Magnetic susceptibility studies of tetrathiofulvalene-tetracyanoquinodimethan (TTF) (TCNQ) and related organic metals*

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The complete temperature dependence of the magnetic susceptibility is reported for pure (TTF)(TCNQ), (ATTF)(TCNQ), and (TMTTF)(TCNQ), [(tetrathiofulvalene-, cis (trans)-dimethyl tetrathiofulvalene-, and tetramethyltetrathiofulvalene-tetracyanoquinodimethan)]. The nonmagnetic ground state and absence of localized-moment formation imply that electron-electron Coulomb interactions are not dominant. The results are analyzed in terms of a two-chain model with a mean-field Peierls-Fröhlich transition temperature $T_P \simeq 450$ K associated with one set of chains, while the second set behaves as a simple metal above 60 K. The susceptibility above 60 K is analyzed in terms of the proposal of Lee, Rice, and Anderson. The transition to a small-band-gap semiconductor at 60 K is interpreted as the onset of three-dimensional ordering. The experimental results show (TTF)(TCNQ) and its dimethyl and tetramethyl derivatives to be a family with quite similar electronic properties.

I. INTRODUCTION

The organic charge-transfer salt tetrathioful-valene-tetracyanoquinodimethan [(TTF)(TCNQ)] at high temperature is a one-dimensional metal.[1,2] A series of detailed experimental studies confirm the one-dimensional properties above 60 K, and show (TTF)(TCNQ) undergoing a metal-insulator transition at 60 K to a small-band-gap semiconducting state.[2-9] Earlier it was suggested that the behavior of (TTF)(TCNQ) is associated with a Peierls[10] instability in which the one-dimensional metallic system is unstable toward a phonon mode driven soft by the divergent response of the electron gas at $q = 2k_F$.

In the event of precisely one electron transferred in the salt, both the anion and cation chains would have half-filled bands with Fermi wave number $k_F = \pi/a$, i.e., commensurate with one another and with the underlying molecular lattice. However, from x-ray studies[11] of the molecular bond lengths and from photoemission data[12,13] one can infer somewhat less than complete charge transfer with the number of electrons and holes between 0.5 and 1, so that the Fermi wave number is expected to be different on the two subsystems. As a result, one can anticipate different electronic properties for the two sets of one-dimensional chains.

The temperature-dependent magnetic susceptibility is a particularly important physical quantity. Susceptibility studies provide insight into the importance of Coulomb correlation effects as well as quantitative information on the band structure. That the observed electronic properties do not involve strong Coulomb correlation effects as is

widely observed in other TCNQ salts[14-16] was inferred from knowledge of the magnitude and temperature dependence of the nuclear relaxation rates[9] and the spin susceptibility. Here we report the complete temperature dependence of the static magnetic susceptibility for pure (TTF)(TCNQ), cis (trans)-dimethyl tetrathiofulvalene TCNQ [(ATTF)(TCNQ)], and tetramethyltetrathiofulvalene TCNQ [(TMTTF)(TCNQ)].

II. EXPERIMENTAL

The static magnetic susceptibility was measured by the Faraday method using a Cahn model RG electrobalance with a rated sensitivity of 0.1 μg and a magnet capable of supplying fields of up to 10 kG with a gradient of 500 G/cm in the vertical direction. The product of the field and gradient ($H \, dH/dz$) was calibrated with a sample of 99.999% pure aluminum and found to be constant to within 3% over a distance of about 1 cm. The magnetic force was reproducible to well within 1 μg, giving a sensitivity of 3×10^{-10} emu. In an 80-mg sample of molecular weight 400 (applicable to the present experiment), this is equivalent to a sensitivity of 2×10^{-6} emu/mole. The absolute accuracy is limited by the presence of ferromagnetic impurities (see Table I). Analysis of a Honda plot of measured susceptibility versus inverse field indicates an over-all absolute accuracy of 2×10^{-5} emu/mole or better, and a relative accuracy (i.e., temperature dependence) approximately an order of magnitude better.

The sample was contained in a quartz sample holder[17] and suspended from the balance beam by a 2-mil tungsten wire. The balance and sample

were pumped to 10^{-6} Torr, typically for three days, to remove residual oxygen, and were subsequently back-filled with helium gas. During an experimental run, the helium exchange gas was kept at about 10 mTorr, and it provided the thermal contact between the sample and a temperature-controlled heat bath consisting of a copper can, thermometer, and heater in partial thermal contact with liquid nitrogen or helium as shown in Fig. 1. The effects of thermomolecular pressure[18] and adsorption of the exchange gas were canceled by sweeping the field up and down at each temperature.

III. RESULTS

Considerable care was taken in the sample preparation of TTF and derivatives, TCNQ, and the resultant charge-transfer salts as a precaution against extrinsic impurity contributions to the measured susceptibilities. The materials were prepared by methods similar to those described earlier[3, 8, 14, 19] which utilize multiple gradient sublimations[20] and handling of the resultant materials in Ar (99.999%) atmospheres. Samples of TTF and TCNQ were measured separately at room temperature as a function of applied fields from 1-10 kG in order to determine the molecular core diamagnetism. The values measured for TTF and TCNQ were $(0.99 \pm 0.04) \times 10^{-4}$ and $(1.21 \pm 0.04) \times 10^{-4}$ emu/mole, respectively, giving a total diamagnetic susceptibility χ_D of $(-2.20 \pm 0.08) \times 10^{-4}$ emu/mole.

