

**dc conductivity of tetrathiofulvalene bromide (TTF-Br<sub>n</sub>) and TTF-I<sub>n</sub> single crystals\***R. J. Warmack<sup>†</sup> and T. A. Callcott<sup>†</sup>*Physics Department, University of Tennessee, Knoxville, Tennessee 37916*

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Tetrathiofulvalene (TTF) combines with the halogens to form crystals with interesting electrical properties due to the segregated stacking of the TTF molecules. The monoclinic forms of TTF-I<sub>n</sub> and TTF-Br<sub>n</sub> ( $n \sim 0.7$ ) have a high conductivity [ $100\text{--}550 (\Omega \text{ cm})^{-1}$ ] which is almost temperature independent for a very broad region near room temperature but display a thermally activated conductivity at low temperature. Unlike monoclinic TTF-Br<sub>n</sub>, monoclinic TTF-I<sub>n</sub> displays a strong hysteresis in its conductivity upon temperature cycling. The conductivity of the orthorhombic form of TTF-I<sub>n</sub> ( $n = 2$ ) is about five orders of magnitude lower than the monoclinic form at room temperature and is thermally activated over the entire temperature range.

A large amount of research has concentrated on highly conductive charge-transfer salts using TCNQ (tetracyanoquinodimethane) as an electron acceptor molecule.<sup>1</sup> In particular, TTF-TCNQ has been investigated extensively due to its high conductivity and unusual physical properties.<sup>2</sup> Much less work has been done on TTF (tetrathiofulvalene) in combination with various acceptor systems. Wudl *et al.*<sup>3</sup> found TTF-chloride to be an excellent solid-state semiconductor (room-temperature resistivity  $3.7 \pm 1 \Omega \text{ cm}$  using compacted microcrystalline samples). This prompted us to look at other halogen analogs of TTF and to obtain their single-crystal properties.

We have grown single crystals of TTF-Br<sub>n</sub> and TTF-I<sub>n</sub> in the form of long (2–6-mm) needles with a monoclinic structure. The three-dimensional crystal structure of TTF-I<sub>n</sub> has been determined using x-ray diffraction and will be published elsewhere.<sup>4</sup> The measured sample had a stoichiometry of  $n = 0.7076$  and was found to be isostructural with TTF-Br<sub>n</sub> whose stoichiometry is known to be variable with  $0.7 < n < 0.8$ .<sup>5</sup> The TTF molecules form segregated stacks in which the plane of each TTF molecule is approximately perpendicular to the stacking axis with an intermolecular separation of about  $3.57 \text{ \AA}$ . Parallel to the TTF stacks are columns of approximately equally spaced ( $\sim 5 \text{ \AA}$ ) halogen ions.

Figure 1 shows the experimental conductivity of monoclinic TTF-I<sub>n</sub> and TTF-Br<sub>n</sub>. These measurements were performed on single crystals using the standard four-probe method with 25- $\mu\text{m}$ -diameter gold electrodes and a silver base paint. Gold strips were evaporated on the samples before the silver paint was applied in order to reduce contact resistance. Both halogen compounds show very broad, almost flat conductances near room temperature with values of 100 to 450  $(\Omega \text{ cm})^{-1}$  for

TTF-I<sub>n</sub> (six samples measured) and to 300 to 550  $(\Omega \text{ cm})^{-1}$  for TTF-Br<sub>n</sub> (two samples measured). The lower-conductivity values correspond to crystals of poorer morphology.

For monoclinic TTF-Br<sub>n</sub>, the conductivity underwent a transition near 180 °K. The curves for the two samples measured were almost identical except for their room-temperature values. At low temperatures (see Fig. 2), the conductance followed the familiar semiconductor relation  $\sigma = \sigma_0 \times \exp(-E_a/kT)$  where  $E_a$  was found to be 0.081 eV (940 °K). A very slight decrease in conductivity was seen as the temperature was raised above 310 °K. No hysteresis or shift in transition temperature observed in repeated temperature cyclings.

