Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 14 Oct 2011.

To cite this article: J. C. Scott (1982): Magnetism of the $(TMTSF)_2X$ Family of Organic Conductors, Molecular Crystals and Liquid Crystals, 79:1, 405-415

To link to this article: http://dx.doi.org/10.1080/00268948208070988

Mol. Cryst. Liq. Cryst., 1982, Vol. 79, pp. 49–59
0026-8941/82/7901–0049$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

MAGNETISM OF THE $(TMTSF)_2X$ FAMILY OF ORGANIC CONDUCTORS

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Received for publication August 31, 1981

The magnetic properties of the $(TMTSF)_2X$ series of conductors have been studied using magnetic susceptibility, electron spin resonance and both CW and pulsed NMR measurements. The results imply the existence of a spin-density-wave ground state, at ambient pressure, in at least the PF_6^-, AsF_6^- and SbF_6^- salts. The amplitude of the SDW, the exchange interaction, the anisotropy energy and the single particle gap are extracted from the experimental data.

I. INTRODUCTION

The magnetic behavior associated with the metal-insulator transition in one-dimensional conductors which undergo the Peierls or charge-density-wave (CDW) transition is quite straightforward. The static susceptibility[1] has the activated temperature dependence typical of semiconductors[2] and the electron spin resonance[3] involves electron-hole pairs excited across the energy gap. There is no anomalous behavior in the nuclear magnetic resonance: the conduction electron contribution to spin-lattice relaxation disappears smoothly as the density of carriers is depleted.[4]

When the family of organic conductors, $(TMTSF)_2X$, first appeared on the scene in 1979,[5] it was natural to assume that their semiconducting ground state also was caused by CDW condensation. However, the earliest magnetic measurements quickly showed that there were striking differences between this series of materials and the

familiar Peierls systems. The initial result of apparent absence of a drop in the static susceptibility[5] of $(TMTSF)_2PF_6$ (it was subsequently[6] shown that there was a relatively small but very sharp anomaly) was in contradiction with the sudden disappearance of the ESR intensity.[7] Further, the low temperature magnetic response was found to be nonlinear in a manner reminiscent of spin-flop behavior in antiferromagnets. It was therefore suggested[6] that the metal-insulator transition was driven by a spin-density-wave (SDW) onset, rather than a CDW. The same conclusion was reached by the Bell Laboratories group[8] based on the reappearance of the ESR signal when a sufficiently large microwave electric field is applied along the conducting axis. That work is the subject of another paper at this conference.

Here I shall review the magnetic susceptibility,[6] low-power ESR,[7,9] and NMR[10,11] evidence which supports the SDW picture, making comparisons between $(TMTSF)_2PF_6$, which is a SDW system, and $(TMTSF)_2ClO_4$, which is a superconductor.[12,13] But first let me summarize the relevant SDW theory as it applies to this novel family of organics.

II. THEORY OF SPIN DENSITY WAVES

The possibility of a SDW instability in one dimension has long been the subject of theoretical investigation.[14] Within the famous g-ology description,[15] it is known that the SDW response dominates for both backward (g_1) and forward (g_2) scattering repulsive, and that the SDW state is stabilized by interchain hopping (in contrast to interchain Coulomb interactions which enhance the CDW). In view of the close interchain Se-Se contact,[5,16] the resulting relatively high transverse bandwidth[17] and conductivity[18] (and with hindsight), it seems that $(TMTSF)_2X$ are ideal SDW candidates.

The 2:1 stoichiometry and the stability of the anions involved (PF_6^-, AsF_6^-, SbF_6^-, ClO_4^-, BF_4^-, etc.) imply half a hole per donor molecule. Since there are two molecules per unit cell along the stacking (a) direction, the Fermi wavevector is $k_F=\pi/2a$. The SDW wavevector is thus $2k_F=\pi/a$, corresponding to a magnetic doubling of the unit cell.[19] The picture in real space consists of moments which are alternately "up" and "down" in adjacent cells, with each moment spread over the two molecules in the cell. The spin density gives rise to an oscillating exchange potential which has the correct periodicity to open a gap in each of the up-spin and down-spin electron spectra.

