Magnetic Properties of the Organic Conductor *bis*-Tetramethyltetraselenafulvalene Hexafluorophosphate [$(TMTSF)_2PF_6$]: A New Phase Transition

J. C. Scott and H. J. Pedersen
Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853

and

K. Bechgaard
Department of General and Organic Chemistry, University of Copenhagen, H. C. Oersted Institute, Universitetsparken, DK-2100 Copenhagen, Denmark

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Magnetic susceptibility measurements on the organic conductor $(TMTSF)_2PF_6$ reveal a new phase transition at 11.5 K. At lower temperature the magnetic response is nonlinear, being more diamagnetic below 6 kOe than at higher fields. At the metal-insulator transition (~17 K) there is no visible anomaly in the static susceptibility, in contrast to the rapid disappearance of the electron-spin-resonance intensity.

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The properties of the new series of charge-transfer conductors, $(TMTSF)_2X$ (TMTSF = tetramethyltetraselenafulvalene and $X = NO_3^-$, ClO_4^-, BF_4^-, PF_6^-, AsF_6^-, SbF_6^-), have aroused renewed interest in organic metals.[1-3] Conductivities exceeding $10^5\ \Omega^{-1}\ cm^{-1}$ are observed[1,4]; the metal-insulator transition temperatures (~20 K) are remarkably low in view of the fact that the stoichiometry implies a commensurate Fermi wave vector[1,4]; and $(TMTSF)_2PF_6$ is superconducting under modest pressure.[2,5] In this Letter we present magnetic susceptibility data for $(TMTSF)_2PF_6$ which show that the low-temperature semiconducting state is not simply Peierls in nature, but has an additional phase transition at 11.5 K, below which the magnetic response is nonlinear.

The present study was motivated by a preliminary report[1] that, in contrast to the intensity of the single observable electron-spin resonance (ESR) line,[3] the static magnetic susceptibility of $(TMTSF)_2PF_6$ has no anomaly at the metal-insulator transition $T_{MI} = 18 \pm 1$ K. Our results confirm this observation, placing more stringent limits on the magnitude of any such magnetic anomaly. In addition, they reveal a previously undiscovered transition at 11.5 ± 0.5 K which has unusual magnetic character.

Measurements were made by the Faraday method on two samples. The first consisted of crystals (40 mg) from several batches, synthesized by electrochemical means several months previously. Crystals from these growths had been used for the transport measurements[1,4] which first identified the metal-insulator transition, and for the ESR study.[3] No special storage precautions were taken. The second sample consisted of 50 mg of material synthesized expressly for magnetic measurements two weeks previously and stored under argon before transfer to the vacuum/He environment of the Faraday apparatus. The sample was exposed to the atmosphere for a maximum of 10 min. Several crystals from this batch were examined by ESR and found to have their transition in the range 16–17 K.

The Faraday apparatus and the method of measurement have been described previously.[6] We have since incorporated additional interfacing whereby signal averaging can be done at fixed temperature, before the computer triggers a change in the setting of the temperature controller. Above 25 K data were taken while sweeping the temperature at 0.2 K/min or slower. Below 25 K the temperature was stabilized to within 50 mK before initiating a measurement sequence. Accuracy of the temperature scale is within 0.5 K.

The results (4–300 K) are shown in Fig. 1. Clearly visible at $T_2 = 11.5$ K (we introduce a notation to distinguish the new transition temperature from $T_1 \equiv T_{MI} = 16$–19 K) is a notchlike anomaly, to which we shall return later. Also shown is the intensity of the ESR absorption signal, in absolute units as determined by comparison with tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ).[7,8] The tabulated Pascal constants[9] for $(TMTSF)_2PF_6$ yield a diamagnetic core correction of $\chi_D = -4.05 \times 10^{-4}$ cm^3/mole. By using the measured value of the diamagnetism for hexamethylene-TSF (HMTSF)[10] and adjusting for the lack of methylene linkage and the Pascal contribution of PF_6 in the present compound, one obtains a core correction

