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Antiferromagnetic Ordering in the Organic Conductor *bis*-Tetramethyltetraselenafulvalene-Hexafluorophosphate [$(TMTSF)_2$-PF_6]

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(Received 12 January 1981)

The anisotropy in the static susceptibility of $(TMTSF)_2$-PF_6 has been investigated above and below the metal-insulator transition for a range of fields between 4 and 25 kOe. The results are consistent with the occurrence of an Overhauser antiferromagnetic transition to a spin-density-wave state with an easiest axis perpendicular to the stacks. Below the transition, evidence for a spin-flop transition is seen. Above the transition, evidence for a crossover, possibly from $n = 3$ to $n = 1$ spin behavior, is seen.

PACS numbers: 75.30.Gw, 71.30.+h, 75.30.Cr, 75.50.Ee

Recently, the new class of organic conductors $(TMTSF)_2$-X has generated extensive interest by exhibiting a number of physical properties different from those observed in chemically related compounds. In particular, $(TMTSF)_2$-PF_6, which is the first organic compound exhibiting superconductivity,[1-4] has been studied in detail. The superconducting state occurs under hydrostatic pressure above 6.5 kbar at temperatures near 1.2 K. At ambient pressure,[5] $(TMTSF)_2$-PF_6 has been observed to undergo a metal-to-insulator (MI) transition in the temperature range 15–19 K, which is remarkably low compared with most other conducting organic charge-transfer salts. More recently, it has been suggested[6] that there is also a magnetic transition at 11.5 K. In our samples, we see only one transition, at 11.5 K, in both the magnetic and transport properties. This transition is the subject of this paper.

Despite considerable experimental work, the nature of the MI transition in $(TMTSF)_2$-PF_6 and its relationship to the superconducting state remain a puzzle. Although the MI transitions occurring in the other known organic metals are believed to be associated with Peierls distortions, no indication of this type of distortion has been seen for $(TMTSF)_2$-PF_6 in diffuse x-ray scattering experiments[7] down to 4 K. The magnetic and transport properties for $T \leq T_c$ have also proved anomalous. At the transition temperature, Pedersen, Scott, and Bechgaard[8] observed a significant reduction of the spin susceptibility, as measured by spin resonance in single crystals, whereas only minor effects were detected in the static susceptibility measured on a powdered sample.[5,6] This is not what is expected from the opening of a Peierls gap. Additional experiments have shown[9,10] that both the dc conductivity and spin paramagnetism are drastically affected by small electric fields (~10 mV/cm) at temperatures below T_c. These observations led to the speculation[6,9] that a spin-density wave might be responsible for the MI transition.

To see if the MI transition is also a magnetic phase transition, we have studied the static magnetic susceptibility in detail, both parallel and perpendicular to the molecular stacking axis (a axis). The results presented in this paper provide the first *direct* evidence that antiferromagnetic ordering takes place in the MI transition. We observe an anisotropic susceptibility at small fields (~4 kOe) for $T < T_c$, an apparent spin-flop transition in somewhat larger fields transverse to a, and the disappearance of anisotropy effects with increasing fields. That the transition is magnetic is in accord with the argument of Scott, Pedersen, and Bechgaard that if there is only one transition, it is magnetic.

Single crystals of $(TMTSF)_2$-PF_6 were grown by an electrochemical technique similar to that described by Bechgaard *et al.*[5] For these crystals, neither the structural properties nor the results of chemical analysis show any significant differences from those previously reported.[5] The source of the difference in measured[10,11] T_c from that given in Ref. 5 is therefore unclear.

The static magnetic susceptibility was measured on a superconducting susceptometer (S.H.E. Corp. 805). Approximately 40 crystals (~5 mg) of $(TMTSF)_2$-PF_6 were placed in a quartz holder (<10 mg). The crystals were mounted with their a axes all aligned but their b and c axes pointing randomly in directions approximately perpendicular to a. An error bar of 10% in the absolute value of the magnetic susceptibility was introduced by the specified uncertainty in the magnetic field (±1%). The relative error bars on the data taken at different temperatures but in a fixed field are less than 1% for $H = 4$ kOe and are even smaller for larger fields.

