

## Effects of isostructural doping of the donor and acceptor stacks on the phase transitions and magnetic and electrical properties of tetrathiafulvalene-tetracyanoquinodimethane

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The roles of the donor (tetrathiafulvalene, TTF) and acceptor (tetracyanoquinodimethane, TCNQ) stacks in the 53- and 38-K phase transitions of TTF-TCNQ and in the phases below each transition are determined by a systematic study of the effects of selectively doping the donor stacks and the acceptor stacks with impurities of similar perturbation strength. Both the magnetic susceptibility and the electrical conductivity of these doped materials were measured as a function of temperature. The experiments indicate that the 53-K transition is a quasi-one-dimensional Peierls transition driven by the acceptor stacks, and that the 38-K transition involves both kinds of stacks but results from long-range order developing on the donor stacks.

### I. INTRODUCTION

Tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), the most extensively studied organic metal, consists of segregated donor (TTF) and acceptor (TCNQ) stacks. Associated with each stack is a partially filled electron band. Theoretically, the quasi-one-dimensional nature of these bands makes both kinds of stacks prone to Peierls distortions. Experimentally, TTF-TCNQ undergoes at least two phase transitions<sup>1-3</sup> at 53 and 38 K, in both of which there is development of a new kind of incommensurate superlattice ordering.<sup>4-7</sup> The nature of these transitions, especially the distinct roles played by the two kinds of stacks in each, have been suggested to be as follows<sup>8</sup>:

(i) The 53-K transition was ascribed to the onset of a three-dimensional TCNQ distortion. No simultaneous transition is induced in the TTF stacks because of an effective decoupling between the TTF stacks and the ordered superlattice on the TCNQ stacks. (ii) The first-order transition at 38 K was ascribed to the incipience of three-dimensional (3D) ordering of the phases of the Peierls fluctuations in the TTF sublattice, which is aided by the presence of the ordered-TCNQ superlattice.

To find out if, indeed, this interpretation of the two phase transitions is correct, it is highly desirable to study *experimentally* the role of each kind of stack in the transitions and to find out how the stacks interact. Previously, this has been attempted by three different methods: (a) Measuring properties in the pure crystal associated with only one kind of stack, which is made possible by the selective introduction of isotopes used as probes. Such measurements can be performed on the NMR relaxation time  $T_1$ ,<sup>9</sup> and the Knight shift<sup>10</sup> of the special isotopes (or of the nuclei they replace). (b) Measuring two combined properties

(i.e., properties of both stacks) of the pure material, so chosen that they allow a decomposition of each into the respective contributions of the different stacks. Such a decomposition can be achieved<sup>11</sup> when the total  $g$  shift and paramagnetic susceptibility are the measured quantities. (c) Modifying only the kind of stack and studying the change in some combined physical property resulting from this modification. Controlled modifications of only the donor stacks have been accomplished by introducing various percentages of tetraselenafulvalene (TSeF),<sup>2</sup> taking advantage of its recent synthesis<sup>12</sup> and the fact that pure TSeF-TCNQ is an isostructural<sup>13</sup> analog of pure TTF-TCNQ. A corresponding modification of the acceptor stacks is reported for the first time<sup>14</sup> in this paper, where we shall present measurements on crystals in which a small percentage of methyl-TCNQ has been introduced into the acceptor stacks.

The first method was applied to TTF-TCNQ by Rybaczewski *et al.*<sup>9</sup> who studied  $T_1$  for proton NMR in samples in which one or the other of the stacks was deuterated. The method was sufficient to indicate the 38-K anomaly on the TTF stacks, but is not adequate for an unambiguous separation of the magnetic susceptibilities of the two stacks because of the uncertainty of the mechanism, especially the possible inapplicability of the Korringa relation to the intermediate phase. Current measurements of the Knight shift on stacks in which <sup>13</sup>C nuclei are selectively introduced appear to be more promising.<sup>10</sup>

The second method was applied to TTF-TCNQ in the semiconducting regime by Tomkiewicz, *et al.*<sup>11</sup> who used the observation of a single Lorentzian EPR line to infer strong coupling between spins of the two stacks, which in turn allowed use of the combined  $g$  shift to determine the fractional susceptibility of each stack. When used in conjunction with the total paramagnetic susceptibili-

ty, also determined by EPR, these fractional susceptibilities in turn yield the desired decomposition into donor and acceptor contributions. In this way, it was shown that the 53-K transition does not affect the TTF susceptibility but strongly affects the TCNQ susceptibility. This fact and the fact that the magnetic activation energy on the TCNQ stacks is much the larger below 53 K imply that the TTF and the TCNQ stacks are decoupled in the vicinity of the metal-insulator transition and that the TCNQ stacks drive this transition. In the same way, it was shown that the 38-K transition strongly affects the TTF susceptibility, demonstrating the involvement of the donor stacks in this transition. The precise nature of the acceptor stacks's involvement is unclear, because their susceptibility is already too small at 38 K to show any measurable anomaly. While this method can distinguish the contributions of the two stacks, the magnetic measurements are not sufficiently accurate to characterize the detailed nature of either transition.<sup>15,16</sup>