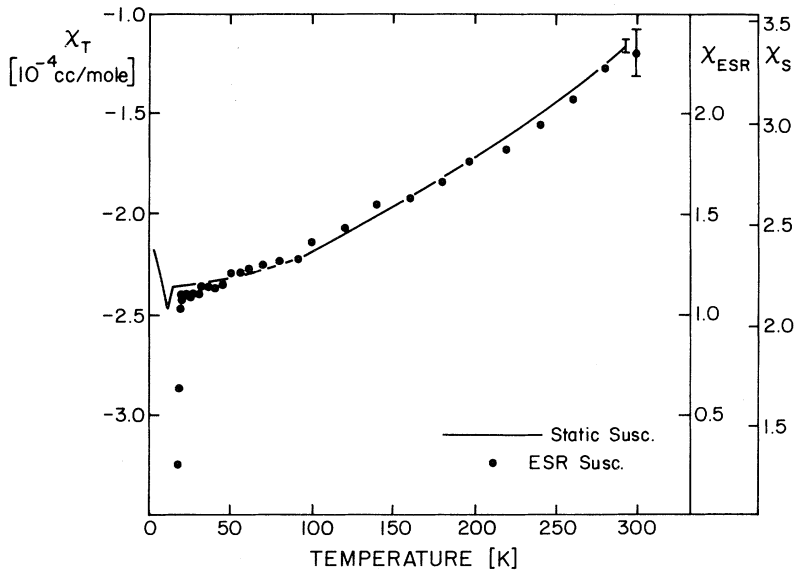

FIG. 1. Total magnetic susceptibility, χ_T (left scale and solid line), of $(TMTSF)_2PF_6$. Correction for the core diamagnetism as explained in the text yields a conduction electron susceptibility, χ_s, as given by the scale on the extreme right. Also shown (solid points and right scale) are the absolute ESR intensity data plotted in such a way that $\chi_{ESR}(300\ K)$ is superimposed on $\chi_T(300\ K)$.

of $\chi_D = -4.55\times10^{-4}$ cm^3/mole. This value has been used to construct the scale on the extreme right of Fig. 1 for the conduction-electron contribution to the susceptibility, χ_s. The relative change in χ_s between 295 and 20 K is then $\Delta\chi_s/\chi_s(295\ K) = 35\%$. On the other hand if one forces χ_s to coincide with χ_{ESR} at room temperature (as shown in Fig. 1) then $\Delta\chi_s/\chi_{ESR} = 50\%$ and moreover the temperature dependences of χ_s and χ_{ESR} agree well over the entire range $20 < T < 300$ K. This observation strongly suggests that the above core corrections are overestimates, and that in this region, above the metal-insulator transition, the single observed ESR spectral line contains all the intensity associated with the (temperature-dependent) conduction-electron susceptibility.

It is thus extremely surprising that the precipitous drop in the ESR intensity at $T_{MI} = 16$ K is not reflected in any way in the static susceptibility (see Fig. 2). The noise level in the Faraday measurement at 15.5 kOe ($\sim 0.4\times10^{-6}$ cm^3/mole) allows us to put an upper limit on the ratio of changes in χ_T and χ_{ESR} at T_{MI} of 3×10^{-3}. Measurements were also made at lower fields, including several below that required to observe nonlinearity at lower temperature (see below), and no anomaly was apparent. For example, at 4.9 kOe the upper bound on this ratio is 3%. Moreover, there is no visible change in the temperature