(TTF) (TCNQ) and the derivative salts prepared from warm acetonitrile solutions in Pyrex glassware were found to contain of the order of 100 ppm of ferromagnetic impurity, which was identified with Fe leached from the glassware specifically during the chemical reaction. For samples prepared in Teflon or quartz ware, the ferromagnetic impurities were reduced to the level of 2-3 ppm

as found from Honda plots of χ vs $1/H$.

Analysis of the salts gave the following results. For (ATTF)(TCNQ): calculated for $C_{20}H_{12}N_4S_4$: 55.02% C, 2.78% H, 12.84% N, 29.37% S; found: 55.00% C, 2.86% H, 12.80% N, 29.64% S. For (TMTTF)(TCNQ): calculated for $C_{22}H_{16}N_4S_4$: 56.86% C, 3.48% H, 12.06% N, 27.60% S; found: 56.96% C, 3.51% H, 12.05% N, 27.49% S.

The complete temperature dependence of the measured magnetic susceptibility of (TTF)(TCNQ) is shown in Fig. 2. Field dependences were measured and Honda plots made to check consistency with the room-temperature Honda analysis. At low temperatures, the measured susceptibility shows a small Curie-like upturn characteristic of extrinsic Curie impurities commonly found in organic charge-transfer salts. The intrinsic susceptibility can then be obtained from the measured values by

$$\chi_{measured} = \chi_{intrinsic} + C/T . \tag{1}$$

A plot of χ vs T^{-1} gives a Curie constant C of 0.6×10^{-4} emu $°K$/mole, corresponding to 0.01% impurity $(S = \frac{1}{2})$ or 0.001% $(S = \frac{5}{2})$ iron impurity. This low value should be compared with the previously reported data of Perlstein, Cowan, and co-workers.[21] The data from Ref. 21 are shown for comparison as the crosses on Fig. 2. The higher purity implied by the data presented here is significant in light of the consistent experimental discrepancies in the transport and microwave properties[22] reported for materials prepared in the different laboratories. The value of low-temperature susceptibility as obtained from extrapolation of χ-vs-T^{-1} plots is $(-2.05 \pm 0.1) \times 10^{-4}$ emu/mole. This value is in excellent agreement with the measured temperature-independent core diamagnetism χ_D of $(-2.20 \pm 0.08) \times 10^{-4}$ emu/mole of the neutral parent compounds TTF and TCNQ, and both are in good agreement with the value

TABLE I. Summary of susceptibility data for the TCNQ compounds.

	Level of ferromagnetic impurity (ppm by weight, iron equivalent)	Level of spin-$\frac{1}{2}$ paramagnetic impurity (% molar)	Diamagnetic susceptibility by extrapolation $(10^{-4}$ emu/mole)	χ_D from Pascal's constants $(10^{-4}$ emu/mole)	Room-temperature paramagnetic susceptibility $(10^{-4}$ emu/mole)
(TTF)(TCNQ)	3	0.01	−2.05 (2.20) [a]	−1.89	6.0
(TMTTF)(TCNQ)	1	0.07	−2.57	−2.38	4.8
(ATTF)(TCNQ)	20	0.24	−1.97	−2.14	3.4

[a] Result obtained by room-temperature measurements on separate parent compounds.

- 1.9×10^{-4} emu/mole estimated from Pascal's constants.[23] We conclude that the material used in the present study is of the highest purity prepared to date, exhibiting magnetic properties intrinsic to pure (TTF)(TCNQ).

With the temperature-independent diamagnetism determined, the temperature dependence of the spin susceptibility of (TTF)(TCNQ) was obtained, as shown in Fig. 3. That this is in fact the spin susceptibility over the entire temperature range was confirmed by a direct measurement of χ_s using the Schumacher-Slichter technique[14] at selected temperatures (the open squares in Fig. 3).

The susceptibilities of (ATTF)(TCNQ) and (TMTTF)(TCNQ) are shown in Figs. 4 and 5. An analysis similar to that presented above was used
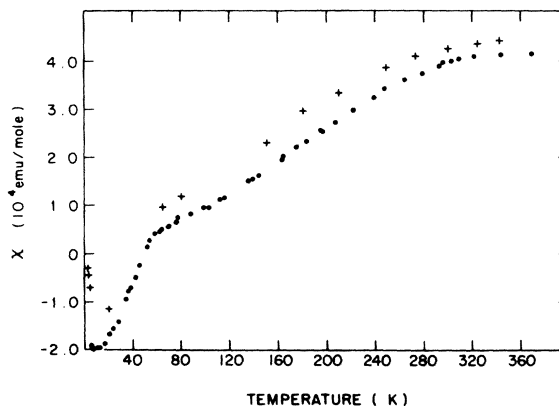
FIG. 2. Temperature dependence of the total magnetic susceptibility of (TTF)(TCNQ). The data of Ref. 21 are shown for comparison (crosses).

to obtain values for χ_D and the concentration of spin-$\frac{1}{2}$ species implied by the low-temperature Curie contribution. The results are presented in Table I. The larger Curie contribution in the ATTF case may be associated with the *cis-trans* disorder acting on the cation chain.[24] The corresponding spin susceptibilities are shown in Figs. 6 and 7.

