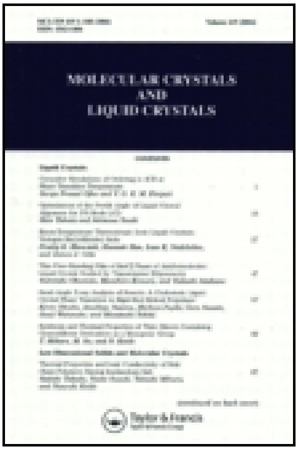

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EVIDENCE FOR A SPIN-PEIERLS-LIKE TRANSITION IN THE 1-D ORGANIC CATION RADICAL SALT :β-(TMTSF)$_2$Re$_6$Se$_5$Cl$_9$

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Abstract The magnetic and low temperature structural properties of the one dimensional organic charge transfer salts β-(TMTSF)$_2$ Re$_6$Se$_5$Cl$_9$ and β-(TMTTF)$_2$ Re$_6$Se$_5$Cl$_9$ are investigated. It is found that the former compound exhibits a spin-Peierls-like transition at ca. 65 K resulting in a tetramerization of the donor stack. No such a phase transition is observed in the TMTTF salt down to 20 K. This is ascribed to a difference in their structure, namely a stronger donor-anion (Se...Se) interaction in the selenium analogue.

INTRODUCTION

Among a series of recently synthetized TTF-based charge-transfer salts of the large chalcohalide metal cluster anion $Re_6Se_5Cl_9^-$, the β phases $(TMTSF)_2^{\dot{+}}$ $Re_6Se_5Cl_9^-$ and $(TMTTF)_2^{\dot{+}}$ $Re_6Se_5Cl_9^-$ (TMTSF : tetramethyltetraselenafulvalene ; TMTTF : tetramethyltetrathiafulvalene) present one-dimensional organic cation radical stacks constrained in a all-inorganic metal cluster network (Figure 1) (1). These are 2 : 1 salts whose architecture and degree of charge transfer (1/2 charge per organic donor) are similar to those of the classical Bechgaard salts (2). However, their structure differs from that of the latter salts by : (i) a significant increase of the

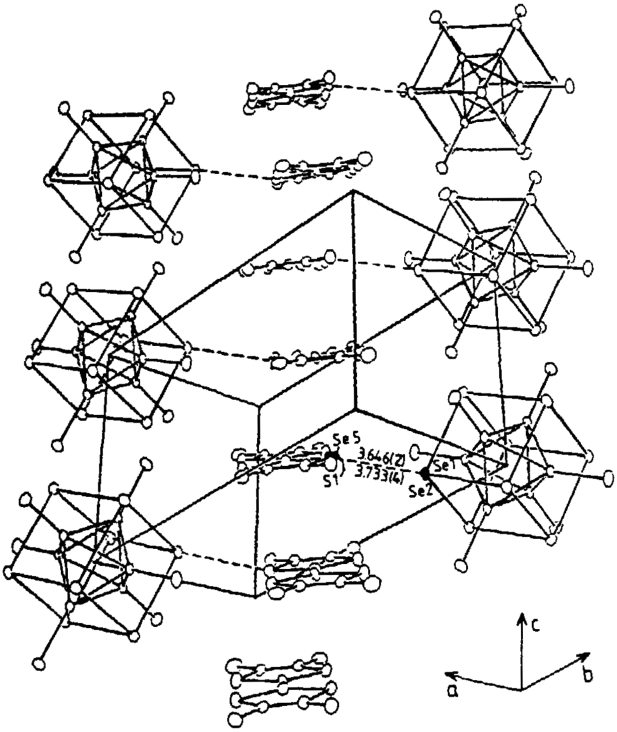

FIGURE 1. Perspective view, normal to the chain axis, of the structure of β-$(TMTTF)_2$ $Re_6Se_5Cl_9$ and β-$(TMTSF)_2$ $Re_6Se_5Cl_9$. The donor-anion shortest distance is indicated for both salts.

dimerization of the organic stack (in order for the stack to accomodate the larger separation between the anions) and (ii) a strong donor-anion interaction (3). Those two features are primarily responsible for their observed semi-conducting properties (1).

This paper reports striking differences in their structural and magnetic properties at low temperature.

MAGNETIC PROPERTIES

For some crystals of each phase the magnetic susceptibility was measured directly using a SQUID susceptometer. The temperature dependence of the net susceptibilities, corrected for the core diamagnetism of both constituents and Van Vleck paramagnetism of the inorganic cluster ($3.9\ 10^{-4}$ emu/mole (3)), are plotted in figure 2. While the spin susceptibility, χ_s, is essentially identical at room temperature for both compounds, it is found to behave differently with temperature. A smooth increase is observed for the TMTTF salt when temperature is lowered, with a broad maximum at ca. 160 K. This behaviour is expected for an Heisenberg chain of spin 1/2 (that is one localized spin per $(TMTTF)_2^{\dot{+}}$). Furthermore, $\chi_s(T)$ for β-$(TMTTF)_2\ Re_6Se_5Cl_9$ can be properly fitted above 50 K by the Bonner and Fisher susceptibility (5) with an antiferromagnetic exchange integral $J \sim 125$ K. The spin susceptibility of β-$(TMTSF)_2\ Re_6Se_5Cl_9$ increases more strongly when the temperature decreases. It shows a sharp maximum at ca. 75 K, before a sharp drop. This unusual low temperature behaviour strongly suggests the occurence of a phase transition at a critical temperature estimated to be ca. 65 K from the change of slope of $\chi_s(T)$. Above 75 K the spin susceptibility (after substraction of a low temperature (Curie tail) is essentially accounted for by a Bonner and Fisher fit (5) with an antiferromagnetic exchange integral $J \sim 50$ K. Note that this value is twice as low as that determined for the TMTTF analogue.

