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Electrical conductivity of tetrathiofulvalinium tetracyanoquinodimethan (TTF) (TCNQ)†

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The temperature dependence of the dc electrical conductivity of tetrathiofulvalinium tetracyanoquinodimethan (TTF)(TCNQ) measured along the crystallographic a, b, and c^* axes and the corresponding anisotropies $\sigma_{\parallel}^{b}/\sigma_{\perp}^{a}$ and $\sigma_{\parallel}^{b}/\sigma_{\perp}^{c^*}$ are reported. Standard four-probe measurements are supplemented by applying the technique of Montgomery to the question of inhomogeneous currents in this anisotropic conductor. We have observed that the intrinsic anisotropy contains two maxima which provide a direct internal method for unambiguously testing the validity of four-probe measurements of the conductivity along the principal conducting b axis. The transverse transport properties are diffusive and yield an electrical anisotropy greater than 500 at room temperature which increases to greater than 10^4 near 58 K. The extreme sensitivity of this one-dimensional metal to crystalline imperfections is experimentally demonstrated through temperature cycling studies. The dc results confirm (TTF)(TCNQ) is a one-dimensional metal exhibiting a strongly temperature-dependent b-axis conductivity that reaches maximum values exceeding 10^5 $(\Omega\ \mathrm{cm})^{-1}$. These data are taken as confirming evidence that above 58 K the metallic state exhibits strong electron correlations associated with a many-body collective state in which the conductivity can greatly exceed the limitations of single-particle scattering.

I. INTRODUCTION

The existence of real physical systems which have the properties of one-dimensional metals is of particular interest because of the exciting possibilities[1,2] associated with the instability of the one-dimensional electron gas.[3-5] The pseudo-one-dimensionality of the electronic properties of tetrathiofulvalinium tetracyanoquinodimethan (TTF)(TCNQ) (Ref. 6) has been established experimentally by a variety of measurements.[7-9] As a highly conducting organic metal which remains metallic to relatively low temperatures, this system is at the focus of work directed toward understanding the nature of the metallic state in pseudo-one-dimensional conductors.

In an earlier publication,[10] we reported the discovery of extraordinary maxima in the dc conductivity of the one-dimensional organic metal (TTF)(TCNQ). Standard four-probe measurements along the crystallographic b axis on all samples showed that with decreasing temperature, the conductivity rapidly increases to a maximum value which varies typically from crystal to crystal. The temperature at which the maximum occurs T_M is in the range 58–60 K. Below the maximum, the conductivity suddenly decreases characteristic of a metal-insulator transition. We interpreted these data as evidence for superconducting fluctuations associated with a Peierls instability in which the one-dimensional metallic system becomes unstable toward a phonon mode driven soft by the divergent response of the electron gas at $q=2k_F$. The variation of the conductivity maximum from crystal to crystal we argued was due to the extreme sensitivity of one-dimensional metals such as (TTF)(TCNQ) to crystalline defects, twinning, and impurities. Although less dramatic, the same kind of sensitivity was previously demonstrated in conductivity studies of the pseudo-one-dimensional conductors (NMP)(TCNQ) [N-methyl phenazinium-tetracyanoquinodimethan][11] and $\mathrm{K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O}$.[12] Recently, other experimental studies on (TTF)(TCNQ) have provided independent evidence of strong electron correlations[13,14] and excess dc conductivity in the metallic state above 60 K.[7,8] Optical reflectivity[7,8] and elastic constant[15] studies show that (TTF)(TCNQ) is a strongly coupled electron-phonon system, with the reflectivity measurements yielding a coupling constant $\lambda_{\mathrm{ph}}=1.3$.

Standard four-probe measurements on (TTF)(TCNQ) can be further examined using the techniques of Montgomery[16] and co-workers[17] on highly anisotropic conductors. Montgomery's results can be applied to the question of inhomogeneous currents wherein a nearly zero current density can result at the surface where the voltage leads contact the anisotropic sample. In this method, one purposely uses a lead configuration designed to give a well-defined inhomogeneous current distribution. When the current is applied with the leads aligned parallel to the principal conducting axis, the voltage drop between the opposite two leads is considerably reduced by the anisotropy. The *apparent* conductivity in this configuration is given by[16,17]

$$\sigma_{\parallel}^{\mathrm{app}}=\sigma_{\parallel}(G/A^{1/2})\exp[\pi(l_{\perp}/l_{\parallel})A^{1/2}], \tag{1}$$

where $\sigma_{\parallel}$ $(\sigma_{\perp})$ is the intrinsic conductivity parallel (perpendicular) to the principal axis; $l_{\parallel}$ $(l_{\perp})$ is the corresponding distance between current and voltage leads; A is the anisotropy $\sigma_{\parallel}/\sigma_{\perp}$; and G is a simple geometric factor. The apparent conduc-

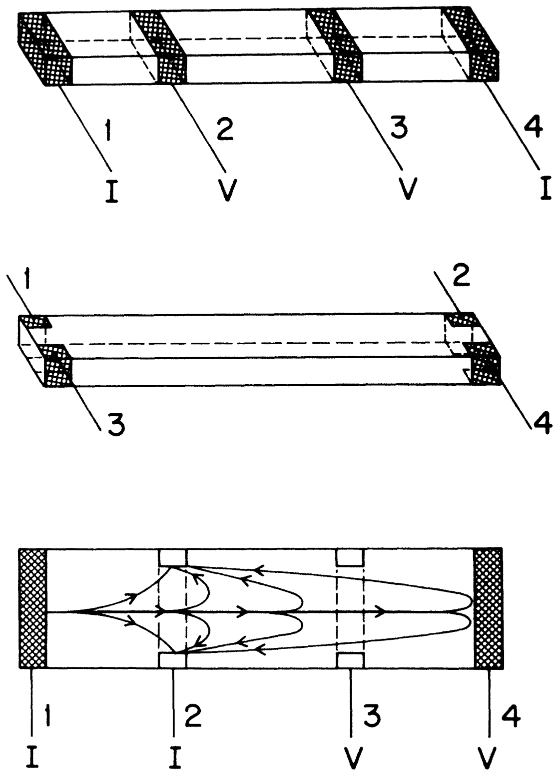


FIG. 1. Schematic diagrams of contact configurations used on single crystals of (TTF)(TCNQ): (a) Standard four-probe configuration; (b) Montgomery configuration; and (c) diagram of current flow induced by lead switching "test."

tivity would then be determined by the magnitude and temperature dependence of the anisotropy $\sigma_\parallel/\sigma_\perp$. Schafer *et al.*[18] have carried out preliminary measurements on (TTF)(TCNQ) down to 70 K using a misaligned configuration to produce a single false conductivity maximum.

