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Magnetic Studies of $(TMTTF)_2X$ (X=PF_6, ClO_4, and Br)

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Abstract

We investigated the magnetic properties of the organic spin-chain compounds $(TMTTF)_2PF_6$, $(TMTTF)_2ClO_4$, and $(TMTTF)_2Br$ in the temperature range 2 K $\leq T \leq$ 500 K by electron-spin-resonance measurements. At high temperatures the spin susceptibility of the compounds can be well described by a spin 1/2 antiferromagnetic Heisenberg chain with exchange constants $J \approx$ 420 K, 430 K and 500 K (X =PF_6, ClO_4, and Br). In $(TMTTF)_2ClO_4$ the first-order structural phase transition at T_{AO} = 72.5 K is accompanied by a dimerization of the spin chain with a singlet-triplet gap $\Delta \approx$ 82 K. At T_{AFM} = 12 K we find an additional transition to an antiferromagnetic ordered state. $(TMTTF)_2PF_6$ undergoes a spin-Peierls transition at T_{SP} = 19 K which can be well described using mean field theory with $\Delta(0) \approx$ 34.5 K. The phase transition in the spin-density-wave state in $(TMTTF)_2Br$ at $T_{SDW} \approx$ 13.5 K is accompanied by visible fluctuations.

Despite twenty years of research, the organic radical cation salts $(TMTCF)_2X$ (C = S or Se, X = PF_6, ClO_4, 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 [1]. By slightly changing the organic molecules or the anions, the physical properties can be varied significantly [2].

The electron-spin-resonance experiments were carried out in a continuous wave X-band spectrometer on single crystals of $(TMTCF)_2PF_6$, $(TMTCF)_2ClO_4$, and $(TMTTF)_2Br$ in the temperature range 1.5 K $\leq T \leq$ 500 K [3]. Here we report on our measurements of the spin-chain compounds $(TMTTF)_2X$, X =ClO_4, PF_6, and Br, at 2 K $\leq T \leq$ 500 K. 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 thermal expansion coefficient along the chain direction has a large temperature dependence, which 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 $(\chi_s)_v$. We used the scaling introduced Wzietek et al. in the case of NMR susceptibility measurements in $(TMTSF)_2PF_6$ [4] for temperatures $T \leq$ 400 K. In the high-temperature regime $(\chi_s)_v$ of the TMTTF salts follows the predicted behavior of a S = 1/2 antiferromagnetic Heisenberg chain (Fig. 1). It is well fitted using the EAT-model [5] with exchange constants $J \approx$ 420 K, 430 K and 500 K for X =PF_6, ClO_4, and Br, respectively.

In $(TMTTF)_2ClO_4$ the alternating order of the anions at T_{AO} = 72.5 K leads to a first-order structural phase transition. This is accompanied by a dimerization of the spin chain leading to a strong decrease of $(\chi_s)_v$ for $T < T_{AO}$ (Fig. 2). The results can be described by the result Bulaevskii obtained for a alternating S = 1/2 AFM Heisenberg chain [6]

$$\chi(T) = \frac{A}{T} \exp\left(-\frac{E}{T}\right) . \qquad (1)$$

A is a constant, $E = J\Delta(\gamma)$, J is the mean value of the exchange integral ($J_{1,2} = J[1 \pm \delta]$), $\Delta(\gamma)$ is tabulated in [6] and $\gamma = (1-\delta)/(1+\delta)$. The singlet-triplet gap Δ is given by the equation $\Delta = 1.637\delta J$ [7]. We determined an alternation parameter γ = 0.83 leading to $J_1 \approx$ 470 K and $J_2 \approx$ 390 K and a singlet-triplet gap $\Delta \approx$ 82 K. At $T \approx$ 15 K, the ESR signal splits into five lines. It is known from ^1H-NMR experiments that the rotation of the methyl groups slows down in this temperature range [8]. Thus the rotational narrowing might be responsible for the hyperfine splitting. Below T_{AFM} = 12 K these lines simultanously decrease. This may indicate an additional transition to an antiferromagnetic ground state ordered in three dimensions.

$(TMTTF)_2PF_6$ undergoes a spin-Peierls transition at T_{SP} = 19 K. Below T_{SP}, the ESR linewidth ΔH increases and $(\chi_s)_v$ vanishes exponentially with decreasing temperature (Fig. 3). Using mean-field theory (Eqn. 1), we obtained an alternation parameter $\gamma(0)$ = 0.91 yielding to $J_1 \approx$ 440 K and $J_2 \approx$ 400 K. The singlet-triplet gap in the T = 0 K limit is given by $\Delta(0) \approx$ 34.5 K. There is a good agreement of $2\Delta(0)/T_{SP}$ = 3.6 with the value of 3.53 predicted by the BCS theory. The decrease of the spin susceptibility along the b and c directions below $T_{SP}^0 \approx$ 62 K can be explained by 1-D lattice fluctuations above the spin-Peierls transition [9]. No fluctuations are observed along the chains.

