

Magnetic susceptibility of tetrathiafulvalene tetracyanoquinodimethane under pressure

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We report high-accuracy static magnetic-susceptibility data $\chi(T, P)$ for tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) over the temperature range 3–400 K at both ambient and applied pressures to 10 kbar. The spin susceptibility χ_s increases with temperature, saturating above 360 K at the value $+(6.05 \pm 0.05) \times 10^{-4}$ emu/mol without passing through a maximum. χ_s decreases rapidly under pressure at all temperatures. The value of the pressure derivative $(-d \ln \chi_s / dP)$ in %/kbar decreases from +8.5 at 75 K to +7 at 300 K and +5 at 360 K. From these pressure dependencies it is possible to show that the thermal contraction of the lattice is sufficiently strong to account for most of the substantial temperature dependence of $\chi_s(T)$ observed at ambient pressure. These results are discussed within the framework of various theoretical models of the susceptibility which take into account band-structure effects, electron-phonon interactions, and electron-electron interactions.

I. INTRODUCTION

The Pauli or spin susceptibility χ_s of tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) has been the subject of numerous experimental and theoretical investigations.¹ For this compound $\chi_s(T)$ is strongly temperature dependent,^{2–5} increasing by a factor of more than 2 from 60 to 300 K with a room-temperature value of $\chi_s \approx +6 \times 10^{-4}$ emu/mol which is enhanced by a factor of 2–3 compared with the value expected for a one-electron tight-binding band.⁶ Enhanced values of χ_s are also observed in other charge-transfer compounds like tetramethyltetrathiafulvalene tetracyanoquinodimethane (TMTTF-TCNQ) and the selenium compounds tetraselenafulvalene tetracyanoquinodimethane (TSF-TCNQ) and tetramethyltetraselenafulvalene tetracyanoquinodimethane (TMTSF-TCNQ), but not in hexamethylene-tetraselenafulvalene tetracyanoquinodimethane (HMTSF-TCNQ).¹

Another reportedly anomalous feature of the spin susceptibility of TTF-TCNQ is its strong pressure dependence $d \ln \chi_s / dP \approx -8\%$ /kbar at room temperature as inferred from ESR (electron spin resonance) experiments.^{4,5} This pressure dependence should be redetermined since it lies well above the values (-2% to -3% per kbar) obtained in relatively accurate static susceptibility studies^{7,8} on other organic conductors such as $(\text{TMTSF})_2X$ ($X = \text{ClO}_4, \text{PF}_6, \text{ReO}_4$), α - and β -(BEDT-TTF)₂I₃ [where BEDT denotes bis(ethylene-dithiolo)] and $(\text{TMTTF})_2\text{BF}_4$. Only TMTTF-TCNQ is believed from ESR studies to have a comparably large pressure dependence of -7% /kbar at room temperature.^{7,9} The apparently strong pressure dependence of χ_s in TTF-TCNQ is accompanied by unusually strong pressure derivatives of

derivatives of other Fermi-level properties such as the longitudinal conductivity σ ($d \ln \sigma / dP \approx +28\%$ /kbar)¹⁰ and the proton relaxation rate $1/T_1$ (-23% /kbar).^{4,11}

In order to explain these and other anomalous properties, several models have been proposed. Torrance *et al.*⁶ invoke Coulomb correlations to account for the enhanced value of χ_s at ambient temperature; an increased screening of these interactions under pressure could lead to a large magnitude of $d \ln \chi_s / dP$. This model was recently extended by Mazumdar and co-workers^{12,13} who include Coulomb interactions between electrons on nearest-neighbor sites into the Hubbard Hamiltonian. The essential effect is a sensitive ρ (charge-transfer) dependence of the effective Hubbard constant U_{eff} , and thus the spin susceptibility χ_s .

In another approach¹⁴ dynamic electron localization arising from quadratic electron-phonon interactions is invoked to account for the observed temperature and pressure dependence of both the electrical conductivity and the spin-susceptibility of TTF-TCNQ. The observed increase of the spin-susceptibility with temperature can be understood as arising from a decreasing mean free path with rising temperature mainly due to the scattering of electrons by "librons." A decrease in the scattering time $\tau \sim T^2 / \omega_L^4$, where the libron frequency ω_L increases with applied pressure, would explain the strong pressure dependence of χ_s .

It is also conceivable that the anomalous temperature and pressure dependences of the physical properties of TTF-TCNQ and other organic metals might arise from sharp structure in the band structure near the Fermi energy E_f . Indeed, a recent band calculation¹⁵ on another organic metal β -(BEDT-TTF)₂I₃ reveals that the energy dependence of the density of states $N(E)$ is quite com-

plex, deviating strongly from simple cosine-band behavior.

The following experiments on TTF-TCNQ would be useful to help test the various theoretical models: (1) High-precision data of $\chi_s(T)$ at ambient pressure over a large temperature range. Whereas the spin susceptibility below 300 K is well known both from static^{2,3} (Faraday) and dynamic (ESR)^{4,5} studies, the high-temperature behavior in the range well above 300 K has received relatively little attention. The evidence³ for a maximum in the susceptibility at temperatures near 350 K would seem quite tenuous since it appears to be based on the accuracy of a single data point at 415 K which is very near the temperature where the sample decomposes. (2) Data of the pressure dependence of χ_s as a function of temperature. As will be shown below, such data are of particular value when testing the correctness of theory. Several measurements of $d \ln \chi_s / dP$ on TTF-TCNQ at ambient^{4,11} and low temperatures⁵ have been reported, but all are based on ESR techniques which possess rather limited accuracy. The ESR studies indicate that $|d \ln \chi_s / dP|$ decreases with decreasing temperatures. We are not aware of any measurement of this pressure derivative at temperatures above 300 K. The strong increase of $\chi_s(T)$ between 60 and 300 K may be at least in part due to the thermal expansion of the lattice, assuming the effect of pressure (volume change) on the spin-susceptibility is as large as reported. An accurate determination of the value of $d \ln \chi_s / dP$ over a wide temperature range would allow one to correct $\chi_s(T)$ to constant volume conditions, thus facilitating a comparison with theoretical models.

