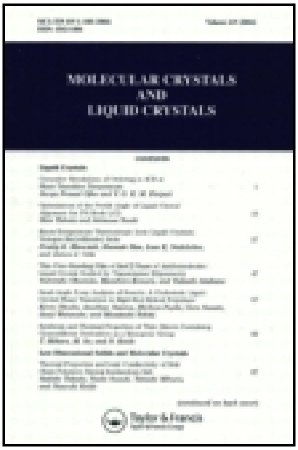

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Pressure Induced Magnetic State in $(TMTTF)_2PF_6$

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PRESSURE INDUCED MAGNETIC STATE IN $(TMTTF)_2PF_6$

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Abstract - We present ^1H NMR relaxation data on $(TMTTF)_2PF_6$. The low temperature insulating state is shown to be non magnetic at ambient pressure and antiferromagnetic (SDW) at 13kbar.

INTRODUCTION

$(TMTSF)_2X$ organic conductors have been of great interest since the discovery of superconductivity in $(TMTSF)_2PF_6$ under pressure .[1] In absence of any anion ordering, the metal insulator transition observed at low temperature in the $(TMTSF)_2X$ series has been characterized as the condensation of a spin-density-wave (SDW) phase [2]. The sulphur analog family $(TMTTF)_2X$ has been interpreted as more one-dimensional at ambient pressure [3] and a study of the temperature-pressure phase diagram [4] has clearly shown the similarities between both series, the critical pressure for the suppression of insulating phase being shifted to higher value for the sulphured compounds. Experimental investigations of the microscopic nature of the insulating state have already extended the comparison, showing for example the magnetic character of the low-temperature semiconducting state in $(TMTTF)_2Br$.[5-6] For $(TMTTF)_2PF_6$, the results at ambient pressure were less convincing and the nature of the insulating state was not clear so far.[5] In the present work, ^1H NMR relaxation rates measurements show unambiguously that the low-temperature state is non-magnetic at ambient pressure. Consequently, the results support the existence of a spin-Peierls (SP) state. We also show that a pressure of 13 kbar is sufficient to induce a spin density wave (SDW)state.

EXPERIMENTAL

We have performed ^1H NMR measurement on single crystals of $(TMTTF)_2PF_6$ with magnetic field perpendicular to the conductivity axis at 1 bar and 13 kbar. It is very important to note that the previous results at ambient pressure reported in ref. 5 were collected using powdered samples prepared by metathesis (anion exchange with $(TMTTF)_2BF_4$) and these probably contain magnetic impurities. As the electronic properties of the Bechgaard salts are very sensitive to impurities [7], a new batch of samples prepared by usual electrochemical method [8] has been used here.

A home-made pulsed NMR spectrometer was operated at a frequency of 45 MHz (resonance field ∿ 10.6 kOe). The free induction and spin-echo signals were digitized and analysed by a microcomputer. The spin-lattice relaxation time T_1 was measured by observing, on more than one decade, the time recovery of the free induction after the saturation comb pulse. The spin-spin relaxation time T_2 has been determined by the echo signal method whereas, assuming an exponential shape, T_2^* is given by the width of the echo.

RESULTS

For the ^1H spin-lattice relaxation measurements in these materials we know that an important contribution is due to the quantum tunnelling of methy-groups [5-9]. At high enough temperature, this contribution is dominant and can be extrapolated with the assumption of an activated behaviour. So, we have plotted on the figures the only point for which this contribution is negligible.

At ambient pressure, no anomaly is detected. The linewidth is constant between 2 and 50 K ($T_2^* \simeq 22$ μs). At low temperature, the relaxation rate is very small and a clear departure is observed at ∿ 14 K (Fig. 1). This temperature corresponds with the drop in static susceptibility [10-11]. These new NMR data show unambigously that the low temperature phase (below 15 K) is non-magnetic in character and its nature will be discussed later. Note that the high-temperature data ($T > 25$ K) are not far from those of ref. 5 and we can interprete the previous large excess of relaxation rate at low temperature as due to magnetic impurities.

A pressure of 13 kbar on $(TMTTF)_2PF_6$ induces important

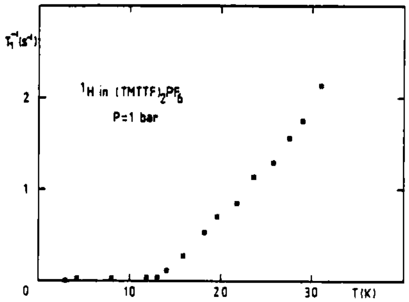

FIGURE 1

^{1}H spin-lattice relaxation at 1 bar.