IV. DISCUSSION

The low-temperature ($T < 60$ K) behavior of the spin susceptibility χ_s shows that (TTF)(TCNQ) exhibits the properties of a nonmagnetic small-band-gap semiconductor. The absence of a finite susceptibility ($\chi_s = 0$) at $T = 0$ K agrees with finding no linear temperature contribution to the measured low-temperature specific heat.[7] These re-

FIG. 1. Schematic diagram of the apparatus showing the sample and thermometry arrangement. A, Dewar; B, stainless steel tube; C, exchange gas adjustable in pressure to control heat flow from D; D, copper can; E, nonmagnetic heater (Ni:Si Janis); F, germanium thermometer (used over temperature range $T \lesssim 25$ K); G, platinum thermometer ($T \gtrsim 25$ K); H, helium exchange gas at 10 mTorr (room-temperature value); I, sample holder (quartz plated with gold to overcome electrostatic problems); J, tungsten wire.
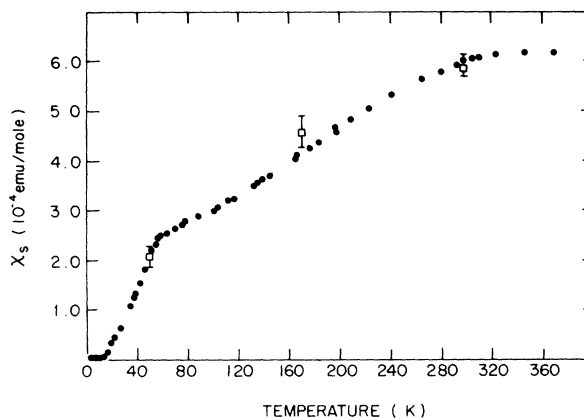
FIG. 3. Spin susceptibility of (TTF)(TCNQ). The open squares represent direct measurements of χ_s by integration of the spin resonance.
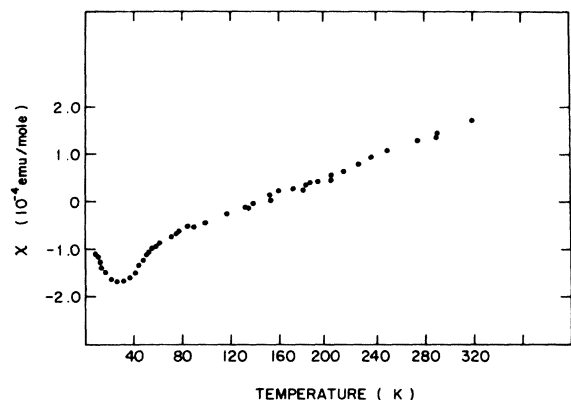
FIG. 4. Temperature dependence of the total magnetic susceptibility of (ATTF)(TCNQ).

FIG. 6. Spin susceptibility of (ATTF)(TCNQ).

sults can be contrasted with the ground-state properties of magnetic Mott-Hubbard insulators, resulting from electron-electron Coulomb correlations. For one electron per site in the uniformly structured one-dimensional case, exact Hubbard-model solutions show the ground state consisting of collective spin-wave modes split off well below the energy for single-particle excitations.[25] The spin-wave modes give rise to a finite susceptibility at low temperatures and a corresponding linear temperature contribution to the low-temperature specific heat.[14] These effects of Coulomb correlations for one-dimensional TCNQ systems were thoroughly studied in (NMP)(TCNQ),[14, 26] where the ground state was experimentally identified with that of a Mott-Hubbard insulator.

The presence of a structural nonuniformity (e.g., a dimerization along the one-dimensional chain) opens a gap at $q = 0$ in the spin-wave excitation mode.[27, 28] The $q = 0$ spin excitations in the strongly
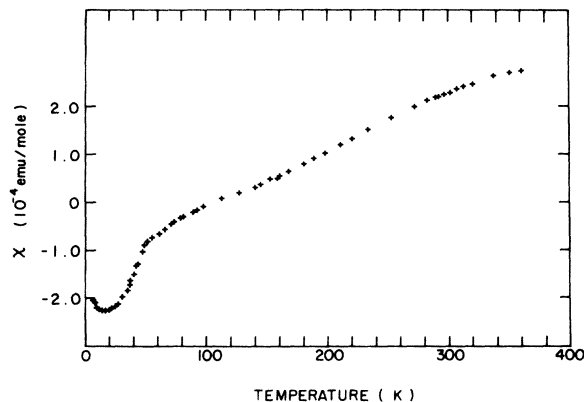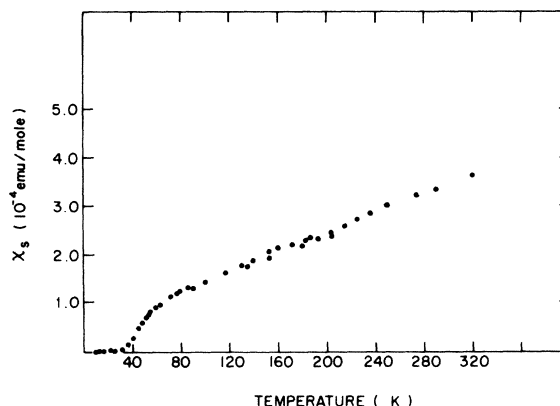
dimerized limit are triplet excitons[29] whose spin susceptibility can be represented in the zero-bandwidth approximation by the expression $\chi = (C/T)$ $\times e^{-\Delta/k_B T}$. Again, the magnetic excitation gap Δ is necessarily much smaller than the single-particle excitation gap. For (TTF)(TCNQ), the low-temperature thermodynamic single-particle gap suggested by the dc and microwave conductivity[8, 30] measurements is 150 ± 30 K. The susceptibility data of Fig. 3 plotted as $\ln \chi T$ vs $1/T$ (Fig. 8) yields an activation gap of 170 K. Since the magnitudes of the respective gaps are comparable, the low-temperature behavior can be viewed as arising from single-particle excitations across a simple semiconducting gap, demonstrating the Coulomb correlations effects in (TTF)(TCNQ) are not of major importance. This is consistent with the results of Rybaczewski et al.[1, 9] who observed Korringa-like nuclear relaxation rates in the high-temperature metallic regime of (TTF)(TCNQ) with $\chi^2 T_1 T$ approximately constant in the metallic state.