Here we present accurate static susceptibility measurements on TTF-TCNQ of both the temperature behavior of $\chi_s(T)$ in the range between 3 and 400 K and the pressure dependence of $\chi_s(T)$ up to 10 kbar at four different temperatures (75, 160, 294, and 378 K). A very large pressure dependence of χ_s at 300 K is found, similar to the ESR results; however, in contrast to these studies, $|d \ln \chi_s / dP|$ is found to increase with decreasing temperature. This finding has important implications with respect to the suitability of various theoretical models.

II. EXPERIMENT

As in previous studies,⁷⁻⁹ the pressure dependence of the static magnetic susceptibility of TTF-TCNQ was determined by the standard Faraday technique using a Cahn R-100 microbalance and a superconducting solenoid with separate gradient-field windings to generate magnetic fields of 5.7 T and 0.064 T/cm, respectively. Pressures to 11 kbar could be generated and retained in a small 45-g pressure clamp made of high-purity binary Cu-Be alloy. The purity of the Cu-Be alloy used is such that its susceptibility changes by less than 1.6×10^{-9} emu/g between 400 and 3 K. The diamagnetism of the clamp is compensated at room temperature to $\sim 1\%$ by a small cylinder of paramagnetic molybdenum bolted to the bottom of the clamp. The maximum hydrostatic pressure attainable with this clamp is ~ 11 kbar at room temperature which reduces to ~ 6 kbar as the tempera-

ture is lowered below 10 K. A calibration run at ambient temperature with an internal manganin manometer revealed that the pressure inside the cell is equal, within a few percent, to the nominal value of the pressure determined from the force-to-area ratio of the pressure piston. See Refs. 7-9 for further details of the measurement and pressure techniques used.

Measurements of the magnetic susceptibility at ambient pressure were carried out in a newly designed lightweight 40-mg crucible made of Al foil with thickness $\sim 2 \mu\text{m}$ which hangs on a $35\text{-}\mu\text{m}$ diameter Pt-wire suspension from the microbalance. The extremely small temperature dependence of the paramagnetic susceptibility of this crucible arises from the fact that nominally magnetic transition-metal impurities (e.g., Fe or Mn) lose their magnetic moment when alloyed into Al.

The sample tube was redesigned to allow the stabilization of temperatures as high as 450 K as well as to sharply reduce eddy current effects when changing the magnetic field. The bottom section of the sample tube is made of Cu-Be alloy into which a slitted Cu tube is inserted to provide a uniform temperature distribution while suppressing eddy currents. Cooling is accomplished by pumping cold He gas through a diffuser which is connected via a capillary tube to the liquid-He bath. Astatically wound heaters on the outside of the sample tube provide further temperature control. The pressure clamp or Al crucible are connected thermally to the sample tube by ~ 1 mbar of He exchange gas. The purity of the exchange gas (no O_2) is monitored by a quadrupole mass spectrometer. Calibrated carbon-glass and platinum resistors are embedded in a Cu-Be cylinder located 1-2 cm below the bottom of the pressure clamp. The mass of this cylinder is approximately the same as that of the pressure clamp (~ 45 g) to minimize thermal lag effects. Measurements were normally taken upon cooling at the rate ~ 1 K/min with the field and field gradient left on. The change in the background signal for $H=0$ between 300 and 3 K was negligible, less than 1% of $\chi_s(300\text{ K})$; in a separate run the field was switched on and off at selected temperatures to verify the accuracy of the susceptibility data taken under constant field conditions.

III. RESULTS OF EXPERIMENT

A. Magnetic susceptibility at ambient pressure

The temperature dependence of the static magnetic susceptibility of TTF-TCNQ at ambient pressure is shown in Fig. 1 and agrees well with the results of previous studies,²⁻⁵ although the experimental resolution in the present studies is clearly superior. The measured susceptibility $\chi = \chi_{\text{core}} + \chi_s$ is the sum of a diamagnetic contribution χ_{core} from the core electrons and a paramagnetic contribution from the conduction electrons, the Pauli spin susceptibility. ESR studies² have shown orbital contributions to be negligible. The value of the core diamagnetism $\chi_{\text{core}} = -1.93 \times 10^{-4}$ emu/mol was determined by measuring the susceptibilities of TTF and TCNQ separately at room temperature. Summing the appropriate Pascal constants¹⁶ leads to χ_{core}

$\approx -1.89 \times 10^{-4}$ emu/mol, whereas a direct determination by using the measured value of the susceptibility in the low-temperature insulating region ($T \leq 15$ K) results in $\chi_{\text{core}} \approx -1.70 \times 10^{-4}$ emu/mol after subtracting the low-temperature Curie tail. The value $\chi_{\text{core}} \approx -1.93 \times 10^{-4}$ emu/mol is used in the subsequent discussion.

