Physica Scripta. Vol. 25, 854–856, 1982

Magnetic Susceptibility of Two Antiferromagnetic Organic Conductors, $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$

Kell Mortensen

Physics Laboratory III, Technical University of Denmark, DK-2800 Lyngby, Denmark

Received August 3, 1981; accepted October 23, 1981

Abstract

The organic conductors, $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ undergo both at ambient pressure a phase transition toward an antiferromagnetically ordered ground state. We review the obtained magnetic susceptibility data and show, that these are almost exactly the same for the two compounds. Both materials have magnetic ordering temperature close to 12 K. In the antiferromagnetically ordered state, spin-flop transitions are seen. The data are discussed on the basis of Overhauser's treatment of itinerant antiferromagnetism.

1. Introduction

The recently synthesized organic conductors based on the TMTSF molecule [1], $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ are members of a new class of compounds which have attracted extensive interests by exhibiting a number of physical properties different from those observed in chemically related compounds. $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ behave very similar. The structure is in both salts triclinic, with rather similar parameters [2, 3]. The interstack selenium distances and interplanar distances reveal, though, that, from a structural point of view, the AsF_6^- salt is slightly more one-dimensional than the PF_6^- salt.

$(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ have both been reported to be superconducting at moderate pressure of 1.2 Pa in the 0.4-1.5 K region [4, 5]. At ambient pressure they undergo a metal-to-insulator (MI) transition at rather low temperatures, $T_{MI} = 12$–19 K [1]. In the metallic state, the d.c.-conductivities reach maximum values beyond $10^5\,\Omega^{-1}\,cm^{-1}$, and below the transition temperature, the d.c.-conductivities remain relatively high [1]. The hexaflourophospate salt has moreover shown unusual nonlinear electric and magnetic field effects [6, 7].

2. Phase transition

Most of the known organic metals related to TTF–TCNQ undergo a transition toward an insulating ground state characterized by the existence of a three-dimensionally ordered lattice distortion. This transition is driven by the Peierls mechanism. A signature of the Peierls instability is the observation of additional reflections in the diffuse X-ray pattern , due to softening of the $2k_F$-modes. No such precursor have, however, been detected by X-ray diffuse scattering in $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ [8, 5]. Moreover, it was observed that while the spin susceptibility obtained by the ESR technique disappears at the phase transition [9], there are only minor effects on the static susceptibility measured on powder [1, 10]. Based on these results, it was speculated that the MI-transition might be of magnetic origin, perhaps due to formation of spin-density waves (SDW) [6, 10]. The possible existence of SDW's may also explain the low transition temperature, since the interstack interaction between spin-density waves is much weaker than between charge-density waves. SDW's have also been proposed to explain the non-ohmic transport properties [6].

3. Magnetic susceptibility

Direct evidence for the magnetic transition of $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ was recently obtained by static magnetic measurements on single crystals [11, 12]. The obtained spin susceptibilities are reshown in Figs. 1–3. The spin terms are calculated from the total susceptibilities by subtracting a constant core diamagnetism, as described in [12]. The measurements were on the hexaflouroarsenate salt done on one single crystal. The magnetic fields were applied parallel to the crystallographic **a**, **b*** and **c*** axes respectively [12]. Since the hexaflourophosphate salt, however, was formed in rather small crystals, these measurements were done on an assembling of single crystals, all with **a** axes aligned, but with **b*** and **c*** axes pointing randomly in directions perpendicular to **a** [11]. The results obtained for $(TMTSF)_2AsF_6$ are consequently somewhat more conclusive than those of $(TMTSF)_2PF_6$. But since all data

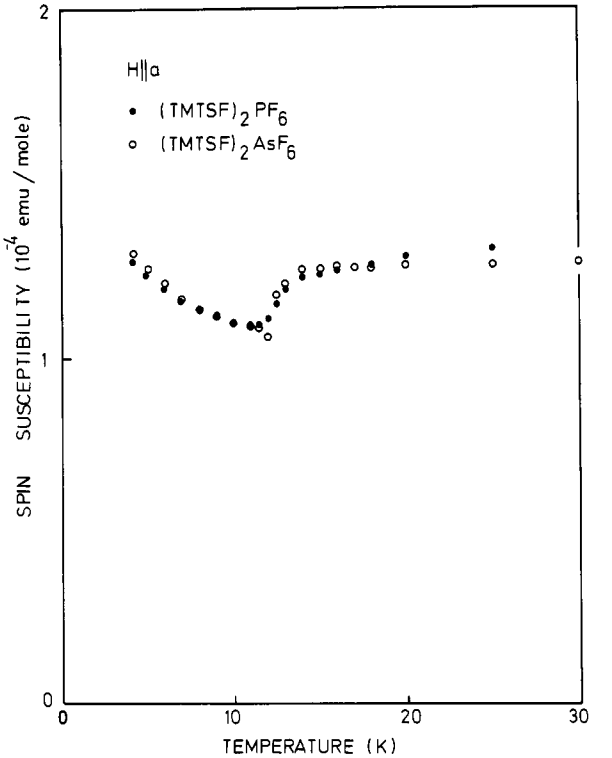

Fig. 1. Spin susceptibilities of $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ versus temperature, as measured with field ($H < H_c$) parallel to **a**.

