teractions in ion-implanted samples, which is widely practiced now, this work indicates the need for caution in ascribing the observation of unique final sites of impurities automatically to substitutional lattice sites. The effectiveness and value of combining lattice-location techniques with hyperfine-interaction studies is clearly brought out with renewed emphasis.

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†Present address: Department of Physics, University of Saskatchewan, Saskatoon, Canada.

[1] P. Raghavan, E. N. Kaufmann, R. S. Raghavan, E. J. Ansaldo, and R. A. Naumann, to be published.

[2] J. A. Davies, in *Channeling*, edited by D. V. Morgan (Wiley, New York, 1973), p. 392.

[3] The obvious exceptions to this are light elements of the first and second periods which are known to form interstitial compounds with the heavier metals.

[4] P. Raghavan, R. S. Raghavan, and E. N. Kaufmann, Phys. Lett. 48A, 131 (1974); R. S. Raghavan, P. Raghavan, and E. N. Kaufmann, Phys. Rev. Lett. 31, 111, 802(E) (1973).

[5] E. N. Kaufmann, P. Raghavan, R. S. Raghavan, K. Krien, and R. A. Naumann, Phys. Status Solidi (b) 63, 719 (1974).

[6] W. Hume-Rothery, *Elements of Structural Metallurgy*, Institute of Metals Monograph and Report Series No. 26 (Institute of Metals, London, 1966), p. 50.

[7] F. W. deWette and G. E. Schacher, Phys. Rev. 137, A78, A92 (1965), and references therein.

[8] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958), and supplements I and II thereof.

[9] Ref. 6, p. 116.

[10] P. Sigmund, Appl. Phys. Lett. 25, 169 (1974).

Low-Temperature Metallic Behavior and Resistance Minimum in a New Quasi One-Dimensional Organic Conductor*

A. N. Bloch,† D. O. Cowan, K. Bechgaard,‡ R. E. Pyle, and R. H. Banks
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

and

T. O. Poehler
Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland 20910

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The dc and microwave conductivities of the new organic charge-transfer salt hexamethylene-tetraselenafulvalinium tetracyanoquinodimethanide (HMTSF-TCNQ) remain metallic in magnitude to temperatures at least as low as 1.1 K. At low T we observe a resistance minimum and thermoelectric anomaly consistent with the theoretical result that density fluctuations can enhance the resistivity of a one-dimensional metal as $T \rightarrow 0$. Implications for $(SN)_x$ and tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) are discussed.

We report the first organic material which behaves electrically as a metal throughout the temperature range 1.1–300 K. The new compound hexamethylene-tetraselenafulvalenium tetracyanoquinodimethanide (HMTSF-TCNQ) (Fig. 1) is an addition to the class of quasi one-dimensional conductors based upon the prototype TTF-TCNQ.[1]

The synthesis and chemistry of HMTSF-TCNQ are presented elsewhere.[2] Electronically, the new donor molecule is indistinguishable from its tetramethyl analog, TMTSF,[3] whose triclinic TCNQ salt becomes insulating below 70 K.[4] Sterically, however, the larger, nonplanar HMTSF is incompatible with the crystal structure[4] of TMTSF-TCNQ. Instead, HMTSF-TCNQ is nearly orthorhombic,[5] with a density of chains per unit area about 20% lower than that of TTF-TCNQ. The structure is disordered along one principal direction perpendicular to the stacking axis.[6] The higher symmetry, reduced interchain

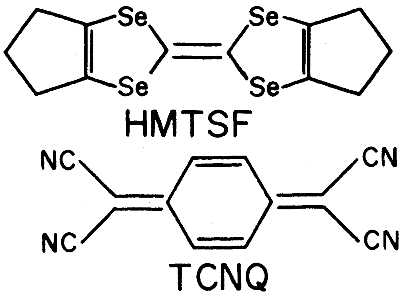

FIG. 1. Molecular structures of HMTSF [hexamethylene-tetraselenafulvalene, or $\Delta^{2,2'}$-*bi*-(4, 5-trimethylene-1, 3-diselenole)] and TCNQ (7, 7, 8, 8-tetracyano-*p*-quinodimethane).

