Classification
Physics Abstracts
75.30 — 75.50

¹H-NMR relaxation measurements in the organic conductors : (TMTTF)₂Br (*) and (TMTTF)₂PF₆ ()**

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(Reçu le 9 juillet 1982, révisé le 20 septembre, accepté le 21 septembre 1982)

Résumé. — Les propriétés électroniques de (TMTTF)₂Br et (TMTTF)₂PF₆ ont été étudiées par des mesures de relaxation du proton en Résonance Magnétique Nucléaire. Par la mise en évidence d'anomalies sur T_1^{-1} , T_2 et T_2^* , nous montrons que l'état semiconducteur dans (TMTTF)₂Br à basse température est un état d'onde de densité de spin, à la pression ambiante et à 13 kbar. Une transition de phase est aussi observée dans (TMTTF)₂PF₆. Cependant, dans ce dernier système, l'amplitude de l'aimantation n'est pas aussi prononcée. Nous considérons comme très probable la coexistence de modulation de spin et de réseau dans l'état basse température de (TMTTF)₂PF₆.

Abstract. — The electronic properties of (TMTTF)₂Br and (TMTTF)₂PF₆ have been studied by ¹H-NMR relaxation measurements. The low temperature semiconducting state in (TMTTF)₂Br is shown to be a SDW state at ambient pressure and at 13 kbar, by the anomalies in T_1^{-1} , T_2 and T_2^* . A phase transition is also observed in (TMTTF)₂PF₆. However, in this latter system, the amplitude of the magnetization is not so pronounced. We consider as very likely the coexistence of spin and lattice modulations in the low temperature state of (TMTTF)₂PF₆.

1. Introduction. — Organic conductors based on the TMTSF (tetramethyl tetraselenafulvalene) molecule are of great interest since superconductivity has been discovered in (TMTSF)₂PF₆ under pressure [1]. In spite of extrinsic effects depending on the behaviour of the inorganic anion, common features are exhibited by all members of the family (TMTSF)₂X. One of them is the magnetic character of insulating state i.e. a spin density wave (SDW)-state [2]. Furthermore, the sulfur analog family (TMTTF)₂X seems to be somewhat different. Although the families are isostructural, experimental results such as conductivity measurements at ambient pressure [3] indicate that (TMTTF)₂X is more one-dimensional, in a good agreement with the comparison of van der Waals radii of selenium and sulfur. Conductivity measurements under high pressure

(*) IUPAC name : Di-(2,2'-bi-4,5-dimethyl-1,3-dithiolyliene) ium-bromide.

(**) IUPAC name : Di-(2,2'-bi-4,5-dimethyl-1,3-dithiolyliene) ium-hexafluorophosphate.

[4, 12] reveal a phase diagram similar to that of the $(\text{TMTSF})_2\text{X}$ series, the critical pressure, for the stabilization of the conducting state at low temperature, being shifted to higher values. This effect has been related to the stronger dimerization of the organic molecules along the chain by theoretical calculations including Umklapp scattering for the electrons [5]. In this respect, $(\text{TMTTF})_2\text{Br}$, with a rather weak dimerization, lies very near the $(\text{TMTSF})_2\text{X}$ family and is therefore an interesting candidate for the investigation of the nature of the insulating state. By proton NMR measurements, we have found clear evidence for the stabilization, below 14 K, of a magnetic phase (SDW), the magnitude of which is enhanced by application of a pressure of 13 kbar.

However, paramagnetic susceptibility [3, 6] and X-ray diffuse scattering [7] data have indicated that, in $(\text{TMTTF})_2\text{PF}_6$, the insulating state is of another nature, with a $2k_F$ lattice distortion and the susceptibility decreasing at the transition temperature. We have found by proton NMR that this phase is much less magnetic than in bromide compound.