The third method has also been applied to TTF-TCNQ. Etamad<sup>2</sup> showed that 3% doping of the TTF stack by TSeF broadens the 38-K transition so as to make it unobservable and decreases the conductivity in the intermediate phase while leaving a well-defined transition at 53 K. These results imply that the conductivity in the intermediate phase ( $38 < T < 53$  K) is mainly on the TTF stack and that the TTF stack is much more involved in the 38-K transition than in the 53-K transition. However, since the conductivity measures a combined property of both the donor and acceptor stacks, it cannot yield a quantitative evaluation of the effects of the doping on each stack separately.<sup>17,18</sup> Also, comparison of the conductivity in the pure and doped systems is inconclusive, because the impurities can affect not only the density of carriers (through their effect on the correlation length) but also the mobility (through their effect on various scattering mechanisms, the introduction of a mobility gap, etc.).

To avoid these shortcomings, we have combined the second and third methods and have determined the contributions of the separate stacks in the doped systems. The purpose of this paper is to report the results of this approach and to discuss their implications. For donor-doped systems (TTF-TCNQ doped with TSeF), susceptibility and  $g$ -value measurements have been made, enabling us to decompose the susceptibility into the separate contributions of the donor and acceptor stacks. For acceptor-doped systems (TTF-TCNQ doped with methyl-TCNQ), where an EPR determination of the total spin susceptibility is not feasible,  $g$ -value measurements alone and a reason-

able assumption about the effect of acceptor doping on donor susceptibility, also allows us to determine the effects of doping on the acceptor susceptibility. These results for the donor-doped and acceptor-doped systems will be compared with similar results for pure TTF-TCNQ. The electrical conductivity for acceptor-doped systems will also be presented and compared with earlier measurements for the pure and donor-doped systems.

The questions of paramount interest will be how the presence of impurities on each kind of stack affects the magnetic and electrical properties of that stack and of stacks of the other kind. The answers to these questions will be analyzed in terms of an existing<sup>8</sup> model for TTF-TCNQ.

In Sec. II, we discuss the preparation of samples, experimental details of  $g$ -shift and EPR susceptibility measurements and the dc conductivity measurements.

In Sec. III, we report the results on total magnetic susceptibility (where available), fractional susceptibilities on the donor and acceptor stacks, magnetic activation energies of the two stacks, and the temperature derivative of the dc conductivity for pure, donor-doped (3-mole% TSeF) and acceptor-doped (3-mole% methyl-TCNQ) TTF-TCNQ.

In Sec. IV, we discuss these results in terms of six basic ideas that have been developed about TTF-TCNQ, reviewing the earlier evidence and discussing the significance of the results reported here for each basic idea.

Finally, in Sec. V, we briefly summarize our findings.

## II. EXPERIMENTAL TECHNIQUES

### A. Sample preparation

Single crystals of TTF-TCNQ doped with methyl-TCNQ (MeTCNQ),<sup>19</sup> and with TSeF<sup>12</sup> were grown in acetonitrile from the purified constituents as described earlier for MeTCNQ doping in TSeF-TCNQ.<sup>19</sup> In the case of donor-stack doping, the amount of TSeF incorporated into TTF-TCNQ could be readily determined within accuracy of  $\pm 0.5\%$  by electron microprobe of the S/Se ratio and by elemental analysis. Single crystals grown from a solution containing 0.03 mole fraction of TSeF relative to TTF were found to have comparable amounts of dopant incorporated. Single crystals of MeTCNQ-doped TTF-TCNQ were also grown with an initial mole fraction of dopant relative to TCNQ of 0.03. However, due to the close similarity of the acceptor stack dopant to TCNQ, we have been unable to make an accurate assessment of the amount of MeTCNQ incorporated into TTF-TCNQ. It is therefore assumed that the concentration of MeTCNQ incorporated into TTF-

TCNQ is similar to the initial mole fraction of MeTCNQ in solution, and henceforth we refer to these crystals as  $(\text{TTF})-(\text{TCNQ})_{0.97}(\text{MeTCNQ})_{0.03}$ , although the exact concentration is not important with respect to the findings of these doping experiments as will be discussed in the subsequent section.

### B. Spin resonance

All investigated compounds exhibit a single EPR absorption line down to 11 K despite the different  $g$  values of the donor and acceptor stacks. The  $g$  value of this absorption line was measured either by using as markers the calibrated positions of  $\text{Mn}^{2+}$  hyperfine lines dispersed in CdSe, or the  $g$  value of N-methylphenazinium-tetracyanoquinodimethanide (NMP-TCNQ). The temperature was varied and controlled by using an Air Products Heli-tran Dewar and Scientific Instrument temperature controller. The temperature dependence of the  $Q$  of the cavity was monitored by the known temperature dependence of the magnetic susceptibilities of the above-mentioned marker.

