SPIN PEIERLS GROUND STATE IN (TMTTF)$_2$PF$_6$

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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 TMTTF (tetramethyl-tetrathiofulvalene) and from TMTSF (tetramethyltetraselenofulvalene) show remarkable quasi one-dimensional (1D) electronic properties. 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]. This gives rise to a large number of competing low-temperature ground states, ranging from antiferro-magnetism (AF) and spin-Peierls (SP) pairing in the localized limit, to spin density wave (SDW) in the metallic limit. At present, all the information concerning the AF or SDW modulation comes from NMR investigations, because the small value ($\approx$ 0.1 μ_B) of the magnetic moment and the small available sample size preclude neutron diffraction measurements.

Very little is known on the SP transition. A first signature of such a transition was found by the observation with X-ray scattering of very weak superlattice reflections in (TMTTF)$_2$PF$_6$ at T=10K [2]. These peaks originate from the tetramerization of the organic stacks, leading to the pairing of localized spins (one spin per dimer of TMTTF molecules) resulting into the formation of non-magnetic singlets, S=0. This is identified by a drop in the spin-susceptibility, observed by EPR [3-5] and NMR [5] below T$_{SP}$ $\approx$ 19 K in (TMTTF)$_2$PF$_6$. However, no accurate study of the structural origin of the SP transition could be performed because of the extreme sensitivity of the TMTTF molecule to X-ray irradiation damages. Up to now, the difficulty to get large samples and the fact that they are hydrogenated have prevented from getting significant results with neutron diffraction.

The synthesis of the organic salts of the TMTSF and TMTTF samples has been strongly improved. A 17mm^3 crystalline sample of (TMTTF)$_2$ PF$_6$ has been elaborated in Orsay, which offered the possibility of a structural study of the SP transition. The experiment has been carried out on the triple axis spectrometer 4F2 of the Orphée reactor at the Laboratoire Léon Brillouin.

The experimental conditions were: k$_i$= 2.662Å^{-1}, 60' collimations on each side of the analyzer, and graphite filters on k$_i$ and k$_f$. The (a*,b*-c*) and the (a*,b*+c*) scattering planes were explored. Such samples are always twinned, but the ratio of (2,0,0) reflections of the two twins indicated that the twinning ratio was 7:1. 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 about 1.4 degree). At T=11K, the intensity of the Bragg reflections of the component used for the measurements was of 7000 c/s for the (0,1,1), 2000 c/s for the (2,0,0), 1200 c/s for the (2,1,1) and 1100 c/s for the (4,0,0), leading to an average Bragg intensity of about 3000 c/s.

At this temperature, a survey of about 20 reciprocal positions expected for the q$_{SP}$ superlattice reflections was performed with a counting time of 645s per step, in both (a*,b*-c*) and (a*,b*+c*) reciprocal planes. Because of a large background of 3 to 5 c/s, due to the incoherent scattering of the hydrogen atoms present in TMTTF molecules, only two very weak superlattice reflections were detected in the (a*,b*-c*) reciprocal plane and none in the (a*,b*+c*) plane. The observed reflections could be indexed as (-4,1,-2)+q$_{SP}$ and (-3,1,-2)+q$_{SP}$, where q$_{SP}$= (1/2,1/2,1/2), and their intensities were about 1/10th of the background.

Figure 1 shows a rocking-curve (ω-scan) and a longitudinal scan around the (-7/2,3/2,-3/2) reciprocal lattice position, which confirm that the observed scattering is a well defined Bragg reflection.
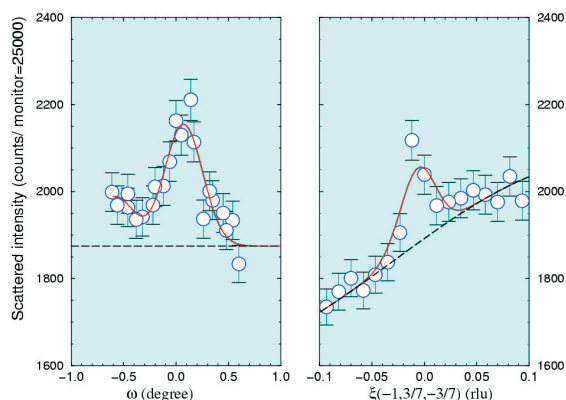

Figure 1. Transverse and longitudinal scans through the (-7/2,3/2,-3/2) superstructure reflection at T=11K. The dashed lines gives the background level.