In Fig. 1 the susceptibility at low temperatures shows a small Curie tail which corresponds to a defect and/or impurity concentration of 300 ppm for $S = \frac{1}{2}$. At temperatures below 60 K the spin susceptibility is seen to decrease rapidly due to the removal of conduction electrons by the Peierls transition. In the inset of Fig. 1 the distinct transitions at $T_H \approx 53$ K and $T_L \approx 38$ K,^{1,10} corresponding to different lattice modulation wavelengths, are clearly seen. We are not able to unequivocally resolve the third transition at the intermediate temperature $T_I \approx 49$ K which was predicted by Ginzburg-Landau theory¹⁷ and experimentally confirmed by inelastic neutron scattering.^{18,19}

In the high-temperature range the magnetic susceptibility of TTF-TCNQ was determined up to 400 K. At these temperatures this fragile organic compound is close to its limit of chemical and physical stability. Particular care, therefore, was taken in measuring $\chi(T)$ in this temperature range. Temperatures between 360 and 400 K were scanned with a heating rate of 0.5 K/min, switching the magnetic field off and on ten times. At the end of this high-temperature scan the room-temperature value was checked again to make sure that no chemical change and/or material loss by sublimation had occurred. Within the resolution of the system ($\pm 0.05 \times 10^{-4}$ emu/mol) the magnetic susceptibility is seen in Fig. 1 to remain constant between 360 and 400 K and thus does not pass through a maximum in the temperature range 3–400 K. This result contrasts with previous findings of Tomkiewicz *et al.*,³ whose data suggest a maximum in $\chi_s(T)$ at 380 K. This suggestion appears to rely on the accuracy of a single data point at 415 K, a temperature

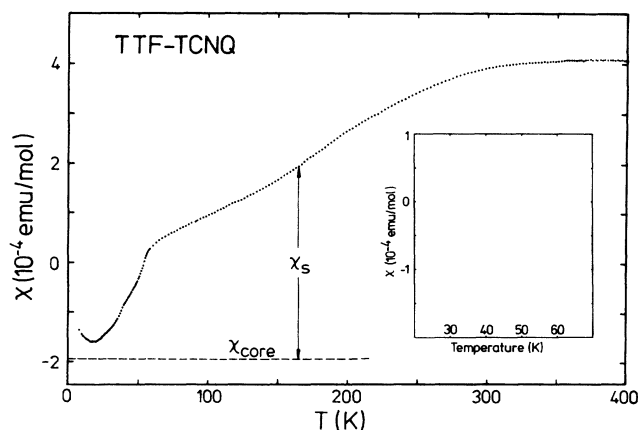


FIG. 1. Data points giving total measured static magnetic susceptibility of TTF-TCNQ vs temperature in magnetic field H of 5.7 T. χ_{core} gives diamagnetic contribution from core electrons (see text). Paramagnetic spin susceptibility χ_s is given by difference $\chi - \chi_{\text{core}}$. Inset shows data on expanded temperature scale.

dangerously close to temperatures where TTF-TCNQ is known to decompose. To our knowledge, there exists no susceptibility data on TTF-TCNQ which proves the existence of a maximum in $\chi_s(T)$. Admittedly, theory predicts that $\chi_s(T)$ should decrease when the temperature has become sufficiently high to render the electron system highly nondegenerate. The data in Fig. 1 do not, of course, rule out the possibility of a susceptibility maximum at temperature above 400 K. We note that $\chi_s(400$ K) takes on a value approximately half the Curie susceptibility $\chi_{\text{Curie}}(400$ K) $\approx +11 \times 10^{-4}$ emu/mol calculated assuming $\rho = 0.6$ and both TTF and TCNQ stacks contributing.

B. Magnetic susceptibility under high pressure

The effect of hydrostatic pressure on the measured room-temperature susceptibility χ of TTF-TCNQ is shown in Fig. 2(a). Data are shown for both increasing and decreasing pressure. Over the pressure range 1–11 kbar the susceptibility is seen to decrease rapidly in a nonlinear fashion with pressure. The applied pressure P can be related to the relative lattice compression $\Delta b/b$ in the stacking direction by fitting the results of Filhol *et al.*²⁰ and Debray *et al.*²¹ to the equation

$$-\Delta b/b = \alpha P + \beta P^2, \quad (1)$$

with $\alpha = +5.9 \times 10^{-3}$ kbar⁻¹ and $\beta = -2.0 \times 10^{-4}$.²² A plot of the susceptibility as a function of $\Delta b/b$ clearly exhibits a linear dependence, as seen in Fig. 2(b); the nonlinearity in the $\Delta b/b$ versus P relationship given by Eq. (1) thus leads to the positive curvature of the $\chi(P)$ data in Fig. 2(a). Since $\chi = \chi_s + \chi_{\text{core}}$, values for $d \ln \chi_s / dP$ can be obtained from the measured values $d \ln \chi / dP$ if the pressure dependence of the core diamagnetism χ_{core} is known. We estimate this derivative by measuring the

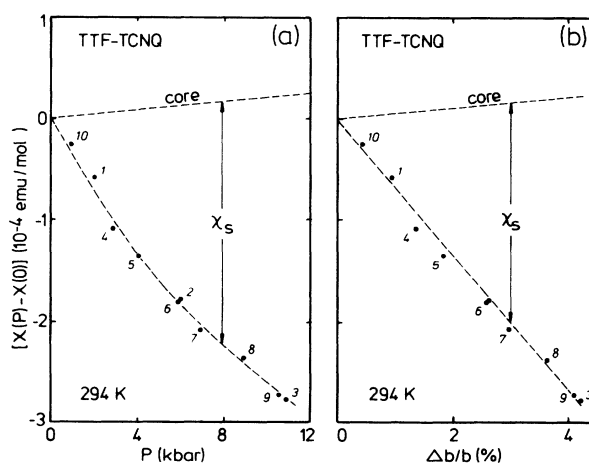


FIG. 2. Data points giving change of the total measured static susceptibility of TTF-TCNQ at ambient temperature as a function of pressure (a) or lattice-parameter change along stack $\Delta b/b$ (b). Numbers give order of measurement. Dashed lines labeled "core" give estimated change under pressure of the core diamagnetism χ_{core} (see text). The difference between the upper and lower curves gives the pressure dependence of the spin susceptibility $\chi_s(P) = \chi(P) - \chi_{\text{core}}(P)$.