We report in this paper measurements of the temperature dependence of the dc conductivity along the crystallographic *a*, *b*, and c^* axes, and the corresponding anisotropies $\sigma^b_\parallel/\sigma^a_\perp$ and $\sigma^b_\parallel/\sigma^{c*}_\perp$. These results provide a direct internal method of unambiguously checking the validity of four-probe measurements of the conductivity $\sigma^b_\parallel$ along the principal conducting *b* axis.

II. EXPERIMENTAL RESULTS

The conductivities were measured by the standard four-probe method, as previously described,[11,12] and by the Montgomery method,[16] as shown in Figs. 1(a) and 1(b). The current and voltage contacts were made with Dupont silver paint.[19] In the standard four-probe measurements [Fig. 1(a)], the current contacts covered the ends of the crystal to assure uniform current distribution, and the voltage contacts were carefully painted completely around the crystal. Currents from 10 to 50 μA were used for the measurements. Contact resistances R_c were typically a few Ω; samples with contact resistance exceeding 10 Ω were considered unsatisfactory and discarded.[20] Figure 2 shows the temperature dependence of the contact resistance. Both the magnitude and temperature dependence suggest that the contact resistance is predominantly a perpendicular spreading resistance. The contacts were ohmic throughout the range 1–100 μA and showed no frequency dependence in the range from dc to 40 kHz.

The transverse conductivities along the *a* and c^* axes, as obtained by four-probe dc methods, are shown in Fig. 3. Normal crystal growth for (TTF)(TCNQ) occurs with the long needle axis of the crystal coincident with the principal conducting (crystallographic *b*) axis of the solid. Single crystals of (TTF)(TCNQ) possessing a transverse habit have been grown in which the long needle axis corresponds to the crystallographic *a* axis [see Fig. 3(a)].[21] This allowed direct measurement by dc and microwave methods[9] of the *a*-axis conductivity. The transverse habit for (TTF)(TCNQ) was identified by carrying out single crystal x-ray studies and verified by polarized optical measurements. As a check on the dc results, the corresponding microwave conductivity[9] was measured along the *a* axis, and the agreement between the dc and ac data is excellent over the entire temperature range [Fig. 3(a)].

The temperature dependences of the anisotropies $\sigma^b_\parallel/\sigma^a_\perp$ and $\sigma^b_\parallel/\sigma^{c*}_\perp$ (Fig. 4) were measured directly using the Montgomery method[16] [see Fig. 1(b)] and

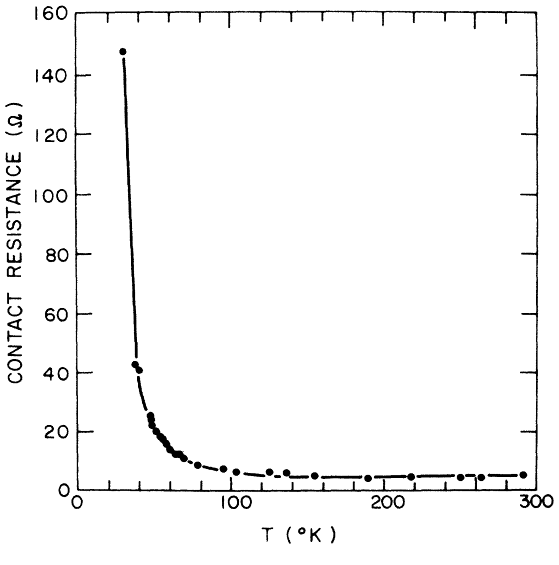


FIG. 2. Temperature dependence of a typical contact resistance for (TTF) (TCNQ).

