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Electrical conductivity of tetrathiafulvalenium-tetracyanoquinodimethanide (TTF-TCNQ)

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New measurements of electrical conductivity along the *b* axis of tetrathiafulvalenium-tetracyanoquinodimethanide (TTF-TCNQ) are combined with published results to provide a comprehensive summary including approximately 600 samples studied at 18 different laboratories. The magnitudes of these measured conductivities do not necessitate the assumption of superconducting fluctuations or any other collective state in which the conductivity exceeds the limitations of single-particle scattering. Since an adequate theory of the limitations of single-particle scattering for TTF-TCNQ does not exist at present, experiment alone does not rule out the possibility that collective effects may somewhat enhance or suppress the conductivity.

The dc electrical conductivity of tetrathiafulvalenium-tetracyanoquinodimethanide (TTF-TCNQ) was first reported by Ferraris, Cowan, Walatka, and Perlstein[1] in 1972. Since that time a number of workers have carefully studied the conductivity in this organic charge-transfer salt. Although the results are not in complete agreement and measurements are continuing in some groups, we would like to summarize the substantial body of work that has been completed. The observed magnitude of the conductivity appears to be comparable to that in common metals and thus, from the limited point of view of an effective mean free path, consistent with a possible contribution to the transport properties from single-particle electron scattering.

The original results of Ferraris *et al.* indicated that TTF-TCNQ was the most highly conducting organic compound known. Its dc conductivity rose with decreasing temperature like a metal and was highly anisotropic. The observed anisotropy was consistent with the crystal structure of other

TABLE I. Codes for sample preparation and purification procedures are the following: *A*, argon or other inert gas atmosphere; *D* distillation; *G*, special glassware; *M*, multiple cycle gradient sublimation; *R*, recrystallization; *S*, sublimation. See references for further information. "Number with σ_{max}" refers to the number observed within the quoted range. Measurement methods were dc conductivity, cavity perturbation, and coaxial resonance.

	σ_{RT} $(\Omega\ \mathrm{cm})^{-1}$	$\sigma_{\mathrm{max}}/\sigma_{\mathrm{RT}}$	$10^{-4}\sigma_{\mathrm{max}}$ $(\Omega\ \mathrm{cm})^{-1}$	Number with σ_{max}	Measurement method	Ref.	Preparation methods
Johns Hopkins Univ.	200–650	15–23	0.3–1.5	4	dc	1	*DRS*
	200–650	15–26	0.3–2.0	40	dc	12	*ADMGRS*
	300–500	15–20	0.5–1.0	60	Cavity pert.	13	
Univ. of Pennsylvania	475–920	30–150	1.4–14.0	7	dc	6, 8	*ADGMR*
	475–920	20–30	0.9–2.8	12	dc	8	
	200–700	10–20	0.2–1.2	250	dc		
	250–750	25–80	0.6–6.0	8	Cavity pert. and Res.	14	
	250–750	15–25	0.4–1.9	8			
Stanford and IBM, San Jose	200–600	10–15	0.2–0.9	9	~dc	15	*DRS*
Bell	300–400	10–15	0.3–0.6	12	dc	7	*ADRS*
DuPont	250–500	12–35	0.3–1.8	35	dc	16	*ADGMRS*
IBM, Yorktown Heights	400–600	10–20	0.4–1.2	11	dc	17, 18	*ADMGRS*
Orsay and IBM, Yorktown Heights	•••	15–60	•••	8	dc	19	
Univ. of Illinois	250–350	8–30	0.2–1.1	5	dc	20	*DGM*
NBS	330–450	18–25	0.6–1.1	4	dc	21	*ADGMR*
	200–400	33–50	0.7–2.0	4	Cavity pert.		
Monsanto	240–650	3–18	0.1–1.2	32	dc	22	*DGR*
Univ. of Chicago	300–500	8–32	0.2–1.6	15	dc	23	*ADGMR*
Univ. of British Columbia	300–700	13–15	0.4–1.1	15	dc	24	*ADGMR*
	250–350	14–25	0.4–0.9	5	Coaxial res.	25	*ADGMR*
IBM, San Jose	425–455	•••	•••	10	dc	26	*ADMR*
	200–600	15–25	0.3–1.5	20	dc		
Hughes	200–600	12–18	0.2–1.1	20	dc	27	*DR*
Clemson	350–450	9–18	0.3–0.8	2	dc	28	*DR*
Tennessee	413–432	8–23	0.3–1.0	5	dc	29	*ADGRS*
Berkeley	300	•••	•••	1	Cavity pert.	30	*ADMR*
Tokyo	300-500	9–11	0.3–0.6	5	dc	31	*ADMR*

