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Spin-density wave ground state in the one-dimensional conductor $(TMTSF)_2PF_6$: microscopic evidence from ^{77}Se and ^{1}H NMR experiments (*)

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Résumé. — L'existence d'ondes de densité de spins dans la phase semiconductrice de $(TMTSF)_2PF_6$ est confirmée par la disparition du signal de résonance magnétique nucléaire de ^{77}Se et l'élargissement de la résonance des protons. Les modes collectifs de l'onde de densité de spins commensurable avec le réseau contribuent notablement à la relaxation spin-réseau des protons. Nous suggérons, en outre, une explication à la très faible valeur de l'amplitude de l'onde de densité de spin, basée sur la coexistence de deux divergences dans ce conducteur unidimensionnel : la supraconductivité et le magnétisme.

Abstract. — The vanishing of the ^{77}Se nuclear resonance signal and the broadening by internal magnetic fields of the proton resonance line establish the existence of spin-density waves in the low temperature semiconducting state of $(TMTSF)_2PF_6$. The thermally activated collective mode of the commensurate spin-density wave contributes significantly to the proton spin-lattice relaxation. It is also suggested that the very small amplitude of the spin-density wave is due to the coexistence of two diverging channels in the conducting state : the SDW and Superconductivity channels.

The existence of a magnetic phase at low temperatures in the organic conductor $(TMTSF)_2PF_6$ has been unambiguously proven by nuclear magnetic resonance studies. These show that (i) the ^{77}Se signal vanishes and (ii) the proton signal is considerably broadened in the low temperature insulating state.

At low temperature all the known quasi-1-D organic conductors belonging to the TTF-TCNQ family undergo a transition towards an insulating ground state characterized by the existence of a three-dimensionally ordered lattice distortion of wave vector $2\,k_F$ along the stacking direction. This phenomenon, the Peierls transition, has been extensively studied in 1-D conductors [1]. A signature of a Peierls instability in a 1-D conductor is the observation in the conducting phase of 1-D structural precursor effects reflecting the softening of a phonon mode with wave vector $2\,k_F$ [2]. Since no such precursor effects have been detected by X-ray diffuse scattering above the metal-insulator transition at 12 K in $(TMTSF)_2PF_6$ [3] it appears that the insulating state in this compound may not be stabilized by a phonon mechanism. However, such an insulating state could be stabilized by other mechanisms, independent of the lattice response as pointed out by Slater in 1951 [4]. Slater considered the particular case of a half-filled band conductor and showed that the self-consistent potential in the Hartree-Fock approximation cannot have the full translational symmetry of the crystalline lattice in the case of an antiferromagnetic metal but that the exchange potential must have the periodicity twice the lattice periodicity. Each energy band is thus split in half with an energy gap in the middle. Slater's picture can easily be extended to an arbitrary band filling. In particular, for a quarter filled one-dimensional band the kinetic energy stabilizes an antiferromagnetic state, with no net macroscopic magnetization, having a magnetic unit cell four times larger than the original lattice cell. Antiferromagnetism can also be viewed as a sinusoidal modulation of the spin-density (spin-density wave, SDW) with wave vector $2\,k_F$ [5]. Such a mechanism for magnetic

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ordering is known to explain the existence of an incommensurate SDW in chromium metal below $T_N = 311$ K, with a spin modulation wave vector which nests the three-dimensional Fermi surface [6]. The nesting wave vector is related to the electronic structure and has, *a priori*, no special relationship with the lattice parameters. But in the stoichiometric $(TMTSF)_2PF_6$ conducting salt, where the TMTSF band is one quarter-filled [7], a commensurate SDW with a wavelength four times that of the primitive unit cell will be energetically favoured. The possible existence of SDW's in $(TMTSF)_2PF_6$ has been proposed to explain its non-linear electronic properties [8]. No measurements on a microscopic scale have yet been made to validate such a hypothesis. It is well known that nuclear magnetic resonance is a useful tool to probe the existence and the dynamics of local magnetic fields [9].