In order to minimize the error due to the uncertainty in the magnetic-field strength, the measurements parallel and perpendicular to the a axis were performed without changing the field between the two orientations. Still, an error we estimate to be less than 5% might have been introduced in the absolute measurements just by the handling of the holder.

In Fig. 1 are shown the susceptibilities measured with fields parallel ($\chi_{\parallel a}$) and perpendicular ($\chi_{\perp a}$) to the stacking axis for two different fields, 4 kOe [Fig. 1(a)] and 25 kOe [Fig. 1(b)]. Significant anisotropy is seen, but only at low temperatures ($<T_c$) and low fields (4 kOe). It cannot come from an anisotropic χ_{diam}, which presumably is temperature and field independent. Above T_c, the temperature dependence agrees well with the previously published data.[7,8]

The magnitudes and field dependences of $\chi_{\parallel a}$ and $\chi_{\perp a}$ can be understood from the phenomenological theory of an antiferromagnet,[12] consistent with expectations[12] for an antiferromagnetic with an easiest axis perpendicular to a. Although the concept of sublattice magnetization in such a theory is more obvious for local spins, it is also appropriate for itinerant spins, which we believe these to be. For low fields, $\chi_{\parallel a}$ is relatively large because the sublattice magnetizations, being all aligned perpendicular to the hard axis (but otherwise randomly oriented due to the random angular orientations of the crystals), are optimally suited to being canted by the weak field. $\chi_{\perp a}$ is smaller either because the canting is into a less favorable direction (if the transverse plane is isotropic) or because some of the sublattice magnetizations are less than optimally oriented for canting (if there is an easiest axis in the transverse plane). It is not possible to distinguish between these two cases from the size of $\chi_{\parallel a} - \chi_{\perp a}$.

More insight into the anisotropy within the transverse plane can be gained from the field dependence of $\chi_{\perp a}$. An overview of $\chi_{\perp a}$ at a weak, an intermediate, and a strong field, over a significant range of temperatures, is shown in Fig. 2(a) and the field dependence of $\chi_{\perp a}$ at 8 K is

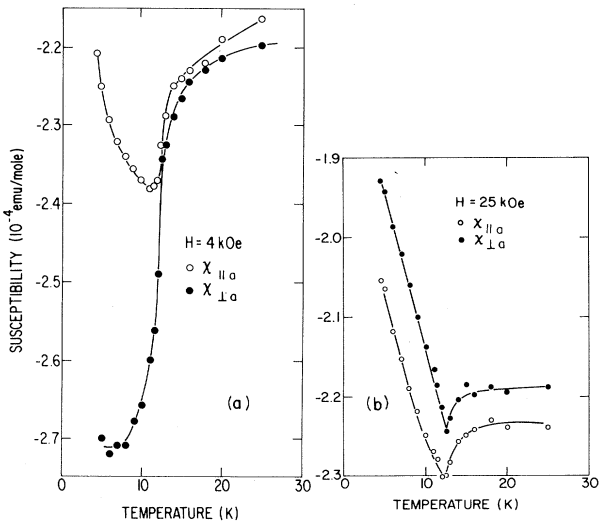

FIG. 1. Static magnetic susceptibility of $(TMTSF)_2$-PF_6 parallel and perpendicular to the stacking axis for two different fields, (a) 4 kOe and (b) 25 kOe.