The spin susceptibility was determined in the following way: The derivative of the EPR absorption line, measured at X-band frequency, was digitized. At least 400 data points for each spectrum were fitted by least squares with a model-Lorentzian derivative line. If this fit is satisfactory, namely, if the fit is better than the experimental noise, then the amplitude and linewidth of the model Lorentzian are used to determine the total area under the absorption line and hence the susceptibility  $\chi_{\text{EPR}}$ . The susceptibility was determined only for temperatures and orientations in which the line is in fact Lorentzian. In principal, one can obtain the area under an absorption line which is neither of Lorentzian nor of Gaussian shape by double integration of the derivative line. However, the signal to noise limits the double integration range leading to loss of intensity which resides in the wings. This loss will be particularly important in case of line shapes which are sums of Lorentzians. The disadvantages of double integration are specially pronounced when both the linewidth and the line shape of the signal are temperature dependent. Maintaining the same number of linewidths over which the double integration is performed helps but does not eliminate the problem because of the loss of the intensity in the wings. Thus, in cases where the susceptibility measurements of non-Lorentzian lines were not essential (because we could obtain the susceptibility by measuring the line for a different orientation of the static magnetic field with regard to the crystallographic axis where the

line is Lorentzian, or by obtaining the same information from an alternative method) these measurements were avoided.

Figure 1 demonstrates the quality of the Lorentzian fits to the actual experimental data at 38 K for both TTF-TCNQ and  $(\text{TTF})_{0.97}(\text{TSeF})_{0.03}-(\text{TCNQ})$ . The susceptibility measurements reported in this paper include data on at least three samples for each dopant concentration. In the case of TTF-TCNQ, six samples of three different batches were measured.

### C. Conductivity measurements

The conductivity measurements were made using a four-probe dc method, with the dc current along the  $b$  axis. The samples were mounted on 0.001-in. gold wires to minimize temperature-dependent strain. Electrical contacts were made by surrounding the needle with silver paint. The data were taken with a computer-controlled device while cooling at 0.5 K/min in the vicinity of the phase transition. Current-voltage curves taken at 4.2 K indicate ohmic behavior for the current densities used in the doped material. Sixteen samples of methyl-doped TTF-TCNQ were measured. The variation in  $\sigma(\text{peak})/\sigma(300 \text{ K})$  was less than 10%.

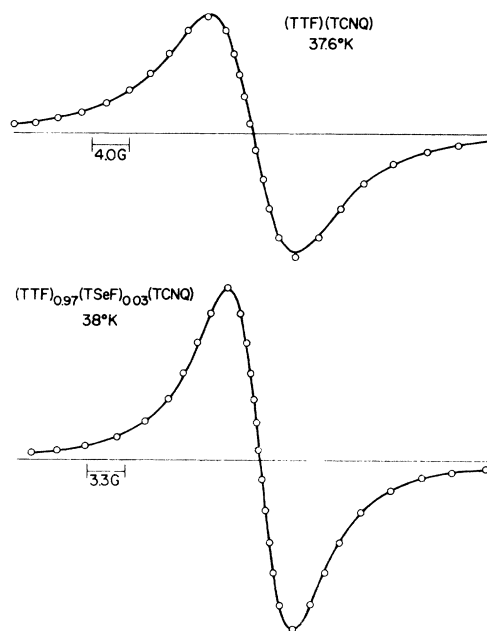


FIG. 1. EPR absorption lines in TTF-TCNQ at 37.6 K and  $(\text{TTF})_{0.97}(\text{TSeF})_{0.03}(\text{TCNQ})$  at 38 K compared with the derivatives of the best two parameter Lorentzian fit. The theoretical curve is represented by a line, the experimental data by points.

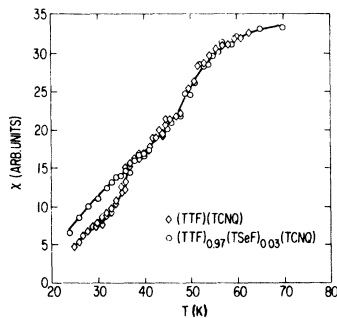


FIG. 2. Temperature dependence of the total spin susceptibility, determined by EPR, for pure TTF-TCNQ and for  $(\text{TTF})_{0.97}(\text{TSeF})_{0.03}(\text{TCNQ})$ . A normalization which makes the susceptibilities the same at 39 K has been chosen in order to emphasize the different temperature dependences.