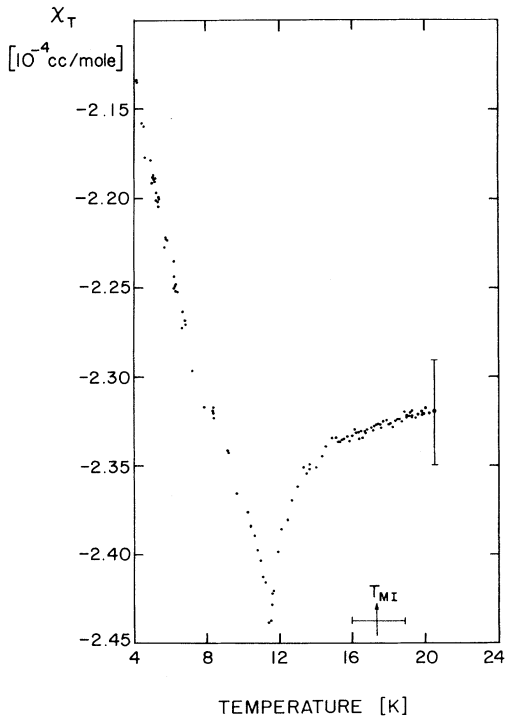

FIG. 2. Total magnetic susceptibility of $(TMTSF)_2PF_6$ at low temperature. Data were taken at a constant magnetic field of 15.5 kOe. The error bar indicates the absolute accuracy of the measurement.

derivative of χ_T. The nature of the metal-insulator transition in $(TMTSF)_2PF_6$ must clearly be reexamined. It is certainly not Peierls-like.

By contrast, at 11.5 K there is a very clear anomaly in the static susceptibility (see Fig. 2). This notch was present in both samples examined, though in the first (and older) sample it rode on a sizable Curie tail. The low temperature increase in the susceptibility of the second sample does not have the C/T behavior of isolated magnetic impurities, and must therefore be assumed to be intrinsic. Note also that there is a point of inflection at 8 K.

Figure 3 demonstrates the magnetic field dependence of the susceptibility in the range $6 \lesssim T \lesssim 15$ K. At fields below about kOe the low-temperature side of the anomaly flattens outs, so that at low fields the material is more diamagnetic than at high fields. (In view of this unusual behavior, it is worth commenting that these data were reproducible from day to day and with recycling to 77 K or room temperature).

One possible explanation of such a diamagnetic anomaly might involve superconducting fluctuations. This is particularly attractive in view of the fact that $(TMTSF)_2PF_6$ does become a superconductor at 0.9 K and 12 kbar.[2,5] Such an explanation is also consistent with greater diamagnetism at lower applied field. However, the existence of the anomaly at high field, the sharpness of the temperature dependence, and the fact that the transition temperature is not depressed by field argue strongly against a superconducting fluctuation picture.

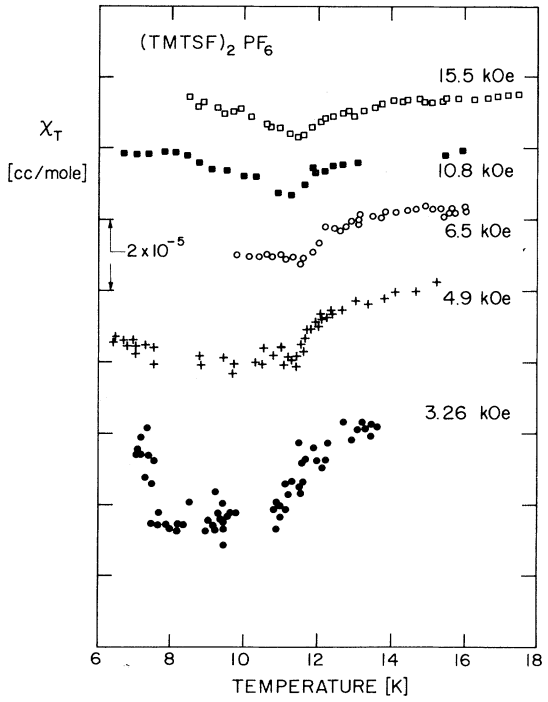

FIG. 3. Variation of the magnetic susceptibility with temperature at several values of applied magnetic field. Successive runs have been offset vertically for clarity. At 15 K all susceptibilities are the same, within the increasing experimental error of the lower-field data.