In the high-temperature region ($60 < T < 360$ K),

FIG. 5. Temperature dependence of the total magnetic susceptibility of (TMTTF)(TCNQ).
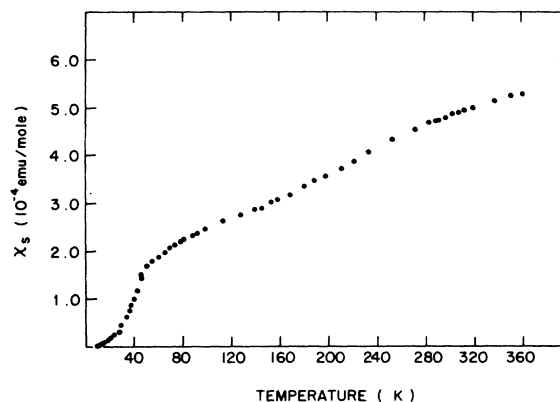

FIG. 7. Spin susceptibility of (TMTTF)(TCNQ).

a definite temperature dependence is observed in χ_s which increases monotonically from 60 K to room temperature with an over-all change in magnitude of approximately a factor of 2. In order to describe the qualitative features, we roughly approximate χ_s for (TTF)(TCNQ) with the simple form $\chi_s = A + Be^{-\Delta/T}$, $A = 2.4 \times 10^{-4}$ emu/mole and $\Delta = 260$ K.

In an attempt to understand the origin of these general features, several different proposals can be considered that involve different local susceptibilities on individual chains, directionally anisotropic susceptibilities, simple band-structure effects, and the effect of the electron-phonon interaction. (i) There may be different local susceptibilities on the cation and anion chains, with one exhibiting a metallic temperature-independent Pauli susceptibility, and the other exhibiting simple semiconducting behavior which would contribute an activated term to χ_s. However, the absence of any sign of magnetic localized moments rules out the possibility of a Coulomb correlation energy gap, and a simple one-electron energy gap is inconsistent with the known uniform chain structure.[11] Thus, simple semiconducting behavior on either chain appears unlikely. (ii) (TTF)(TCNQ) is known to be highly anisotropic in its electrical,[2,8] optical,[4,5] and dielectric[8] properties. This anisotropy might be reflected in the susceptibility with a Pauli-like contribution in the principal conducting direction and an activated term contributing from the perpendicular direction. However, spin-resonance measurements[31] (30 GHz) on oriented single crystals of (TTF)(TCNQ) reveal that the necessary g-value anisotropy is more than two orders of magnitude too small to account for the susceptibilities to be assigned. (iii) Simple band-structure effects may lead to temperature dependence through averaging the density of states within kT of the Fermi energy. Such simple band effects seem unlikely since the scale of energies for the bandwidth involved is large compared to kT. From thermopower[6] and optical[4,5] studies, the Fermi energy for (TTF)(TCNQ) along the principal axis is of the order of 2×10^3 K, whereas the observed temperature dependence of χ occurs below room temperature. Other evidence comes from the normalized susceptibility for (TTF)(TCNQ), (ATTF)(TCNQ), and (TMTTF)(TCNQ) shown in Fig. 9. One of the effects of methyl substitution on TTF is to introduce more electron density into the TTF rings, resulting in lower ionization potentials for ATTF and TMTTF relative to the parent TTF compound. This should lead to relative band shifts in the solid state. Moreover, some differences in bandwidth are expected on general grounds since the intermolecular overlap should not be precisely

the same. These differences would be reflected in the magnitude of the spin susceptibility of the three salts, and indeed, χ_s at room temperature is noticeably different for the three systems (TTF, 6.0×10^{-4} emu/mole; ATTF, 3.4×10^{-4} emu/mole; and TMTTF, 4.8×10^{-4} emu/mole). However, the normalized spin susceptibilities (Fig. 9) are nearly identical over the entire temperature range, indicating that another more general mechanism is responsible for the major features of the observed temperature dependence.

V. ANALYSIS OF THE TEMPERATURE DEPENDENCE OF χ

A. $T > 60$ K

We consider here the effect of the electron-phonon (el-ph) interaction on the susceptibility for $T > 60$ K. Whereas in three-dimensional systems, the electron-phonon interaction leads to mass renormalization without effect on the magnetic susceptibility,[32] the strong-coupling one-dimensional case is fundamentally different. In this case, electron-phonon coupling qualitatively alters the band structure via the Peierls-Fröhlich instability.[33,34] As a result, χ_s becomes temperature dependent, reflecting the nature of the coupled system.