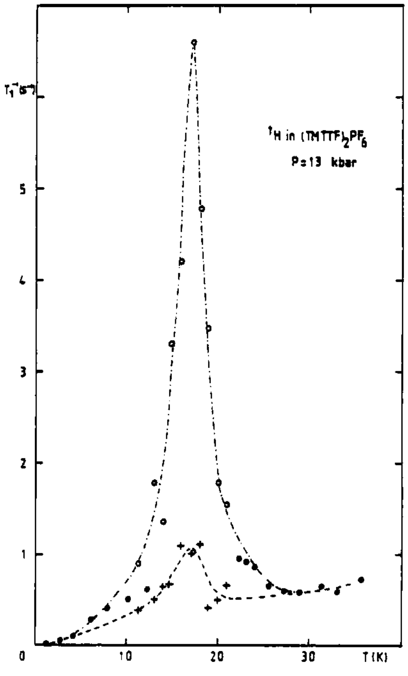

FIGURE 2

^{1}H spin-lattice relaxation at 13 kbar.

changes. From resistivity measurements [4], a nearly metallic phase is stabilized down to ∿ 19 K, temperature at which a metal-insulator transition occurs. NMR data show a clear peak of the spin lattice relaxation rate around T $\sim$ 17 K (Fig. 2). In a narrow temperature region (± 5 K), the relaxation was found non exponential, but we can define the initial (0) and the final (+) slopes of the decay. We note the apparent constant value of T_1^{-1} above the transition (25-35 K). The anomalies of T_2 and T_2^* (Fig. 3) are

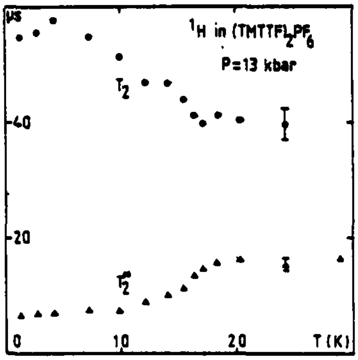

FIGURE 3

evidences for the onset of an inhomogeneous local field. T_2 increases by about 30 % while T_2^* decreases by a factor 3. With T_2^{*-1} values, we can estimate the increase of the inhomogeneous local field at ^{1}H sites as about 40 Oe. The increase of T_2 below 17 K is the consequence of nuclear spin decoupling due to the inhomogeneous local fields. All these results allow us to associate the metal-insulator transition with the condensation of a magnetic (SDW)phase. We want to point out that, by many features, $(TMTTF)_2PF_6$ at 13 kbar behaves like $(TMTTF)_2Br$ at 1 bar. Especially the amplitude of the magnetization and the constant value of T_1^{-1} above the transition are the same. This is in agreement with the picture already mentionned [4] that the T-P phase diagrams of $(TMTSF)_2X$ and $(TMTTF)_2X$ series are identical (without anion effect) but shifted in pressure.

DISCUSSION

At ambient pressure, the resistivity measurements clearly show the existence of a well defined Hubbard correlation gap at high temperature ($T \lesssim 200$ K). This has been interpreted by a weak localization of the electrons on the chain, which is consistent with the prediction of a 4 k_F charge density wave in a g-dogy model, when the Umklapp scattering processes (related to the dimerization of the organic molecules along the stack) are relevant. At this point, the observation of weak diffuse sheat at 2 k_F by X-ray measurementsbelow 60 K [13] and the absence of any magnetic effect by NMR strongly suggest that the low temperature state is of Spin-Peierls type in agreement with susceptibility measurements [14].

At 13 kbar, the present work shows that the low-T state is characterized as a SDW state. This possibility of a pressure induced magnetic state strongly support the interpretation of the T-P phase diagrams [4-5]. In absence of anion ordering effects,the phase diagrams and the nature of the low-T phases are identical for both $(TMTSF)_2X$ and $(TMTTF)_2X$ families but are shifted on the pressure axis. Apparently, the critical pressure depends on the magnitude of the resistivity correlation gap or the relevance of Umklapp processes. From a theoretical point of view [14], the constant value of T_1^{-1} above the transition may be attributed to the existence of a small correlation gap, which can be infered from a flat variation of the resistivity between 50 and 19 K at this pressure [4]. In this sense, the depression of the relaxation rate observed in $(TMTTF)_2Br$ between 1 bar and 13 kbar above the transition, may be attributed to a gradual reduction of the correlation gap. This should be correlated with the reduction of the Umklapp scattering under pressure [12-15].

CONCLUSION

The present resultsconfirm that the properties of the electron gas in $(TMTTF)_2X$ and $(TMTSF)_2X$ are quite similar with an appropriate change of the pressure scale. Furthermore, the $(TMTTF)_2PF_6$ compound seems to be a nice candidate to check the predictions of theories, as it undergoes by a continuous change of the lattice parameters, non magnetic, magnetic and possibly superconducting low temperature states. We believe that the most relevant effect of pressure is the reduction of the Umklapp scattering [12] (and consequently the Hubbard gap) while SDW phase appears and finally superconductivity takes place.

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