The interaction Hamiltonian which gives rise to the SDW can be written, in the mean field approximation,[20,21] as

$$H_{SDW} = -(\tilde{U}/2\mu_B)\sum_{k,\sigma}(\sigma\mu c^{+}_{k\sigma}c_{k+Q,\sigma} + \text{h.c.}), \quad (1)$$

where the order parameter, i.e., the sublattice magnetization is

$$\mu = \mu_B\sum_{k,\sigma}\sigma\langle c^{+}_{k\sigma}c_{k+Q,\sigma}\rangle . \quad (2)$$

$\tilde{U}$ is the average Coulomb repulsion, $Q=2k_F$, $\sigma=\pm1$ and μ_B is the Bohr magneton. Hence, up (down) spin electron states, k, are mixed with down (up) spin hole states, k+Q. The single particle gap, 2Δ, and the transition temperature, T_{SDW}, are found by an analysis analogous to the BCS theory:

$$\Delta_o = 1.76kT_{SDW} = (\mu_o/\mu_B)\tilde{U} = \varepsilon_F e^{-1/\rho(\varepsilon_F)\tilde{U}}, \quad (3)$$

where Δ_o, μ_o indicate the zero temperature values and $\rho(\varepsilon_F)$ is the single-spin density of states at the Fermi energy, ε_F.

In the ordered state, the sublattice magnetization, $\underline{\mu}$, is locked along the "easy" direction by anisotropies which arise from dipolar interactions. The effect can be described to a good approximation in terms of the usual single ion anisotropy energies, D and E. Hence, the Hamiltonian describing the spins in the SDW phase can be written:

$$H = x^2J\sum_i \underline{S}_i \cdot \underline{S}_{i+1} - x^2D\sum_i S^2_{iz}$$

$$+ x^2E\sum_i (S^2_{ix} - S^2_{iy}) - gx\mu_B\sum_i \underline{H} \cdot \underline{S}_i . \quad (4)$$

The form of the first three terms has been chosen in such a way as to show explicitly the dependence on SDW amplitude, $x=\mu/\mu_B$. The zero-field, zero-temperature antiferromagnetic resonance (AFMR) energies

$$\hbar\omega_{\pm} = x[2J(D\pm E)]^{1/2} \quad (5)$$

are reduced because the effective "molecular" fields are less by a factor x.[22] The perpendicular susceptibility (at T=0 K)

$$\chi_{\perp} = \frac{Ng^2\mu^2}{2x^2J} = \frac{Ng^2\mu_B^2}{2J} \quad (6)$$

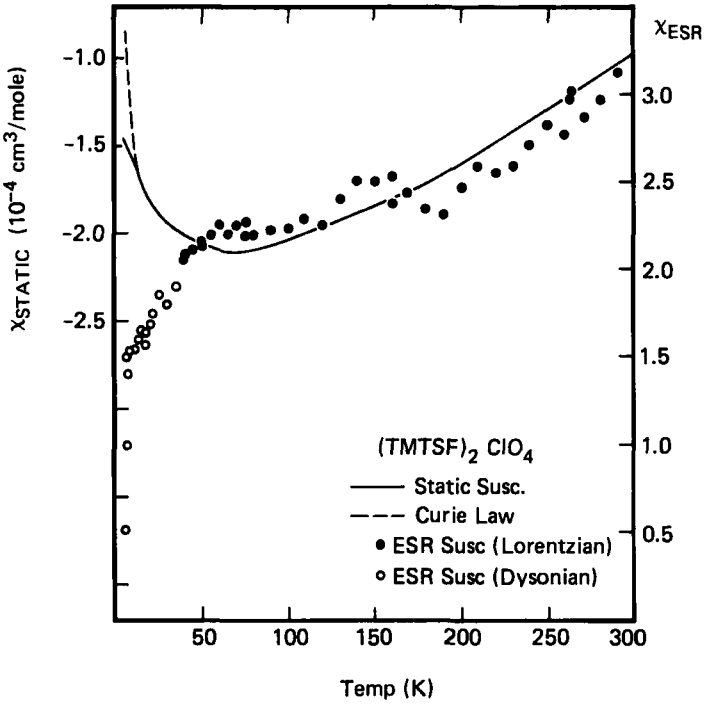

FIGURE 1 The susceptibility of $(TMTSF)_2ClO_4$. The dotted line indicates Curie behavior corresponding to a spin concentration of 0.8%, chosen to fit the temperature range $20 \lesssim T \lesssim 50K$. The scales for χ_{STATIC} and χ_{ESR} are offset by a core diamagnetic contribution of -4.2×10^{-4} cm^3/mole.

is independent of x, as is the relation between spin-flop field and AFMR frequency:

$$\mu_B H_{SF} = x[2J(D - E)]^{1/2} = \hbar\omega_- . \quad (7)$$

III. STATIC SUSCEPTIBILITY

The static susceptilibity of $(TMTSF)_2PF_6$ was reported at the Helsingor conference a year ago.[6] The important points to notice are: (1) the anomaly at $T_{SDW}=12.5K$, which signals the onset of the SDW; (2) the nonlinear behavior below T_{SDW}, which can be described in terms of a spin-flop field $H_{SF}\simeq 6$ kgauss; and (3) the low-temperature, high-field susceptibility $\chi_\perp = 1.2\times10^{-4}$ cm^3/mole. Subsequent work by