We have performed NMR experiments on two nuclear species forming part of the TMTSF molecule, (i) the ^{77}Se ($I = \frac{1}{2}$) nuclei which are located on the aromatic rings of the cation radical and (ii) the protons ^1H ($I = \frac{1}{2}$) belonging to the CH_3 groups. In these studies a carefully prepared ground powder of $(TMTSF)_2PF_6$ was used. The measurements were performed with a high-power phase coherent pulsed spectrometer at a fixed frequency of 45 MHz. Free precession and spin echo techniques were used to measure the proton line width and proton transverse relaxation rate $1/T_2$ respectively. The proton spin-lattice relaxation rate, $1/T_1$, was derived from the time dependence of the recovery of the magnetization after saturation by a comb of 90° pulses. Spin echo and box-car integrator techniques were used to observe the ^{77}Se signal.

The most striking feature exhibited by figure 1 is that while the proton line width increases below 12.5 K, the homogeneous line width, given by $1/T_2$, becomes significantly smaller. At the same temperature there is also a large increase of the spin-lattice

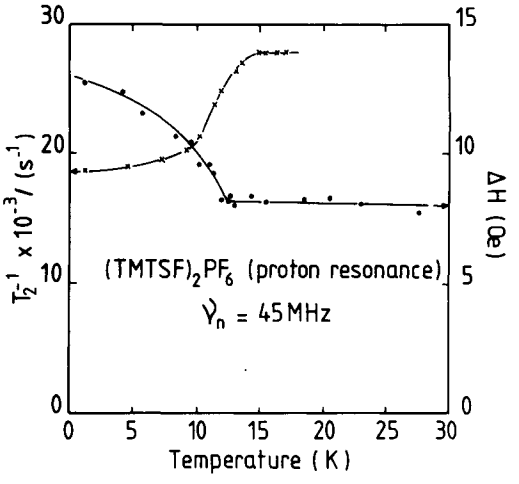

Fig. 1. — Proton resonance line width *versus* temperature in a field of 10.57 kOe (ν_n = 45 MHz) (right scale). Spin echo $1/T_2$ (left scale).

relaxation, whereas between 15 and 25 K $1/T_1$ follows, almost exactly, a Korringa behaviour ($1/T_1 \propto T$), (Fig. 2). The ^{77}Se resonance amplitude,

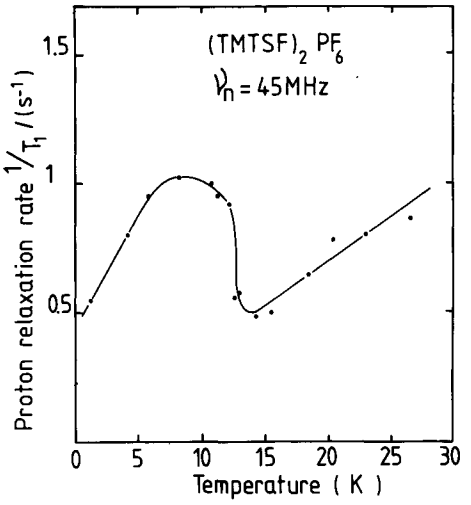

Fig. 2. — Proton spin-lattice relaxation rate *versus* temperature.

shown in figure 3, decrease abruptly at about 13 K and below 11 K the signal is too small to be measured above the noise. As can be seen in figure 3, between 27 and 20 K the amplitude of the ^{77}Se signal follows a Curie law ($A^{-1} \propto T$), showing that the number of selenium nuclei contributing to the constant width resonance line is unchanged. The ^{77}Se resonance is broadened at 13 K, without noticeable change of the resonance field ($H = 55.4$ kOe).

