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Robert V. Gemmer [a], Dwaine O. Cowan [a], Aaron N. Bloch [a], Ronald E. Pyle [a] & Rodney H. Banks [a]
[a] Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland, 21218, U.S.A.
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Some Comments on the Electrical Conductivity of TTF–TCNQ

ROBERT V. GEMMER, DWAINE O. COWAN, AARON N. BLOCH, RONALD E. PYLE, and RODNEY H. BANKS

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, U.S.A.

The best organic conductors of electricity known are the charge-transfer salt TTF–TCNQ (tetrathiafulvalinium tetracyanoquinodimethanide) (**1**), first prepared in these laboratories,[1–7] and several of its derivatives[8] and analogs.[9,10] The chain-like structures[4] of these materials lead to conductivities

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which are highly anisotropic, but metallic in magnitude along the chain axis. Since the propagation of conduction electrons is thus restricted effectively to one dimension, it is natural to expect chemical impurities and lattice defects to influence transport more profoundly here than in conventional three-dimensional metals.

Interest in the problem of purification has sharpened with the observation[1,11–13] that the conductivity of TTF–TCNQ is strongly sample-dependent. Although it now appears that early reports[11] of truly giant conductivities in occasional crystals were overstated,[14–16] the variation among specimens is still large enough that the intrinsic conductivity of TTF–TCNQ remains in some doubt. Compounding the uncertainty are claims by at least one laboratory[11,12,17] of extreme chemical purity, based solely upon accounts of the methods of purification and care employed in synthesis.

Toward a resolution of these questions, we have undertaken to evaluate the methods currently used by various laboratories for purification of the

neutral molecules TTF° and TCNQ°. Using newly available techniques of high-pressure gel permeation chromatography, we obtain separations of 4000–5000 theoretical plates, and by differential ultraviolet detection we are able to monitor impurity concentrations as low as 1 ppm.

Three methods of purification were examined in this study: (a) recrystallization in an inert atmosphere using dry, purified solvents, (b) non-fractionating sublimation onto teflon, and (c) fractionating, or gradient sublimation onto teflon. We find that conventional techniques of recrystallization and sublimation are sufficient to reduce impurity levels in TTF° below the sensitivity of our instruments. The same is true of TCNQ° except for a tendency to complex weakly with acetonitrile. The acetonitrile is removed upon formation of the TTF–TCNQ salt. The gradient sublimation technique introduced by McGhie, *et. al.*,[17] offers no improvement for TTF° or TCNQ°.

As a test of the importance of impurities in the TTF–TCNQ salts, we compared the conductivities of crystals grown under various conditions. The conductivities of TTF–TCNQ crystals of maximum purity are the same as reported previously,[1,13,14] and not significantly different from those of deliberately contaminated samples, and no significant variations are observed among the classes of crystals. However, a substantial variation is observed in the ratio of the conductivity at the maximum to the room temperature conductivity (σ_{max}/σ_{RT}) within each type. We conclude that most of the variation in conductivity among sample of TTF–TCNQ is due to lattice imperfections rather than chemical purity.[18]

Our results also bear upon reports of occasional crystals whose apparent conductivities are much higher ($> 10^5\ \Omega^{-1}\ cm^{-1}$) than those of our maximum-purity samples. Schafer, *et al.*, have shown how inhomogeneous current distributions can give rise to artificially high apparent conductivities in small, highly anisotropic crystals measured by the standard four-probe technique.[14] Further, by computer simulations which also take account of contact inhomogeneity, they have produced a single, giant peak in the apparent conductivity which essentially matches the Pennsylvania results at all temperatures.[19] We have achieved a similar result experimentally, as shown in Figure 1. Plotted along with the apparent conductivity are the voltage checks suggested by Schafer, *et. al.*[14] In most of our samples, the check voltages are near zero, indicating reliable measurements; the large values near the peak in Figure 1 indicate unambiguously that we are dealing with an experimental artifact.

This is not to imply that many-body effects are completely unimportant for electron transport in this material. Fukuyama, *et. al.*,[19] have argued that the onset of a Peierls distortion can give rise to a dynamic enhancement of the *resistivity* due to impurities or defects. The resulting temperature-dependent impurity resistivity would limit the conductivity just above the

transition. Consistent with such an effect, we and others[12] find that the conductivity maximum decreases and moves to higher temperature with diminishing sample quality.

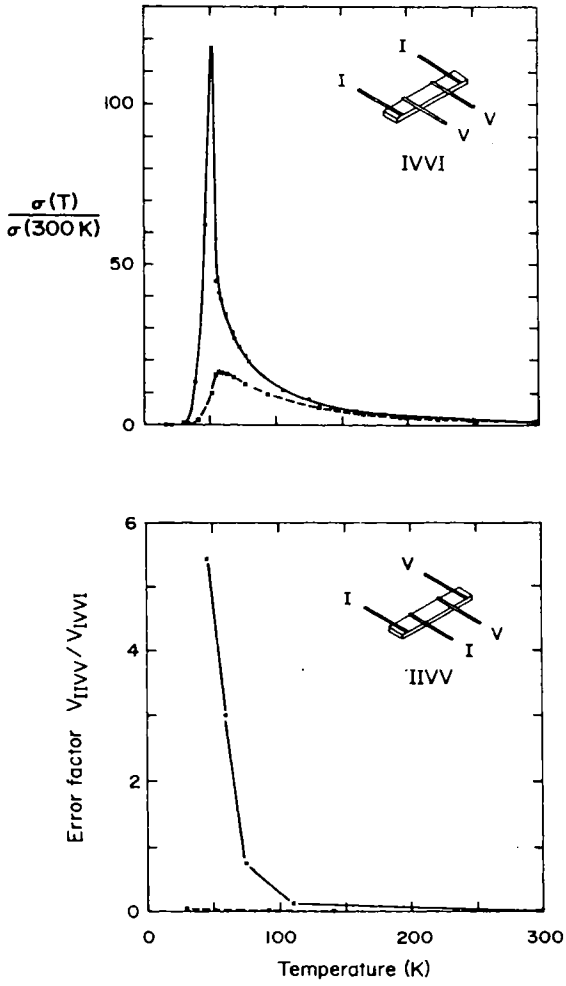

FIGURE 1

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