similar compounds of TCNQ consisting of separated stacks of planar molecules along which electrons moved easily. This quasi-one-dimensional picture led Ferraris *et al.* to suggest that the transition from metallic to semiconducting behavior, which occurred near 60 K, might be due to (among several possibilities) a periodic distortion of the crystal lattice driven by the conduction electrons, called a Peierls distortion.[2–5]

Subsequently, Coleman, Cohen, Sandman, Yamagishi, Garito, and Heeger,[6] reported large dc electrical conductivities in three of the seventy crystals studied. They interpreted the observed magnitude and temperature dependence in terms of BCS superconducting fluctuations. One of these three samples reached a maximum conductivity of 10^6 $(\Omega\ \mathrm{cm})^{-1}$—a factor of about 70 larger than observed previously.[1] Coleman *et al.* stressed that sample purity and crystalline perfection were the crucial factors which accounted for the wide variation that they and the earlier workers observed among samples.

Commenting on the large conductivities, Schafer, Wudl, Thomas, Ferraris, and Cowan[7] warned that anomalously large apparent conductivities along the *b* axis could occur if the applied current missed the points on the sample where the voltage was probed. They found that such problems were particularly severe in anisotropic materials such as the small TTF-TCNQ crystals that were then available, and they observed a spurious apparent conductivity rise in one sample to a maximum