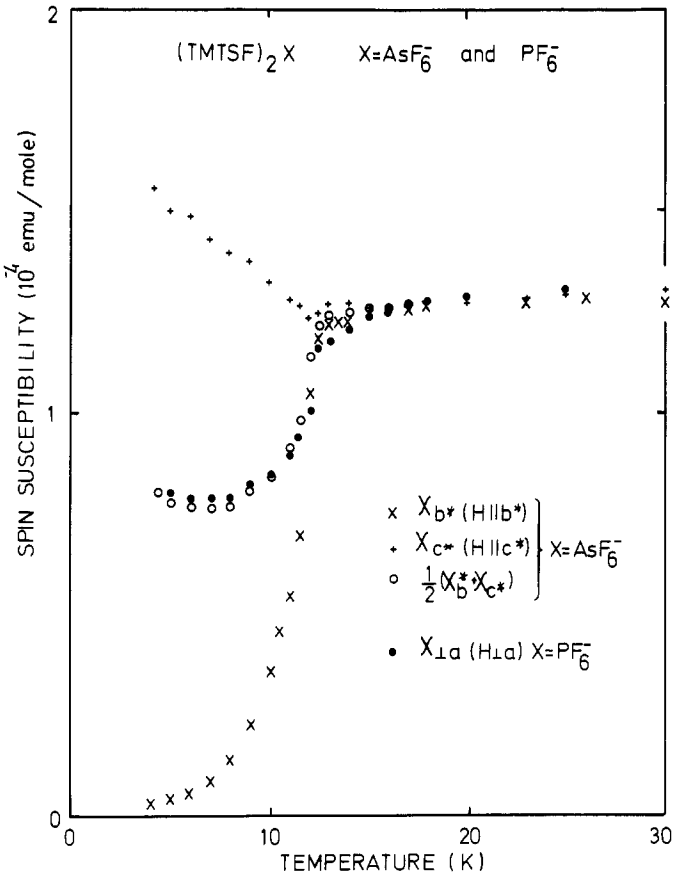

Fig. 2. Spin susceptibility of $(TMTSF)_2PF_6$ as measured with field ($H < H_c$) perpendicular to **a**, and spin susceptibilities of $(TMTSF)_2AsF_6$ as measured with field ($H < H_c$) parallel to **b*** and **c***.

indicate that the detailed magnetic properties of the two materials are the same, we believe that our conclusion on the AsF_6^--salt also account for the properties of $(TMTSF)_2PF_6$.

In Figs. 1 and 2 are shown the spin susceptibilities versus temperature as measured at relatively low magnetic fields ($H \leqslant 4$ kG). While the spin susceptibilities between 15 and 30 K are isotropic and relatively temperature independent, we observe significant T-dependences below 15 K. Close to 12 K, markedly anisotropy develops.

Below 15 K, $\chi(H \| \mathbf{b}^*)$ of $(TMTSF)_2AsF_6$ decreases monotonically with decreasing temperature, but with a sharp maximum in slope at 12 K. Close to zero temperature, $\chi(H \| \mathbf{b}^*)$ approach zero. $\chi(H \| \mathbf{a})$ and $\chi(H \| \mathbf{c}^*)$ have several common properties. At 12 K, they both show a characteristic anomaly, and going to zero temperature, the susceptibilities remain large. The stacking axis component of the susceptibility, $\chi(H \| \mathbf{a})$, of $(TMTSF)_2PF_6$ is within the errorbar equal to that of $(TMTSF)_2AsF_6$ (see Fig. 1). Correspondingly, $\chi(H \perp \mathbf{a})$ of the PF_6-salt is equal to the average of the two components of $\chi(H \perp \mathbf{a})$ of $(TMTSF)_2AsF_6$; $\chi(H \| \mathbf{b}^*)$ and $\chi(H \| \mathbf{c}^*)$ (Fig. 2). The exact value of the transition temperature, T_c, as detected by the anomalies in $\chi(T)$, seems though to be slightly different for the two materials. We find $T_c = 11.5$ and 12 K for $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ respectively [11, 12].