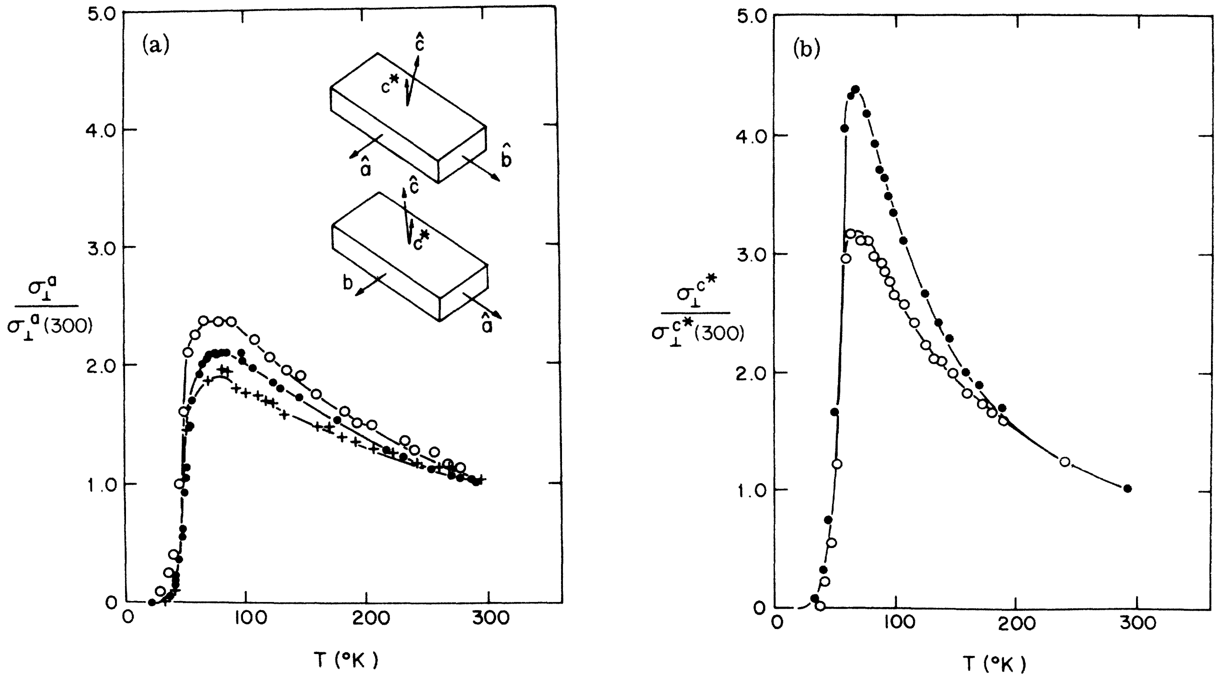
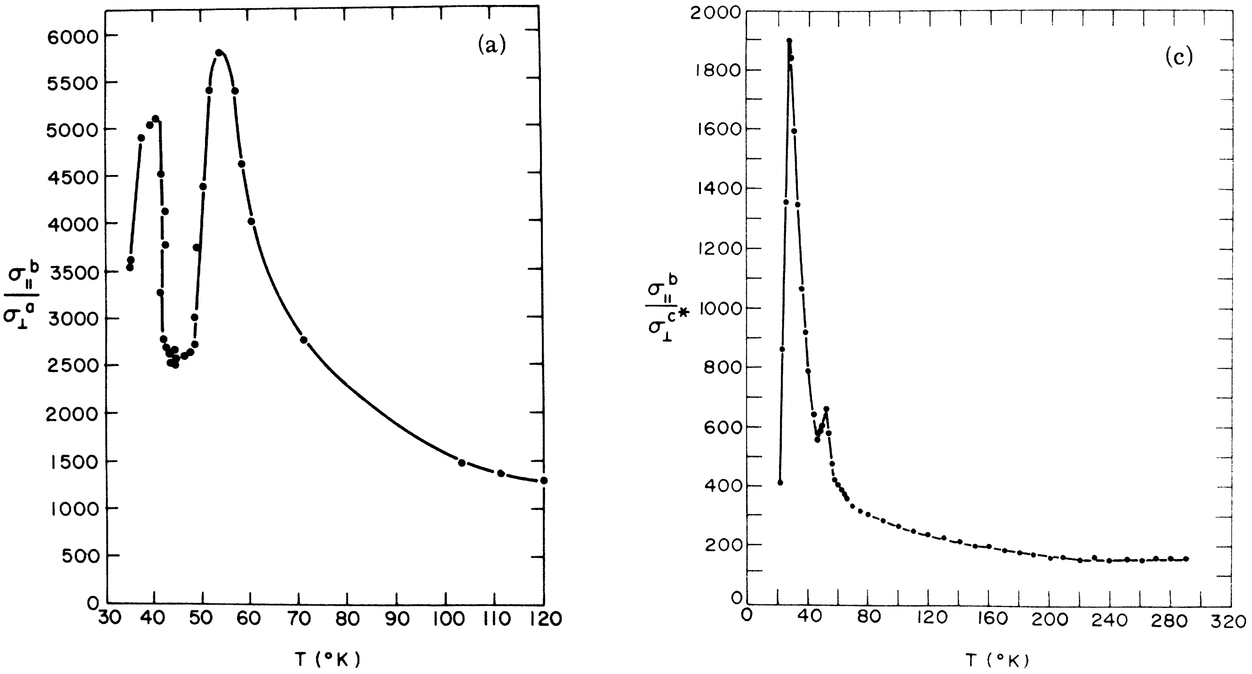


FIG. 3. Temperature dependence of the transverse conductivities normalized to their room-temperature values: $\sigma_\perp^a \simeq 0.5$–1 $(\Omega\ \mathrm{cm})^{-1}$ and $\sigma_\perp^{c*} = 4$–6 $(\Omega\ \mathrm{cm})^{-1}$. (a) $\sigma_\perp^a$ as obtained by the standard four-probe method (-•-•-•-); microwave technique (10 GHz) (-o-o-o-); and Montgometry method (-+-+-+-). The two crystal habits of (TTF) (TCNQ) are shown. (b) $\sigma_\perp^{c*}$ as obtained by the four-probe method (-o-o-o-) and the Montgomery method (-•-•-•-).

independently checked using the ratio of standard four-probe data obtained from different crystals. $\sigma_\parallel^b/\sigma_\perp^a$ exhibits the marked feature of two maxima located near 55 and 40 K. The data for $\sigma_\parallel^b/\sigma_\perp^{c*}$ show a similar low-temperature maximum at 25 K. The b-c^* data [Fig. 4(b)] were obtained from a sample with $\sigma_\parallel^b(T_M)/\sigma_\parallel^b(300) = 8$; for a better sample with $\sigma_\parallel^b(T_M)/\sigma_\parallel^b(300) > 15$ [Fig. 4(c)], a maximum appears in the vicinity of T_M. These maxima originate from the intrinsic temperature dependences of the individual conductivity components. The high-temperature maximum is due to $\sigma_\parallel^b(T)$ reaching its largest values at these temperatures. At lower temperatures, although $\sigma_\parallel^b$ and the transverse conductivities $\sigma_\perp^a$ and $\sigma_\perp^{c*}$ are decreasing, the temperature dependence of $\sigma_\parallel^b$ is different from that of either $\sigma_\perp^a$ or $\sigma_\perp^{c*}$, resulting in a second low-temperature maximum.

Moreover, there exist experimental checks which are internal to the same crystal. The temperature dependences of the normalized conductivity components $\sigma_\parallel^b$, $\sigma_\perp^a$, and $\sigma_\perp^{c*}$ were obtained from the corresponding anisotropy ratios following Montgomery. In each case, the resultant transverse conductivity was in good agreement with data obtained by the standard four-probe method on other crystals (see Fig. 3). $\sigma_\parallel^b$ behaved characteristically from crystal to crystal, exhibiting as usual a common overall temperature dependence but varying in magnitude at the maximum normalized conductivity.

