole-induced flip-flop transitions for this pair is given by the expression

$$W = (\pi/2)\omega_1^2 f(\omega_0), \qquad \omega_1 = (\gamma^2\hbar/2r^3)(1-3\cos^2\theta),$$

where the NMR lineshape function $f(\omega)$ is normalized to unity and has a maximum at $\omega = \omega_0$ (Ref. 10, p. 138). We have $f(\omega_0) = 1.67(2\pi\Delta f)^{-1}$ and $0.636(2\pi\Delta f)^{-1}$ for Gaussian and Lorentzian lines, respectively, and we obtain

$$W=(1/2\Delta f)(\gamma^2\hbar/r^3)^2\approx 140\ \mathrm{s}^{-1}$$

if we use the approximation $f(\omega_0) = (2\pi\Delta f)^{-1}$ (where $\Delta f \approx 50$ kHz is the linewidth at half-maximum), average $\omega_1^2$ over all angles $\theta$ in the polycrystalline specimen, and substitute the minimum value $r\approx 4$ Å (Ref. 6) for the distance between the protons in the stationary and vibrating ethylene groups in two neighboring molecules in the crystal. Since this value of $W$ is an order of magnitude larger than the maximum observed relaxation rate $T_1^{-1} = 14\ \mathrm{s}^{-1}$, we conclude that the relaxation time is identical for all the protons because of the spin diffusion.

The onset of NMR line narrowing at $T = 140$ K is consistent with structural distortion in $\beta$-(BEDT-TTF)$_2$I$_3$ even below the temperature at which the structural transition occurs.[8] If we use the experimentally observed exponential temperature dependence of the correlation time, we get an estimate for the temperature at which the line starts to narrow which is 40 K below the experimentally observed value. This discrepancy could reflect a decrease in the conformational transition frequency in the incommensurate phase present at low temperatures.

## 5. CONCLUSIONS

We have found that spin-lattice relaxation in $\beta$-(BEDT-TTF)$_2$I$_3$ is caused by dipole-dipole coupling, which indicates that intramolecular motion must occur at low frequencies (comparable to the Larmor frequency of the protons). Nuclear relaxation due to the conduction electrons is typical of metals, but in the case of $\beta$-(BEDT-TTF)$_2$I$_3$ it has features that reflect the quasi-two-dimensional nature of the electron system and the small carrier mean-free path at high temperatures.

We are grateful to É. B. Yagubskiĭ for supplying the $\beta$-(BEDT-TTF)$_2$I$_3$ crystals, and to L. I. Buravov and I. F. Shchegolev for helpful discussions and assistance in building the NMR cryostat.

*Note added in proof (27 March 1986):* After this paper was submitted, results on the crystal structure of $\beta$-(BEDT-TTF)$_2$I$_3$ at $T = 120$ K were reported by P. C. W. Leung, T. J. Emge, M. A. Beno, *et al.* [J. Am. Chem. Soc. **107**, 6184 (1985)]. These data confirm that conformational changes occur in the BEDT-TTF molecule—a transition of the half-chair inversion type occurs in one of the two six-membered $C_2S_2C_2H_4$ rings of the molecule. It is noteworthy that our thermal activation energy $E_0 = 2100$ K for the conformational transition is comparable to the height of the barrier (2700 K) for half-chair inversion in a cyclohexane molecule.

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Translated by A. Mason