pressure dependence of equal amounts of thoroughly mixed TTF and TCNQ insulating crystals to obtain $d \ln |\chi_{\text{core}}| / dP = -1.1 \pm 0.3\%/\text{kbar}$, as indicated by the dashed line in Figs. 2(a) and 2(b). The change in the diamagnetism of the pressure cell components (pressure fluid and Delrin sheath) under applied pressure was negligible within experimental error. Thus from the data in Fig. 2(a) we obtain $d \ln \chi_s / dP = -7 \pm 1\%/\text{kbar}$ at ambient temperature, in quite good agreement with the value -8 from ESR studies.^{3,4}

The temperature dependence of the measured susceptibility is shown in Fig. 3 for three different values of the pressure at room temperature. The strong pressure dependence of χ at ambient temperature is clearly visible as well as the shift of the transition at T_L towards lower temperatures, T_H remaining approximately constant up to about 6 kbar. This latter behavior is in agreement with phase diagrams derived from transport data.¹ The kinks at about 180 K and 220 K in the two high pressure curves are due to the freezing of the pressure fluid and correspond to a pressure loss of about 0.5 kbar. The observed shift of the kink under pressure is consistent with measurements of Reeves *et al.*²³ of the pressure dependence of the melting point of related organic pressure fluids.

The pressure dependence of χ_s was also determined at three other temperatures: 75, 160 and 378 K. It is well known that the pressure stored in the type of pressure clamp used here decreases with decreasing temperature. Knowing the pressure at ambient temperature (derived from the force-to-area ratio with a small 2% correction for friction) and at 7 K (derived from the value of the superconducting transition temperature of Pb), the pressures at 75 and 160 K were estimated by assuming that the pressure decreases linearly with temperature between 300 to 400 and 70 K, remaining constant below. The correctness of this procedure is supported by previous calibration studies on a similar pressure clamp²⁴ as well as by measurements of the temperature T_p of the metal-insulator phase transition in compounds, for example $(\text{TMTSF})_2\text{ReO}_4$,²⁵ whose value of dT_p/dP is known from

transport data. The pressure at high temperatures was estimated by a linear extrapolation of the value from 70 to 300 to 400 K. A lower estimate for the pressure at 400 K (upper bound on $d \ln \chi_s / dP$) is obtained by assuming the pressure remains constant between 300 and 400 K. This uncertainty in the value of the pressure at 400 K is included in the error given in Fig. 4 for the value of $d \ln \chi_s / dP$. The values of the initial pressure derivative at four different temperatures are shown in Fig. 4. The magnitude of $d \ln \chi_s / dP$ is seen to be very large (7–8 %/kbar) at all temperatures below 300 K, falling off somewhat at higher temperatures.

C. Correction to constant b value

Cooper²⁶ has pointed out that the $T^{2.3}$ dependence observed in the electrical conductivity $\sigma(T)$ of TTF-TCNQ at constant ambient pressure changes to a qualitatively different behavior if the $\sigma(T)$ data are corrected to constant- b lattice parameter (stacking direction). Knowing the value of the logarithmic derivative $d \ln \chi_s / dP$ as a function of temperature, an estimate of the temperature dependence of the spin susceptibility at constant- b lattice parameter can now be made by correcting the constant pressure data of Fig. 1 to constant- b lattice parameter. The correctness of this procedure will be discussed below. To obtain the constant- b correction, we start directly from Fig. 2(b), rather than from Fig. 2(a), where the non-linearity of the compressibility has been accounted for. Using the fact that the compressibility in the b direction ($K_b = -d \ln b / dP$) decreases upon cooling from 300 to 10 K by approximately a factor of 2 (Ref. 27) and assuming K_b depends linearly on temperature between these limits, values for $d \ln \chi_s / d \ln b$ can be derived over the entire temperature range of our measurements, as shown below in Fig. 6(a). The constant- b correction $\Delta \chi_s$ of the data in Fig. 1 is then obtained by use of thermal expansion data for $b(T)$ in the temperature range above 70 K, i.e.,

$$\Delta b / b = [b(T) - b(70 \text{ K})] / b(70 \text{ K}),$$

and the relation

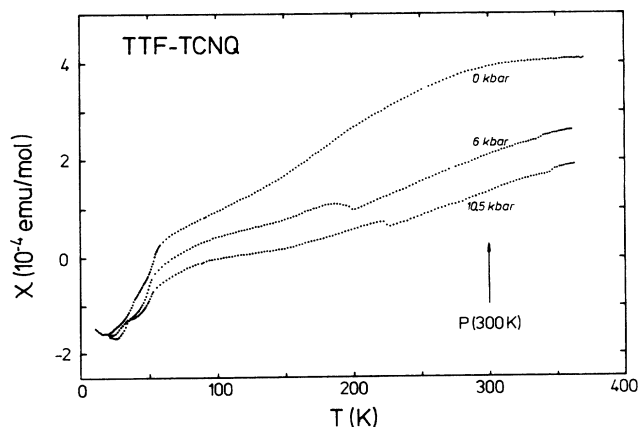


FIG. 3. Temperature dependence of the total measured static susceptibility of TTF-TCNQ at three different pressures: The pressures at 300 K (0, 6, and 10.5 kbar) reduce to 0, 2.4, and 6.4 kbar, respectively, at low temperatures (7 K).