The temperatures of both maxima and the magnitude of the high-temperature maximum are influenced by the magnitude of the maximum normalized b-axis conductivity $\sigma_\parallel^b(T_M)/\sigma_\parallel^b(300)$, which occurs near the metal-insulator transition. For $\sigma_\parallel^b/\sigma_\perp^a$, the maxima can be moved up (down) by 3 K for crystals with smaller (greater) values of $\sigma_\parallel^b(T_M)/\sigma_\parallel^b(300)$. For a crystal with $\sigma_\parallel^b(T_M)/\sigma_\parallel^b(300) \simeq 4.2$, no high temperature maximum occurs in $\sigma_\parallel^b/\sigma_\perp^a$, whereas for crystals with $\sigma_\parallel^b(T_M)/\sigma_\parallel^b(300) \geq 12$, this peak begins to appear. For $\sigma_\parallel^b/\sigma_\perp^{c*}$, the high-temperature peak appears when $\sigma_\parallel^b(T_M)/\sigma_\parallel^b(300) > 15$. The data in Fig. 4(b) correspond to $\sigma_\parallel^b(T_M)/\sigma_\parallel^b(300) \simeq 8$. Figure 4(c) shows the b-c^* anisotropy as obtained from direct measurement of $\sigma_\perp^{c*}$ and $\sigma_\parallel^b$ on different crystals using typical b-axis data where $\sigma_\parallel^b(T_M)/\sigma_\parallel^b(300) = 16$. The double maximum is clearly observed. We consider these data evidence that the low-temperature maximum is determined by the intrinsic difference between the temperature dependence of $\sigma_\parallel^b$ and that of $\sigma_\perp^a$ or $\sigma_\perp^{c*}$ at temperatures well separated from the $\sigma_\parallel^b$ maximum. We note that the preliminary $\sigma_\parallel^b/\sigma_\perp^a$ data reported by



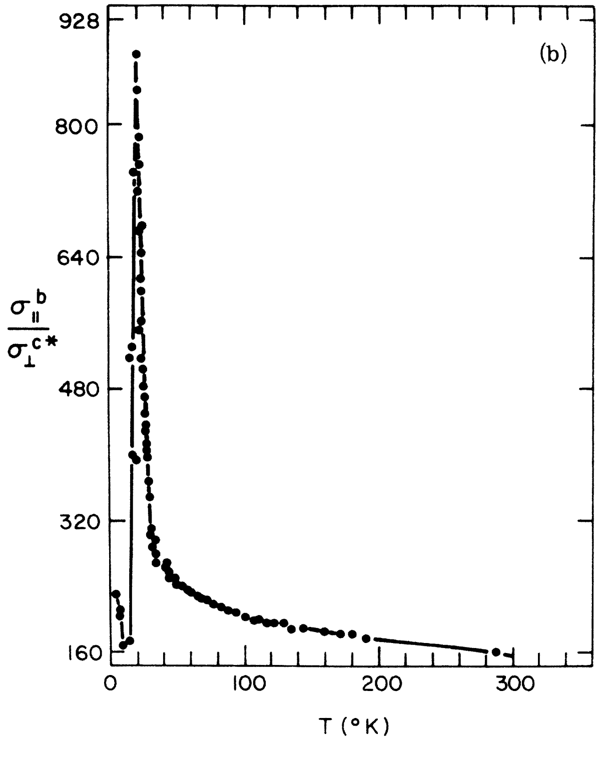


FIG. 4. Anisotropy as a function of temperature. (a) $\sigma_{\parallel}^{b}/\sigma_{\perp}^{a}$ showing the double maximum, $\sigma_{\parallel}^{b}/\sigma_{\perp}^{a}(300) \simeq 500$; (b) $\sigma_{\parallel}^{b}/\sigma_{\perp}^{c*}$ using Montgomery's technique on a cyrstal with $\sigma_{\parallel}^{b}(T_M)/\sigma_{\parallel}^{b}(300) \simeq 8$. The room-temperature value is approximately 160: (c) $\sigma_{\parallel}^{b}/\sigma_{\perp}^{c*}$ obtained directly from the ratio of $\sigma_{\perp}^{c*}$ and $\sigma_{\parallel}^{b}$ with $\sigma_{\parallel}^{b}(T_M)/\sigma_{\parallel}^{b}(300) = 16$.

Schafer *et al.*[18] extend down only to 50 K, so that they were unable to observe the second low-temperature maximum near 40 K. We conclude that the two maxima are intrinsic properties of the anisotropy of pure (TTF)(TCNQ).

The experimental observation of double maxima in the anisotropies can be used as a convenient internal check on the validity of $\sigma_{\parallel}^{b}(T)$ four-probe measurements. We have generated false giant conductivity maxima using a completely misaligned lead configuration similar to that used by Schafer *et al.*, which is nothing more than a slightly modified Montgomery configuration. Data for the *b*-*a* configuration are shown in Fig. 5 along with the *b*-*a* data down to 70 K of Ref. 18.[22] The fact that the anisotropy dominates the measurements is clearly signified by the double maximum in the false conductivity. To demonstrate the one-to-one relation between the anisotropy and the false conductivity, we note that the data on Fig. 5(a) can be generated from the *b*-*a* anisotropy [Fig. 4(a)] using Montgomery's analysis. Thus, whenever there is structure in the anisotropy, there will be corresponding structure in the apparent conductivity using the misaligned contact configuration. Equivalent false conductivity curves appropriate to the *b*-*c** configuration have been generated numerically from the *b*-*c** anisotropy data shown in Fig. 4(c). The structure in $\sigma_{\parallel}^{b}/\sigma_{\perp}^{c*}$ between 40 and 50 K always results in similar structure in σ_{apparent} whenever significant anisotropy related enhance-