In $(TMTTF)_2Br$ the phase transition in the antiferro-

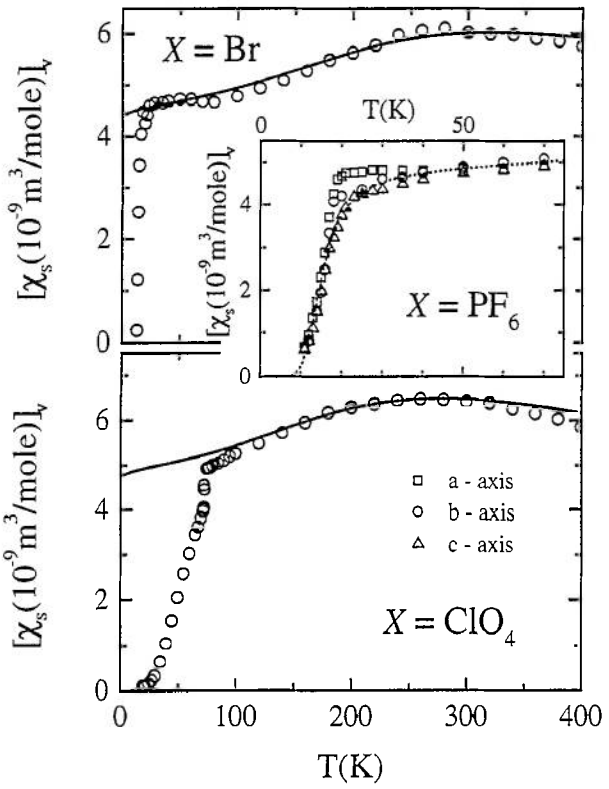

Fig. 1: Temperature dependence of $(\chi_s)_v$ of $(TMTTF)_2X$, $X = ClO_4$ and Br. The lines correspond to fits using the EAT-model for a $S = 1/2$ AFM Heisenberg chain [5] with $J = 430$ K and $J = 500$ K. The absolute values of χ_s were obtained by scaling the integrated intensity at its maximum value using the relation $\chi_{max} = C/T_{max}$, with $C = 1.782 \times 10^{-6} m^3 K/mole$. The inset indicates the fluctuations above the spin-Peierls transition in $(TMTTF)_2PF_6$; a good description of χ_s in the SP pseudo-gap regime is given by the line [9].

magnetic ground state of the spin-density-wave (SDW) at $T_{SDW} \approx 13.5$ K leads to a decrease of the spin susceptibility. The inset of Fig. 3 indicates that the phase transition is smeared out and that there are at fluctuations above the phase transition. This is in contrast to the behavior of the metallic selenium compound $(TMTSF)_2PF_6$ where the signal fully vanishes within 1 K at T_{SDW}.

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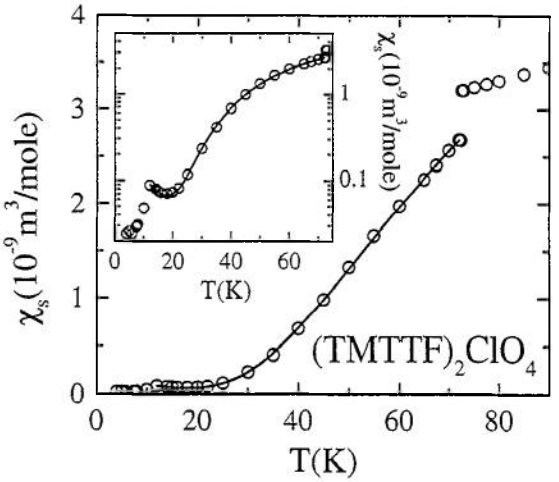

Fig. 2: Low temperature behavior of the spin susceptibility of $(TMTTF)_2ClO_4$. The decreasing intensity below $T_{AO} = 72.5$ K is fitted by Bulaevskii's model [6] with $\gamma = 0.83$ and $\Delta(0) \approx 82$ K (line). The inset shows the same data on a logarithmic scale in order to stress the saturation of the signal below 22 K and the second transition at $T_c = 12$ K.

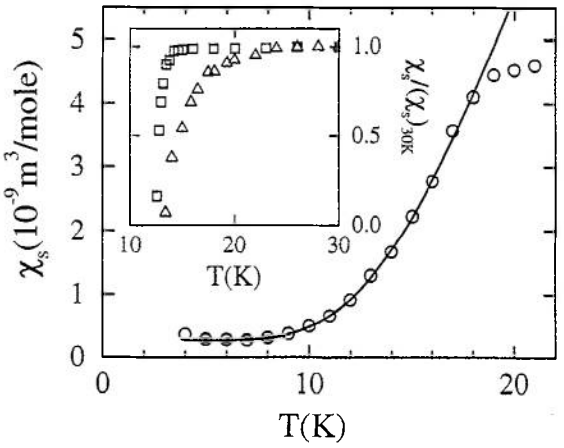

Fig. 3: Low temperature behavior of the spin susceptibility of $(TMTTF)_2PF_6$. The line corresponds to a fit of χ_s below the spin-Peierls transition using Eqn. (1). The inset shows the spin susceptibility normalized at 30 K of $(TMTTF)_2Br$ near the phase transition in the SDW state (triangles). In comparison the data of the SDW compound $(TMTSF)_2PF_6$ are plotted (squares).

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