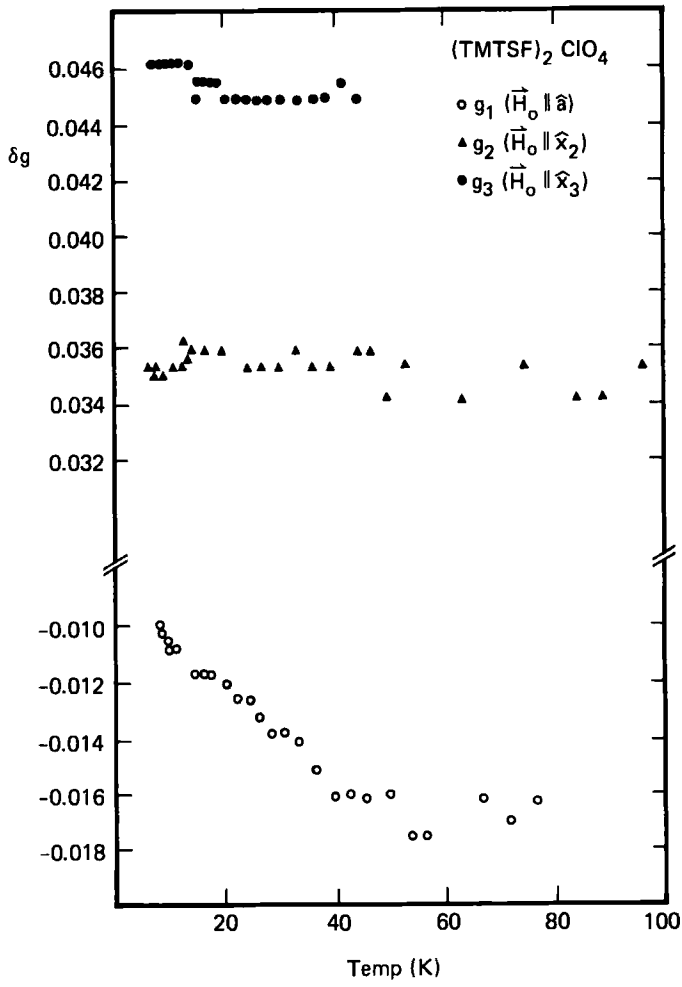

FIGURE 2 Principal-component g-shifts for $(TMTSF)_2ClO_4$. $\hat{x}_1 \simeq \hat{a}$, $\hat{x}_2$ and $\hat{x}_3$ are aligned with the axes of the TMTSF molecule.

Mortensen et al.[23] has confirmed the existence of a spin-flop field and has demonstrated the anisotropic susceptibility expected of an antiferromagnet.

The values of T_{SDW}, $\chi_\perp$ and H_{SF} can be used to extract U, μ_o, Δ_o, J and D from Eqs. (3), (6) and (7). Using the value of ε_F=1 eV from thermoelectric power[5] and plasma frequency[18] measurements, we obtain U≃300K, $\mu_o/\mu_B \simeq 0.07$, $\Delta_o \simeq 21$K, J≃700K and (D-E)≃0.02K. The value of U is such that $U/\varepsilon_F << 1$, in keeping with a "small-u"

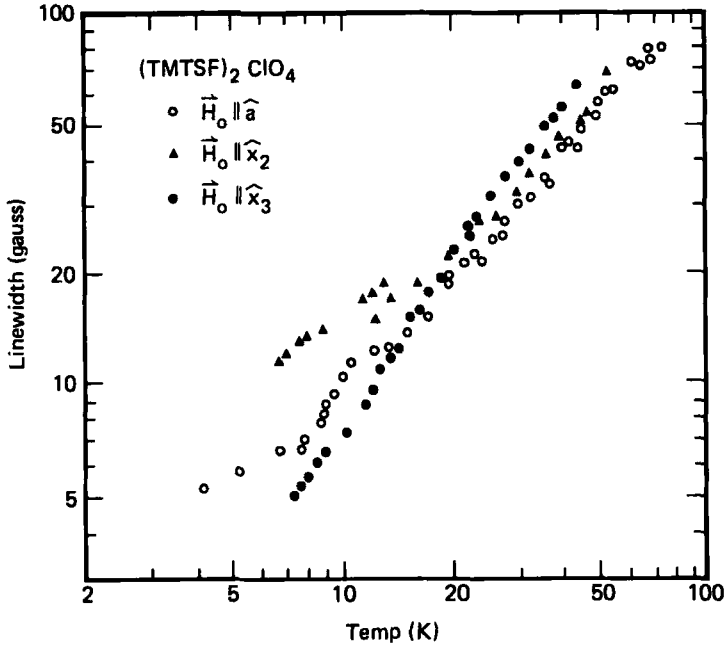

FIGURE 3 ESR linewidth of $(TMTSF)_2ClO_4$.