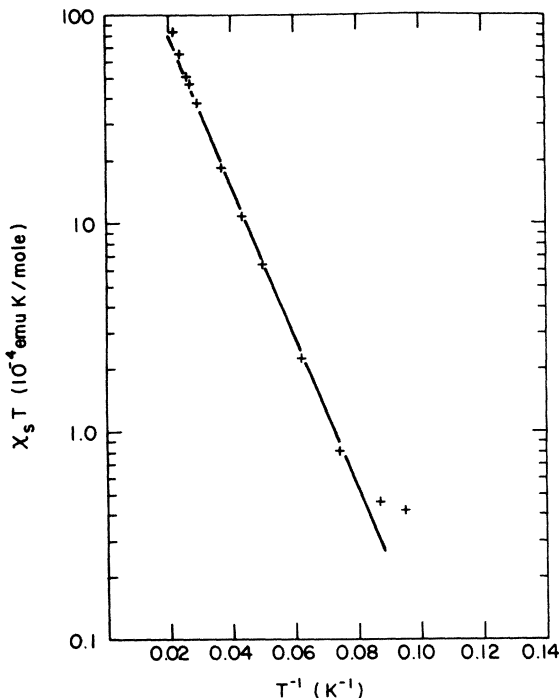The analysis of the temperature dependence of

FIG. 8. $\ln \chi_s T$ vs $1/T$ for (TTF)(TCNQ) showing the exponential temperature dependence at low temperatures.

the metallic reflectivity near the plasma edge[4,5] leads to a value for the electron-phonon coupling constant, $\lambda \simeq 1.3$, implying a Peierls-Fröhlich transition temperature well above room temperature. Lee, Rice, and Anderson[35] observed that if the Peierls-Fröhlich transition were in fact this high, the qualitative temperature dependence of χ_S found experimentally would be expected.

Comparison of the temperature dependence of the optical conductivity (obtained from the Drude analysis near ω_p) and the dc conductivity led us to conclude that at all temperatures above the 60 K transition, the dc conductivity is not dominated by single-particle scattering, but there is excess dc conductivity arising from a collective many-body effect.[5] This excess collective conductivity might arise from superconducting fluctuations (either pairing or a giant density-wave mechanism like that of Fröhlich) at temperatures *above* a mean-field transition temperature, or, alternatively, from fluctuations from the collective state in a one-dimensional system well *below* the mean-field transition. The qualitative temperature dependence of the susceptibility suggests the latter alternative, and we shall analyze the data in these terms below.

However, we note that there is no reason to assume identical behavior on the cation and anion chains. In fact, nuclear relaxation measurements on (TTF)(TCNQ)[9] and the deuterated analog (TTF)(TCNQD_4)[36,37] indicate more rapid relaxation on the TTF chains, implying a larger susceptibility.[38] Moreover, there is clearly another characteristic temperature in the problem, the transition temperature at 60 K.

As a model, therefore, we assume that above 60 K (TTF)(TCNQ) consists of two sets of chains.[39] The first set (probably the TCNQ chains) are in the Peierls-Fröhlich state, well below the mean-field temperature T_P. The second set (probably the TTF chains) behave as simple one-dimensional metallic chains. With this picture, the 60 K transition is a three-dimensional ordering in which interchain coupling pins the two sets of chains and leads to the small energy gap observed at low temperatures.

This description is consistent with the optical properties[40] which suggest a dynamic energy gap of the order of 1000 cm^{-1} even at room temperature. This is taken to be the Peierls-Fröhlich gap in the TCNQ chains. In addition, there is a metalliclike contribution to $\sigma_1(\omega)$ at long wavelengths which vanishes below 60 K, consistent with the opening of an energy gap in the second set of chains.

The spin susceptibility in this model for $T > 60$ K would be a sum of two parts,

$$\chi = \chi_P + \chi_{LRA} \, , \tag{2}$$

where χ_P represents the (approximately) constant Pauli susceptibility of the metallic chains, and χ_{LRA} represents the Lee-Rice-Anderson susceptibility of the dynamically distorted chains.[35] The experimental data are consistent with this decomposition. Examination of χ_S for (TTF)(TCNQ) implies a constant term χ_P^{exp} of magnitude $\chi_P^{exp} = 2.4 \times 10^{-4}$ emu/mole. In Fig. 10 we plot the difference $\chi_{LRA}^{exp} = \chi_S - \chi_P^{exp}$ (normalized for a best fit) as a function of T/T_P and compare it with the theoretical Lee-Rice-Anderson function (solid curve). Fixing $T_P = 450$ K, the agreement is satisfactory over the entire temperature range, although there is some deviation at the lowest temperatures. This small discrepancy might arise from lifetime broadening, which would smooth the square-root singularity to a peak and thus reduce the over-all curvature in $\chi(T)$ somewhat. There are only three adjustable parameters involved in obtaining the comparison shown in Fig. 10: the magnitude of χ_P, the value for T_P, and the normalization constant. The first is fixed by the data for T approaching 60 K to better than $\pm 10\%$. Thus, although there are assumptions involved in the decomposition described by Eq. (2), there are only two free parameters. However, the consistency of the analysis with other aspects of the experimental picture must await a more detailed study of the *local* susceptibilities of both nuclear- and electron-spin resonance.