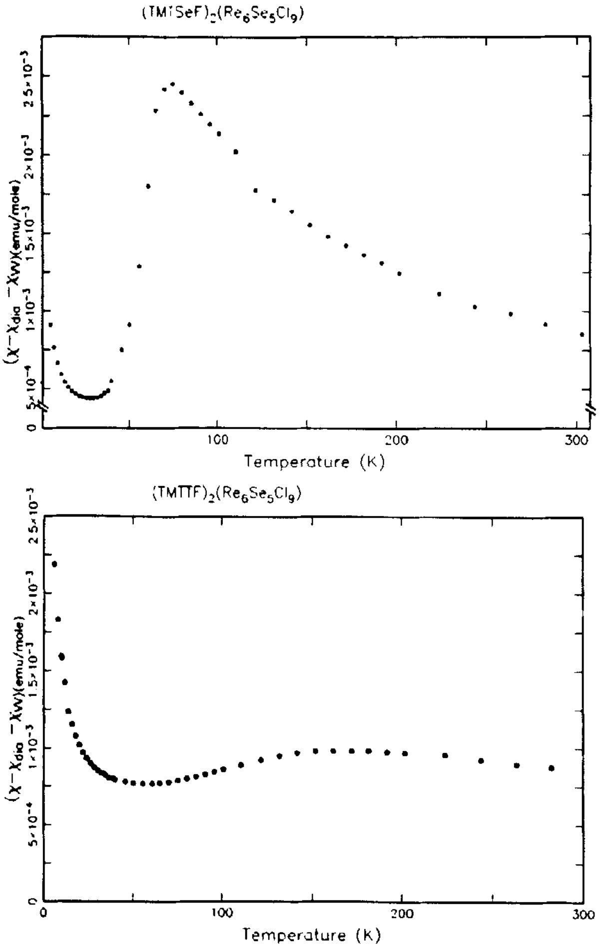

FIGURE 2. Temperature dependence of the magnetic susceptibility of β-(TMTSF)$_2$ Re$_6$Se$_5$Cl$_9$ (up) and β-(TMTTF)$_2$ Re$_6$Se$_5$Cl$_9$ (down) corrected for core diamagnetism and Van Vleck paramagnetism of the inorganic cluster.

LOW TEMPERATURE STRUCTURAL INVESTIGATION

Series of X-ray "monochromatic Laue" photographs of single-crystals of both compounds were taken down to 20 K. Investigation of the TMTSF salt reveals the occurence at ca. 60 K of new superlattice satellite reflections (arrows in Figure 3) with the in-chain wave vector component of $\frac{c^*}{2}$.
This indicates that a doubling of the stacking periodicity occurs at this temperature, which most likely results from a tetramerization of the donor stack. Further cooling leads to irreversible breaking of the crystal which can be associated with stresses occuring during the phase transition. By contrast, the TMTTF salt does not reveal any additional structural features in this temperature range.

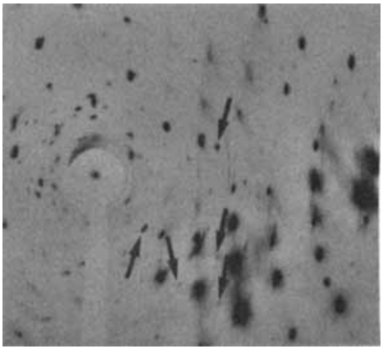

FIGURE 3. Cu-Kα X-ray pattern from β-$(TMTSF)_2$ $Re_6Se_5Cl_9$ at 60 K. Arrows point towards additional superstructure reflections (the chain axis c is horizontal).

CONCLUSION

Clearly, this investigation demonstrates that a structural phase transition is associated with the observed drastic drop of the magnetic susceptibility of β-$(TMTSF)_2Re_6Se_5Cl_9$ at 65 K. A likely consequence of such a phase transition is that the magnetic susceptibility vanishes as a result of the pairing of the otherwise localized spin 1/2 per each dimer. Indeed, although those features are characteristics of a conventional Spin-Peierls transition (4), the presence of (i) strong organic stack-inorganic cluster chalcogen-chalcogen interactions in the TMTSF salt and (ii) sizeable tensions during the transition suggest that the constraints imposed by the anion sublattice on the organic stacks have a key influence on the mechanism of the phase transition of β-$(TMTSF)_2$ $Re_6Se_5Cl_9$. Also, a weaker organic stack-inorganic anion coupling in the TMTTF salt (S (organic) - Se (inorganic) = 3.733 (4) Å) than in the TMTSF analogue (Se (organic) - Se (inorganic) = 3.646 (2) Å), see Fig.1, might explain why such a structural transition is not observed in β-$(TMTTF)_2$ $Re_6Se_5Cl_9$, in spite of a larger value of the interdimer exchange integral J.

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