description and the weak-coupling approximation which is implicit in the mean field analysis of Section II. The Hubbard model expression for the exchange, $2t^2/U \sim 10^5$K, is clearly then inappropriate for these materials. The single particle gap, Δ_o, is in agreement with the results of transport measurements.[24] The value of D is just what one would expect for the dipolar interaction between electrons spread over a unit cell of 7Å.

By contrast, the static susceptibility (Fig. 1) of $(TMTSF)_2ClO_4$, which does not undergo a SDW transition but rather remains metallic down to a superconducting transition at 1.2K,[12,13] shows no anomalous behavior, other than a tendency to drop as the temperature is lowered below about 10K. This latter behavior hints that SDW fluctuations may be present in this material also, but that, for some reason, the actual transition never occurs and that the superconducting instability dominates.

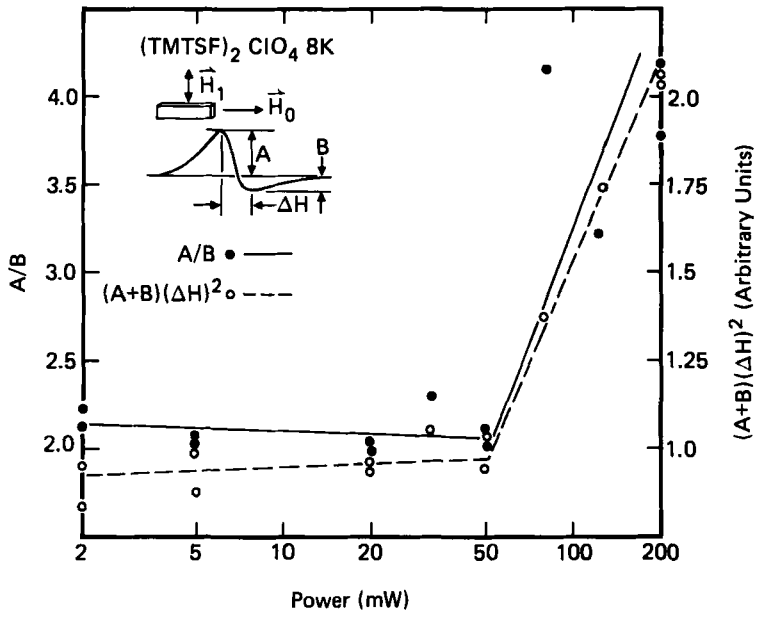

FIGURE 4 Power dependence of ESR signal in $(TMTSF)_2ClO_4$. A, B and ΔH are indicated in the inset. $(A+B)(\Delta H)^2$ is used as an approximate measure of total intensity. The lines guide the eye.

IV. ELECTRON SPIN RESONANCE

The results of extensive studies of the ESR parameters, g, linewidth and intensity for the series of salts $(TMTSF)_2X$, $X = PF_6^-$, AsF_6^-, SbF_6^-, BF_4^- and NO_3^-, have been presented previously.[6,7,9] In this section, I shall summarize the data on the PF_6^- salt and contrast them with new results on the perchlorate.

The ESR signature of the SDW transition is the rapid disappearance of the ESR line within 1-2K of T_{SDW}. As the line vanishes, it also broadens and shifts to lower field. Since the ESR intensity is proportional to the static susceptibility, the loss in signal must be accompanied by a reappearance of the oscillator strength elsewhere. Torrance et al.[25] have recently observed the antiferromagnetic resonance at Q-band, confirming the predictions of Section II. Direct, quantitative results relating to the SDW cannot be readily extracted from the metallic state ESR. However, the line-broadening and resonance shift are clear signatures that the

metal-insulator transition is accompanied by the development of internal fields, in marked contrast to the case of a Peierls distortion.