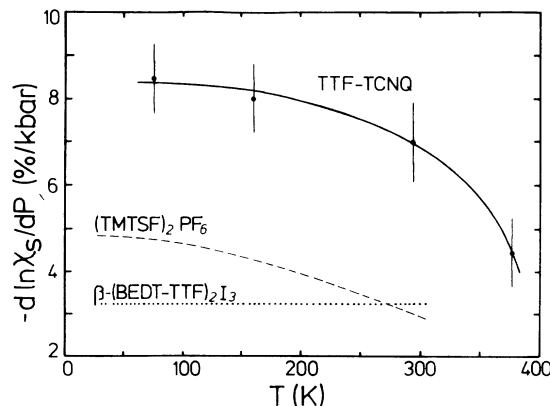


FIG. 4. Large dots (●) giving fractional change under pressure of the spin susceptibility of TTF-TCNQ as a function of temperature. Solid line is guide to eye. Dashed line and small dots give fractional change of χ_s under pressure for $(\text{TMTSF})_2\text{PF}_6$ (Refs. 7 and 9) and $\beta\text{-(BEDT-TTF)}_2\text{I}_3$ (Refs. 7–9).

$$\Delta\chi_s = \chi_s (d \ln \chi_s / d \ln b) (\Delta b / b).$$

Two studies^{28,29} for $b(T)$ agree that there is 2.0% thermal expansion of $b(T)$ between 160 and 300 K, but differ rather strongly at lower temperatures, giving the values 2.3% (Ref. 28) and 3.3% (Ref. 29) between 70 and 300 K, respectively. We use here 1%, 3%, and 4.2% thermal expansion of $b(T)$ between 70 K and $T = 160$ K, 294 K, and 378 K, respectively. The value for 378 K is a linear extrapolation of the data up to 300 K. Multiplying the values of the thermal expansion $\Delta b/b$ with $\chi_s d \ln \chi_s / d \ln b$ gives the corrections $\Delta\chi_s = -0.8 \times 10^{-4}$ emu/mol, -2.3×10^{-4} emu/mol, and -1.6×10^{-4} emu/mol at the temperatures 160 K, 294 K, and 378 K, respectively, as shown in Fig. 5(a). Correcting the ambient pressure data of TTF-TCNQ for the effects of thermal expansion is seen to largely remove the anomalous rise of χ_s with temperature.

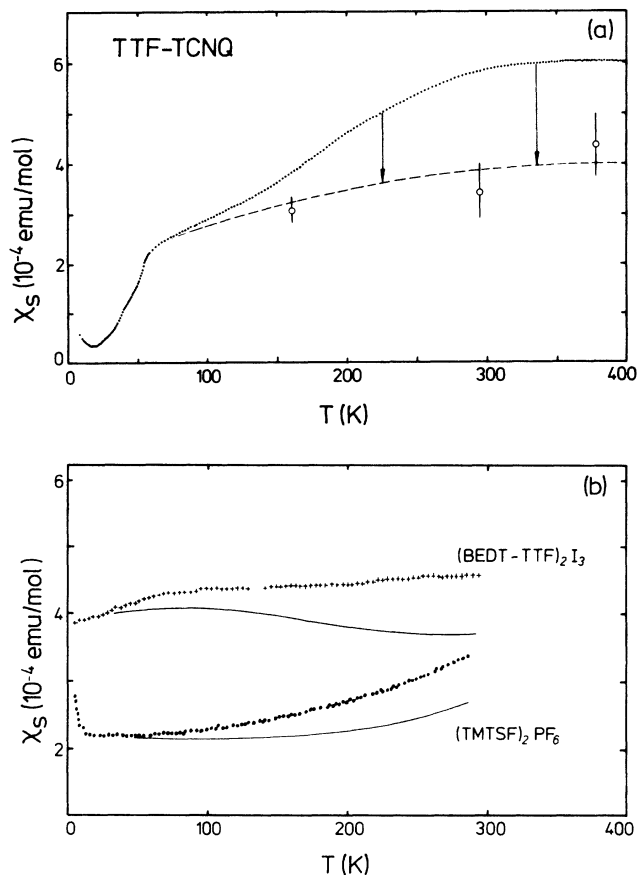


FIG. 5. (a) Data points (●) give measured temperature dependence of spin susceptibility $\chi_s(T)$ for TTF-TCNQ at ambient pressure, as shown in Fig. 1. Circles (○) give susceptibility data χ_s at selected temperatures after correction to constant volume at ambient pressure. Dashed line gives estimated temperature dependence of the constant-volume spin susceptibility $\chi_s^V(T)$. Arrows indicate direction of correction of data from constant pressure to constant-volume conditions. (b) crosses (+) and dots (●) give $\chi_s(T)$ at ambient pressure for (BEDT-TTF)₂I₃ and (TMTSF)₂PF₆, respectively. Solid lines give estimated temperature dependence of spin susceptibility after correction for lattice-parameter expansion.

In the above correction procedure of the data to constant- b lattice parameter the changes of the a and c lattice parameters have been ignored. Strictly speaking, the experimental data at ambient pressure should be corrected to constant a and c values as well as to constant b . The thermal contraction along the a , b , and c directions between 300 and 70 K is 1.1%, 2.45%, and 0.8% according to Ref. 30, whereas 6-kbar pressure leads to a contraction of 1.4%, 2.45%, and 1.7% in the a , b , and c lattice parameters at room temperature.²¹ The inequivalence of pressure and temperature is restricted mainly to the c axis. Since like molecules lie along the c direction, an equivalent pressure shift of about 2 kbar along this direction would not be expected to cause important changes in the charge-transfer and relevant band-structure properties. In addition, the tilt angle between the normal to the molecules and the stacking direction is independent of *both* temperature and pressure.^{30,31} It would thus seem reasonable to assume that the above procedure properly corrects the susceptibility data for the effects of thermal expansion and in this sense we refer to the thus corrected susceptibility as the “constant-volume” susceptibility $\chi_s^V(T)$.

