

Neutron-scattering evidence for a spin-Peierls ground state in $(\text{TMTTF})_2\text{PF}_6$

P. Foury-Leykian,¹ D. Le Bolloc'h,¹ B. Hennion,² S. Ravy,^{1,3} A. Moradpour,¹ and J.-P. Pouget¹

¹Laboratoire de Physique des Solides, CNRS UMR 8502, Batiment 510, Université Paris Sud, 91405 Orsay Cedex, France

²Laboratoire Léon Brillouin, CEA-CNRS UMR 12, 91191 Gif-sur-Yvette Cedex, France

³Synchrotron Soleil, L'orme des merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France

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We present a study of the spin-Peierls (SP) transition in the $(\text{TMTTF})_2\text{PF}_6$ organic conductor by elastic neutron scattering. The $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ superstructure reflection associated with the SP transition is clearly detected up to 18 K. The intensity of the satellite reflection is particularly small compared to other similar organic systems. Several explanations are proposed to account for the weakness of the three-dimensional SP amplitude of distortion in the $(\text{TMTTF})_2\text{PF}_6$ system.

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The isostructural series of 2:1 cation radical salts based on monovalent anions X such as PF_6 , AsF_6 , ReO_4 , NO_3 , SCN , and Br , and deriving from tetramethyltetrafulvalene (TMTTF) and from tetramethyltetraselenofulvalene (TMTSF), show remarkable quasi-one-dimensional (1D) electronic properties. Indeed, these salts are made of slightly dimerized zig-zag stacks of TMTTF or TMTSF running along the a direction, which delimit cavities in which the monovalent anions X are located.¹ From stoichiometry there is one charge per dimer of organic molecules. This series exhibit extremely rich physical phenomena which span from Mott-Hubbard charge localization phenomena in $(\text{TMTTF})_2X$, to metallic delocalization and superconductivity in $(\text{TMTSF})_2X$.² This leads to quite a large number of competing low-temperature ground states, ranging from antiferromagnetism (AF) and spin-Peierls (SP) pairing in the localized limit, to spin-density wave (SDW) in the metallic limit. In addition, when the anions such as ReO_4 , NO_3 , and SCN are noncentrosymmetric, the salt undergoes an anion ordering (AO) transition below room temperature, which leads to the orientational ordering of the anions in their cavities, generally accompanied by a charge-density wave (CDW) or bond order wave (BOW) stack distortion.¹

At present, all the information concerning the AF or the SDW modulation comes from NMR investigations, since no neutron-diffraction study could be performed due to the fairly small value ($\approx 0.1\mu_B$) of the magnetic moment and due to the small crystal volume. NMR measurements indicate that the AF modulation is commensurate in $(\text{TMTTF})_2\text{Br}$ and SCN ,³ and that the SDW is incommensurate in $(\text{TMTSF})_2\text{PF}_6$.⁴ More recently, an x-ray diffuse scattering investigation has shown that the ground state of $(\text{TMTSF})_2\text{PF}_6$ presents an unexpected mix of spin and charge-density wave-like character.⁵

Very little is known on the SP transition of $(\text{TMTTF})_2\text{PF}_6$, even though its signature was found by the observation of very weak superlattice reflections at 10 K more than 20 years ago.⁶ In $(\text{TMTTF})_2\text{PF}_6$, the SP instability leads to the pairing of localized spins $\frac{1}{2}$ (one spin per dimer of TMTTF molecules) into nonmagnetic singlets, $S=0$, via a tetramerization of the organic stacks (i.e., cell doubling along a , corresponding to the $\frac{1}{2}a^*$ component of the superlattice wave vector

q_{SP}). The formation of nonmagnetic singlets is identified by a drop in the spin susceptibility as observed by EPR (Refs. 7–9) and NMR (Ref. 9) below $T_{SP} \approx 19$ K in $(\text{TMTTF})_2\text{PF}_6$. However, no accurate study of the structural counterpart of the SP transition could be performed because of the extreme sensitivity of the TMTTF molecule to x-ray irradiation damages, which irreversibly lead to the destruction of the SP transition.