2. Experimental. — Powdered samples (~ 20 mg) of $(\text{TMTTF})_2\text{Br}$ and $(\text{TMTTF})_2\text{PF}_6$ prepared by the same method as described elsewhere [8] were used for the ^1H -NMR measurements. A home-made pulsed-NMR spectrometer was operated at a frequency of 45 MHz (the resonance field ~ 10.6 kOe). The amplitude of the RF field determined by the $\pi/2$ -condition is $2H_1 \sim 120$ G. The NMR free induction decay and the spin-echo signals detected by the receiver with the dead time less than $8\ \mu\text{s}$ were digitally sampled on a transient recorder DL 905 of data-lab and analysed with a mini computer Apple II.

The spin lattice relaxation time T_1 was measured by observing the time recovery of the free induction after the saturation comb pulse. The spin-spin relaxation time T_2 was determined by the usual pulse method. T_2^* was determined by the half width at half maximum (HWHM) of the echo signal times $(\ln 2)^{-1}$ assuming a simple exponential echo-shape; the observed echo-shape is somewhere between exponential and Gaussian.

3. Results. — ^1H -NMR relaxation times T_1^{-1} , T_2 and T_2^* on $(\text{TMTTF})_2\text{Br}$ at ambient pressure are plotted *versus* temperature in figure 1a, b, c. A clear peak of the spin-lattice relaxation rate T_1^{-1} is seen at $T \sim 14$ K. In a narrow temperature region (± 4 K) around this temperature, the relaxation was found non-single exponential. The initial and final slopes are plotted and connected by a dashed line. We believe that the non-single exponential behaviour comes from the anisotropic T_1 due to random orientation in the powdered sample. Except in this narrow temperature region, the relaxation is fairly exponential, over more than one decade.

Below 14 K, T_2 increases by about 20 % up to $40\ \mu\text{s}$ (at 4.2 K), while T_2^* decreases by a factor three ($6\ \mu\text{s}$ at 4.2 K). These anomalies in the ^1H -NMR relaxation clearly indicate the onset of the inhomogeneous local field, below 14 K. Since T_2^{*-1} is a measure of the NMR absorption line-width, we can estimate the increase of the local field at ^1H -sites as about 4 Oe. The increase of T_2 below 14 K is ascribed to the nuclear spin decoupling by the microscopic variation of the resonance field [9]; it is a clear evidence of the inhomogeneous nature of the local field. These results enable us to conclude that the SDW phase exists below 14 K.

The results at a pressure of 13 kbar on the same sample of $(\text{TMTTF})_2\text{Br}$ are shown in figure 2a, b, c. Now, the magnetic transition occurs at $T \sim 16$ K, i.e. at temperature higher than at ambient pressure. We also notice that the transition looks narrower than at ambient pressure as indicated by the width of the T_1^{-1} peak and the rapid variation in T_2 . The value of the excess local field below the transition temperature estimated by T_2^{*-1} is larger by 60 % (~ 6.4 Oe). This point seems rather surprising since T_{M-1} does not vary that much with pressure. The depression of the spin-lattice relaxation in the region of $18 < T < 30$ K by the application of the pressure is also noted.

The ^1H -NMR relaxation measurements on $(\text{TMTTF})_2\text{PF}_6$ were performed at ambient pressure. The results are quite different from the case of $(\text{TMTTF})_2\text{Br}$, as shown in figure 3a, b, c.

Fig. 1. — ^1H -NMR relaxation times at low temperatures in $(\text{TMTTF})_2\text{Br}$ at ambient pressure. (a) The spin-lattice relaxation rate T_1^{-1} vs. temperature. The non-single exponential behaviour observed around the peak is expressed by a dashed line connecting the initial and final slopes. (b) The temperature dependence of T_2^* determined by the echo width. (c) The spin-spin relaxation time T_2 vs. temperature.