### III. RESULTS

The total spin susceptibility versus  $T$  for single crystals of  $(\text{TSeF})_{0.03}(\text{TTF})_{0.97}(\text{TCNQ})$  is compared with similar measurements on a single crystal of pure TTF-TCNQ in Fig. 2, where the temperature dependence of the susceptibility for the pure and doped crystals is exhibited. Both susceptibilities were obtained for the orientation  $\vec{H}_{DC} \parallel \vec{c}^*$  and were arbitrarily normalized to agree at 38 K.

Two distinct temperature regimes emerge, above and below the transition at 38 K. In the range  $T > 38$  K, the total spin susceptibilities of the pure and doped systems exhibit the same temperature dependence. This behavior is strikingly different from the one found<sup>2</sup> for the temperature

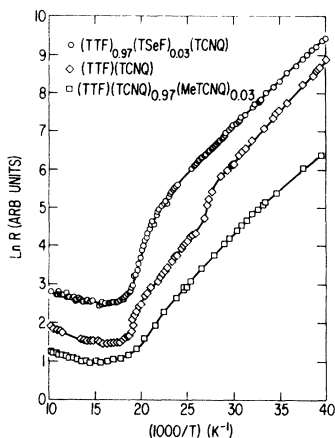


FIG. 3. Comparison of the temperature dependence of the resistivity for pure, donor-doped (3-mole % TSeF), and acceptor-doped (3-mole % MeTCNQ) TTF-TCNQ. The pure and donor-doped curves are taken from Etemad (Ref. 2). Normalization for each type of sample has been chosen which displaces the data in a vertical direction so that a clear comparison between the three can be made.

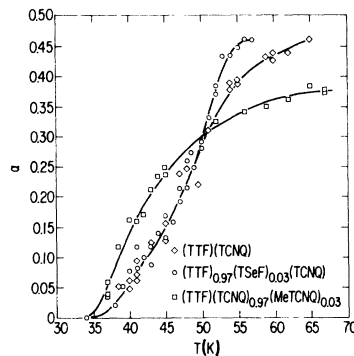


FIG. 4. Ratio between the acceptor stack susceptibility and the total susceptibility as a function of temperature in pure, donor-doped (3-mole % TSeF), and acceptor-doped (3-mole % MeTCNQ) TTF-TCNQ, as determined from  $g$ -shift measurements. Below 34 K this ratio is zero within the error of the measurement.

dependence of the conductivities of the two systems in which the donor-doped system showed a much greater rise in the resistivity as  $T$  is lowered through 53 K than did the pure system, but no sudden additional rise at 38 K in contrast to the sharp rise seen in the pure system (Fig. 3). In the range  $T < 38$  K, the decrease of the susceptibility with decreasing temperature is much slower in the doped crystal than in pure TTF-TCNQ.

More detailed information can be obtained by determining the susceptibilities of the TTF and TCNQ stacks separately. This can be achieved by measuring the temperature dependence of the  $g$  value in the temperature regime of interest.<sup>11</sup> In the strong-coupling approximation (characterized by a single Lorentzian line), the relationship between  $g(\theta, T)$  measured at an angle  $\theta$  with respect to a crystallographic axis and the  $g$  values of the donor and acceptor stacks,  $g_D(\theta)$  and  $g_A(\theta)$ , is determined by the fractional susceptibilities of the two stacks:

$$g(T, \theta) = [1 - \alpha(T)]g_D(\theta) + \alpha(T)g_A(\theta), \quad (1)$$

where  $\alpha(T)$  is the fraction of the susceptibility on the acceptor stacks:

$$\alpha(T) = \chi_A(T) / [\chi_A(T) + \chi_D(T)]. \quad (2)$$

Figure 4 shows  $\alpha(T)$  for the pure and donor-doped systems. To determine  $\alpha(T)$ ,  $g(T)$  was measured in these experiments,  $g_A(\theta)$  was determined from  $g$ -tensor measurements of NMP-TCNQ, and  $g_D(\theta)$  was determined from the temperature-independent  $g$  values measured for these compounds at sufficiently low temperatures [temperatures at which  $\chi_A(T)$  is negligible].

Combining the value of  $\alpha(T)$  so determined and the measured susceptibilities, we are able to decompose the total susceptibility into acceptor and

donor contributions. The results of the decomposition are shown in Fig. 5 for the pure and donor-doped systems. The susceptibility data used for the doped compound are normalized to the susceptibility of pure TTF-TCNQ at 38 K. The purpose of this normalization<sup>20</sup> is to emphasize the difference between the temperature dependences of these susceptibilities.

Consider first the effects of doping the donor stacks. We observe first that the TCNQ susceptibility is affected above 50 K. The susceptibility of this stack maintains its metallic value to a lower temperature in the doped system than in the pure one. This behavior can be attributed to the smearing of the phase transition at 53 K as indicated in the conductivity data in Fig. 6. Secondly, we note that in spite of the donor-doping effects on the 53-K transition, the activation energy of the acceptor stack for  $T < 50$  K does not change as a consequence of donor doping.