For monoclinic TTF-I<sub>n</sub>, the transition occurred between 200 and 270 °K for different samples and was not constant for repeated temperature cycles of the same sample (see Fig. 1). Below the transition, some samples then showed a very sharp fall in conductance into an exponential region in which  $E_a$  varied from about 0.12 eV (1400 °K) to 0.084 eV (980 °K) as the temperature was lowered further. Upon heating the samples, a hysteresis loop was formed which could always be made to close on the original room-temperature conductance. This hysteresis was observable in any temperature region.

Another crystalline form of TTF-I<sub>n</sub> with  $n = 2$  has an orthorhombic unit cell<sup>4</sup> and is observed as flat platelets ( $\sim 0.5 \times 0.5 \times 0.05 \text{ mm}^3$ ). The TTF molecules form segregated stacks (intermolecular distance  $3.52 \text{ \AA}$ ) with the plane of each molecule approximately perpendicular to the stacking axis which is along the thin dimension of the samples. The iodine columns contain small polyiodide species, probably predominately I<sub>3</sub><sup>-</sup> (trimers).<sup>5</sup> The conductivity along the stacking axis was measured

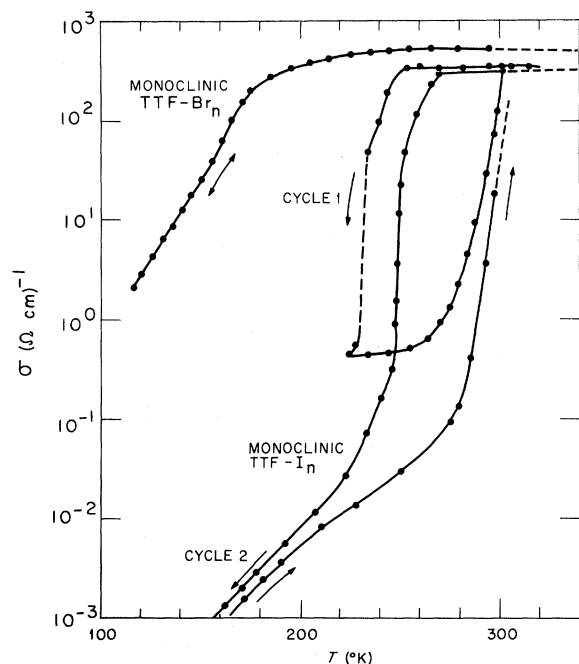


FIG. 1. Temperature dependence of the conductivity along the stacking axes of monoclinic TTF-Br<sub>n</sub> and TTF-I<sub>n</sub>. Two temperature cycles of the TTF-I<sub>n</sub> sample are shown. Arrows indicate the direction of temperature change.

by evaporating gold on both faces of the samples to act as current electrodes for the overlap region, and taking the voltage on faces opposite each current electrode so as to obtain a four-probe measurement (see Fig. 3). This unusual electrode arrangement gave good results because the conductivity in the directions perpendicular to the stacking axis was about  $10^{-5} (\Omega \text{ cm})^{-1}$  or about two orders of magnitude lower than along the stacking axis. Two samples were made with voltage electrodes directly across the thin dimension of the sample, and the opposing voltage due to the proximity of the current electrodes was found to be at least four orders of magnitude less than that observed in the arrangement of Fig. 3. Also, with correction for contact resistance, two-probe measurements agreed well with the four-probe results. At 300°K the conductivity was measured to be between  $1 \times 10^{-3} (\Omega \text{ cm})^{-1}$  and  $2 \times 10^{-3} (\Omega \text{ cm})^{-1}$  for four samples measured. The temperature dependence showed constant exponential behavior (except for a slight deviation above 250°K) with  $E_a = 0.24 \text{ eV}$  (2800°K).