IV. DISCUSSION

In the preceding section we have seen that correcting the measured spin susceptibility $\chi_s^V(T)$ of TTF-TCNQ for the effects of thermal contraction removes almost all of the anomalous temperature dependence, leaving a corrected susceptibility $\chi_s^V(T)$ which is nearly temperature independent, i.e., Pauli-like, as seen in Fig. 5(a). It is thus not surprising that previous attempts^{2,3} to fit the results of theoretical calculations of $\chi_s(T)$ to uncorrected experimental data have met with little success; only the small polaron model of Entin-Wohlmann *et al.*,¹⁴ which includes the possibility of progressive band narrowing as the electronic mean free path is reduced at higher temperatures, is able to account for the large increase in the measured $\chi_s(T)$ with temperature. Thus Torrance *et al.*⁶ find that the calculated susceptibility $\chi_s(T)$ from a Hubbard model with onsite Coulomb repulsion energy U is capable of reproducing the measured value of the spin-susceptibility at room temperature, but is notably unable to account for the large positive temperature dependence of $\chi_s(T)$, irrespective of whether U is chosen to be zero, small, or large. Taking into account the differing susceptibilities of the TTF and TCNQ stacks³² does not improve the poor agreement between experiment and theory. It is interesting to note, on the other hand, that the corrected susceptibility $\chi_s^V(T)$ is essentially temperature independent and can be readily fit, within experimental error, by both large- and small- U theories.⁶ If V is the volume at 70 K for ambient pressure, we can fit $\chi_s^V(T)$ within a $U = 0$ tight-binding model for bandwidth $4t \simeq 0.32$ eV, within a small- U Hubbard model for $4t \simeq 0.35$ eV and $U \simeq 0.10$ eV, or within a large- U model for the value of the exchange parameter $J \simeq 350$ K (this value of J corresponds to, for example, $4t \simeq 0.5$ eV and $U \simeq 0.7$ eV). From a fit to the corrected $\chi_s^V(T)$ data alone it is thus not possible to determine which U approxima-

tion is the most appropriate—all fit rather nicely. As we will see below, important additional information is contained in the magnitude and temperature dependence of the pressure derivative $d \ln \chi_s / dP$.

Before considering in more detail the significance of the measured pressure derivative of χ_s , we would like to establish whether the above conclusions are restricted to TTF-TCNQ or are more generally applicable. We now proceed to derive corrected values of $\chi_s(T)$ for two further classes of organic metals, the Bechgaard salts, represented by $(\text{TMTSF})_2\text{PF}_6$, and the quasi-two-dimensional compounds with donor cation BEDT-TTF, represented by the β phase of $(\text{BEDT-TTF})_2\text{I}_3$. As seen in Fig. 5(b), the measured $\chi_s(T)$ data^{7,9} for the Bechgaard salts show an anomalous increase with temperature, whereas the spin susceptibility of the latter compound shows little temperature dependence.⁸ Values for the pressure derivative $d \ln \chi_s / dP$ for these compounds have been determined in previous studies⁷⁻⁹ and are shown in Fig. 4. The value of the pressure derivative $d \ln \chi_s / dP$ is, within experimental error, equal for the three Bechgaard salts $(\text{TMTSF})_2X$ for $X = \text{PF}_6$, ClO_4 , and ReO_4 in the temperature range studied $T \leq 300$ K.^{7,9} For the β phase of $(\text{BEDT-TTF})_2\text{I}_3$ we obtained⁸ $d \ln \chi_s / dP \approx -3\%/kbar$, independent of temperature below 300 K. The pressure dependence of χ_s for TTF-TCNQ clearly dominates over that found for the other systems studied.

A comparison of the temperature and pressure dependences of χ_s in Figs. 4 and 5 reveals that $\chi_s(T)$ increases with temperature most rapidly in those systems where the pressure derivative $-d \ln \chi_s / dP$ is large. This correlation between the magnitude of temperature and pressure effects is what would be expected if the temperature dependence of $\chi_s(T)$ in an organic metal were dictated by its large thermal contraction upon cooling. This expectation is confirmed by the results in Fig. 5(b), where the measured temperature dependences $\chi_s(T)$ for $(\text{BEDT-TTF})_2\text{I}_3$ and $(\text{TMTSF})_2\text{PF}_6$ are corrected for the effects of thermal contraction.^{33,34} For these compounds, as found for TTF-TCNQ, the corrected spin susceptibility is seen to depend only weakly on temperature. We thus conclude that in TTF-TCNQ and the Bechgaard salts the anomalous increase of the spin susceptibility with temperature arises from the large magnitude of both the thermal expansion coefficient and the pressure derivative $d \ln \chi_s / dP$ in these systems. The corrected susceptibility is almost independent of temperature (Pauli-like) and can be accounted for by both big- U and small- U theories. Without accurate information on the bare density of electron states at the Fermi energy E_f it is difficult to determine whether the measured spin susceptibility is weakly or strongly enhanced by electron-electron or other correlation effects. We now proceed to show that the measured values of the pressure derivatives $d \ln \chi_s / dP$ provide further information.

In Fig. 6(a) the magnitude of the logarithmic derivative $\gamma \equiv d \ln \chi_s / d \ln s$ at constant intermolecular separation s along the highly conducting direction is plotted versus temperature for the three system classes studied.³⁵ γ can be as large as $\gamma \approx +25$ at lower temperatures which

means that under pressure the magnitude of the spin susceptibility decreases approximately 25 times faster than the intermolecular separation s along the stacking axis. For the three system classes studied here the value of γ at low temperatures differs by more than a factor of 2. However, in all three cases the value of γ tends to decrease with increasing temperature. We would now like to compare these salient features to the predictions of several theoretical models.