In contrast to the insensitivity of the acceptor's magnetic activation energy to donor doping, the donor's activation energy is very sensitive, at least in the low-temperature phase. The activation energy is lowered significantly, as can be judged from a comparison of the slopes of the susceptibility versus temperature in the pure and donor-doped systems. This lowering of the activation energy is related to the smearing of the transition at 38 K, evident in both the susceptibility curves and the conductivity curves.

Let us now turn to the effects of doping the acceptor stacks with MeTCNQ. This dopant seems to be appropriate for our purpose, because its salt with TTF consists of segregated stacks of MeTCNQ and of TTF so the MeTCNQ molecules<sup>21</sup>

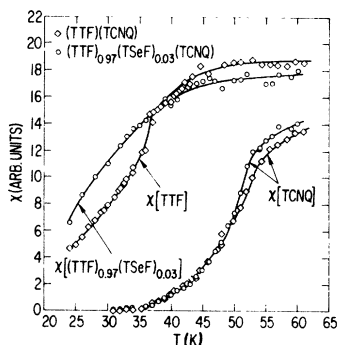


FIG. 5. Separate spin susceptibilities, determined by EPR in combination with  $g$ -shift measurements, on the donor and acceptor stacks in pure TTF-TCNQ and in  $(\text{TTF})_{0.97}(\text{TSeF})_{0.03}(\text{TCNQ})$ . The total susceptibilities of these materials were normalized to agree at 39 K, before the  $g$ -shift measurements were used to separate the contribution from each stack.

are expected to enter the acceptor stacks. The MeTCNQ will cause a perturbation on the acceptor stacks, because TTF-MeTCNQ undergoes its metal-insulator transition at a different temperature<sup>21</sup> from TTF-TCNQ. However, this perturbation occurs without introducing severe changes<sup>19</sup> in the crystal structure of TTF-TCNQ, because the steric requirements of the host stack and the guest molecule are very similar.

The temperature dependence of the fraction  $\alpha$  of the susceptibility on the acceptor stacks, as determined from  $g$ -value measurements, is given in Fig. 4 for  $(\text{TTF})-(\text{TCNQ})_{0.97}(\text{MeTCNQ})_{0.03}$ . The temperature dependence of  $\alpha(T)$  gives a rough indication of the value of the activation energy on the acceptor stacks. To see this, let us assume that in the intermediate phase ( $38 < T < 53$  K) the donor susceptibility remains temperature independent under acceptor doping, as was found previously (Fig. 5) for the pure and donor-doped systems. Then the temperature dependence of  $\alpha$  clearly indicates that the susceptibility on the acceptor stacks falls off much more slowly with decreasing temperature for the acceptor-doped system than for the pure one, similar to the behavior of the donor susceptibility with donor doping below 38 K. Therefore, impurity doping of the acceptor stack has qualitatively the same effect on the susceptibility as impurity doping in the donor stack—reduction of the activation energy on the stack into which the impurity is introduced.

Some better understanding of the two transitions can be obtained if one studies the effects of donor and acceptor doping on the position and sharpness of the transition, and in particular, if one can compare the effects of the two kinds of doping. However, in order to make this comparison meaningful, one should have a measure for the relative strength of the perturbation of each impurity on its own kind of stack. The strength of such an in-stack perturbation depends not only on the impurities concentration, but also on many parameters (e.g., ionization energy or electron affinity, respective bandwidths, densities of states at the Fermi energy, the  $2k_F$  Fourier component of the perturbing potential of the impurity, etc.) some of which are hard to determine experimentally. In this respect one might expect that MeTCNQ would constitute a much smaller perturbation on the acceptor band than the same concentration of TSeF is on the donor band because the band-forming orbitals of MeTCNQ and TCNQ are more similar than the bond forming orbitals of TSeF and TTF. Therefore, the accurate knowledge of the concentrations of TSeF and MeTCNQ is useless in terms of comparing their relative perturbation strengths.

As a rough experimental indication of the strength of the perturbation, we use the relative change in the value of the magnetic activation energy of the appropriate stack that results from the introduction of a fixed concentration of impurities on that stack. The physical reasoning behind this criterion is the following: the impurities reduce the correlation length of the charge density waves, hence, smear out the  $k$  vectors associated with one electron state and modify the density of states in the neighborhood of the edges of the Peierls subbands (i.e., "smear the Peierls gap"), introducing states within the gap and reducing the density of states within the subbands. This all has the effect of reducing the effective activation energy. To see quantitatively the effect of donor doping on donor activation energy, the susceptibilities of the donor stacks in TTF-TCNQ and in  $(\text{TTF})_{0.97}(\text{TSeF})_{0.03}(\text{TCNQ})$  are fitted with expressions of the form

$$\chi_D = (c/\sqrt{T}) \exp(-\Delta_D/T) \quad (3)$$

below 38 K. The origin of  $\sqrt{T}$  factor is the 1D nature of the band structure. The value of the magnetic activation energy  $\Delta$  obtained from this fit can be considered only as a very rough measure of the real activation energy, because its temperature dependence has been neglected. The value of  $\Delta$  for the donor stack was found in the temperature regime  $25 < T < 38$  K to be  $60 \pm 10$  K for  $(\text{TTF})_{0.97}(\text{TSeF})_{0.03}(\text{TCNQ})$  in comparison to  $110 \pm 10$  K found for TTF-TCNQ.