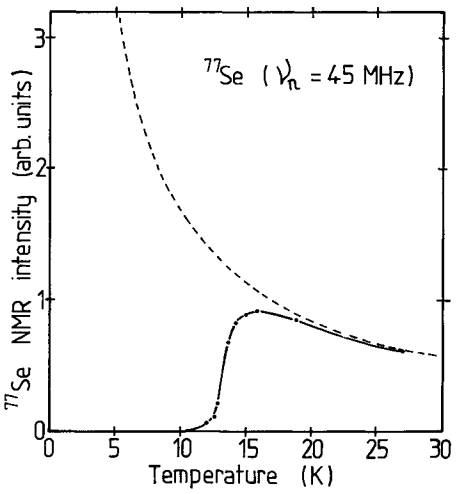

Fig. 3. — ^{77}Se signal amplitude *versus* temperature below 30 K and the Curie law behaviour (dashed curve).

Since ^{77}Se is a spin one half nucleus, the broadening of the line below 13 K cannot be of quadrupolar origin but must imply the existence of strong local magnetic fields of hyperfine origin. The growth of internal magnetic fields is also reflected in the broadening of the proton resonance line below 12.5 K. The inhomogeneous nature of this broadening is illus-

trated by the temperature dependence of $1/T_2$ which exhibits just the opposite behaviour. The sharp anomaly in the proton relaxation rate seen at 12.5 K, figure 2 is clearly related to the change in the electronic properties which takes place at low temperatures. Methyl group rotation can contribute to the proton spin-lattice relaxation and can give rise to maxima in $1/T_1$, at low temperature. This effect has been carefully studied for the CH_3 groups in TMTTF-TCNQ (D_4) where maxima are found at 24 K and 54 K with a resonance frequency of 14 MHz [10]. Within traditional theory of nuclear relaxation through molecular motion [9], these peaks will be shifted to higher temperatures, at higher frequencies. We believe therefore that below 25 K with $\nu_n = 45$ MHz, $1/T_1$ is not influenced by relaxation mechanisms others than those of hyperfine origin [9, 10], (see Fig. 2). In the case of the more commonly found, non-magnetic Peierls ground state in 1-D conductors the nuclear relaxation drops in the low temperature insulating state as a result of the reduction in charge carriers (see for example, proton relaxation [11] or ^{13}C relaxation in TTF-TCNQ(^{13}C)) [13]. Therefore, the large increase (as opposed to a decrease) of $1/T_1$ seen in the low temperature insulating state again implies the existence of thermally populated magnetic modes. In the conducting domain the relaxation obeys the law $1/T_1 = 0.03\,T$ where T_1 and T are expressed in units of seconds and Kelvin respectively. The increase of 4.5 Oe in the local field seen by the methyl group protons at 1.2 K is unlikely to be associated with hyperfine fields for the following reasons : first, the hyperfine fields for protons are probably too small (≈ 1.5 Oe/μ_B) to explain the magnitude of low temperature line broadening and second, the substantial increase of the spin-spin relaxation time as the temperature is decreased (Fig. 1) is indicative of local magnetic field inhomogeneities which are sufficient to partially detune the nuclear spins of the methyl groups.

Similar increases of T_2 have been observed in the mixed state of superconductors where they have attributed to the detuning of spins on a microscopic scale by the magnetic field variations induced by an Abrikosov-type fluxoid structure [14]. Consequently, the local fields seen by the proton probably originate from the dipolar field due to the electronic magnetization of the nearest atoms on the molecular ring. If we take 2.5 Å as the shortest distance between a proton and an atom (C or Se) of the ring [15], a dipolar field of 4.5 Oe is produced by a moment of $\approx 2 \times 10^{-3}$ μ_B. This implies that the amplitude of the spin-density wave is extraordinary small even-though the microscopic magnetization of an entire molecule may be somewhat bigger.

The existence of an extremely weak SDW is in reasonable agreement with the measured band gap in the low temperature insulating phase. The stoichiometry of $(TMTSF)_2PF_6$ means that the SDW will be commensurate with the underlying lattice, the magnetization varying as $m(R) = m \cos\left(\frac{\pi}{2a} R + \varphi\right)$ where a is the lattice constant along the stacking direction (ignoring the weak dimerization of the chain [15] and φ is an unknown phase factor).