In all forms of the TTF-halides reported here, we believe conduction must occur along stacks of TTF molecules because of the large orbital overlap between adjacent molecules within each stack. In the iodine columns, the overlap is very small

since the distance between adjacent iodide ions is about 5 Å in the monoclinic form and either 4 or 5 Å for the spacing between small polyiodide units in the orthorhombic form. In a separate publication, we will show that a partial charge transfer of electrons from the TTF stacks to the iodine columns is indicated by optical data.<sup>7</sup> The stoichiometry of the monoclinic form should give the charge transfer directly since iodine has a high electron affinity compared to the ionization potential of TTF and would exist as isolated ions. Thus the TTF molecules have an average charge of about +0.7 e, depending upon the exact stoichiometry. The charge transfer in the orthorhombic form is less well defined, since the exact population of each polyiodide species in the iodine columns is uncertain. For pure I<sub>3</sub><sup>-</sup> species 0.67e per TTF would be transferred while 0.80e per TTF would be transferred for (I<sub>3</sub><sup>-</sup>)<sub>2</sub>(I<sup>-</sup>)<sub>2</sub>(I<sub>2</sub><sup>0</sup>) species.<sup>5</sup> A charge transfer of about this magnitude is indicated by optical data.<sup>7</sup> Thus structural and optical information shows that the spacing and charge transfer in the TTF stacks is very similar in the monoclinic and orthorhombic forms of TTF-I<sub>n</sub>.

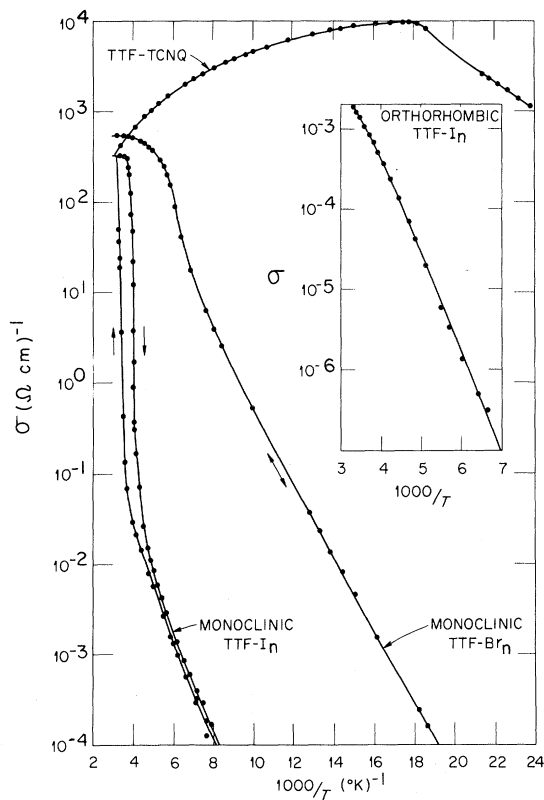


FIG. 2. Temperature dependence of the conductivity along the stacking axes of monoclinic TTF-I<sub>n</sub>, monoclinic TTF-Br<sub>n</sub>, and orthorhombic TTF-I<sub>n</sub> plotted as  $T^{-1}$ . Also shown is the conductivity of a typical sample of TTF-TCNQ.

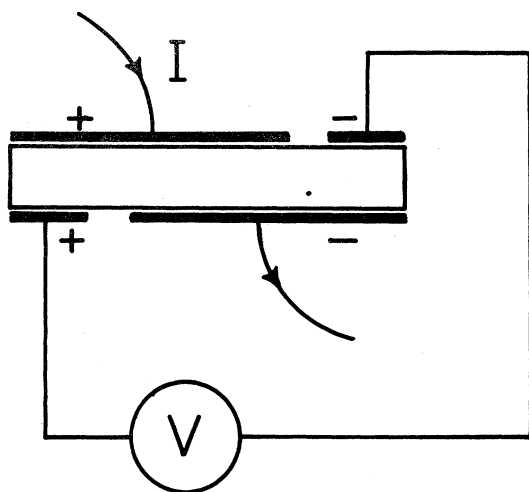


FIG. 3. Schematic drawing of the conductivity measurement for orthorhombic TTF- $I_n$ . The edge of the sample is shown (stacking axis vertical). Locations of gold evaporated onto the faces of the crystal are shown as broad lines. Also indicated are the polarities observed during a conductivity measurement.