The absolute magnitudes of the two contributions can be used to estimate the bandwidths associated with the different chains. Using $\chi_P = 2\mu_B^2\rho(0)$ with a tight-binding density of states given by $\rho(0) = (\pi E_F)^{-1}$ per molecule for the one-dimensional metal in the vicinity of the center of the band leads to $E_F/k_B \sim 950$ K. A constant-density-of-states model gives $E_F/k_B \sim 3000$ K. These values are
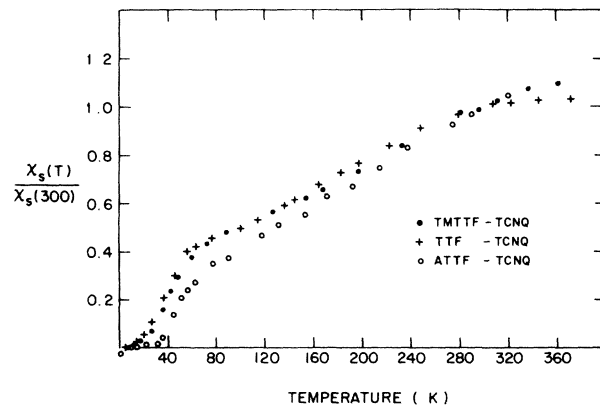

FIG. 9. Comparison of the spin susceptibilities of (TTF)(TCNQ), (ATTF)(TCNQ), and (TMTTF)(TCNQ). The values are normalized to the point at 300 K. (For clarity not all points from Figs. 3, 6, and 7 are included.)

comparable to, but somewhat smaller than, es-
timates obtained from other measurements.[4-6]
Values obtained from the susceptibility data must
be considered lower limits, since exchange en-
hancement from residual electron-electron inter-
actions can be expected to increase $\chi(q=0)$ some-
what over the band value. Since the high-tempera-
ture limit of the total susceptibility is about two
times the value of χ_P^{exp}, the bandwidths of the two
sets of chains are comparable. The corresponding
results for the dimethyl and tetramethyl deriva-
tives are $E_F/k_B = 1600$ K (tight binding) or E_F/k_B
$= 5000$ K (constant density of states) for (ATTF)
(TCNQ); and $E_F/k_B = 1250$ K (tight binding) or
$E_F/k_B = 3750$ K (constant density of states) for
(TMTTF) (TCNQ).

B. $T < 60$ K

As demonstrated above, the susceptibility for
$T < 60$ K is that of a small-band-gap nonmagnetic
semiconductor for which $\chi(T)$ is dominated by the
exponential temperature dependence of the number
of single-particle excitations. We consider this
temperature regime in more detail.

The question naturally arises as to how the low-
temperature semiconducting gap changes with in-
creasing temperature. Earlier studies of the low-
temperature dielectric constant implied the semi-
conducting gap renormalized toward zero as T
approached 60 K.[8] Such a renormalization pre-
sumably reflects the direct similarity between the
large number of states at a BCS gap edge and the
singularity of the density of states for one-dimen-
sional systems.

In general, the susceptibility of an electronic
system is given by

$$\chi = -\tfrac{1}{2} g^2 \mu_B^2 \int_{-\infty}^{\infty} \frac{\partial f}{\partial \epsilon} \rho(\epsilon) d\epsilon , \tag{3}$$

where $\rho(\epsilon)$ is the density of states for a single sign
of the spin. In the case of a one-dimensional tight-
binding band (arbitrary band filling) perturbed by
a weak lattice distortion at $k = \pm k_F$, the dispersion
relation is

$$\epsilon = 2t \cos k_F a \cos(k_F - k)a$$
$$\pm [4t^2 \sin^2 k_F a \sin^2(k_F - k)a + \delta^2]^{1/2} ; \tag{4}$$

i.e., a gap 2δ opens up at the Fermi surface and
the system becomes semiconducting. The density
of states for energies near the gap can be calcu-
lated to order $\delta^2/4t^2$ as

$$\rho(\epsilon') = \frac{N}{2\pi}$$
$$\times \frac{|\epsilon'|}{[(\epsilon')^2 - \delta^2]^{1/2} [4t^2 \sin^2 k_F a - (\epsilon')^2 - \delta^2]^{1/2}} , \tag{5}$$

where $\epsilon' = \epsilon - 2t \cos k_F a$ is the energy relative to the
Fermi energy. The susceptibility (per molecule)
may be expressed as

$$\chi = \chi_P \int_0^{\infty} \tfrac{1}{2} \cosh^{-2} \tfrac{1}{2} (x^2 + \beta^2 \delta^2)^{1/2} dx , \tag{6}$$

where

$$\chi_P = 2\mu_B^2 \rho(0) \tag{7}$$

is the Pauli susceptibility for the chains in ques-
tion.

The experimental data were fitted to the above
expression (integrated numerically) choosing χ_P
as obtained for the metallic chains in the previous
section. The gap, $2\delta(T)$, was renormalized ac-
cording to mean-field theory,[41,42] becoming zero
at $T_c = 58$ K. The best fit was obtained with $2\delta(0)/$
$k_B = 160 \pm 40$ K. The low-temperature data and the
computer fit are shown in Fig. 11. For compari-
son, the expression with a constant gap is also
plotted where the magnitude of the gap is fixed by
the lowest temperature points. The susceptibility
of (TTF)(TCNQ) for $T < 60$ K can be viewed as that
of a nonmagnetic small-gap semiconductor with the
gap going smoothly to zero as T approaches 60 K.