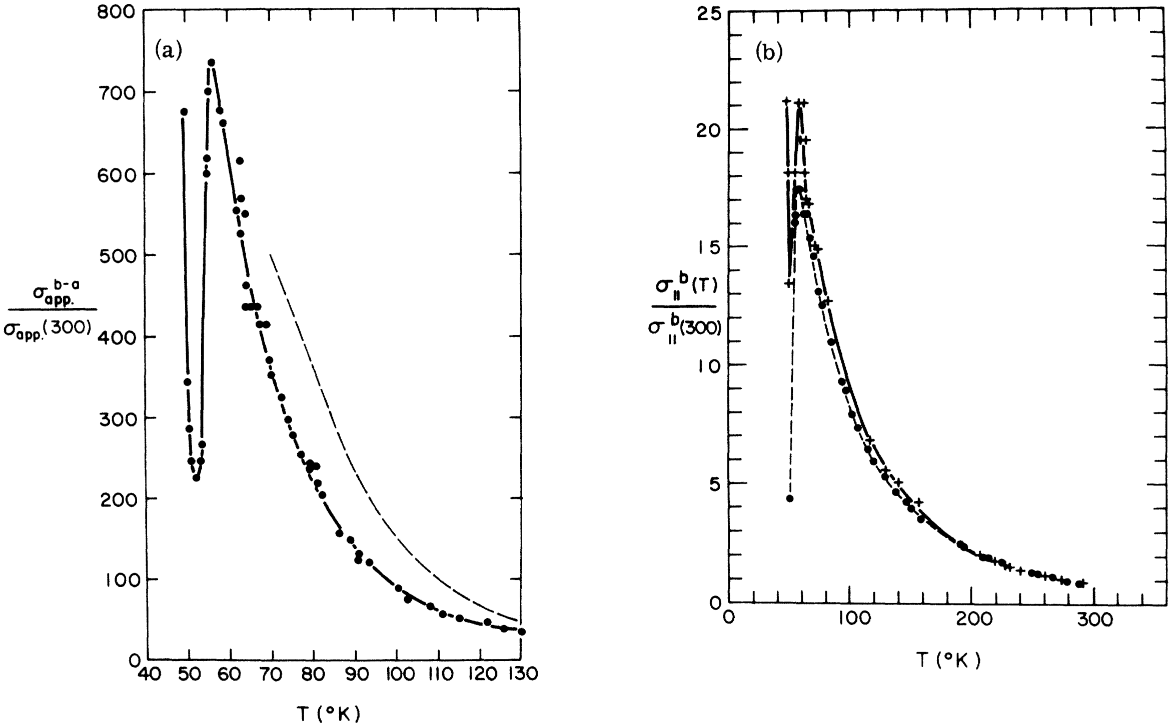


FIG. 5. (a) Apparent conductivity resulting from misaligned contacts in the *b*-*a* plane. Note the clear signature of the double maximum of the *b*-*a* anisotropy. The dashed curve corresponds to the data of Ref. 18. (b) Standard four-probe conductivity on a (TTF)(TCNQ) single crystal showing the sensitivity to anisotropy distortions of the data. An enhancement of the peak by only 20% carries the signature of the second maximum in the anisotropy (see text).

ment is present. In general, the *b*-*a* anisotropy enhancement is expected to dominate rather than the *b*-c^* enhancement, since the sample thickness along c^* is approximately an order of magnitude smaller than the width along *a*, and the measured ratio $\sigma_\parallel^b/\sigma_\perp^{c*}$ is smaller than the corresponding *b*-*a* ratio. However, since $\sigma_\parallel^b/\sigma_\perp^a$ and $\sigma_\parallel^b/\sigma_\perp^{c*}$ each show the characteristic double maximum, inhomogeneous currents of any origin will always result in corresponding structure in the apparent conductivity. Correspondingly, the absence of such structure in the range from 40 to 50 K provides an internal test of the validity of four-probe *b*-axis data.

In samples containing a large number of defects, inhomogeneous current distributions naturally give rise to non-uniform surface equipotential lines. The same false double maximum produced by lead misalignment (Fig. 5) has also been produced in defective samples purposely selected for studying inhomogeneous currents using the standard lead configuration.

The sensitivity of the double anisotropy maxima as a self-consistent check on the validity of $\sigma_\parallel^b$ data is illustrated in Fig. 5(b). On the first temperature run, a value of $\sigma_\parallel^b(T_M)/\sigma_\parallel^b(300) = 17.5$ was obtained, which was enhanced to 21.0 on a subsequent run. Cycling the crystal in this case damaged the contacts and allowed the anisotropy to affect the measurements. The data show that even a slight enhancement due to inhomogeneous currents is accompanied by the clear signature of the second peak in the data near 40 K.

We note that similar maxima have been observed in two recent studies of the pressure dependence of $\sigma_\parallel^b$ for (TTF)(TCNQ) reported by Chu *et al.*[23] and Jerome *et al.*[24] Both sets of data contain evidence of two maxima in the metal-insulator transition region, and both studies accepted their presence as direct evidence for two transitions taking place in (TTF)(TCNQ). Comparison of these data with those of Fig. 5 demonstrates that the pressure data are not intrinsic to the *b* axis, and points out the real experimental hazards in four-probe measurements. Craven *et al.*[25] have reported specific-heat studies in the transition region and observed only a single peak in the specific heat, not two.

Both pressure studies[23,24] reported using a lead switching test suggested by Schafer *et al.*[18] to guard against inhomogeneous current distributions. The test consists of applying current through two leads [1 and 2 on Fig. 1(c)] on one end of the crystal while measuring the voltage drop on the other

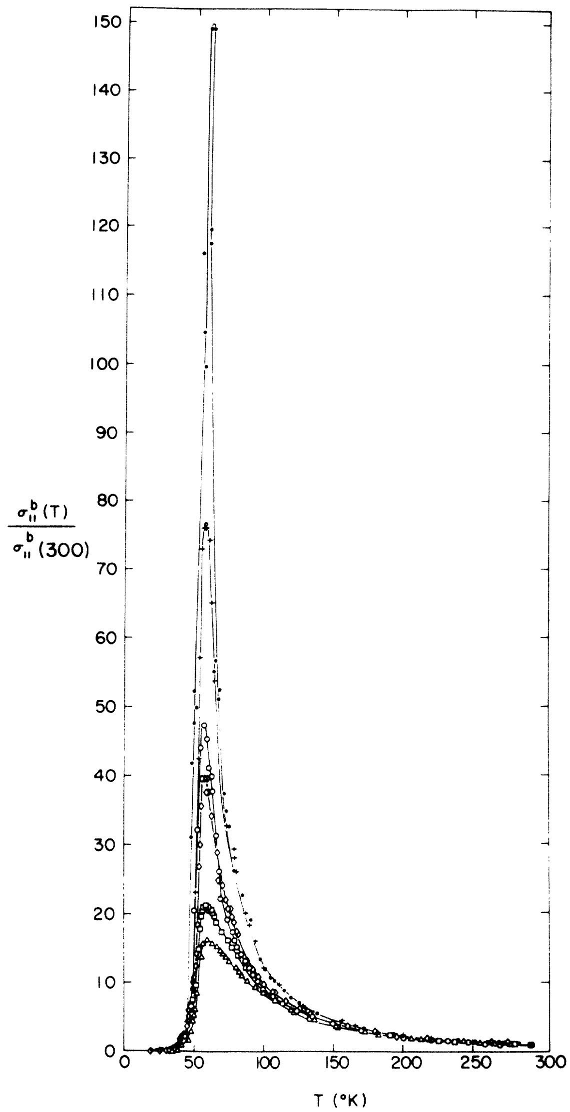


FIG. 6. Normalized four-probe data showing the *b*-axis conductivity as a function of temperature. There is no trace of a second low-temperature maximum.

end (3 and 4). Schafer *et al.*[18] assert that a nonzero voltage reading implies the data are invalid. Although correct for an isotropic conductor, this "test" is invalid in the presence of high anisotropy as shown schematically in Fig. 1(c). With anisotropies in excess of 10^3, the "test" configuration grossly distorts the current flow pattern with current lines running virtually all the way to the end of the crystal before looping back to the second contact. This kind of flow pattern has been observed in model resitor networks. Using the four-probe lead configuration shown in Fig. 1(c), a negative voltage drop is expected across 3 and 4, and indeed has been observed in a variety of typical crystals where $\sigma_{\parallel}^{b}(T_M)/\sigma_{\parallel}^{b}(300) < 20$. Thus, lead switching "tests" are misleading, and their usefulness is limited to testing only the Ohmic behavior of the sample and contacts through the reciprocity theorem.