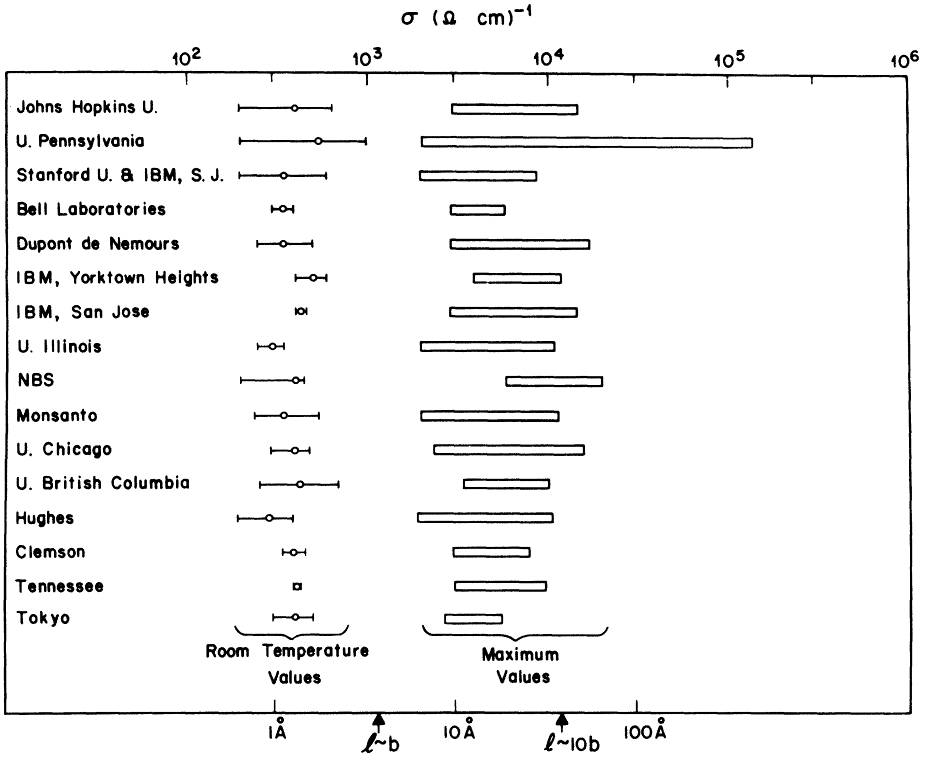

FIG. 1. Plot summarizing the values of room-temperature conductivities σ_{RT} and maximum conductivities σ_{max} along the b axis in TTF-TCNQ as listed in Table I. Microwave and dc measurements are combined. The effective mean free path (see text) is shown on the lower axis.

value of about 3×10^6 $(\Omega\,\mathrm{cm})^{-1}$ near 70 K. Schafer *et al.* agreed with the earlier workers that improved sample purification and crystalline quality could also increase the measured conductivity. Cohen, Coleman, Garito, and Heeger[8] studied these possibilities and concluded that spurious conductivity problems could be ruled out in their measurements[9] up to maximum conductivities of 1.5×10^5 $(\Omega\,\mathrm{cm})^{-1}$. They stated in conclusion[8,10] that the magnitude of the conductivity can greatly exceed the limitations of single-particle electron scattering processes.

Since the original report of Ferraris *et al.*, a large number of investigations of the b-axis dc and microwave electrical conductivity of TTF-TCNQ have been carried out. The results of these studies are listed in Table I and illustrated in Fig. 1. According to these data, the experimental range of b-axis conductivities (at T near 60 K) reproduced in more than one laboratory is $(0.3-2)\times10^4$ $(\Omega\,\mathrm{cm})^{-1}$, in reasonable agreement with the original range measured by Ferraris *et al.*[1] of $(0.3-1.5)\times10^4$ $(\Omega\,\mathrm{cm})^{-1}$. The fact that the measurements of 18 laboratories fall within this range does not, of course, determine unequivocally the intrinsic conductivity. In any case the maximum low-temperature conductivity is remarkably large compared to previously known organic conductors, e.g., *N*-methylphenazenium-tetracyanoquinodimethanide.

Although the unusual behavior of the phonons[3,5] suggests the possibility that collective effects may modify the transport properties, it is perhaps useful to consider whether the observed magnitude of the conductivity can be described by a reasonable value of the usual effective mean free path in one dimension,[6,7,11]

$$l=(\pi\hbar/2e^2)(\sigma/s),$$

where s is the number of conducting chains per unit area (four per unit cell). Using this relation, the lower axis of Fig. 1 is labeled in units of l. Since the b-axis lattice spacing[4] is $b=3.819$ Å, all of the observed conductivities at room temperature imply values of l smaller than b. Thus, the conductivity of TTF-TCNQ near room temperature should properly be described as diffusive.[11] As the temperature is lowered the values of l exceed b so that a band conduction picture becomes a possibility. The mean free path increases to a value at $\sigma=\sigma_{max}$ of $l=7-70$ Å or approximately $(2-18)b$. In comparison, as an example of a common metal with a substantial amount of electron scattering, the mean free path of Pb at $T=60$ K is about 100 Å, or 28 lattice spacings.

Since the observed effective mean free paths in TTF-TCNQ are smaller than those in Pb and many normal materials, they are consistent with single-particle scattering processes.[17,20] Thus, we can conclude that the magnitude of the conductivity of TTF-TCNQ summarized here does not necessitate the assumption of superconducting fluctuations or any other collective state in which the conductivity exceeds the limitations of single-particle scattering. On the other hand, since an adequate theory of the limitations of single-particle scattering for TTF-TCNQ does not exist at present, experiment alone does not rule out the possibility that collective effects may enhance or suppress the conductivity.