The spin-lattice relaxation rate reveals a weak step-like anomaly around $T \sim 15 \text{ K} \sim 19 \text{ K}$ instead of a peak. Again in the transition region, the relaxation is non-single exponential (we plotted both of the initial and final slopes of the relaxation curve as before). The relaxation rate below the transition is very high compared with $(\text{TMTTF})_2\text{Br}$ and less temperature dependent. (The scattering of the data below 4.2 K does not seem to be due to the experimental error. The precise measurements in the lower temperature region are left for a forthcoming work.) The small changes in T_2 and T_2^* are also observed but the estimated value of excess local field is nearly one-order of magnitude smaller ($\sim 0.5 \text{ Oe}$) than $(\text{TMTTF})_2\text{Br}$ (note the difference in the vertical scale).

T > 20 K region. — The ^1H spin-lattice relaxation rate in the higher temperature region is shown in figure 4a, b, c. We can observe two broad peaks of T_1^{-1} around 50 K and 100 K for all cases. Since the proton spins are on the methyl groups of the TMTTF molecules, the methyl rotation (as well as other molecular motions) contribute to the ^1H spin-lattice relaxation. Similar behaviours have been reported on $(\text{TMTSF})_2\text{PF}_6$ at ambient pressure [10]. The solid curves have been obtained by assuming the classical picture of the motion which gives [11]:

$$T_1^{-1} = c \left[\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4 \tau_c}{1 + 4 \omega_0^2 \tau_c^2} \right]$$

with the Arrhenius-type correlation time $\tau_c = \tau_0 \exp(E/kT)$.

Fig. 2. — ^1H -NMR relaxation times at low temperatures in $(\text{TMTTF})_2\text{Br}$ at 13 kbar. (a) The spin-lattice relaxation rate T_1^{-1} vs. temperature. The dashed line indicates the non-single exponential behaviour as in figure 1. (b) The temperature dependence of T_2^* determined by the echo width. (c) The temperature dependence of the spin-spin relaxation time T_2 .

4. Discussion. — The present relaxation data on $(\text{TMTTF})_2\text{Br}$ at ambient pressure and at 13 kbar clearly show that the low temperature semiconducting phase is a magnetic SDW-phase. The onset of the microscopic inhomogeneous local field indicated by the line-broadening of the proton resonance (T_2^{*-1}) the nuclear spin-decoupling (increase of T_2) and the spin-lattice relaxation peak ascribed to the critical slowing-down of the magnetic fluctuations are good evidences of the SDW-nature of the low temperature phase. These results are in a very good agreement with the observation of an antiferromagnetic resonance in $(\text{TMTTF})_2\text{Br}$ at ambient pressure [12]. The Néel temperature was found to be $T = 13 \pm 1$ K, which agrees well with the transition temperature observed here.

These data strongly support the suggestion given by the pressure investigations on the phase diagram of $(\text{TMTTF})_2\text{Br}$ [13] namely that there exists a close similarity between $(\text{TMTTF})_2\text{Br}$ and the $(\text{TMTSF})_2\text{X}$ family apart from the difference in the critical pressure to suppress the SDW-semiconducting phase. Furthermore, the highly conducting state at 25 kbar may also be related to the occurrence of superconductivity, as it is the case in the $(\text{TMTSF})_2\text{X}$ family, while there exists still some unsolved problems as to the sample dependence of the observed phenomena [4].

The apparent increase of the transition temperature under pressure (increase of ~ 2 K at 13 kbar) is not clear so far : according to the conductivity measurements at zero field, the phase

Fig. 3. — $^1\text{H-NMR}$ relaxation times at low temperatures in $(\text{TMTTF})_2\text{PF}_6$ at ambient pressure. (a) The spin-lattice relaxation rate T_1^{-1} vs. temperature. The dashed line indicates the non-single exponential behaviour. (b) T_2^* determined by the spin-echo width and (c) the temperature dependence of the spin-spin relaxation time T_2 .

boundary is suggested as almost pressure independent in this low pressure region [13]. However, the sharper transition (the narrower critical region) and the larger amplitude of the SDW under pressure suggest that the low temperature phase is more magnetic at 13 kbar than at ambient pressure. We are rather confident that the increase of the transition temperature with pressure, at least below 13 kbar, is an intrinsic effect. Possibly, the application of the pressure may enhance the magnetic interchain coupling which leads to the increase of the SDW transition, at least in the low pressure region. We should not rule out a magnetic field dependence of the phase diagram.