Schafer *et al.* have furthermore proposed that the best contact configuration for dc conductivity measurements consists of four point contacts in line. Aside from the obvious difficulties in achieving precise alignment, we note that from Eq. (1), the measured (apparent) conductivity would be *reduced* by the square root of the anisotropy, $A(T)^{1/2}$. Thus, the point-contact technique utilized by Schafer *et al.* measures the temperature dependence of the geometric mean $(\sigma_{\parallel}\sigma_{\perp})^{1/2}$, and thereby seriously underestimates the *b*-axis conductivity. Applying the Montgomery analysis of Eq. (1) (with $l_{\perp}/l_{\parallel} = 0$) to the published data of Schafer *et al.* (Fig. 4 of Ref. 18) together with the known temperature dependence of $\sigma_{\perp}^{a}$, yields $\sigma_{\parallel}^{b}(T_M)/\sigma_{\parallel}^{b}(300) \simeq 40$.

Normalized four-probe dc conductivity data $\sigma_{\parallel}^{b}(T)/\sigma_{\parallel}^{b}(300)$ are given in Fig. 6. We find these results intrinsic to (TTF)(TCNQ) undistorted by anisotropy-related effects. Included are data which reach peak normalized values of 17, 21, 40, 48, 75, and 150. The normalized conductivities are nearly identical over the temperature range from 300 down to 140 K, where, for crystals which show larger values of $\sigma_{\parallel}^{b}(T_M)/\sigma_{\parallel}^{b}(300)$, the conductivity continues to increase with decreasing temperature while the lower values successively nest underneath. Each crystal cleanly undergoes the metal-insulator transition near 58 K, and $\sigma_{\perp}^{b}/\sigma_{\parallel}^{b}(300)$ sharply decreases below 58 K. *There is no trace of a second low-temperature maximum arising from anisotropy effects, and all the data are qualitatively different from the false conductivity data shown in Fig.* 5. The room temperature values were all in the typical range from 500 to 1000 $(\Omega\ \mathrm{cm})^{-1}$. The earlier data[10] with $\sigma_{\parallel}^{b}(T_M)/\sigma_{\parallel}^{b}(300) \simeq 500$ does not extend to sufficiently low temperatures to definitively test for anisotropic enhancements. However, we note that the temperature dependence of the previous data[10] above 60 K is the same as that for the best sample shown in Fig. 6. As another diagnostic test, $\sigma_{\parallel}^{b}(T)$ was measured as a function of frequency up to 40 kHz. In contrast to well-known frequency dependent conductivities observed for doped semiconductors[26] and for doped ferroelectrics exhibiting PTC anomalies,[27] no frequency dependence was observed for the (TTF)(TCNQ) samples, including those which exhibited large conductivities. In all cases, the measured resistances were Ohmic through 100 μA.

The value of the maximum normalized conductivity $\sigma_{\parallel}^{b}(T_M)/\sigma_{\parallel}^{b}(300)$ varies from crystal to crystal, and, as suggested in our earlier publication,[8–10] is associated with the extreme sensitivity of one-di-

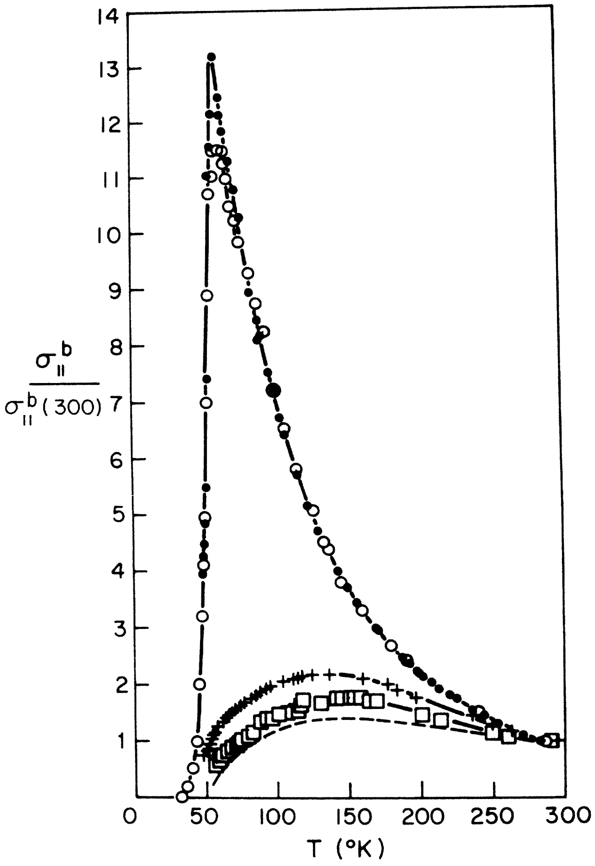


FIG. 7. Cycling experiment showing degradation of the conductivity maximum: (-•-•-•-) first cycle [$\sigma(300) = 685 (\Omega\ \mathrm{cm})^{-1}$]; (-o-o-o-) fourth cycle [$\sigma(300) = 685 (\Omega\ \mathrm{cm})^{-1}$]; (-+-+-+-) sixth cycle [$\sigma(300) = 325 (\Omega\ \mathrm{cm})^{-1}$]; (-□-□-□-) eighth cycle [$\sigma(300) = 165 (\Omega\ \mathrm{cm})^{-1}$]; and (------) polycrystalline data.

mensional metals to crystalline defects, twinning, and impurities. The intrinsic anisotropy $\sigma_{\parallel}^{b}/\sigma_{\perp}^{a} \gg 10^4$ near 58 K makes (TTF)(TCNQ) extremely sensitive, and crystal perfection at the level of parts per million is required, for any defects will either remove a given chain altogether, force carriers to tunnel through the defect, or force transverse current flow between chains. We note, further, that the strain field around a defect can be expected to be effective in scattering both electrons and $2k_F$ phonons in a narrow band anisotropic solid. An extreme example of crystal imperfection limiting the maximum conductivity is presented in Fig. 7, where $\sigma_{\parallel}^{b}/\sigma_{\parallel}^{b}(300)$ for a single crystal temperature cycled several times from 300 to 50 K becomes essentially equivalent to that of a polycrystalline compaction in the final cycle. This kind of degradation is commonly observed, with the highest conductivity specimens being particularly sensitive.