Likewise, a SP transition occurs at $T_{SP} \approx 13$ K in $(\text{TMTTF})_2\text{AsF}_6$ (Refs. 10 and 11) and in the isostructural 2:1 cation radical series $(\text{BCPTTF})_2\text{PF}_6$ and AsF_6 (BCPTTF stands for benzocyclopentyltetrafulvalene). This latter series has been studied more extensively because BCPTTF is less sensitive to x-ray irradiation.¹² In the BCPTTF's, the SP transition occurs at higher critical temperatures than in the TMTTF's ($T_{SP}=36$ and 32.5 K for the PF_6 and AsF_6 salts, respectively). The SP instability, also observed in 2:1 anion radical organic salts, such as $\text{MEM}(\text{TCNQ})_2$, and in the inorganic compound CuGeO_3 , is a quantum cooperative phenomena of current interest (see, for example, Ref. 13). In the case of the $(\text{TMTTF})_2X$, the situation is all the more interesting since this series undergoes a high-temperature charge disproportionation transition (occurring at 70 and 105 K in the PF_6 and AsF_6 salts,¹⁴ respectively) which corresponds to a $4k_F$ charge ordering on the molecular sites, usually denoted as $4k_F$ -CDW ($k_F = \frac{1}{4}a^*$ is the Fermi wave vector of the non-interacting 1D electron gas associated with these salts). This $4k_F$ -CDW phenomena seems to provide a subtle control over the SP and AF instabilities of the $(\text{TMTTF})_2X$.^{15,16}

In the present paper, we report a structural study of the SP transition of $(\text{TMTTF})_2\text{PF}_6$ using elastic neutron scattering. This study was made possible thanks to the outstandingly large single crystals elaborated in Orsay.¹⁷ The experiment was conducted on the triple axis spectrometer 4F2 of the reactor Orphée at the Laboratoire Leon Brillouin. The experimental conditions were: $k_i = 2.662 \text{ \AA}^{-1}$, $60'$ collimations on each side of the analyzer, and graphite filters on k_i and k_f . The sample was fixed with silver glue onto the cold finger of a cryogenerator, which was able to cool down to 11 K. Two $(a^*, b^*, -c^*)$ and the $(a^*, b^*, +c^*)$ scattering planes were explored. The lattice parameters were taken from a previous determination of the average structure of $(\text{TMTTF})_2\text{PF}_6$ at 4 K.¹⁸

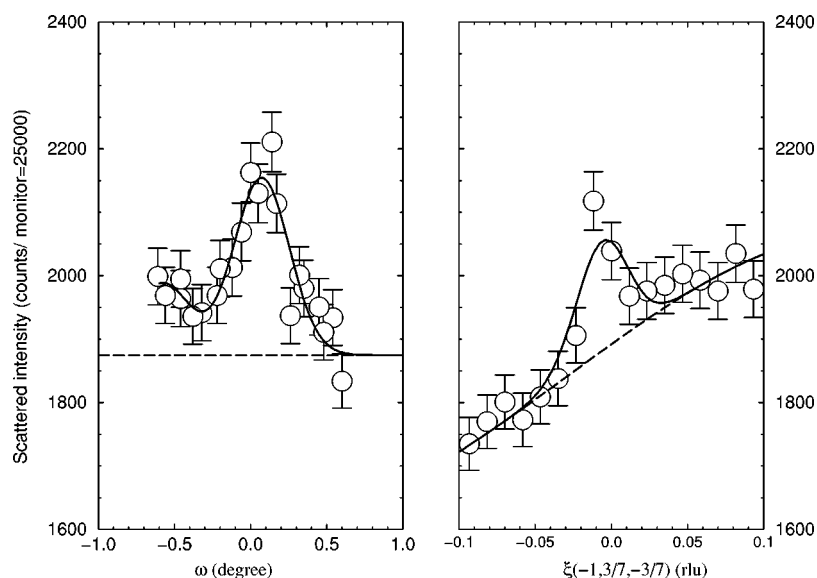


FIG. 1. Transverse (ω scan) and longitudinal scans (ξ scan) through the $(-\frac{7}{2}, \frac{3}{2}, -\frac{3}{2})$ superstructure reflection, at $T=11$ K. The dashed line gives the background intensity.