VI. CONCLUSION

Measurements of the temperature dependence of
the magnetic susceptibility of (TTF)(TCNQ) and its
dimethyl and tetramethyl derivatives show these
to be a family with quite similar electronic prop-
erties. The nonmagnetic ground state and the
absence of localized-moment formation imply that
electron-electron Coulomb interactions are not
dominant. This is consistent with the relatively
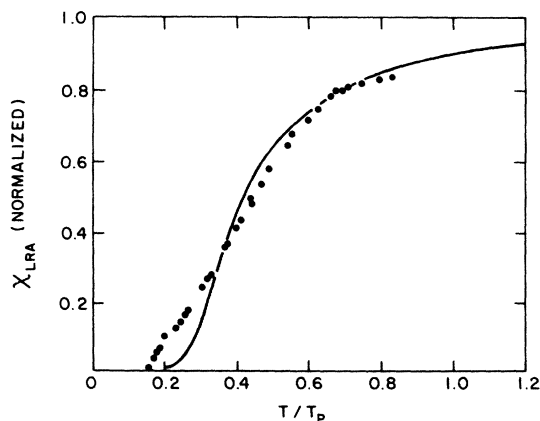large molecular polarizability and the associated

FIG. 10. Spin susceptibility χ_{LRA} according to Eq. (2)
(see text). The data are compared with the theoretical
results of Lee, Rice, and Anderson (Ref. 33) with T_P
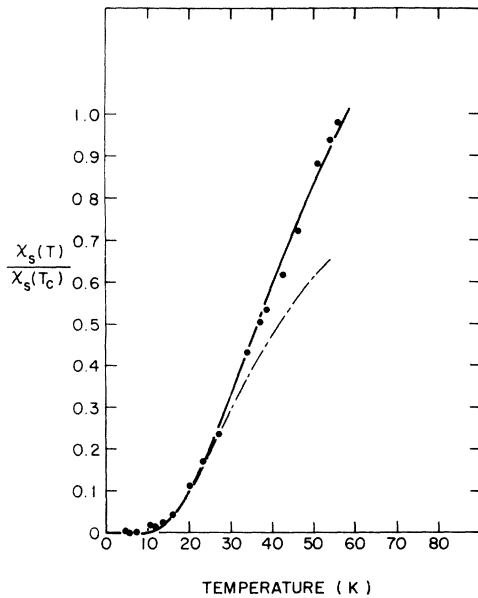$= 450$ K.

FIG. 11. Spin susceptibility of (TTF)(TCNQ) at low temperatures. The solid curve represents the one-dimensional small-band-gap semiconductor with temperature-dependent gap renormalized according to the BCS form; the dashed curve assumes a temperature-independent gap.

reduction of U_{eff} by polarization via excitonic polarons.[43,44] Although such screening effects would not likely be complete, the residual Coulomb interaction appears to have little effect on measured properties. Evidently the strong electron-phonon interaction dominates, and the one-dimensional divergence (at $q = 2k_F$) in the susceptibility response function is removed.[45]

The analyses in the high- ($60 < T < 360$ K) and low- ($T < 60$ K) temperature regions demonstrate that the magnetic properties are consistent with a two-chain model. Following the proposal of Lee, Rice, and Anderson,[35] the 60-K transition is probably a three-dimensional ordering in which inter-

chain coupling pins the two sets of chains and leads to the small energy gap observed at low temperatures. From $\chi_s(T)$ for $T < 60$ K, evidence is found for a temperature-dependent energy gap with $2\delta(T)$ roughly following the BCS mean-field form.

Some temperature dependence can be expected for χ_s in the metallic regime from thermal effects in narrow bands, especially with two independent bands and the possibility of band crossing.[46] In the absence of knowledge of the detailed band structure, it is difficult to rule this out. However, two facts weigh against such effects playing a dominant role. First, temperature dependence is observed at relatively low temperatures ($\sim 10^2$ K) whereas the Fermi energies are much higher ($> 10^3$ K). Second, the normalized temperature dependences of (TTF)(TCNQ) and the ATTF and TMTTF derivatives are nearly identical, whereas the absolute magnitudes vary from one to the other by a factor of 2. Thus, although there may be come contribution to the temperature dependence from simple thermal population in an energy-dependent density of states, the over-all features appear to be dominated by the strong electron-phonon coupling which would qualitatively lead to a nontrivial temperature-dependent band structure via the Peierls-Fröhlich instability.

ACKNOWLEDGMENTS

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[1]A. F. Garito and A. J. Heeger, Nobel Symp. 24, 129 (1973).
[2]M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 1298 (1974).
[3]L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, Solid State Commun. 12, 1125 (1973).
[4]A. A. Bright, A. F. Garito, and A. J. Heeger, Solid State Commun. 13, 943 (1973).
[5]A. A. Bright, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 1328 (1974).
[6]P. M. Chaikin, J. F. Kwak, T. E. Jones, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 31, 601 (1973).
[7]T. Wei, S. Etemad, A. F. Garito, and A. J. Heeger, Phys. Lett. A 45, 269 (1973).
[8]S. K. Khanna, E. Ehrenfreund, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 2205 (1974).
[9]E. F. Rybaczewski, A. F. Garito, and A. J. Heeger,

Bull. Am. Phys. Soc. 18, 450 (1973).