As expected, there are no such signatures in the ESR data for $(TMTSF)_2ClO_4$ (Figs. 1-3). Nevertheless, there are features which indicate that there may be spin-density fluctuations in some samples of this salt too. In our original samples,[12] the ESR intensity decreased by 70% below 10K, qualitatively similar to the static susceptibility, and the linewidth levelled off in the same range. Recent single crystal work (Fig. 3) shows a linewidth which decreases, approximately linearly down to the lowest temperature, without significant loss of ESR signal. There is a slight shift of the line for $H_0 \| \hat{a}$ at temperatures below about 30K (Fig. 2). These features suggest the presence of fluctuations, the magnitude of which vary from sample to sample.

At high power and low temperature, and with $H_0 \| \hat{a}$ so that a component of the microwave field is also parallel to the highly conducting direction, it is possible to observe an ESR signal of a much more asymmetric shape and of higher intensity than at low power. At 8K, the threshold power for this change in the ESR characteristics is 100 mW (see Fig. 4). Walsh[8] gives much more detail of this "spin-resurrection" phenomenon.

The magnitude of the ESR linewidth in $(TMTSF)_2ClO_4$ is systematically larger than that in the PF_6 salt (compare Fig. 3 with Fig. 4 of Ref. 9), the difference being most apparent at low temperature. This indicates greater interchain interaction in the perchlorate, consistent with the suppression of the SDW instability.

V. NUCLEAR MAGNETIC RESONANCE

The proton NMR of $(TMTSF)_2PF_6$ has been studied as a function of temperature and frequency.[10,11,26] CW measurements[11] at 10 MHz (H_0=2.3 kgauss) yield a linewidth of 6 gauss (FWHM) above T_{SDW} and 7.5 gauss below. Since it is expected that the conduction electron density at the methyl protons is negligible for TMTSF, the interaction between the electronic moment and protons is dipolar. The additional broadening due to the SDW moment, at a distance of roughly 5Å from the protons, therefore corresponds to a SDW amplitude, μ/μ_B, of order a few percent. This result is in accord with that of the mean field evaluation of Section III.

The fact that the linewidth below T_{SDW} is indeed inhomogeneous is confirmed by spin-echo experiments[10] (see Fig. 1 of Ref. 26). For $T>T_{SDW}$, $T_2 \simeq T_2^*$ consistent with the homogeneously broadened line one expects from proton-proton dipolar interactions. For $T \lesssim T_{SDW}$, T_2 increases, while T_2^* (which is inversely proportional to the linewidth)

decreases. This is exactly as expected for an antiferromagnet, where the local field at each proton site, due to the electronic moment, shifts the resonance of each inequivalent proton by a different amount and "detunes" the otherwise resonant interaction between them.

The fluctuations in spin-density near T_{SDW} provides an additional spin-lattice relaxation channel for the protons, in contrast again to the case of a CDW transition where there is no direct coupling of the order parameter to the nuclear moments. Details of this effect are given in another paper in these proceedings,[26] and discussed theoretically by Morawitz and me.[27]

VI. CONCLUSION

The experimental evidence for a spin-density-wave ground state in $(TMTSF)_2PF_6$ includes nonzero magnetic susceptibility, spin-flop behavior, the shift of the ESR oscillator strength and the onset of internal fields as seen by g-shift, ESR linewidth, NMR linewidth and relaxation. The data on the AsF_6^- [9,19,23] and SbF_6^- [9] salts are less complete, but, so far, are similar in all respects. Other results, including the susceptibility anisotropy,[23] the antiferromagnetic resonance,[25] the nonexistence of a CDW superlattice,[19] and the magnitude of the single particle gap, complete a consist picture of the SDW state.

The data on the salts of tetrahedral anions such as BF_4^- [5,9] and ReO_4^- [28] are rather different, and indicate that the metal-insulator transition is driven by an ordering of the anions in a manner which doubles the size of the unit cell and therefore creates a $2k_F$ distortion. Although this leads to a superlattice and a semiconducting ground state, it is not, strictly speaking, a Peierls distortion, but rather has much more first-order character typical of a structural phase transition.

The perchlorate is an interesting case. Although it too is tetrahedral, it does not undergo an ordering transition, but rather is the only salt of the series to remain metallic, and to become superconducting, at ambient pressure. There is some evidence in the magnetic properties that SDW fluctuations may exist at low temperature. One therefore concludes that the SDW instability is not quite so strong as superconductivity, perhaps because it is suppressed by stronger interchain coupling and by the residual disorder in orientation of the anions.

ACKNOWLEDGMENTS

Part of this work was performed at Cornell University with support from the NSF-MRL grant number DMR-76-81083. Work at IBM received partial support from ONR. It is a great pleasure to acknowledge the important contributions of my collaborators in this work, especially Drs. H. J. Pedersen, K. Bechgaard and W. G. Clark.

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