To see the effect of acceptor doping on the acceptor activation energy, we must proceed more indirectly, because we have no EPR measurement of the total susceptibility. The magnetic activation energy of the acceptor stack in  $(\text{TTF})-(\text{TCNQ})_{0.97}(\text{MeTCNQ})_{0.03}$  is evaluated by fitting  $\alpha(T)$  with an expression of the form

$$\alpha(T) = \frac{(B/\sqrt{T}) \exp(-\Delta_A/T)}{C + (B/\sqrt{T}) \exp(-\Delta_A/T)}. \quad (4)$$

Implicit are the assumptions of a temperature-independent activation energy on the acceptor stack and a temperature-independent susceptibility on the donor stack in the temperature regime  $38 < T < 53$  K. The latter assumption will be better satisfied the further one moves above 38 K. For  $45 < T < 53$  K,  $\Delta_A$  was found to be  $220 \pm 10$  K ( $\Delta_A$  evaluated for  $38 < T < 53$  K was  $280 \pm 20$  K for the acceptor-doped system, compared with  $410 \pm 20$  K in the pure system.<sup>11</sup>

We conclude that because the relative change in the magnetic activation energies of the appropriate stacks as a consequence of doping is roughly the same, the perturbation produced by MeTCNQ on the TCNQ stacks is similar in strength to that

produced by TSeF on the TTF stacks. *This conclusion makes meaningful the effects of 3% donor and acceptor dopings on the two phase transitions of TTF-TCNQ.*

The effects of doping on the position and sharpness of the phase transitions are obvious in the conductivity data shown in Fig. 3 and 6. Most instructive is Fig. 6, showing the derivative of the normalized conductivity of the pure, donor-doped, and acceptor-doped material. The data reflect the existence of three phase transitions for TTF-TCNQ at 53, 46,<sup>22,23</sup> and 38 K. Acceptor and donor doping have similar effects on both the 46- and 38-K transitions, viz., they completely broaden out the transitions. However, the metal-insulator transition at 53 K is affected differently by selective doping. While donor-doping broadens it without shifting the temperature of the transition, acceptor-doping broadened it markedly and in addition shifts the transition to about 47 K.

It is instructive to compare the effects of the different dopings on the effective activation energy of the conductivity. These effects are demonstrated in Fig. 3 where the resistance on a logarithmic scale is shown versus  $1/T$ . The slopes of the respective curves correspond to the effective activation energies. The data for the pure and donor-doped systems are taken from Etemad.<sup>2</sup> Two different temperature regimes emerge from the comparison:

1.  $T < 38$  K. Both acceptor- and donor-doping reduce the effective activation energy from that measured for the pure system. This reduction reflects the smearing of the Peierls gap by impurities and is consistent with the magnetic results.
2.  $38 < T < 53$  K. Acceptor doping reduces the effective activation energy while donor doping increases it. However, the analysis of the magnetic data does not indicate any increase of mag-

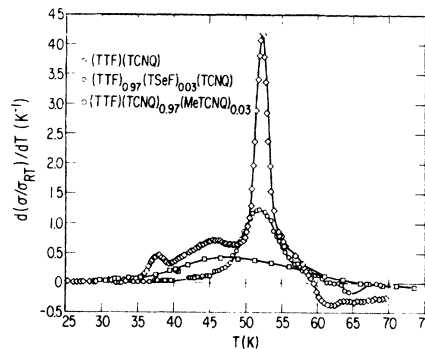


FIG. 6.  $d(\sigma/\sigma_{RT})/dT$  vs  $T$  for pure, donor-doped (3-mole % TSeF), and acceptor-doped (3-mole % MeTCNQ) TTF-TCNQ, a sensitive measure of the position and sharpness of a Peierls transition.

netic activation energy upon doping. Therefore the effect of donor doping on the conductivity is indicative of effects on the mobility. The lowering of the activation energy of the acceptor-doped system is consistent with the magnetic measurements and reflects the smearing of the gap on the acceptor stacks. The nonobservable effects on the mobility are probably related to the negligible contribution of the TCNQ stacks to the conductivity of pure TTF-TCNQ for  $T < 53$  K.

#### IV. DISCUSSION

Let us now consider the picture that emerges from these and earlier experiments about the roles of donor and acceptor stacks in the two phase transitions and in the intermediate- and low-temperature phases of TTF-TCNQ. We list the six principal ideas in this general picture and summarize the evidence leading to each.