Another conceivable model would be based on a singlet ground state and a very low-lying triplet-exciton band. Such a spectrum arises from a spin-Peierls type[11] of distortion in a one-dimensional antiferromagnetic (or perhaps more precisely spin-density-wave[12]) system. The effect of a magnetic field is to induce a level crossing between the $M_s = -1$ subband of the triplet state and the $S = 0$ ground state, and hence to restore paramagnetic behavior. Note, however, that the spin-Peierls gap required to explain the low level-crossing field is of order $\frac{1}{2}$ K, or 5% of T. This, in addition to arguments similar to those against superconductivity, leads to the conclusion that the field dependence is not merely a depression of the spin-Peierls state. An alternative explanation, within the framework of a spin-Peierls description, is that the 6 kOe field represents the onset of a "devil's staircase" of commensurability transitions as recently proposed for TTF-$CuS_4C_4(CF_3)_4$ (TTF-CuBDT).[13] Further work is in progress to examine, in more detail, the nonlinear magnetic response.

To summarize, magnetic susceptibility measurements have revealed a new phase transition in $(TMTSF)_2PF_6$ at 11.5 K. In the low-temperature phase, the magnetic response is more diamagnetic below about 6 kOe than at higher fields. The metal-insulator transition at 17 K where the ESR intensity drops sharply, is not visible in the static magnetic behavior. These results should encourage closer examination and renewed consideration of the instabilities of organic conductors in general and the series $(TMTSF)_2X$ in particular.

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Itinerant-Electron Ferromagnetism in $R\,Rh_6B_4$ (R = Y,Lu,La,Eu^{3+})

Israel Felner and Israel Nowik
Racah Institute of Physics, The Hebrew University, Jerusalem, Israel
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X-ray, magnetization, and Mössbauer studies of new hexagonal compounds RRh_6B_4 (R = rare earth) were performed. YRh_6B_4 and $LuRh_6B_4$ exhibit strongly enhanced itinerant paramagnetism. $LaRh_6B_4$ and $Eu^{3+}Rh_6B_4$ exhibit itinerant-electron ferromagnetism (T_c = 6 and 19 K) with large magnetic anisotropy and hysteresis [$H_c(EuRh_6B_4)$ = 2.1 kOe at 4.1 K]. All systems, when doped with 0.5 at.% Fe, show very high Curie points (100 to 300 K) and moments per Fe ion of up to $8\mu_B$.

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We prepared a new family of intermetallic compounds of the form RRh_6B_4, (R = Y, or any rare-earth element). They exhibit extremely unusual magnetic phenomena. $LaRh_6B_4$ and $EuRh_6B_4$ are anisotropic itinerant-electron ferromagnets[1] with Curie points at 6 and 19 K, respectively. YRh_6B_4 and $LuRh_6B_4$ are itinerant paramagnets with susceptibilities much higher than that of Pd metal. An addition of 0.5 at.% Fe to all systems induces ferromagnetic order up to very high temperatures (300 K in $LuRh_6B_4$).

Following the discovery of the unique properties of the RRh_4B_4 compounds by Matthias *et al.*[2] the R-Rh-B system has attracted great interest by many groups.[3] In an attempt to prepare $EuRh_4B_4$, we found this composition to crystallize in a new unknown hexagonal-type structure with some additional phases. For the composition $EuRh_6B_4$, the powdered x-ray pattern could be indexed with this hexagonal system without any extra lines. The elements were of a high-purity (99.9% R, 99.999% Rh and B) and were melted in an induction furnace. The new ternary RRh_6B_4 system is stable and well defined for all the rare-earth elements with $a \sim 5.65$ Å and $c \sim 17.1$ Å. The measured density is about 10.2 g/cm^3. The polycrystalline samples obtained from the melt contained relatively large single crystals which were separated for x-ray studies. The detailed structure is not yet clear. However, Mössbauer-effect studies (ME) of ^{151}Eu and ^{155}Gd indicated that these crystals contain a single rare-earth site. Some of the samples prepared were doped with 0.5 at.% Fe to allow ME studies of the ^{57}Fe probe. Samples, as obtained from the melt, and crushed fine powders, were studied by magnetic-susceptibility measurements at temperatures 1.6 to 300 K in fields of up to 17.5 kOe by a PAR Model No. 155 vibrating-sample magnetometer and up to 50 kOe in a PAR Model No. 156 magnetometer.[4] The samples containing ^{57}Fe, ^{151}Eu, and ^{155}Gd were also studied by the ME technique. We now proceed to discuss our results in what follows.