This information is difficult to reconcile with the observed conductivities of the two forms which differ by five orders of magnitude at room temperature. If a band picture is applicable to these systems, the upper band would be partially filled and thus conducting. It may be that small distortions within the TTF stacks or disorder introduced by the iodine columns acting to localize charge carriers<sup>8</sup> so that conduction proceeds with a much lower efficiency via a hopping mechanism. The detailed three-dimensional structure reveals that, for the monoclinic form, each TTF is rotated slightly about the stacking axis so that the angle of rotation between adjacent TTF molecules in each

stack can be as much as about  $10^\circ$ . According to the present refinement of the orthorhombic form, some distortion is present, most probably as slight rotations about the low-inertial axis of the TTF molecules.<sup>11</sup> Another difference between these two crystal structures is that adjacent TTF stacks are rotated  $90^\circ$  about their stacking axes in the monoclinic form but are aligned in the orthorhombic form. These crystals therefore can provide a study of how subtle changes in structure can affect the conductivity.

The temperature dependence of the conductivity of monoclinic TTF- $Br_n$  is quite similar to that observed for N-methylphenazinium-TCNQ (NMP-TCNQ).<sup>9</sup> Both compounds have segregated stacks of closely spaced molecules in which only one molecular species participates in conduction.<sup>10</sup> In NMP-TCNQ the NMP molecules are highly polarizable, as are the adjacent stacks of TTF molecules which are rotated  $90^\circ$  about the stacking axis in monoclinic TTF- $Br_n$ . It is tempting to speculate about similar interpretations of the conduction mechanism, but this must await further experimentation.

The hysteresis in monoclinic TTF- $I_n$  is indicative of a phase transition which is affected by an uncontrolled parameter, perhaps by thermal stresses on the sample. Preliminary x-ray results of TTF- $I_n$  at low temperature reveal no major change in crystal structure,<sup>11</sup> but very significant changes in conductivity are possible with only minor changes in x-ray structure.<sup>12</sup> It is interesting to note that this hysteresis is not present in the isostructural bromine analogue.

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<sup>3</sup>F. Wudl, D. Wobschall, E. J. Hufnagel, *J. Am. Chem. Soc.* **94**, 670 (1972).

<sup>4</sup>C. K. Johnson, C. R. Watson, and R. J. Warmack, *Am. Crystallogr. Assoc. Meeting Program and Abstracts* **3**, 19 (1975); C. K. Johnson and C. R. Watson (unpublished).

<sup>5</sup>The x-ray data of C. K. Johnson indicates that monomers and possibly dimers may be present in orthorhombic

TTF- $I_n$  in addition to the  $I_3^-$  trimers. The scheme which fits the data most closely repeats two trimers, two dimers, and one dimer.

<sup>6</sup>S. J. LaPlaca, J. E. Weidenborner, B. A. Scott, and P. Cornfield, *Bull. Am. Phys. Soc.* **20**, 496 (1975).

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<sup>8</sup>A. N. Bloch and C. M. Varma, *J. Phys. C* **6**, 1849 (1973).

<sup>9</sup>E. Ehrenfreund, S. Etemad, L. B. Coleman, E. F. Rybaczewski, A. F. Garito, and A. J. Heeger, *Phys. Rev. Lett.* **29**, 269 (1972); see Fig. 1(b).

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<sup>11</sup>C. K. Johnson (private communication).

<sup>12</sup>R. H. Blessing and P. Coppens, *Solid State Commun.* **15**, 215 (1974).