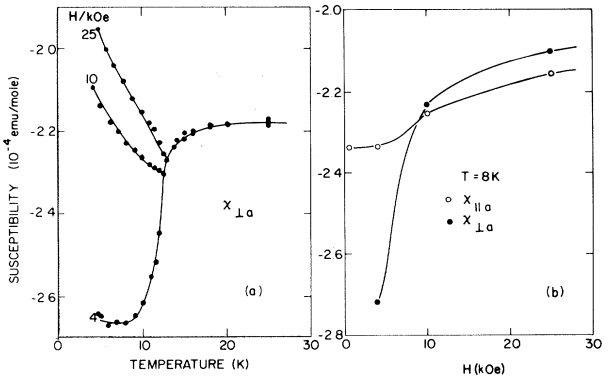

FIG. 2. Evidence for spin flop in $(TMTSF)_2$-PF_6. (a) $\chi_{\perp a}$ vs T at 4, 10, and 25 kOe. (b) $\chi_{\perp a}$ and $\chi_{\parallel a}$ vs H at 8 K.

shown explicitly in Fig. 2(b). If the crystals were magnetically isotropic in the transverse plane, the canting and, therefore, the magnetization would grow linearly with H, at least for small H, so that $\chi_{\perp a}$ would be independent of H, in contrast to what is seen in Fig. 2(b). If the crystals had an easiest axis in the transverse plane, then because of their random orientations around the a axis, they would undergo variously broadened spin-flop transitions to a state with a much larger $\chi_{\perp a}$. The expected $\chi_{\perp a}$ would have a distinctly nonlinear behavior near the spin-flop critical field and increase by roughly a factor of 2 in going to saturation, in agreement with Fig. 2(b). More detailed experiments on the field dependence of $\chi_{\perp a}$ are in progress to see if the actual behavior agrees with that predicted.

For H parallel to a, one would expect $\chi_{\parallel a} \simeq$ const $\neq 0$ for small H, because the canting would grow continuously from 0 as H increased from 0. The slight S-shaped behavior of $\chi_{\parallel a}$ might be a matter of misalignment relative to the hard axis. For large fields (~25 kOe), the absence of any significant difference between the susceptibilities for different orientations is compatible with having overcome all anisotropy fields.

The phenomenological theory, including the notion of sublattice magnetizations, can be based on the Hubbard model for a one dimensional chain which, within Overhauser's Hartree-Fock treatment,[13] has an antiferromagnetic ground state. One way, although not the only way, to introduce anisotropy into such a chain would be to include a nearest-neighbor, spin-dependent, *ferro* magnetic, Ising interaction like

$$V_{1,\,\mathrm{anis}} \sum_{jss'} ss' n_{j,s} n_{j+1,\,s'}, \qquad (1)$$

where $n_{j,s}$ is the occupation-number operator at site j for spin $S_z \equiv s = \pm\frac{1}{2}$, the z axis in spin space being in some definite direction. A term like (1) with the z axis along a could arise from a dipole-dipole interaction between spins on neighboring sites along the stacks.[14] If a single chain or a weakly-coupled system of such chains is treated in the manner of Overhauser, anisotropy effects similar to those of the phenomenological theory are found [the inclusion of (1) leads to an easy xy plane in spin space]. The precise orientations of the principal axes of the susceptibility tensor and their microscopic origin must still be investigated. The Overhauser mechanism would also account for the insulating character below T_c, because in a quasi-one-dimensional system the Overhauser gap covers the whole Fermi surface.

The disappearance below T_c of the EPR absorption signal at X band may also be explained by the development of anisotropic antiferromagnetic order. Previously, it was attributed[9] to extensive line broadening, although recent measurements[11] indicate that despite the line broadening occurring for $T < T_c$, the linewidth remains finite. We now propose that the resonance becomes an antiferromagnetic resonance. In zero field, this would occur at $g\mu_B (2H_{\mathrm{exch}} H_{\mathrm{anis}})^{1/2} \simeq 17$ GHz, which we obtain from the spin-flop field $\equiv (2H_{\mathrm{exch}} H_{\mathrm{anis}})^{1/2} \simeq 6$ kG.