Moreover, the data of Fig. 7 show that with increasing degradation, the temperature at the conductivity maximum T_M shifts away from 59 K to higher temperatures. Values of T_M have been reported which are higher[18,28–31] (up to 72 K) than the 58 K reported in this study. Poehler *et al.*[31] have concluded that the highest T_M measured (72 K) is the intrinsic value. However, our results indicate that $T_M = 58$ K is the intrinsic value for (TTF)(TCNQ). Along with the degradation experiments, we have found that our purest samples consistently give $T_M = 58$–59 K, whereas crystals prepared from unpurified starting materials as well as crystals exposed to air for long periods of time (of order of weeks) show $T_M > 60$ K. A value for T_M near 58 K is further supported by numerous independent experiments ranging from studies of the specific heat[25] and thermopower[13] to susceptibility[14] and far infrared properties[32] which show the metal-insulator transition is below 60 K with nothing taking place at 72 K.

The absolute value of the intrinsic room-temperature conductivity is required, since it sets the scale for all the data. Measurements from a large number of crystals yield an average value of 550 $(\Omega\ \mathrm{cm})^{-1}$, with values ranging to above 10^3. The measured crystals contain microcrystalline imperfections, from imperfect growth or sample handling and mounting, which leads to smaller effective cross-sectional areas than inferred from the actual dimensions. Thus, the intrinsic value of $\sigma_{\parallel}^{b}(300)$ is greater than the unrestricted average. Direct evidence comes from the fact that for crystals with room temperature values differing by a factor of 5, the normalized temperature dependences $(150 < T < 300\ \mathrm{K})$ are identical. The maximum room-temperature value obtained with contactless microwave measurements is 1000 $(\Omega\ \mathrm{cm})^{-1}$, where the true microwave value is necessarily higher since edge and corner effects enhance the internal field over that for a simple ellipsoid. We conclude that the intrinsic value of $\sigma_{\parallel}^{b}(300)$ is approximately 10^3 $(\Omega\ \mathrm{cm})^{-1}$.

III. DISCUSSION

The transverse conductivities along the *a* and *c** axes are diffusive and yield an anisotropy greater than 500 at room temperature which increases to greater than 10^4 near 58 K. From the crystal structure[33] and general electronic properties of (TTF)(TCNQ), the tight-binding transfer integrals associated with *interchain* coupling are expected to be small. Thus the bandwidths associated with vectors along the *a* and *c** axes should be much less than that associated with the *b* axis, and the effective mass correspondingly anisotropic. Transport in such narrow bands (i.e., $W_a < W_c < k\Theta_D$, where Θ_D is the Debye temperature) is not metallic but diffusive,[34] being severely limited by phonon thermal disorder. That a diffusion-theory[9] approach to the transverse conductivity is necessary can be seen from an estimate of the mean free path Λ along the a and c^* axes. Using the measured conductivity and the known electron density, one estimates from tight-binding theory[11] $\Lambda < 0.01$ Å. The estimated value for Λ is much less than one lattice constant, which suggests that the carriers do not propagate as in a metal but remain on a given chain for relatively long times, eventually hopping from one chain to the next in a diffusive manner. The transport properties thus support the treatment of (TTF)(TCNQ) as a one-dimensional metal in which the transverse transport is severely inhibited by the weak interchain coupling and the relatively strong electron-phonon interaction. These results are consistent with the remarkable anisotropy obtained for the low-temperature dielectric constants[9] $\epsilon_1^b/\epsilon_1^a \simeq 500$, where, even in the insulating state, the oscillator strength is principally along the b axis.

The dc results thus confirm (TTF)(TCNQ) as a one-dimensional metal exhibiting a strongly temperature-dependent b-axis conductivity that reaches maximum values exceeding 10^5 $(\Omega\ \mathrm{cm})^{-1}$. Given the existence of this strong temperature dependence and the giant conductivity maximum, the fundamental question is whether a collective many-body effect is involved in which single-particle scattering is inhibited. The peak value itself implies a mean free path greater than 100 lattice constants, a value which is surely unusual and difficult to understand for a soft[35] narrow band solid[7,8,13] at the temperatures in question. Moreover, comparison of the temperature dependences and magnitudes of the optical and dc conductivities[8] above 58 K demonstrates the existence of excess dc conductivity not limited by single-particle scattering in that the *residual* single-particle mean free path due to strains and defects never exceeds five lattice constants, even in our purest material. Recent specific-heat studies[25] at the metal-insulator boundary have confirmed our analysis[6,9,10,14] that (TTF)(TCNQ) undergoes a second-order phase transition. In general, in a system undergoing a continuous phase transition, fluctuations cause extra scattering resulting in a decreased conductivity, not a dramatic increase as observed in (TTF)(TCNQ). Thus, we conclude that there are strong electron correlations that lead to a collective many-body enhancement of the conductivity.

Without the dc and optical results as well as the related microwave data, there is little experimental justification for asserting the existence of such correlations. The data of Bloch, Cowan, and coworkers[18,28–31] on unpurified materials[36] do not exhibit the enhanced dc and microwave properties[9] intrinsic to pure (TTF)(TCNQ). The modest magnitude and temperature dependence obtained in their studies led Bloch *et al.*[30] to conclude that (TTF)(TCNQ) behaved simply as a metal with a T^2 temperature dependent conductivity[29] as emphasized by Patton and Sham.[37]

The strong electron correlations in the metallic state may result from superconducting fluctuations associated with either BCS pairing[38] or a giant density wave mechanism like that of Fröhlich[1,39] above a mean-field transition; or, alternatively, from fluctuations in the collective state of the one-dimensional system well below the mean-field transition. Lee, Rice, and Anderson[40] have demonstrated that the Fröhlich giant density wave mechanism can lead to enhanced conductivity, contrary to the results of Patton and Sham.[37]

Analysis of the temperature dependence of the spin susceptibility[14] above 58 K yields a mean-field transition temperature $T_p = 450 \pm 50$ K. Moreover, Anderson *et al.*[41] argued in general that conductivities of the observed magnitude in a one-dimensional system cannot be obtained unless the system is well below the mean field transition temperature T_p. Thus, we compare the temperature dependence of the conductivity with the expression suggested by Anderson, Lee, and Saitoh[41] for $T < T_p$.