*a. Transition at 53 K is a quasi-one-dimensional Peierls transition.* This idea rests first on recent x-ray<sup>4,5</sup> and neutron<sup>6,24</sup> scattering experiments that have demonstrated the existence of a large correlation length along the stacking axis direction at temperatures above 53 K and the development of three-dimensional long-range order below 53 K. The fact that the transition is likely to result from the Peierls instability of the one-dimensional stacks is indicated by the incommensurability of the superlattice and the higher-temperature Kohn anomaly.<sup>5,24</sup> The present experiments add support to the idea of a quasi-one-dimensional Peierls transition in two ways: (a) the anomaly in the conductivity at 53 K is markedly broadened by only a few percent acceptor doping, and (b) the transition temperature appears to be lowered and the TCNQ magnetic activation energy below the transition is significantly decreased by a few percent acceptor doping.

While a genuinely three-dimensional transition would also be sensitive to doping, a quasi-one-dimensional transition is much more sensitive, depending as it does on the development of a sufficiently large correlation length within the 1D stacks (even if interstack couplings are neglected) to insure that the correlated regions on different stacks, although very weakly coupled *per unit length*, will still undergo a 3D cooperative transition. The introduction of impurities can be expected<sup>25</sup> to lower the transition temperature and broaden the transition of a quasi-1D Peierls transition for three reasons: first, through their tendency to pin the phases of Peierls distortions, they limit the correlation lengths to values related to the mean separation between impurities; second, the pinning of phases within stacks at random

values also inhibits the correlation of phases on adjacent stacks, necessary for the development of 3D order; third, by limiting the correlation lengths within stacks, impurities smear the edges of any developing Peierls gap, thereby reducing the tendency of the electron gas to drive a Peierls instability. This latter effect is expected not only to lower the transition temperature but also to result in a smaller Peierls gap at all temperatures below the transition.

*b. 53-K transition is on the TCNQ stacks, not on the TTF stacks.* This idea rests primarily on the previous observation of a large magnetic activation energy on the TCNQ stacks and a small or negligible activation energy on the TTF stacks<sup>11</sup> below 53 K. It was also based on the fact that while a 3% concentration of TSeF broadens the 53-K transition, it does not appear to lower the transition temperature nor does any percentage of TSeF so broaden the transition as to make it undetectable in conductivity measurements.<sup>2</sup> The present experiments give considerable support to this idea because they show acceptor doping to have a much greater effect on the breadth of the transition as well as to lower its temperature markedly.

What may seem surprising is that a TSeF impurity, while presumably inducing only a short-range charge density wave on its TTF stack is able to have as large an effect as it does on the TCNQ stacks. That such an effect should occur is consistent with the notion, advanced earlier,<sup>26</sup> that the conduction-band wave functions of the larger TSeF molecules hybridize much more effectively with the corresponding wave functions of the TCNQ stacks, especially for small percentages of TSeF, at which concentrations the average separation of TTF and TCNQ stacks has not yet grown significantly<sup>27,28</sup> from the separation in pure TTF-TCNQ.

*c. The 38-K transition appears also to be a quasi-one-dimensional transition.* That is, it arises from a rapidly increasing correlation length along the stacks. Earlier evidence for this idea included the broadening of the conductivity anomaly at 38 K and the lowering of its temperature achieved by a few percent donor doping.<sup>2</sup> The idea was also supported by an appreciable amount of mainly one-dimensional order above 38 K. The present experiments add support to this idea in two ways. First, it is seen that small percentages of acceptor doping also broaden the conductivity anomaly. Second, it is seen that both 3-mole% donor and 3-mole% acceptor doping broaden the transition to unobservability, as seen in the donor susceptibility, and lower the donor magnetic activation energy at temperatures below the transition.

*d. The long-range order that develops in the*

38-K transition is on the TTF stacks, and hence is driven by this development. This follows first from the inference above that it is the TTF stacks that fail to have long-range order above 38 K. It was also indicated by earlier experiments<sup>11</sup> that showed an appreciable magnetic activation energy developing on the donor stacks during this transition. The fact that the long-range order that develops is at least on the TTF stacks is confirmed now by the decrease in the TTF magnetic activation energy by doping of the donor stack.

*e. In the intermediate phase, the TCNQ's have long-range 3D order while the TTF's manifest some sort of quasi-one-dimensional fluctuations, presumably with a correlation length that increases with decreasing temperature and with a pseudogap leading to a small magnetic activation energy.* The fact that both donor and acceptor doping have little effect on the donor susceptibility supports this idea, because any decrease in activation energy that such doping might produce would be unobservable. The marked increase in resistivity in this phase with donor doping must then be attributed to a marked increase in the scattering rate of excited holes. Equivalently, the doping of the donor chain can be viewed as increasing the mobility gap and thereby decreasing the number of mobile holes.