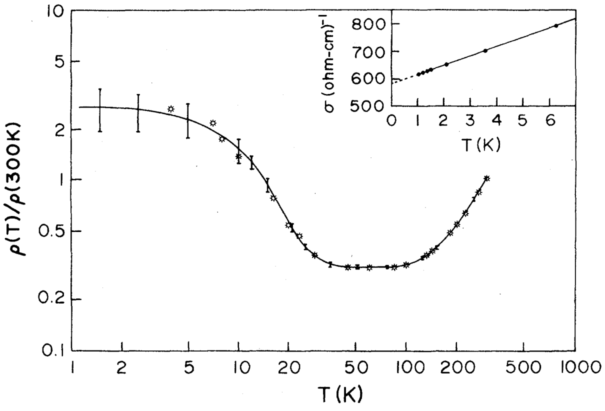

FIG. 2. Normalized dc (solid line) and microwave (*) resistivities of HMTSF-TCNQ. Error bars represent standard deviations among nine crystals. Inset: dc conductivity of a typical crystal extrapolated to $T=0$.

coupling, and lack of three-dimsnsional long-range order suggest natural rationalizations for suppression of the insulating state.

The room-temperature dc conductivity of HMTSF-TCNQ is the largest of any known organic substance. Measurements[7] ranged from 1391 to 2178 Ω^{-1} cm^{-1}, with no distinction between two separately synthesized crystal batches. This spread is within our error in measuring the sample dimensions (typically 3.5 mm×0.04 mm ×0.02 mm), and we correct by normalizing the resistivity $\rho(T)$ for each crystal to its room-temperature value. The average result for nine typical samples is plotted in Fig. 2, with error bars representing standard deviations at selected temperatures.

With cooling from 300 K, $\rho(T)$ drops rapidly. Below 110 K, however, the curve flattens and passes through a broad minimum between 45 and 75 K, where the conductivity is about 3.4 times its room-temperature value. With further cooling the resistivity rises again, but extrapolation from 1.1 K to $T=0$ (inset) yields values still in the metallic range. We observe no hysteresis in $\rho(T)$ during thermal cycling.

In close agreement with the dc results is the normalized microwave resistivity at 10 GHz,[8, 9] presented in Fig. 2 for two additional crystals. The microwave dielectric constant remains large and negative, as for a metal, throughout the temperature range.

The resistivity appears to consist of at least two distinct contributions. Above 100 K, the normalized curves are remarkably reproducible, with standard deviation about 1%. We take this behavior to be intrinsic. In contrast, the standard deviation below 45 K rises to more than 25%, with variations of nearly a factor of 4 among individual samples.[10] Here we presume that conduction is limited by impurities[11] and lattice defects. The simplest inference is that $\rho(T)$ is everywhere the sum of an intrinsic part which decreases and an "impurity" part which increases as the temperature is lowered, forming the minimum at their crossing point.

Recent data[12, 13] for the quasi one-dimensional inorganic polymer $(\mathrm{SN})_x$ invite similar analysis. Consistent with this interpretation, the minimum becomes shallower and moves to higher temperatures with deteriorating sample quality.[12, 13]

By least-squares analysis we find that with correlation coefficient 0.999 96, the intrinsic resistivity of HMTSF-TCNQ above 110 K is described by

$$\rho(T)/\rho(300\ \mathrm{K}) = a + bT^{\gamma}, \qquad (1)$$

where $a=0.264$, $b=8.84\times10^{-7}$, and $\gamma=2.39\pm0.01$. Previous studies have shown that the high-temperature resistivities of other compounds in this class also obey Eq. (1), with $\gamma=2.33\pm0.14$ (TTF-TCNQ),[14] 2.34 ± 0.04 (TMTTF-TCNQ),[15] and 2.4 ±0.2 (TMTSF-TCNQ).[4]

