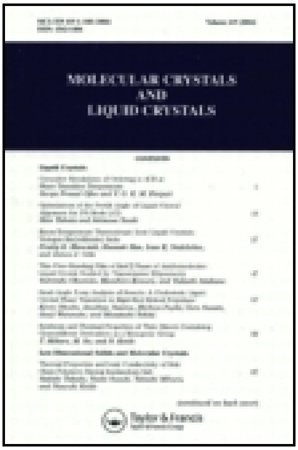

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Antiferromagnetic Resonance in $(TMTTF)_2SbF_6$ and $(TMTTF)_2SCN$

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ANTIFERROMAGNETIC RESONANCE IN $(TMTTF)_2SbF_6$ AND $(TMTTF)_2SCN$

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Abstract Antiferromagnetic resonance has been observed in the two Bechgaard salts, $(TMTTF)_2SbF_6$ and $(TMTTF)_2SCN$, below 7 and 9 K, respectively. For the thiocyanate the spin-flop field is found to be at 4.7 kOe, and the easy axis is near the crystallographic b' direction. The upper zero field mode is estimated to lie at approximately 6 kOe. The analysis for the SbF_6 salt is more difficult because the easy magnetic axis does not coincide with a principal crystallographic direction, and because the spin-flop field is less than 3.3 kOe.

The existence of an antiferromagnetic ground state has been demonstrated in many of the 2:1 salts of the electron donors TMTSF and TMTTF.[1] In general, ESR and susceptibility data have been cited as evidence, and the number of materials in which antiferromagnetic resonance (AFMR) has been observed remains rather small.[2-4] In this paper, we present AFMR results recently obtained on two more salts of TMTTF: $(TMTTF)_2SCN$ which was previously known, on the basis of susceptibility measurements,[5] to have an antiferromagnetic ground state; and $(TMTTF)_2SbF_6$ which, until the present study and that of Maaroufi *et al.*,[6] was only suspected of being antiferromagnetic from its ESR properties[7] below 10 K.

Antiferromagnetic resonance is conveniently performed, in this class of materials, using a conventional ESR spectrometer, in our case operating at 9.3 GHz. The single crystal sample is cooled to below its Néel temperature using a Oxford instrument ESR-900 continuous flow cryostat, and may be rotated about an axis perpendicular to the applied static magnetic field. In general, the AFMR(s) are shifted in field far from the $g=2$ position, and are strongly dependent on orientation.[8] The nature of the rotation pattern for the resonances depends on the relationship between the microwave frequency

(ω_0) and the zero-field uniform (k=0) spin-wave frequencies:[9]

$$\Omega_{\pm} = (\mu/\mu_B)\sqrt{2J(D \pm E)} \qquad (1)$$

where in a localized spin Hamiltonian, J is the nearest neighbour exchange interaction, D and E are the magnetocrystalline anisotropy parameters, and μ is the magnitude of the local magnetic moment, which has been shown to be of order 0.1 Bohr Magnetons.[10] For some values of ω_0, Ω_-, and Ω_+ and in certain orientations, it is possible that no resonance will be observed at all.

The behaviour of the resonant fields *vs* angle of rotation about the crystallographic *a* axis of $(TMTTF)_2SCN$ is shown in figure 1. The existence of two resonances which converge and disappear beyond a critical angle on either side of a "special" orientation (4°, i.e. close to b') occurs uniquely for the case that $\omega_0 < \Omega_-$ and the magnetic easy axis is close that direction. Computer simulation is required in order to fit the detailed shape of the experimental rotation pattern, including the cusp in the higher field mode at 4°, the asymmetry, and the overall width of the "bubble", depending upon the values of four parameters: $\Omega_{\pm}$ and two angles giving the orientation of the rotation (a) axis with respect to the magnetic easy, intermediate and hard axes. We find, in addition to the assignment of the easy axis near b', that the hard axis is close to a and the parameters Ω_-/γ and Ω_+/γ are 4.7 and 6.0 (both ±0.5) kGauss. (The electron gyromagnetic ratio, γ=2.8 MHz/Gauss, is used to convert to magnetic field units.) Further refinement is underway, and the complete results of the computer analysis will be presented in a later, more comprehensive, publication.