The sinusoidal antiferromagnetic ordering opens up a gap at the Fermi surface, $Q = \pm k_F$ [5, 16]. In the Hartree-Fock approximation for the SDW state, the band gap 2Δ is related to the exchange energy U through the relation $2\Delta = 2mU$, where m is a measure of the staggered magnetization. Assuming, for example, $U/4t_{\parallel} = 1$ and with $4t_{\parallel} = 500$ meV [7], we obtain $U = 0.5$ eV and using $2\Delta = 60$ meV as derived from anomalies in the dynamic conductance observed by tunnelling of electrons into $(TMTSF)_2PF_6$ at low temperature [17], we calculate a staggered molecular moment of 6×10^{-3} μ_B. Considering the diffuse character of the spin-density over the entire molecular ring the value of the staggered molecular moment calculated in this way agrees very well with that derived from the proton NMR. The latter, a moment « per atom », is only 3 times smaller. Thus, the small value of the SDW amplitude in $(TMTSF)_2PF_6$ at low temperature is well established. Although it is a rather surprizing result, since the almost perfect « nesting » of the 1-D Fermi surface should favour the establishment of large amplitude SDW's with a nearly complete participation of the Fermi surface in the spin-density. Other important results are (i) the existence of a magnetic field dependence of the staggered magnetization, as derived from low field proton NMR experiments [18] and (ii) the observation of a very large positive magnetoresistance in the insulating state of $(TMTSF)_2PF_6$ [19].

It appears that the nature of the antiferromagnetic state in $(TMTSF)_2PF_6$ is different from that observed in typical itinerant antiferromagnets. One might postulate that as far as $(TMTSF)_2PF_6$ is concerned the antiferromagnetic and the superconducting divergences must be considered together, even under ambient pressure conditions. Thus, a large divergence of the superconducting channel could lead in the conducting domain to the formation of a pseudo-gap at the Fermi level (with the possibility of para-conductive fluctuations [20]) and a concomitant reduction of the Fermi surface area available for the magnetic instability.

It seems likely that in the insulating state the nuclear spin-lattice relaxation will proceed through coupling of the nuclear spins to the SDW collective mode. However in a commensurate ($\times$ 4) SDW the phason mode at $q = 0$ will have a finite energy (the pinning energy) [21]. Therefore if $1/T_1$ depends on thermal activation of the phason mode it will have a temperature dependence which will depend on the magnitude of the pinning energy. The pinning energy

is estimated to be about 0.1 meV from the data in figure 2.

Above the metal-insulator transition, the Korringa behaviour followed by the proton relaxation rate ($1/T_1 \propto T$) suggests the absence of strong spin fluctuations. This result is somewhat surprizing since large precursor effects can be expected for a 1-D system above the 3-D ordering temperature. However, $(TMTSF)_2PF_6$ cannot be considered as an ordinary 1-D conductor, since both SDW and Superconducting divergences (3-D ordering and 1-D precursor effects) must be considered simultaneously.

Therefore, despite the existence of a transition towards a 3-D ordered SDW state at ambient pressure, it has been suggested that superconducting fluctuations are dominant in the 1-D fluctuating regime [20] and they may not affect the spin-lattice nuclear relaxation rate as strongly as spin fluctuations.

Finally, we wish to point out that the low temperature antiferromagnetic ground state in $(TMTSF)_2PF_6$ confirms the theoretical interpretation of its electronic properties based on the dominant role of Coulomb interactions [22].

In conclusion, NMR studies have shown the existence of an antiferromagnetic insulating ground state in a one-dimensional conductor. The discovery of such a state confirms the applicability of Hartree-Fock theory in lower dimensions [4]. It can also be considered as a manifestation of an excitonic instability [23].

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