In an attempt to obtain the temperature dependence of the intrinsic b-axis conductivity, we schematically represent the effects of crystalline imperfections and impurities by a temperature-independent resistance (R_s) in series with the intrinsic resistance; i.e., $R_{\mathrm{measured}} = R_{\mathrm{intrinsic}} + R_s$. Since considerable variation of R_s with temperature and from chain to chain is expected, the simple model is a rough approximation. However, using the value of R_s as the single free parameter, all of the data of Fig. 6 may be fit to

$$\sigma = \sigma_0 (T/T_p) e^{T_p/T}\,, \tag{2}$$

with $T_p = 525 \pm 50$ K.[41,42] The temperature dependences of the conductivities (from Fig. 6) having values of $\sigma_\parallel^b(T_M)/\sigma_\parallel^b(300)$, which range from 16 to 150 are replotted in Fig. 8 in the form of Eq. (2). The agreement between the various data on Fig. 8 suggests that the same conductivity mechanism is operating in all samples. For comparison, we show the false conductivity generated by Schafer *et al.*,[18] which differs qualitatively from the intrinsic b-axis data.

With this picture, the Peierls transition occurs at a temperature of order 500 K. However, there is clearly another characteristic temperature in the problem, the phase transition near 58 K. Following the proposal of Lee, Rice, and Anderson,[43] we suggest that the 58-K transition is probably three-dimensional ordering in which interchain coupling pins the two sets of chains and leads to

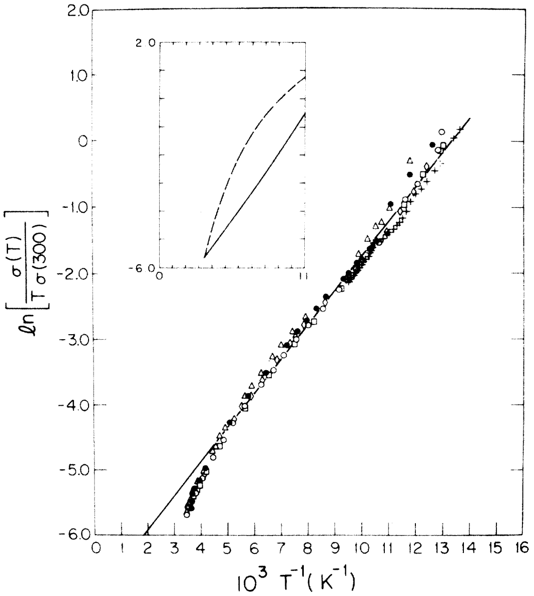


FIG. 8. Data of Fig. 6 replotted in the form of Eq. (2). In each case, a series resistance is assumed (see text). The results are consistent with the expression of Anderson Lee, and Saitoh with $T_p = 525 \pm 50$ K. Inset shows the false conductivity data (dashed line) of Ref. 18 plotted in the form of Eq. (2) with $T_p = 525$ K. The fact that the data line lies entirely above the theoretical line and is concave downward means that it cannot be fit to this curve with only R_s as a free parameter. The inset is plotted with the same axes as the main figure.

the small energy gap observed at low temperatures. The spin susceptibility[14] and dielectric constant[9] results indicate a low-temperature energy gap which renormalizes continuously to zero as T approaches 58 K. For $T > 58$ K, the temperature dependence of the spin susceptibility suggests a two-chain model with one set of chains (probably TCNQ)[14] in the Peierls-Fröhlich state well below the mean-field temperature.

IV. CONCLUSION

We have observed that the intrinsic anisotropy of (TTF)(TCNQ) contains two maxima which provide a sensitive internal test for the validity of $\sigma_{\parallel}^{b}(T)$ data. In case of inhomogeneous current distribution due to poor contacts or crystal defects and cracks, the false anisotropy enhanced conductivity exhibits two maxima while the temperature dependence above 60 K is distinctly different from $\sigma_{\parallel}^{b}(T)$ data. With reasonable care in constructing contacts to well-formed crystals, such effects can be avoided so that four-probe measurements of $\sigma_{\parallel}^{b}$ can be trusted. We will separately report contactless rf and microwave measurements in progress to supplement the dc data.

We have taken considerable care in obtaining materials of the highest purity. Gradient sublimation techniques,[9,44] together with handling the materials and chemical reactions (using quartz or Teflon ware[14]) under inert atmosphere, lead to high-purity (TTF)(TCNQ). Nevertheless, within a given batch of crystals, there is considerable variation in $\sigma_{\parallel}^{b}(T_M)$. Thus, although necessary, high purity is not sufficient, and crystal perfection becomes the limiting factor. This sensitivity of the peak conductivity to crystal imperfections is suggestive of the Fröhlich mechanism wherein the $2k_F$ phonon mean free path limits the conductivity.

In conclusion, the conductivity studies reported here confirm that (TTF)(TCNQ) above 58 K is a one-dimensional metal with strong electron correlations associated with a collective state in which the conductivity can greatly exceed the limitations of single-particle scattering. Because of the lack of long-range order in one-dimension and the existence of dissipative processes for the giant density wave mechanism, true persistent currents cannot be expected. However, the existence of enhanced conductivities[45,46] in a new class of materials,[47] one-dimensional metals, can be anticipated.

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[22] Schafer *et al.* (Ref. 18) report an apparent room-temperature conductivity of 5000 $(\Omega\ \mathrm{cm})^{-1}$ due to misaligned contacts. Because the room-temperature anisotropy intrinsic to crystals grown in our laboratory exceeds 500 in contrast to the value of 60 reported by Schafer *et al.*, the apparent (false) conductivity in the misaligned lead configuration is 5×10^4 $(\Omega\ \mathrm{cm})^{-1}$. We have never observed four-probe room-temperature conductivities of this magnitude; the data shown in Fig. 6 corresponds to measured room-temperature values below 10^3 $(\Omega\,\mathrm{cm})^{-1}$.

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