From the trend in the coefficient b, which decreases with increasing molecular weight, we infer that the second term in (1) is phonon dominated. For a simple one-dimensional metal above the Debye temperature, the usual one-electron–acoustic-phonon interaction leads to a resistivity proportional to T, as observed[12] in $(\mathrm{SN})_x$. We suspect, then, that the large γ found for our materials is not a general feature of the one-dimensional metallic state, but rather a peculiarity of the two-band[8, 16, 17] organic systems. A strong temperature dependence for the phonon part of the resistivity is expected if the density of electronic states is strongly energy dependent near the Fermi level,[16] as implied by approximate band-structure calculations,[17] or if low-lying intramolecular optical modes play an important role in the scattering, as suggested by recent spectroscopic results.[18] In any event this contribution should become exponentially small in the low-temperature regime, as the short-wavelength phonons responsible for the resistivity are forzen out.

The strong temperature dependence of the impurity resistance below 45 K is less easy to rationalize. Special energy dependences for the density of states or scattering potential are possible, but unlikely to recur in systems so disparate chemically as $(SN)_x$ and HMTSF-TCNQ. Further, at low temperatures the apparent mean free path in both materials typically falls to about 1 lattice constant, too small to arise from simple scattering by any reasonable concentration of defects or impurities.

On the other hand, Fukuyama *et al.*[19] have argued that the divergence of the electronic polarizability at $q=2k_F$ can lead to a dynamic enhancement of the impurity scattering, and hence the resistivity, of a one-dimensional metal at $T\to 0$. An exact calculation[20] affirms this conclusion for a simple model over a certain range of physically reasonable coupling constants. The effect bears a mathematical[20] and experimental[12] resemblance to the Kondo phenomenon.

Within the Born approximation, the theory predicts an inverse power-law dependence of the resistivity on the temperature.[19,20] Such a law is obeyed by HMTSF-TCNQ with exponent ~ 1.7, but only over a limited temperature range above 12 K. At low temperature, the Born approximation must fail as the scattering rate increases. Quantitative estimates are especially difficult for the present case of two narrow overlapping conduction bands,[16,17] but self-consistency requires that the higher-order terms limit the enhanced rate so as not to exceed the electronic bandwidth as $T\to 0$. In HMTSF-TCNQ, this limit corresponds to $\sigma(0)=875\ \Omega^{-1}\ \mathrm{cm}^{-1}$ if all the chains are conducting, in good agreement with experiment for our best samples.

Since the energy dependence of the scattering rate in this description enters chiefly through the parameter E_F/T, we expect a low-temperature thermoelectric power roughly proportional to $T^2\,\partial\ln\rho/\partial T$ and nearly independent of impurity concentration. This is observed. Figure 3 presents the absolute thermoelectric power $S(T)$ for crystals from two separately synthesized batches of HMTSF-TCNQ. The small, positive, nearly linear, high-temperature thermopower is typical of selenium analogs of TTF-TCNQ[4,21] but the strong negative peak near 16 K [the inflection point in $\ln\rho(T)$] suggests that a different scattering mechanism has emerged. A weaker negative peak has been reported[13] for $(SN)_x$ at low temperatures.

In those quasi one-dimensional conductors where a metal-to-insulator transition does occur at a finite temperature T_c, the divergence of the leading term in the impurity scattering should arise[19] as $T\to T_c$. In TTF-TCNQ, where $T_c\sim 54$ K,[22] the conductivity maximum σ_{max} usually occurs at $T_{\mathrm{max}}\sim 59$ K, but diminishes and moves to higher temperature with decreasing sample quality.[23,11] Likewise, the weakly disordered sulfur-selenium compound, DSDTF-TCNQ,[24] has a lower σ_{max} and higher T_{max} than either of its ordered isostructural analogs TTF-TCNQ and TSF-TCNQ.[24] It is possible, then, that in these materials σ_{max} represents a crossing of phonon and enhanced impurity resistance curves as in $(SN)_x$ and HMTSF-TCNQ, and that the region $T_c < T < T_{\mathrm{max}}$ is characterized by fluctuation resis-

