

## Spin dynamics of organic linear chain compounds

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# Spin dynamics of organic linear chain compounds

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Despite many years of research, the organic radical cation salts  $(\text{TMTCF})_2\text{X}$  ( $C = \text{S}$  or  $\text{Se}$ ,  $\text{X} = \text{PF}_6$ ,  $\text{ClO}_4$ ,  $\text{Br}$ , ...) attract considerable interest. The reduced dimensionality leads to instabilities in the electronic and magnetic system, various ground states like spin–Peierls, spin-density wave, or superconductivity develop at low temperatures. By slightly changing the organic molecules or the anions, the physical properties can be changed significantly [1,8].

We carried out electron-spin-resonance experiments in a continuous wave X-band spectrometer on single crystals of  $(\text{TMTCF})_2\text{PF}_6$ ,  $(\text{TMTCF})_2\text{ClO}_4$ , and  $(\text{TMTTF})_2\text{Br}$  in the temperature range  $1.5 \text{ K} \leq T \leq 500 \text{ K}$  [2]. Here we report about our measurements of the spin-chain compounds  $(\text{TMTTF})_2\text{ClO}_4$  and  $(\text{TMTTF})_2\text{PF}_6$  at  $2 \text{ K} \leq T \leq 400 \text{ K}$  (Fig. 1). In contrast to their selenium analogs TMTSF which are one-dimensional metals, the sulfur salts are semiconductors with localized spins on the TMTTF dimers.

The large temperature dependence of the thermal expansion coefficient along the chain direction has significant effects on the temperature dependence of the spin susceptibility. To compare the experimental results with the theoretical predictions it is necessary to calculate the spin susceptibility at constant volume  $(\chi_s)_V$  using the scaling introduced by Wzietek et al. in the case of NMR susceptibility measurements in  $(\text{TMTSF})_2\text{PF}_6$  [6]. In the high-temperature regime  $(\chi_s)_V$  of both compounds follows the predicted behavior of a  $S = \frac{1}{2}$  antiferromagnetic Heisenberg chain with an exchange constant  $J \approx 420 \text{ K}$ .

In  $(\text{TMTTF})_2\text{ClO}_4$  the ordering of the anions leads to a first-order structural phase transition at  $T_{\text{AO}} = 72.5 \text{ K}$ . This is accompanied by a dimerization of the spin chain leading to a strong decrease of  $(\chi_s)_V$  for  $T < T_{\text{AO}}$ . We determined an alternation parameter  $\gamma = 0.83$  and a singlet–triplet gap  $\Delta \approx 82 \text{ K}$ . At  $T \approx 15 \text{ K}$ , the ESR signal splits into five lines. It is known from  $^1\text{H-NMR}$  experiments that the rotation of the methyl groups slow down in this temperature range [7]. Thus, the rotational narrowing might be responsible for the hyperfine splitting. Below  $T_{\text{AFM}} = 12 \text{ K}$  these lines simultaneously decrease. This may indicate an additional transition to an antiferromagnetically state ordered in three dimensions.

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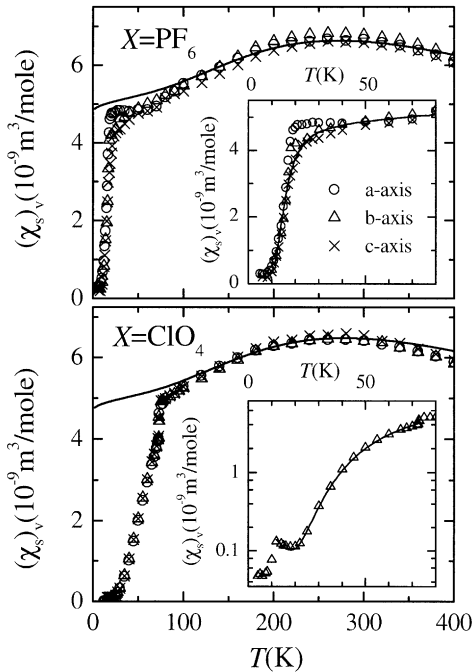


Fig. 1. Temperature dependence of  $(\chi_s)_V$  of  $(\text{TMTTF})_2X$ ,  $X = \text{PF}_6$  and  $\text{ClO}_4$ , along the three crystal axes. The lines correspond to fits using the EAT-model for a  $S = \frac{1}{2}$  AFM Heisenberg chain [3] with  $J = 420$  K. The absolute values of  $(\chi_s)_V$  were obtained by scaling the integrated intensity at its maximum value using the relation  $\chi_{\text{max}} = C/T_{\text{max}}$ ,  $C = 1.782 \times 10^{-6} \text{m}^3 \text{K}/\text{mole}$ . The upper inset indicates the fluctuations above the spin-Peierls transition in  $(\text{TMTTF})_2\text{PF}_6$ ; a good description of  $\chi_s$  in the SP pseudo-gap regime is given by the line [4]. The lower inset gives an enlarged view on the decreasing intensity below the anion-order transition in  $(\text{TMTTF})_2\text{ClO}_4$ . The line represents a fit using Bulaevskii's model of an alternating spin chain [5].

$(\text{TMTTF})_2\text{PF}_6$  undergoes a spin-Peierls transition at  $T_{\text{SP}} = 19$  K. Below  $T_{\text{SP}}$ , the ESR linewidth  $\Delta H$  increases and  $(\chi_s)_V$  vanishes exponentially with decreasing temperature. Using mean-field theory, we determined an alternation parameter  $\gamma(0) = 0.91$  and a singlet-triplet gap  $\Delta(0) \approx 34.5$  K. The decrease of the spin susceptibility along the  $b$  and  $c$ -directions below  $T_{\text{SP}}^0 \approx 62$  K can be explained by 1D lattice fluctuations above the spin-Peierls transition [4]. No fluctuations are observed along the chains.

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