The sample studied had a volume of 17 mm^3 , with a twinning ratio of 7:1 as determined from the ratio of intensities of the $(-2, 0, 0)$ reflection of the two twins. At room temperature, the intensity of Bragg reflections of the main twin was 9600 cps for the $(0, -1, -1)$, and 4100 cps for the $(-2, 0, 0)$. Upon cooling, due to the constraint of the fixing procedure, the main twin was found to split into three components (a small component and two large ones separated by an angle of about 1.4°). At 11 K, the intensity of the Bragg reflections of the component used for the measurements was of 7000 cps for the $(0, -1, -1)$, 2000 cps for the $(-2, 0, 0)$, 1200 cps for the $(-2, -1, -1)$, and 1100 cps for the $(-4, 0, 0)$, leading to an average Bragg intensity of about 3000 cps. At this temperature, a survey of about 20 reciprocal positions expected for the q_{SP} superlattice reflections was performed with a counting time of 645 s/point, in each of the $(a^*, b^*, -c^*)$ and $(a^*, b^*, +c^*)$ reciprocal planes. Due to the presence of a large background of 3–5 cps from the incoherent scattering of the hydrogen atoms present in the TMTTF molecule, only two very weak superlattice reflections were detected in the $(a^*, b^*, -c^*)$ reciprocal plane; one at $(-4, 1, -2) + q_{SP}$ and one at $(-3, 1, -2) + q_{SP}$ reciprocal lattice positions, where $q_{SP} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and both with intensities of about 1/10th of the background. No superlattice reflection could be detected in the $(a^*, b^*, +c^*)$ scattering plane.

Figure 1 shows a rocking curve (ω scan) and a longitudinal (ξ scan) around the $(-\frac{7}{2}, \frac{3}{2}, -\frac{3}{2})$ reciprocal lattice position, which confirm that the observed scattering is a well-defined Bragg reflection. In order to check that this peak was not the contribution of the $(-7, 3, -3)$ Bragg reflection with the second harmonic of the incoming beam, we removed one graphite filter whose transmission for the second harmonic is about 5×10^{-3} . The only change was an increase in intensity corresponding to the absorption of the filter for the first harmonic. This shows that the reduced component of the SP reflection is $q_{SP} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The profile displayed in Fig. 1 is resolution limited, which proves the presence of a three-dimensional (3D) long-range SP order (i.e., $>1000 \text{ \AA}$). Fig-

ure 1 shows also that the peak intensity of this superlattice reflection amounts to 220 counts in 645 s (i.e., 0.35 cps; monitor 25 000 in Figs. 1 and 2). This reflection has about 10^{-4} times the intensity of an average Bragg reflection. The weakness of the SP reflections explains why they could not be detected in previous neutron-scattering investigations of $(\text{TMTTF})_2\text{PF}_6$ at 4 K.¹⁸ Finally, Fig. 2 shows that the superlattice intensity vanishes upon heating above about 18 ± 1 K. This corresponds to the critical temperature T_{SP} , where a gap opens in the spin susceptibility,^{7,8} and where the derivative of the thermal expansion (a quantity proportional to the specific heat) exhibits a λ -type anomaly.¹⁹

First, it is interesting to compare the SP transition of $(\text{TMTTF})_2\text{PF}_6$ with that of the isostructural salts $(\text{BCPTTF})_2X$ (with $X = \text{PF}_6$ and AsF_6).¹² In spite of the increase of T_{SP} by a factor of 2, a sizeable difference in the intensity of the superlattice reflections exists between the BCPTTF series ($I_S/I_B = 1/30$ for the AsF_6 salt²⁰) and the TMTTF series ($I_S/I_B = 10^{-4}$ for the PF_6 salt). The intensity of the SP superlattice reflections of the BCPTTF salts is comparable to that observed at the AO transition of

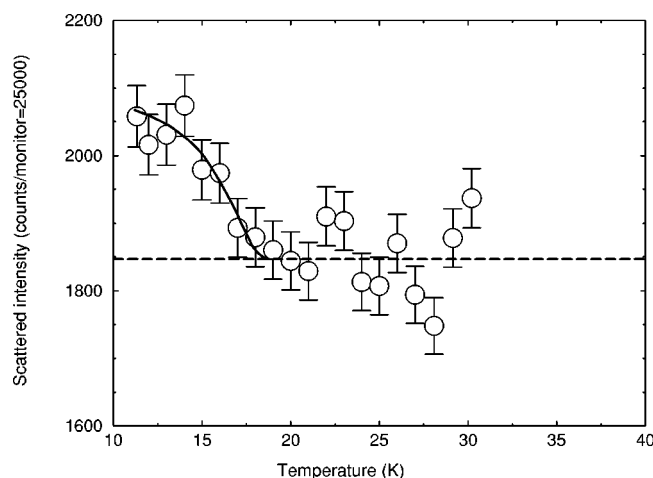


FIG. 2. Temperature dependence of the $(-\frac{7}{2}, \frac{3}{2}, -\frac{3}{2})$ peak intensity. The dashed line gives the background intensity.