[10] R. E. Peierls, *Quantum Theory of Solids* (Oxford U. P., London, 1955), p. 108.

[11] T. E. Phillips, T. J. Kistenmacher, J. P. Ferraris, and D. O. Cowan, Chem. Commun. xx, 471 (1973).

[12] W. D. Grobman, R. A. Pollak, D. E. Eastman, E. T. Maas, Jr., and B. A. Scott, Phys. Rev. Lett. 32, 534 (1974).

[13] A. J. Epstein, P. Nielsen, N. O. Lipari, and D. J. Sandman, Bull. Am. Phys. Soc. 19, 295 (1974).

[14] A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, Phys. Rev. B 5, 952 (1972).

[15] P. J. Strebel and Z. Soos, J. Chem. Phys. 53, 4077 (1970).

[16] P. Pincus, in *Selected Topics in Physics, Astrophysics, and Biophysics*, edited by Abecassis de Laredo and N. Jurisic (D. Reidel, Dardrecht, Holland, 1973), pp. 138–172.

[17] Supplied by Worden Quartz, Houston, Tex.

[18] A. N. Gerritsen and D. H. Damon, Rev. Sci. Instrum. 33, 301 (1962).

[19] L. B. Coleman, J. A. Cohen, A. F. Garito, and A. J. Heeger, Phys. Rev. B 7, 2122 (1973).

[20] A. R. McGhie, A. F. Garito, and A. J. Heeger, J. Crystal Growth 22, 295 (1974).

[21] J. H. Perlstein, J. P. Ferraris, V. V. Walatka, D. O. Cowan, and G. A. Candela, AIP Conf. Proc. 10, 1494 (1973).

[22] A. N. Bloch, J. P. Ferraris, D. O. Cowan, and T. O. Poehler, Solid State Commun. 13, 753 (1973).

[23] The values of Pascal's constants used were taken from *Modern Coordination Chemistry*, edited by J. Lewis and R. G. Wilkins (Interscience, New York, 1960), p. 403. (All in units of 10^{-6} emu/mole.) H, 2.93; C, 6.00; N, 5.57; S, 15.0. Constitutive corrections C=C, −5.5.

[24] A. N. Bloch, R. B. Weisman, and C. M. Varma, Phys. Rev. Lett. 28, 753 (1972).

[25] A. A. Ovchinnikov, Zh. Eksp. Teor. Fiz. 57, 2137 (1969) [Sov. Phys.—JETP 30, 1160 (1970)]. See also M. Takahashi, Prog. Theor. Phys. 43, 1619 (1970); 42, 1098 (1969); 43, 860(E) (1970).

[26] A. J. Heeger and A. F. Garito, AIP Conf. Proc. 10,

1476 (1973).

[27] L. N. Bulaevskii, Fiz. Tverd. Tela 11, 1132 (1969) [Sov. Phys.-Solid State 11, 921 (1969)].

[28] A. B. Harris, Phys. Rev. B 7, 3166 (1973).

[29] P. L. Nordio, Z. G. Soos, and H. M. McConnell, Annu. Rev. Phys. Chem. 17, 237 (1966).

[30] J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, J. Am. Chem. Soc. 95, 948 (1973).

[31] S. K. Khanna (unpublished).

[32] G. Gladstone, M. A. Jensen, and J. R. Schrieffer, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), Vol. II, Chap. 13.

[33] H. Fröhlich, Proc. R. Soc. A 223, 296 (1954).

[34] J. Bardeen, Solid State Commun. 13, 357 (1973); D. Allender, J. W. Bray, and J. Bardeen, Phys. Rev. B 9, 119 (1974).

[35] P. A. Lee, T. M. Rice, and P. W. Anderson, Phys. Rev. Lett. 31, 462 (1973).

[36] These data were presented at the Gatlinburg Conference on Superconductivity and Lattice Instabilities, 1973 (unpublished).

[37] E. F. Rybaczewski, E. Ehrenfreund, A. F. Garito, and A. J. Heeger, Bull. Am. Phys. Soc. 19, 222 (1974).

[38] Solution EPR studies show the hyperfine coupling to the protons in the two ions to be similar: $a_H(TTF^+)$ = 1.26, F. Wudl, G. M. Smith, and E. J. Hufnagel, Chem. Commun. 1453 (1970); $a_H(TCNQ^-)$ = 1.57, P. H. Rieger and G. K. Fraenkel, J. Chem. Phys. 37, 2795 (1962).

[39] Variations of the two-chain model have been proposed by many people: see, for example, Refs. 21 and 35.

[40] D. B. Tanner, C. S. Jacobsen, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 32, 1301 (1974).

[41] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[42] C. G. Kuper, Proc. R. Soc. A 227, 214 (1955).

[43] P. M. Chaikin, A. F. Garito, and A. J. Heeger, Phys. Rev. B 5, 4966 (1972).

[44] P. M. Chaikin, A. F. Garito, and A. J. Heeger, J. Chem. Phys. 58, 2336 (1973).

[45] A. Luther and I. Peschel, Phys. Rev. B 9, 2911 (1974).

[46] P. Pincus (private communication).