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[3] The first measurements of the crystal structure at room temperature by Phillips, Kistenmacher, Ferraris, and Cowan (Ref. 4) showed that the molecular arrangement indeed consisted of segregated stacks along the *b* axis of TTF and TCNQ molecules. Recently, studies below the metal-semiconductor transition (Ref. 5) reveal x-ray scattering from a new lattice periodicity, which the authors interpret as a Peierls distortion; neutron scattering data also support this interpretation [R. Comès, S. M. Shapiro, G. Shirane, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 35, 1518 (1975)].

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[9] Thomas has rejected the check (Ref. 8) for true conductivity based on two peaks in the apparent conductivity. On the one hand, two maxima in the anisotropy (Refs. 8 and 17) and intrinsic structure in the *b*-axis σ near 38 K (Refs. 15, 18, and 25) have been confirmed. On the other hand, spurious enhancement of a *single* apparent conductivity peak can occur in a computer model of TTF-TCNQ, since contact problems tend to be suppressed when $\sigma/\sigma_{max} \ll 1$ [G. A. Thomas, in Conference on One-Dimensional Conductors, Arrowhead Lake, California, 1974 (unpublished)]. Such behavior has been observed (Ref. 12); and Mol. Cryst. Liq. Cryst. 32, 237 (1976).

[10] The data of Refs. 16, 19, and 21 have been interpreted [A. J. Heeger and A. F. Garito (private communication)] to confirm a range (Ref. 8) of $(3\text{–}10)\times 10^4$ $(\Omega\text{-cm})^{-1}$ and, in conjunction with data from other types of experiments to support their belief that the electrical transport is dominated by "superconducting fluctuations" associated with a Peierls instability.

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[20] M. B. Salamon, J. W. Bray, G. DePasquali, R. A. Craven, Ray Herman, G. Stucky, and A. Schultz, Phys. Rev. B 11, 619 (1975); and previously unpublished results. This study of the thermal conductivity of TTF-TCNQ indicated that the average rise in the electrical conductivity ($\sigma_{\max}/\sigma_{\mathrm{RT}} = 10$–$35$) is consistent with normal single particle scattering processes. The samples were grown in quartz vessels by recrystallization of triple-gradient-sublimed constituents and freshly distilled acetonitrile solutions. The electrical conductivities were measured after the samples had been thermally cycled for the thermal-conductivity experiment.

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[22] G. R. Johnson, M. G. Miles, and J. D. Wilson (previously unpublished results). Crystals of TTF-TCNQ were prepared by means of the following operations conducted under nitrogen in quartz apparatus: TTF was purified by liquid chromatography and triple recrystallization from spectromethylcyclohexane. TCNQ was triply recrystallized from spectroacetonitrile (dried over 3-Å molecular sieves), containing a trace of bromine. Crystals of TTF-TCNQ were grown in an asymmetric *H* tube by introducing the starting materials into the limbs, filling with spectroacetonitrile and immersing in a thermostatic bath. For some crystals the resistance was measured independently on both smooth faces; for these the crystal resistance is taken to be the average of the face resistances. The highest observed value, $\sigma_{\max}/\sigma_{\mathrm{RT}} = 29$, for a single face was paired with a value of 13 for the opposite face; the over-all crystal value was $\sigma_{\max}/\sigma_{\mathrm{RT}} = 18$.

[23] P. M. Horn and B. Rimai (previously unpublished results). Part of the samples for this study were supplied by M. G. Miles and J. D. Wilson, Monsanto Co. and R. P. Groff, Du Pont Corp. Samples were also prepared by multiple gradient sublimation under argon.

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[27] L. Roth, F. Yamaghishi, and A. Pastor (private communication). We have observed a strong correlation between the crystalline perfection, hence the dc conductivity in our TTF-TCNQ crystals, and the purity of the starting materials, i.e., the TTF·TCNQ complex and acetonitrile, that we used in our free convection growth method. Because we are aware that our TCNQ purity is low, less then 99.78%, we expect that significant increases in dc conductivity will be achieved once

this purity problem is remedied.

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