(TMTSF)₂ReO₄ ($I_S/I_B=10^{-1}$), which stabilizes a superstructure at the same critical wave vector $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ as the SP transition of the TMTTF's and the BCPTTF's.²¹ Structural refinement of the (TMTSF)₂ReO₄ superstructure shows that the AO transition (in addition to the orientational ordering of the ReO₄) consists of a tetramerization of the organic stacks (usually denoted as $2k_F$ BOW) with a molecular displacement of $\approx 3 \times 10^{-2}$ Å (mostly in the long direction of the molecule), and of a concomitant shift of the ReO₄ by about 5×10^{-2} Å from the center of the organic cavities where they are located.²¹ The SP transition of (BCPTTF)₂AsF₆ and (TMTTF)₂PF₆ also involves a tetramerization of the organic stack. With similar ratios of I_S/I_B , one would expect a distortion of the molecular stack in (BCPTTF)₂AsF₆ and in (TMTSF)₂ReO₄ to be of similar amplitudes. As the superlattice reflection intensity is proportional to the square of the long-range (i.e., 3D averaged) atomic displacement, it can be inferred that the organic stack in (TMTTF)₂PF₆ undergoes an amplitude of distortion, u_{3D} , one order of magnitude smaller than in (BCPTTF)₂AsF₆. In MEM(TCNQ)₂ and CuGeO₃, the SP superlattice reflections are three orders of magnitude less intense ($I_S/I_B=10^{-3}$) than the main Bragg reflections.²² The refinement of their superstructure shows that the SP distortion consists of a displacement in the TCNQ molecule of 10^{-2} Å for MEM(TCNQ)₂,²³ and displacement in Cu of 7×10^{-3} Å for CuGeO₃.^{24,25} With an order-of-magnitude smaller ratio of I_S/I_B in (TMTTF)₂PF₆, one would expect the TMTTF shift to be three times smaller: $u_{3D} \sim 3 \times 10^{-3}$ Å, a value consistent with the previous estimate.

According to these estimates, however, the 3D-SP distortion appears to be particularly weak in (TMTTF)₂PF₆. A sizeable reduction of the amplitude of the SP distortion is expected in the presence of strong quantum fluctuations in the vicinity of the critical point separating the SP dimerized phase from the nondimerized spin-fluid (magnetic) phase.^{27,28} This last effect is probably not important at ambient pressure in (TMTTF)₂PF₆ since the crossover from the SP to the AF ground states takes place under pressures as large as 1 GPa.^{29,30}

The SP ground state of (TMTTF)₂PF₆ is unusual because the organic stack stabilizes a $4k_F$ charge ordering at 70 K.¹⁴ The reason is that the $4k_F$ -CDW creates an heteropolar charge distribution which weakens the $2k_F$ BOW response, as shown by numerical calculations¹⁶ and experimental studies of the TMTTF-TMTSF ReO₄ alloy.²⁶ As the $2k_F$ BOW response governs the SP dimerization, one would expect a SP distortion of smaller amplitude in (TMTTF)₂PF₆.

However, the strong reduction in amplitude u_{3D} , when going from the BCPTTF family to the TMTTF family, does not scale with the small reduction of T_{SP} and the value of the spin gap Δ_σ , which governs the singlet-triplet excitations of the SP ground state. In (BCPTTF)₂PF₆, $\Delta_\sigma=97$ K (Ref. 31) is only slightly larger than $\Delta_\sigma=70$ K (Ref. 9)–90 K (Ref. 8) in (TMTTF)₂PF₆. The amount of (intrachain) dimerization (δ defined below) can be obtained from the spin gap value Δ_σ given the value of the near-neighbor exchange interaction J of the $S=\frac{1}{2}$ AF Heisenberg chain undergoing the SP instability. More explicitly, if for small atomic intrachain displacements u_{1D} (i.e., 1D), the dimerization leads to the staggered