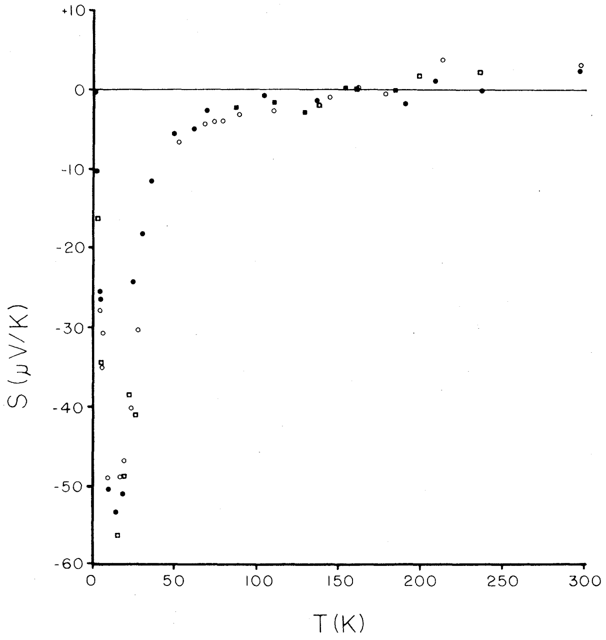

FIG. 3. Absolute thermoelectric power of HMTSF-TCNQ. Data-point symbols distinguish warming and cooling runs for two crystals.

tivity.[22,19]

Our conjectures cannot be valid unless the average interchain bandwidth, $W_\perp$, is small enough for the one-dimensional response functions to obtain, yet large enough to lift the one-dimensional constraint[25] that all states in an imperfect lattice be localized. The former condition is $W_\perp \ll E_F$, and Shante[26] has found that the latter has the approximate form $W_\parallel W_\perp \gg \delta^2$, with $W_\parallel$ the intrachain bandwidth and δ the rms potential fluctuation. For the anisotropy of the TTF-TCNQ compounds[17] and reasonable concentrations of defects and impurities,[11] the two conditions are compatible.

HMTSF also forms a conducting salt with the electron acceptor TNAP,[27] the napththo-analog of TCNQ. Preliminary dc and microwave measurements indicate that HMTSF-TNAP remains apparently metallic to 1.1 K and displays a resistance minimum at somewhat higher temperature and lower conductivity than HMTSF-TCNQ.

Note added.—Since this paper was submitted, R. L. Greene and W. A. Little have extended the dc conductivity measurements of our HMTSF-TCNQ samples to 45 mK, with no qualitative departure from Fig. 2. We thank them as well as V. K. S. Shante and M. H. Cohen, T. E. Phillips and T. J. Kistenmacher, R. Schumaker, and S. J. La Placa for useful comments and for permission to quote their respective unpublished results.

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†Alfred P. Sloan Foundation Fellow.

‡Present address: H. C. Oersted Institutet, Universitetsparken 5, DK-2100, Copenhagen, Denmark.

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

[2] K. Bechgaard, D. O. Cowan, A. N. Bloch, R. E. Pyle, and R. H. Banks, to be published.

[3] K. Bechgaard, D. O. Cowan, and A. N. Bloch, Chem. Commun. 1974, 937.

[4] R. E. Pyle, A. N. Bloch, D. O. Cowan, K. Bechgaard, T. O. Poehler, T. J. Kistenmacher, V. V. Walatka, R. Banks, W. Krug, and T. E. Phillips, Bull. Amer. Phys. Soc. 20, 415 (1975).

[5] T. E. Phillips and T. J. Kistenmacher, private communication.