In the first approximation we ignore the electron-electron repulsion ($U=0$) and attempt to analyze the spin susceptibility in terms of the simple tight-binding formula¹ for two equal stacks

$$\chi_s = \chi_{\text{TB}} = 2N_A \mu_B^2 [\pi t \sin(\pi\rho/2)]^{-1} \quad (2)$$

where $4t$ gives the bare bandwidth, ρ is the charge transfer ($\rho \approx 0.57$ electrons per formula unit for TTF-

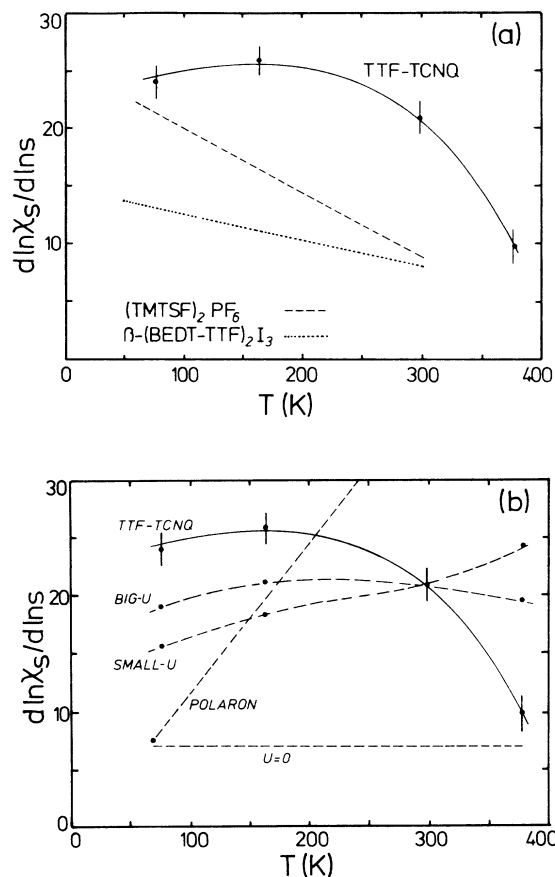


FIG. 6. (a) Temperature dependence of the logarithmic derivative $d \ln \chi_s / d \ln s$ at a constant value of the high-conductivity direction s for the three organic conductors TTF-TCNQ, $(\text{TMTSF})_2\text{PF}_6$, and β -(BEDT-TTF) $_2\text{I}_3$. The curves for $(\text{TMTSF})_2\text{PF}_6$ and β -(BEDT-TTF) $_2\text{I}_3$ were obtained from the data in Fig. 4 using the expression $d \ln \chi_s / d \ln s = (d \ln \chi_s / dP) K_s^{-1}$, where K_s is the temperature-dependent compressibility along the s direction. The curves for TTF-TCNQ were obtained from the data in Figs. 2(b) and 5(a). (b) Temperature dependence of the logarithmic derivative of χ_s with respect to s for TTF-TCNQ in comparison with the dependence estimated for four different theoretical models (see text).

TCNQ at 300 K), and N_A is Avogadro's number. Since within this approximation the square of the plasma frequency ω_p^2 is proportional to the bandwidth $4t$, it follows from Eq. (2) that $d \ln \chi_s / dP \simeq -d \ln t / dP \simeq -2d \ln \omega_p / dP \simeq -2.5\% / \text{kbar}$, as estimated from the measured³⁶ pressure dependence of the plasma frequency of TTF-TCNQ at room temperature [the inclusion of the pressure dependence of ρ ($d \ln \rho / dP \simeq +0.7\% / \text{kbar}$ from Ref. 1) in Eq. (2) leads to only a minor correction ($\sim 0.5\% / \text{kbar}$) in the estimated pressure dependence of the susceptibility]. The measured pressure dependence of the spin susceptibility given in Fig. 4 is far too large to be accounted for by the increase in bandwidth under pressure. A similar conclusion can be reached for the Bechgaard salts and BEDT-TTF systems, where the anticipated pressure dependence of the bandwidth should be even less than for TTF-TCNQ due to their larger bandwidths and nearly free electron values of the effective mass, as noted in previous work.⁷⁻⁹ We note here that Mazumdar and co-workers^{12,13} predict a sensitive dependence of the effective Hubbard constant U_{eff} on the amount of charge transfer, which is, in fact, largest for $\rho \simeq 0.5$; this model includes Coulomb interactions between electrons on nearest-neighbor sites. Such effects may account for at least part of the large value of $d \ln \chi_s / dP$ for TTF-TCNQ, but not for β -(BEDT-TTF)₂I₃ or the Bechgaard salts because in the latter compounds ρ is fixed and not dependent on pressure. From the above pressure dependence we obtain for TTF-TCNQ the value of the logarithmic derivative

$$\begin{aligned} \gamma &= d \ln \chi_s / d \ln b \\ &= -(d \ln \chi_s / dP) K_b^{-1} \\ &\simeq (+2.5\% / \text{kbar}) / (0.34\% / \text{kbar}) \simeq +7 \end{aligned}$$

at room temperature, as seen in Fig. 6(b).³⁷ This value is in quite reasonable agreement with that obtained from Eq. (2) using the calculated³⁸ b -axis dependence of the bandwidth ($d \ln t / d \ln b$) which takes on the values -7 and -3.5 for the TCNQ and TTF bands, respectively.