The temperature dependences of the measured anisotropic susceptibilities are consistent with expectations for a simple antiferromagnet, characterized by having three principal magnetic axes. The easy axis is close to the crystallographic **b***-direction. The susceptibilities measured with applied magnetic fields perpendicular to **b*** are relatively large, because the sublattices in these configurations are optimally suited to being canted by the field. In contrast, the spin susceptibility of $H \| \mathbf{b}^*$ is small since any finite spin-moment can only occur as a result of some spins turning over, which is more or less prevented by the exchange field.

The markedly T-dependent and slightly anisotropic susceptibilities observed in a region above T_c reveal a magnetic precursor developing below approximately 15 K. Careful inspections of the data may suggest that the spins in this narrow precursor range condense into the **ab***-plane [12].

4. Spin–flop transition

More insight into the antiferromagnetic groundstates of $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ is gained from the field dependences of the susceptibilities. In Fig. 3 are χ vs. H shown for $H \| \mathbf{b}^*$ and $H \| \mathbf{c}^*$ for $(TMTSF)_2AsF_6$ and for $H \perp \mathbf{a}$ for $(TMTSF)_2PF_6$. No significant field dependence was seen for $H \| \mathbf{a}$ in any of the salts, as well as for $H \| \mathbf{c}^*$ for the AsF_6 salt. The susceptibility, $\chi(H \| \mathbf{b}^*)$ of $(TMTSF)_2AsF_6$ show in contrast a drastic field dependence, with a sharp increase in susceptibility close to 4.5 kG. Like the behaviour of the temperature dependences of χ, the field dependence of $\chi(H \perp \mathbf{a})$ of $(TMTSF)_2PF_6$ is equal to the average of $\chi(H \| \mathbf{b}^*)$ and $\chi(H \| \mathbf{c}^*)$ of $(TMTSF)_2AsF_6$.

The field dependences are indicative of spin–flop transitions. When the applied magnetic field exceeds a critical value, given by the exchange field (H_E) and the anisotropy field (H_A); $H_c = \sqrt{2H_E H_A}$, the spins turn from the direction of the easy axis (**b***) toward a predominantly perpendicular one, most probably close to **a** [12].

5. Overhauser transition

A phenomenological theory which describes the antiferromagnetic ordering in $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ may be based on Overhauser's Hartree–Fock treatment of an itinerant

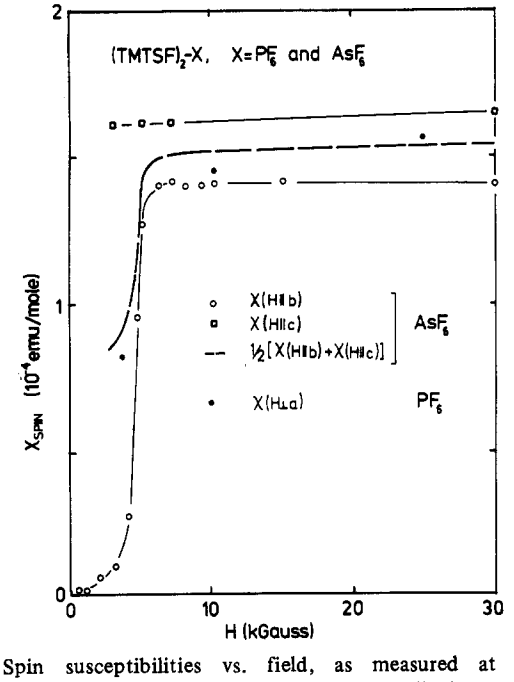

Fig. 3. Spin susceptibilities vs. field, as measured at 4.2 K for $(TMTSF)_2PF_6$, the field is applied perpendicular to **a**. For $(TMTSF)_2AsF_6$, the field is applied parallel to **b*** and **c***.

electron gas [13]. The antiferromagnetic SDW ground state is in this model energetically favored with a spin modulation wave vector which nests the almost planar Fermi surface of these quasi-one dimensional metals. In the 2:1 stochiometric $(TMTSF)_2X$ salts, where the TMTSF bands are quarter filled, a commensurate SDW with a wavelength four times that of the primitive unit cell will be cormed. Since the antiferromagnetic SDW ordering opens up a gap at the Fermi surface, the Overhauser mechanism will also account for the semiconducting transport behavior observed below T_c [1].