Inspection of Fig. 2(a) reveals a precursor to the 11.5 K transition developing below 15 K. This could, of course, reflect a crossover from one-dimensional to three-dimensional ordering, i.e., $d = 1$ to $d = 3$ in the usual notation of second-order transitions. Because of the existence of an easiest axis, this narrow precursor range could also reflect a crossover from three-dimensional to one-dimensional spin motion, i.e., $n = 3$ to $n = 1$. Such a crossover is expected when the anisotropic part of the interaction energy for all spins within a correlation length is or order kT. As the spin behavior becomes more one dimensional, the correlation length grows rapidly as it crosses from $1/T$ behavior ($n = 3$) to $\exp(T_c/T)$ behavior ($n = 1$). We suggest that the rapid fall in $\chi_{\perp a}$ just above the transition may be due to this effect. The n crossover can also hasten the crossover in d and thereby hasten the phase transition itself. Without this effect of spin anisotropy, the transition would be at an even lower temperature, which could be due at least partly to the absence of Coulomb interactions between spin-density waves.

Although precursor effects are seen in static-susceptibility and transport[10,11] measurements, none is seen in the g value. This, and the possibility of a Q-band resonance, must be further investigated.

From the sharp anomaly in $\chi_{\parallel a}$ vs T, Fig. 3(a), we obtain T_c and its magnetic-field dependence, Fig. 3(b). At zero field, $T_c \simeq 11.5 \pm 0.5$ K, in contrast to previous results[5,6,8] but in agreement with conductivity,[10,11] thermopower,[11] and spin-susceptibility[11] results in samples of the same batch. Furthermore, no other transition has been seen, so we do not have the problem of explaining two transitions posed by Scott, Pedersen, and Bechgaard[6] [Fig. 3(b)]. We find very slight, if any, field dependence, in agreement with previous conductivity measurements.[15] The apparent

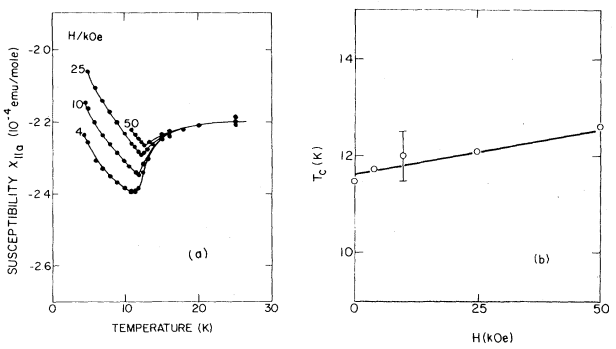

FIG. 3. Phase transition in $(TMTSF)_2$-PF_6 as a function of H. (a) $\chi_{\parallel a}$ vs T for various fields. (b) T_c vs H as detected by anomaly in (a).

increase in T_c with increasing H is not unusual for antiferromagnets and can be due to an increase in the staggered susceptibility of individual chains.[16]

We summarize our principal conclusions about $(TMTSF)_2$-PF_6. (1) There is a single phase transition occuring at $T_c \cong 11.5$ K for $H = 0$ and ambient pressure. (2) This transition is not only a MI transition but is marked by the development of antiferromagnetic order having an easiest axis perpendicular to a. In this sense, $(TMTSF)_2$-PF_6 is different from other organic metals where the MI transition is believed due to a charge-density-wave instability. (3) The transition temperature is so low at least in part because the interstack interaction between spin-density waves is much weaker than between charge-density waves. (4) There may be a crossover from $n = 3$ to $n = 1$ spin behavior below 15 K. (5) T_c is prevented from being even lower by this $n = 1$ behavior, which enhances the correlation length and, thereby, the effective interchain interaction.

We wish to thank Dr. J. B. Torrance, Jr., and Dr. M. Pomerantz for valuable conversations. This work was supported in part by the Office of Naval Research. One of us (K. M.) is an IBM World Trade Fellow.

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