[6] In this respect HMTSF-TCNQ differs from its sulfur analog HMTTF-TCNQ, which is insulating at low temperature. [R. Schumaker, M. Ebenhahn, G. Castro, and R. L. Greene, Bull. Amer. Phys. Soc. 20, 495 (1975); R. Schumaker and R. L. Greene, to be published.]

[7] Our four-probe measurements included the voltage checks suggested by D. E. Schafer *et al.* [Solid State Commun. 14, 347 (1974)], to test for inhomogeneous current distributions in anisotropic crystals. We have found these to be sensitive indicators of spuriously large apparent conductivities in TTF-TCNQ and TMTSF-TCNQ (R. V. Gemmers, D. O. Cowan, A. N. Bloch, R. E. Pyle, and R. Banks, to be published). In all samples of HMTSF-TCNQ studied, the checks indicated that such errors were negligible.

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

[9] Here the crystals chosen for study were thinner (< 10 μm) than a skin depth, so that the complex conductivity could be determined by a cavity-perturbation technique according to the dielectric formalism, as in Ref. 8. Where this condition is violated, no simple analysis of the data is accurate for the quasi–one-dimensional case. [T. O. Poehler, A. N. Bloch, J. Bohandy, D. O. Cowan, V. V. Walatka, Y. Tomkiewicz, and D. Garrod, Bull. Amer. Phys. Soc. 20, 440 (1975), and to be published.]

[10] The resistivity of one sample among the sixteen measured left the curve of Fig. 2 below 100 K and rose to 0.5 Ω cm at 4 K.

[11] Gemmer *et al.*, Ref. 7.

[12] V. V. Walatka, M. M. Labes, and J. H. Perlstein, Phys. Rev. Lett. 31, 1139 (1973); C. Hsu and M. M. Labes, J. Chem. Phys. 61, 4640 (1974).

[13] R. L. Greene, P. M. Grant, and G. B. Street, Phys. Rev. Lett. 34, 89 (1975).

[14] R. P. Groff, A. Suna, and R. E. Merrifield, Phys. Rev. Lett. 33, 318 (1974).

[15] R. E. Pyle and R. H. Banks, unpublished.

[16] M. H. Cohen, J. A. Hertz, P. M. Horn, and V. K. S. Shante, Int. J. Quantum Chem. Symp. 1974, 491, and to be published; U. Bernstein, P. M. Chaikin, and P. Pincus, Phys. Rev. Lett. 34, 271 (1975).

[17] A. J. Berlinsky, J. F. Carolan, and L. Weiler, Solid State Commun. 15, 795 (1974); W. Lee, S. I. Choi, and A. N. Bloch, unpublished.

[18] J. B. Torrance and A. N. Bloch, to be published.

[19] H. Fukuyama, T. M. Rice, and C. M. Varma, Phys. Rev. Lett. 33, 305 (1974).

[20] A. Luther and V. J. Emery, Phys. Rev. Lett. 33, 589 (1974).

[21] P. M. Chaikin, J. F. Kwak, R. L. Greene, S. Etemad, and E. Engler, Bull. Amer. Phys. Soc. 20, 495 (1975), and to be published.

[22] R. A. Craven, M. B. Salamon, G. DePasquali, R. M. Herman, G. Stucky, and A. Schultz, Phys. Rev. Lett. 32, 769 (1974).

[23] M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, Phys. Rev. B10, 1298 (1974).

[24] S. Etemad, T. Penney, E. M. Engler, B. A. Scott, and P. E. Seiden, Phys. Rev. Lett. 34, 741 (1975).

[25] R. E. Borland, Proc. Roy. Soc., Ser. A 274, 529 (1963).

[26] V. K. S. Shante, private communication.

[27] 11, 11, 12, 12-tetracyano-2, 6-naphthoquinodimethane. J. Diekmann, W. R. Hertler, and R. E. Benson, J. Org. Chem. 28, 2719 (1963).