Itinerant spin-density wave antiferromagnetism has generally successfully been studied by neutron diffraction technique. On $(TMTSF)_2PF_6$, however, scattering experiments have so far failed to show the SDW superstructure [14]. In order to know whether the SDW is expected to be seen directly by neutrons, an attempt to estimate the SDW amplitude is important. An approach would be to assume that the magnetic anisotropy arises largely from dipole–dipole interactions between spins. Metzger has calculated this dipolar anisotropy assuming maximum amplitude SDW, namely spins localized on every other TMTSF molecule [15]. The calculated anisotropy within the **ab**-plane is of the order of 10^{-4} K. By using this number, and the exchange integral $J = 600$ K as got from a Bonner–Fisher analysis of the spin-susceptibility, one should expect a spin-flop field equal 8 kG. Since the magnitude of the dipolar anisotropy goes as the square of the SDW amplitide, the experimental value of $H_{SF} = 4.5$ kG predicts a SDW amplitude of approximately 50%. The dipolar anisotropy calculations [15] did, however, not give the correct hard and easy magnetic axes. The estimation given above is therefore somewhat doubtful, and we should emphasize that NMR analysis have predicted a SDW amplitude of less than 1% [16].

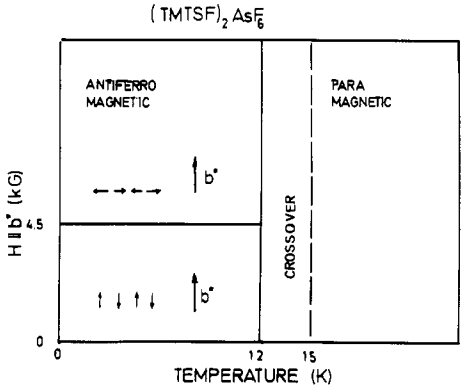

Fig. 4. Phase diagram of $(TMTSF)_2AsF_6$.

6. Conclusion

We summarize our principal conclusions about $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$. The two materials behave very similar. The spin susceptibilities of the two salts are both qualitatively and quantitatively almost exactly the same. Close to 12 K, they both undergo a phase transiton into an antiferromagnetic ground-state. The ordered spins are in this state aligned close to the b^* axis. Upon increasing magnetic fields, the salts undergo a spin-flop transition. For $(TMTSF)_2AsF_6$ the spin-flop critical field is 4.5 kG. The phase-diagram corresponding to these observations is schematically shown in Fig. 4.

Acknowledgements

We are pleased to acknowledge discussions with Dr K. Bechgaard, Dr Y. Tomkiewicz, Dr T. D. Schultz, and Dr E. M. Engler.

References

1. Bechgaard, K., Jacobsen, C. S., Mortensen, K., Pedersen, H. J. and Thorup, N., Solid State Commun. **33**, 1119 (1980).
2. Thorup, N., Rindorf, G., Soling, H. and Bechgaard, K., Acta Cryst. B (in press).
3. Wudl, F., Preprint (1981).
4. Jérome, D., Mazaud, A., Ribault, M. and Bechgaard, K., J. Phys. (Paris), Lett. **41**, L95 (1980).
5. Ribault, M., Pouget, J. -R., Jérome, D. and Bechgaard, K., J. Phys. (Paris), Lett. **41**, L607 (1980).
6. Walsh, W. M., Wudl, F., Thomas, G. A., Nalewajek, D., Hauser, J. J., Lee, P. A. and Poehler, T., Phys. Rev. Lett. **45**, 829 (1980).
7. Jacobsen, C. S., Mortensen, K., Weger, M. and Bechgaard, K., Solid State Commun. **38**, 423 (1981).
8. Suter, R. S. and Horn, P. M., Private communication.
9. Pedersen, H. J., Scott, J. C. and Bechgaard, K., Solid State Commun. **35**, 207 (1980).
10. Scott, J. C., Pedersen, H. J. and Bechgaard, K., Phys. Rev. Lett. **45**, 2125 (1980).
11. Mortensen, K., Tomkiewicz, Y., Schultz, T. D. and Engler, E. M., Phys. Rev. Lett. **46**, 1234 (1981).
12. Mortensen, K., Tomkiewicz, Y. and Bechgaard, K., Phys. Rev. B (in press).
13. Overhauser, A. W., Phys. Rev. **128**, 1437 (1962); Fedders, P. A. and Martin, P. C., Phys. Rev. **143**, 245 (1966).
14. Kjems, J., Private communication.
15. Metzger, R. M., J. Chem. Phys. **75**, 482 (1981).
16. Andrieux, A., Jerome, D. and Bechgaard, K., J. Phys (Paris), Lett. **42**, L87 (1981).