exchange interactions $J(1 \pm \delta)$, it is possible to deduce the following: $\delta=2[d \ln(J)/du]u_{1D}=2[d \ln(J)/d \ln(u)]$ from the Δ_σ/J ratio. Using the numerical calculations of Ref. 32, one gets $\delta=4.5\%$ in (TMTTF)₂PF₆, where $J=420$ K,⁸ and $\delta=8\%$ in (BCPTTF)₂PF₆, where $J=330$ K.¹² The δ value of (TMTTF)₂PF₆ is only two times smaller than δ in (BCPTTF)₂PF₆. In those two isostructural salts, δ (or more likely the total energy of the dimerized chain; see Fig. 17 in Ref. 32), which is proportional to u_{1D} , scales with T_{SP} , and not with the estimate of u_{3D} above.

The main question is that δ does not scale with the amplitude (u_{3D}) of the 3D-SP distortion. One explanation is that the 3D-averaged amplitude of distortion, u_{3D} (whose square is proportional to the satellite intensity), should be much smaller than the intrachain one, u_{1D} (proportional to δ), due to the existence of an interchain disorder as a result of the difficulty in achieving the optimal π phasing between the SP distortion on neighboring chains. In the presently considered salts, the $q_b=q_c=\frac{1}{2}$ components of q_{SP} do not lead to a perfect interchain π phasing because of the triclinic arrangement of the organic chains. In this respect, since the triclinic angles deviate further from 90° in (TMTTF)₂PF₆ than in (BCPTTF)₂PF₆, one expects greater difficulty in setting an optimal 3D coupling between the individual SP distortions in the case of the TMTTF family.

A second possibility is that $d \ln(J)/du$ could be larger in (TMTTF)₂PF₆ than in (BCPTTF)₂PF₆. As the TMTTF and BCPTTF stacks are very similar, this could be due to the stabilization of a different mode of displacement. For example, in (BCPTTF)₂PF₆, the SP displacement could be directed along the long direction of the BCPTTF molecule, as for the stack distortion at the AO transition of (TMTSF)₂ReO₄,²¹ while in (TMTTF)₂PF₆, it could occur along the short direction of the TMTTF molecule. This last statement agrees with the observation of strongest SP reflections in the (a^* , b^* , $-c^*$) reciprocal plane nearly perpendicular to the long direction of the TMTTF molecules. In addition, the SP distortion of the organic sublattice should deform the cavities where the anions X are located. This certainly leads to a shift of the anion, as suggested by the observation of a critical divergence of the NMR relaxation rate T_1^{-1} of the ⁷⁵As nucleus at the SP transition of (TMTTF)₂AsF₆.¹¹ With stack distortions of different polarization and amplitude, the direction of the anionic shift should also be different in the TMTTF's and the BCPTTF's. All these speculations of course need to be confirmed by a structural refinement of the SP superstructure of (TMTTF)₂PF₆. When using neutron scattering, such a structural determination requires the collection of a large number of reflections on large deuterated single crystals, where the incoherent scattering is expected to be one order of magnitude smaller. With such samples it should also be interesting to study the lattice dynamics (and especially the presence of a soft mode) associated with the 1D-SP pretransitional fluctuations which have been detected up to about 60 K by x-ray diffuse scattering,⁶ and the coupling of these structural fluctuations with the magnetic ones which can also be probed by neutron scattering.

In conclusion, the SP superlattice reflections of (TMTTF)₂PF₆ have been observed by elastic neutron scatter-

ing. However, the amplitude of the SP stack distortion appears to be much smaller in the TMTTF's compared to the ones observed in other SP systems studied to date. Another result of this study is to show that from a deuterated sample of the same volume as the hydrogenated one used here, it should be possible by neutron scattering to detect superlat-

tice reflections of about 10^{-5} the intensity of an average Bragg reflection. Such an intensity ratio is the one expected for magnetic reflections of an antiferromagnet with a staggered magnetization of about $0.1\mu_B$. This opens the possibility of studying the AF and SDW modulations in the $(\text{TMTTF})_2\text{X}$ and $(\text{TMTSF})_2\text{X}$ salts, respectively.

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