In $(\text{TMTTF})_2\text{PF}_6$ the behaviours are completely different: below the transition at $T_m \sim 17 \pm 2 \text{ K}$, the spin-lattice relaxation is nearly constant and the anomalies in T_2 and T_2^* are very small.

The recent observation of the weak diffuse sheet with $2 k_F$ by X-ray measurements at low temperatures may suggest that the low temperature phase is a CDW or Spin-Peierls state accompanied by a $2 k_F$ lattice distortion. However, neither of them can explain the temperature dependence of the relaxation rate, since a rapid reduction of the relaxation rate below the transition would be expected in these states. We believe that the low temperature semiconducting phase of $(\text{TMTTF})_2\text{PF}_6$ is a complex state exhibiting some magnetic character. As suggested by Emery *et al.* [5], the low temperature state of this family may have different nature depending on the strength of Umklapp scattering. It seems reasonable to suppose that there exists somewhere a crossover point of different instabilities [3] and that $(\text{TMTTF})_2\text{PF}_6$ is near the region where the

Fig. 4. — ^1H -NMR relaxation rate at high temperatures ($17\text{ K} < T < 200\text{ K}$). (a) In $(\text{TMTTF})_2\text{Br}$ at ambient pressure, (b) in $(\text{TMTTF})_2\text{Br}$ at 13 kbar and (c) in $(\text{TMTTF})_2\text{PF}_6$ at ambient pressure. The curves are calculated using the classical formula for the motional effect on the relaxation.

magnetic SDW-state and another state with $2k_F$ lattice distortion such as CDW or Spin-Peierls (as suggested by Emery) are competing. Because of the competition between these two instabilities, the amplitude of the SDW may be very small and a low-lying collective mode (with a frequency of the order of the proton Zeeman frequency) may contribute to the relaxation rate in the entire domain of the semiconducting state. It is also possible that the SDW instability exists only as short range fluctuations. In order to clarify the low temperature phase in $(\text{TMTTF})_2\text{PF}_6$, more experimental informations are necessary. The forthcoming relaxation measurements under pressure in this material may help to solve this problem.

At higher temperatures ($T > 20\text{ K}$) the ^1H spin-lattice relaxation rate exhibits complex behaviours, with two clear peaks around 50 K and 100 K. Numerous investigations on the motions of the methyl groups in organic compounds have revealed that the hindered rotation of the methyl groups in a fixed potential barrier gives rise to two ^1H -NMR relaxation peaks; one is associated to the classical rotational motions [14] and the other to the quantum mechanical tunnelling motions. Other kinds of molecular motions can also contribute to the ^1H -relaxation, so that the situation is not simple. Since the detailed discussions on the molecular dynamics require more informations, especially on the frequency dependence of ^1H -relaxation, we only give some comments here, concerning the present analysis of the low temperature phase.

(i) The effect of methyl rotations on ¹H-relaxation at 45 MHz is important only at high temperatures well above 20 K.

(ii) There is no temperature region where the ¹H spin-lattice relaxation rate follows the usual Korringa law.

(iii) The remarkable depression by pressure of the relaxation rate in (TMTTF)₂Br in the region of 20 K < T < 30 K may be related to the quantum rotational effect [14] : in (TMTTF)₂PF₆ a broad maximum around T ~ 28 K can be seen more clearly.

5. Conclusion. — The present results confirm that the properties of the quasi-1D electron gas in (TMTSF)₂X and (TMTTF)₂X families are quite similar. As pointed out in the previous works [3, 13], the difference in the members of these families should be primarily attributed to the one-dimensionality of the system, which can be controlled by the application of high pressure or slight chemical change. A systematic measurement for various compounds including the pressure investigations are now under progress.

Acknowledgments. — We thank C. Coulon and C. Bourbonnais for valuable discussions and C. Andrzejewski and A. Andrieux for skilful technical support.

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