*f. Perturbations in the TCNQ stacks have big effects on the TTF stacks, comparable with the effects of perturbations directly in the TTF stacks.* This is in marked contrast to the effect of TTF stack perturbations on the TCNQ stacks. It is also in apparent conflict with the idea that the TTF stacks remain essentially disordered below 53 K, despite the development of a Peierls superlattice on the interleaved TCNQ sublattice. When viewed in terms of a model recently proposed to correlate recent structural experiments with earlier magnetic and electrical experiments,<sup>8</sup> these difficulties become more apparent than real. In that model, it is assumed that both kinds of stacks have a tendency to a Peierls distortion, that of the TCNQ stacks being the larger. When the TCNQ quasi-1D Peierls transition takes place at 53 K, the coupling to the TTF Peierls fluctuations is reduced essentially to zero by the symmetry of the TCNQ superlattice (which has a lattice constant of  $2a$  along  $\vec{a}$ , in turn, a consequence of the much larger amplitude charge density waves on the TCNQ stacks). As the temperature is lowered, this superlattice dimension begins to increase slowly, so that a single phase for the TTF Peierls fluctuations is preferred throughout, and some average order begins to develop throughout, but the fluctuations still interact mostly with themselves, their correlation length growing. Ultimately a

quasi-1D Peierls transition on the TTF sublattice might be expected to take place, broadened by the presence of the ordering field of the TCNQ superlattice. The tendency to this transition is interrupted by a first-order transition in the superlattice when the growing superlattice dimension along  $\vec{a}$  suddenly jumps to  $4a$ . The 38-K transition can therefore be viewed as being driven by the TTF fluctuations, but according to this model it involves the TCNQ stacks in an average way. This is in agreement with the fact that when the Peierls vector characterizing the superlattice changes discontinuously, it describes a change in the superlattice on both donor and acceptor stacks.

Within this model, an impurity on one stack can affect the other stack both directly and also indirectly by inducing order (especially by pinning the phase of the order parameter) on its own stack over some distance, which then acts on the neighboring stacks of the other kind. For donor stack impurities near 53 K, this effect is small, because donor correlation lengths are presumably small, and because the amplitude of the order parameter on the donor stacks is never as large as on the acceptor stacks. For acceptor stack impurities, where correlation lengths and charge density waves are both much larger, this indirect perturbation of the donor stacks can be much larger. This would be the case especially when the effect of the impurity is to break the symmetry associated with superlattice doubling ( $2a$ ) by interrupting the short-range order between TCNQ stacks separated by  $a$ , a symmetry that is so important in decoupling donor fluctuations from the acceptor superlattice at temperatures  $\leq 53$  K. At temperatures nearer 38 K, where the symmetry has already been lost and the TTF and TCNQ charge density waves are weakly coupled, this effect would be weaker, but nevertheless more noticeable through its effect of broadening the 38-K transition.

## V. CONCLUSIONS

Measurements indicating the effect of acceptor and donor doping of similar perturbation strength on the magnetic susceptibility and electrical conductivity of TTF-TCNQ have been presented and interpreted. The measurements support earlier inferences based on magnetic measurements in undoped TTF-TCNQ.

1. The donor and acceptor stacks are to lowest order decoupled in the vicinity of the 53-K transition.
2. The 53-K transition occurs only on the acceptor (TCNQ) stacks, and is therefore driven by these stacks.



3. The 38-K transition, although it involves both kinds of stacks, reflects the development of long-range order (i.e., an infinite correlation length for the Peierls fluctuations) on the TTF stack.

In addition, these results lead to two new conclusions:

4. Doping one stack causes a smearing of the gap and a lowering of the transition temperature associated with that stack, although doping the acceptor stack also affects the gap and transition associated with the donor stack for reasons discussed.

5. Donor doping, in the intermediate phase, reduces the hole mobility while increasing the excited hole concentration on the donor chain.

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- <sup>15</sup>Another attempt to use the second method, i.e., to decompose a combined property, has been carried out by Chaikin *et al.* (Ref. 16). They have measured the total thermoelectric power ("thermopower")  $S$  which is a weighted average of the thermopowers  $S_F$  and  $S_Q$  of the TTF and TCNQ stacks, the weighting factors being the fractional conductivities  $\sigma_F/(\sigma_F + \sigma_Q)$  and  $\sigma_Q/(\sigma_F + \sigma_Q)$  of the two stacks. If there were independent knowledge of  $S_F(T)$  and  $S_Q(T)$ , the thermopower could be used to decompose the total conductivity into the respective contributions of the TCNQ and TTF stacks. Unfortunately, independent knowledge of  $S_F(T)$  and  $S_Q(T)$  is lacking. However for sufficiently high temperatures under some simplifying assumptions both of these quantities are proportional to  $T$ . In this case the sign of the thermopower can give qualitative information as to which stack is dominating the conductivity process.
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