The preceding analysis depends heavily on the assumption that the spin susceptibility is inversely proportional to the electron bandwidth and is thus directly related to the plasma frequency, as is the case for simple cosine bands within the tight-binding model. If, however, the energy dependence of the electron density of states $N(E)$ shows a peaked structure near the Fermi energy E_F , neither the value of χ_s , nor its pressure dependence, need be correlated in any simple way with the bandwidth or its pressure dependence. Recent band calculations¹⁵ for the compound β -(BEDT-TTF)₂I₃ reveal that $N(E)$ is indeed quite complex, deviating strongly from simple cosine-band behavior. If such band structure effects are important, one would anticipate considerably enhanced pressure derivatives of χ_s , particularly at low temperatures where thermal smearing effects are minimal. Band structure effects can thus, at least in principle, account for the magnitude and temperature dependence of $d \ln \chi_s / d \ln s$ for the three classes of organic compounds given in Fig. 6(a).

In a second model we relax the condition $U=0$ and assume U to be finite but small, i.e., $U \ll 4t$. The relevant equation for χ_s is then⁶

$$\chi_s = \chi_{\text{TB}} / (1 - U/4\pi t), \quad (3)$$

where χ_{TB} is the tight-binding susceptibility given by Eq. (2). In this approximation the increase in the measured spin susceptibility with increasing temperature would originate from an increase in the value of the ratio $U/4t$ due to the expansion of the lattice. Since at low temperatures, where the spin susceptibility is essentially unenhanced, the value of χ_s according to Eq. (3) is primarily determined by the bandwidth $4t$, $d \ln \chi_s / dP \simeq -2.5$, a small value. Because within this model the lattice expansion with increasing temperature would lead to an appreciable enhancement of χ_s , the value of the pressure derivative $d \ln \chi_s / dP$ should also be strongly enhanced at room temperature (pressure reverses the effect of the lattice expansion). Within the "small U " model, therefore, the magnitude of the pressure dependence of the spin susceptibility would be expected to increase markedly with increasing temperature. This expectation stands in direct contrast to the experimental results in Fig. 4, where $|d \ln \chi_s / dP|$ is seen to decrease with increasing temperature. A calculation³⁹ of the logarithmic derivative $\gamma = d \ln \chi_s / d \ln s$ for the "small- U " model shows [see Fig. 6(b)] that γ decreases with temperature even at constant s . The small- U prediction of an increased pressure derivative of χ_s at elevated temperatures is diametrically opposed to the experimental results in Fig. 6(a), where γ is seen to decrease with increasing temperature.

A similar conclusion can be reached when considering the small polaron model of Entin-Wohlman *et al.*¹⁴ Although the basic physical mechanism for the enhancement of the susceptibility at higher temperatures is completely different than in the small- U model, both models describe an unenhanced susceptibility at low temperatures which is strongly enhanced at elevated temperatures. In the small- U model the lattice expansion upon warming increases the ratio $U/4t$ leading to the enhancement, whereas in the small polaron model the enhancement at elevated temperatures originates from dynamic band narrowing arising from the reduced electronic mean free path at higher temperatures. Within the latter model the enhanced susceptibility at elevated temperatures should decrease rapidly under pressure due to the known increase in the mean free path under pressure, as evidenced by the rapid pressure-induced increase in the electrical conductivity of TTF-TCNQ and most other organic metals. Within the small polaron model, therefore, the most rapid pressure dependence of the susceptibility should occur at elevated temperatures where the mean free path is the shortest. The pressure dependence of χ_s should be smallest at low temperatures where it no longer depends on the mean free path. The fact that the experimentally determined pressure derivative shows just the opposite temperature dependence (see Fig. 4) gives strong evidence against the appropriateness of this model in describing the anomalous temperature dependence of the

susceptibility in TTF-TCNQ and other organic metals. A quantitative analysis⁴⁰⁻⁴² of the anticipated pressure dependence of χ_s from the small polaron model [see Fig. 6(b)] supports the above conclusions.

Torrance *et al.*⁶ have calculated the temperature dependence of χ_s for various values of the effective exchange interaction $J = (2t^2/U)\rho[1 - (\sin 2\pi\rho)/2\pi\rho]$ in the "big= U " limit ($U \gg 4t$) for $\rho = 0.59$. The calculated⁴³ big- U temperature dependence of the pressure derivative $d \ln \chi_s / d \ln s$ is shown in Fig. 6(b). In comparison to the small- U and small polaron theories, the predicted temperature dependence of $\gamma(T)$ in the big- U limit appears to agree somewhat better with experiment, showing a decrease in magnitude at temperatures above 250 K.

In summary, the present experiments have clearly shown that the anomalous temperature dependence of the spin susceptibility of TTF-TCNQ and other organic metals can be understood as arising from strong thermal contraction coupled with a large dependence of χ_s on the lattice parameter. The magnitude and temperature depen-

dence of the measured pressure derivative $d \ln \chi_s / dP$ allows one to conclude that tight-binding $U = 0$ and small- U theories, as well as the small-polaron model, are not appropriate descriptions of the spin susceptibility of the organic metals considered. On the basis of the present results, theories which include band-structure effects, as well as possibly theories with strong electron-electron correlations, have the potential to describe the anomalous properties of organic metals. Further band-structure calculations on organic metals would be highly desirable.

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⁴⁰We use the formula from Ref. 41 $t_{\text{eff}} = t \exp(-b/l)$, where $l \propto \omega_L^2 / T^2$ and $\chi_s \propto (t_{\text{eff}})^{-1}$. Taking the values of $d \ln t / d \ln b = -5$ (see text) and $d \ln \omega_L / d \ln b = +8$ (from Ref. 41; $\Delta \omega_L / \omega_L \approx 25\%$ for an applied pressure $\Delta P = 7$ kbar, i.e., $\Delta b/b = 3\%$ at 300 K) we thus obtain $d \ln \chi_s / d \ln b \approx +38$ at 300 K, where $b/l \approx 1$ (Ref. 42) and $d \ln \chi_s / d \ln b \approx +8$ at 70 K, where $b/l \approx 0.1$ (Ref. 42).

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