The results for $(TMTTF)_2SbF_6$ are shown in figure 2. Antiferromagnetic resonance is observed below a transition temperature, $T_N = 7 \pm 1$ K. Extrema in the resonances are observed at 2 kOe along c^*, at 5 kOe 110° from a and perpendicular to the direction of g_{MAX}, and at 2 kOe near a, with

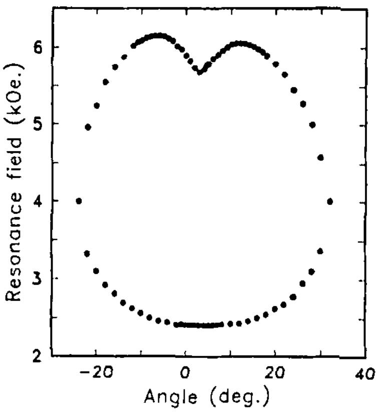
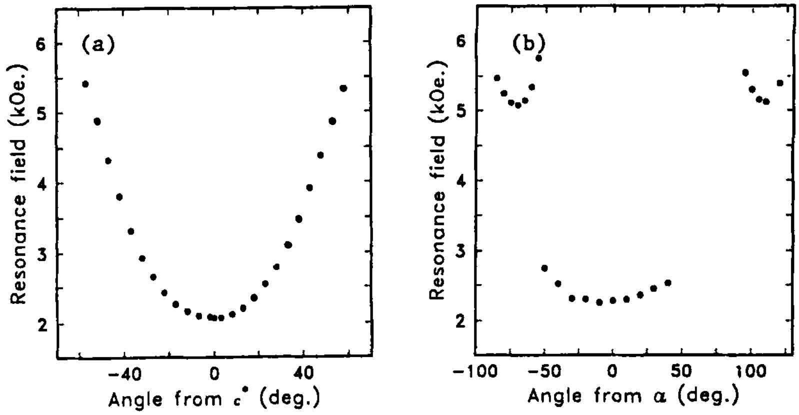


FIGURE 1. Antiferromagnetic rotation pattern of $(TMTTF)_2SCN$ at 3.8 K about the a-axis. 0° corresponds to b', which is therefore close to the easy axis.



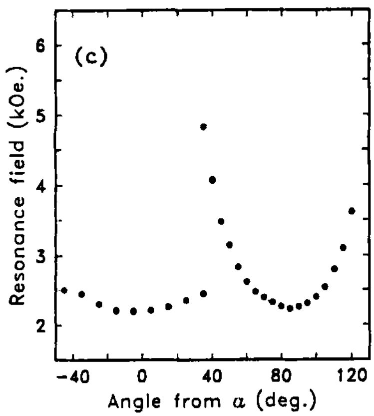


FIGURE 2. AFMR rotation patterns of $(TMTTF)_2SbF_6$ at 3.8 K: (a) about the a-axis; (b) about the direction corresponding to the high temperature g_{MAX}, which is 22° from c^* in the b'-c^* plane; (c) about the axis of g_{INT}, which is 22° from b'.

the last mode being rather weak and having less orientation dependence. Three observable resonances, in three (nearly) mutually perpendicular directions, can occur only when the microwave frequency, ω_0, lies between Ω_- and Ω_+. Therefore the spin-flop field is less than 3.3 kOe, and the strong mode seen along c^* can only be associated with the behaviour close to the intermediate axis. No mode should be visible when the field is along the hard axis. The rotation around the direction of g_{MAX} is rather difficult to understand: one possibility is that the resonance near a is due the spin-flop behaviour of the higher frequency mode, when the field is along the easy axis. In any case, it is clear from both the a-axis and g_{MAX} rotations that there is no spin-flop mode along the direction of the short molecular axis, as expected from the assignment of the easy-axis by Maaroufi *et al.*[6]

Further information on the magnetic parameters is obtained from the temperature dependence of the resonances. This indicates that the upper frequency, Ω_+, drops below the observation frequency ω_0, just above 4 K.

The zero temperature value of Ω_+/γ cannot therefore be much greater than 3.3 kOe. Further analysis to clarify the orientation and temperature dependences, and to determine the magnetic parameters and axes is in progress and will be presented in a future publication.

Regardless of the exact values of the magnetic parameters of $(TMTTF)_2SbF_6$, our AFRM results show conclusively that the ground state of this material is antiferromagnetic. The magnetic phase transtion cannot be associated with a spin-density-wave instability of the Fermi-surface,[11,12] because conductivity measurements show that there is a gap which opens below about 160 K.[13] Thus the low temperature properties should be described in terms of a Mott-Hubbard semiconductor, with a small energy gap for charge excitations, and localized magnetic moments which become three dimensionally ordered at 7 K. In this picture, it is interesting to speculate whether the metal-to-insulator change at 160 K is a true phase transition, or merely a one-dimensional crossover temperature from a regime of extended electronic states to one of localized states.

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