The experimental width of the peak corresponds to the instrumental resolution, which implies a long range 3D SP order (i.e. > 1000 Å). The absence of second harmonic contamination has been checked. Finally the temperature dependence of the peak has been determined, as shown in the Figure 2, which unambiguously evidences the intensity drop at a temperature about 18-19 K. This ascertained the value of $q_{SP}=(1/2,/12,1/2)$.
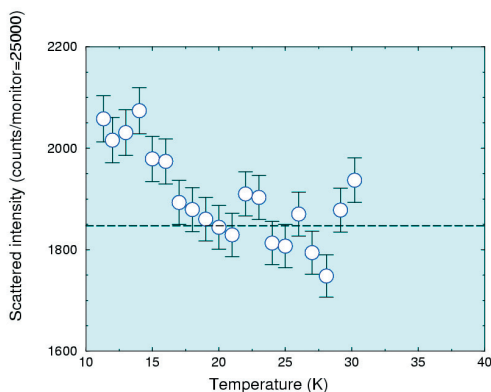

Figure 2. Temperature dependence of the (-7/2,3/2,-3/2) peak intensity. The dashed line gives the background level

The peak intensity I_S of the superlattice reflection is ~ 0.35 c/s. This is about 10^{-4} times the intensity I_B of an average Bragg reflection measured in the same experimental conditions. As the superlattice reflection intensity is proportional to the square of the long range atomic displacement, this means that the distortion undergone by the organic stack in $(TMTTF)_2PF_6$ is quite small compared to similar compounds, e.g. one order of magnitude smaller than in $(BCPTTF)_2AsF_6$. For comparison the ratio I_S/I_B in $MEM(TCNQ)_2$ and $CuGeO_3$ is ~10^{-3}. The shift u_{3D} of the TMTTF molecules is thus estimated to ~3 10^{-3} Å.

On the other hand, the amount of dimerization δ may be deduced from the spin gap value and the near neighbor exchange interaction J of the S=1/2 AF Heisenberg chain undergoing the Peierls instability. This gives another parameter u_{1D} corresponding to the intrachain displacement, with $\delta=2u_{1D}dln(J)/du$. Numerical calculations [6] yield $\delta=4.5\%$ in $(TMTTF)_2PF_6$, about two times smaller than $\delta=8\%$ found in $(BCPTTF)_2PF_6$, while there is about one order of magnitude between their respective u_{3D}.

Why the δ value does not scale with the amplitude u_{3D} of the 3D-SP distortion in $(TMTTF)_2PF_6$ opens new issues in the under-standing of this organic conductor. Several assumptions may be done. This could for instance point out the stabilization of a different mode of displacement. For example, in $(BCPTTF)_2PF_6$, the SP distortion could be directed along the long direction of the BCPTTF molecule, while in $(TMTTF)_2PF_6$, along the short direction of the TMTTF molecule. On the other hand, the SP distortion of the organic sublattice should deform the cavities where the anion X are located. This could lead to different shifts of the anions.

A better understanding of this problem would require a structural refinement of the SP superstructure of $(TMTTF)_2PF_6$. This could be achieved on large deuterated single crystals, with a strong reduction of the incoherent elastic scattering.

Finally, the present study demonstrates that deuterated samples of comparable volume that the hydrogenated used here, would make it possible to observe superlattice reflections of about 10^{-5} of an average Bragg reflections. This opens interesting perspective for the study of AF and SDW modulations in the $(TMTTF)_2X$ and $(TMTSF)_2X$ salts, respectively.

References
[1] J.P. Pouget and S. Ravy, J. Phys. I **6**, 1501 (1996).
[2] J.P. Pouget, R. Moret, R. Comès, K. Bechgaard, J.M. Fabre and L. Giral. Mol. Cryst. Liq. Cryst. **79**, 129 (1982).
[3] C. Coulon, P. Delhaes, S. Flandrois, R. Lagnier, E. Bonjour, and J.M. Fabre, J. Phys. Lett. (France), **43**, 1059 (1982).
[4] M. Dumm, A. Loidl, B.W. Fravel, K.P.Stanley, L.K. Montgomery and M.Dressel, Phys. Rev. B **61**, 511 (2000).
[5] F. Creuset, C. Bourbonnais, L.G. Caron, D. Jérome and K.Bechgaard, Synth. Met. **19**, 289 (1987).
[6] Yokoyama and Saiga, J. Phys. Soc. Japan **66**, 3617 (1997).