with photoemitted electrons and, on the basis of the observed trap filling and depopulating kinetics, propose that at fields as low as 5×10^5 V/cm some excess electrons have sufficient kinetic energy to ionize an occupied trap. Our data clearly show that the average electron at the highest fields has less than 0.15 eV energy, but of course there will be a distribution of electrons with higher kinetic energies the shape of which is not predicted by the TF theory. There is also the possibility as suggested by both DiMaria, Feigl, and Butler[10] and TF[1] that electrons which have much more than 0.15 eV upon injection will be in the unstable part of the energy-loss versus energy curve and will be accelerated by the field until some other energy-loss mechanism drops them into the stable part of the curve. Evidence for impact ionization by hot electrons in the oxide layer has been obtained in the switching studies of Shatzkes, Av-Ron, and Anderson,[11] but only for fields over 10^7 V/cm which can be maintained by the space charge of the low-mobility holes.[12]

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[1] K. K. Thornber and R. P. Feynman, Phys. Rev. B 1, 4099 (1970).

[2] R. C. Hughes, Phys. Rev. Lett. 30, 1333 (1973).

[3] J. J. O'Dwyer, *The Theory of Electrical Conduction and Breakdown in Solid Dielectrics* (Clarendon, Oxford, England, 1973).

[4] E. M. Conwell, in *Solid State Physics,* edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1967), Vol. 20, Suppl. 1.

[5] A. G. Chynoweth, in *Semiconductors and Semimetals,* edited by R. K. Willardson and A. C. Beer (Academic, New York, 1968), p. 263.

[6] W. T. Lynch, J. Appl. Phys. 43, 3274 (1972), and thesis, Princeton University, 1971 (University Microfilms, Ann Arbor, Michigan, No. 72-2731).

[7] K. L. Yip and W. B. Fowler, Phys. Rev. B 10, 1400 (1974).

[8] O. L. Curtis, Jr., J. R. Srour, and K. Y. Chiu, J. Appl. Phys. 45, 4506 (1974). Our high-field data agree with Curtis, Srour, and Chiu who did not resolve the separate contributions of the electrons and holes to the total charge.

[9] Z. A. Weinberg, W. C. Johnson, and M. A. Lampert, Appl. Phys. Lett. 25, 42 (1974).

[10] D. J. DiMaria, F. J. Feigl, and S. R. Butler, Appl. Phys. Lett. 24, 459 (1974), and Phys. Rev. B 11, 5023 (1975).

[11] W. Shatzkes, M. Av-Ron, and R. M. Anderson, J. Appl. Phys. 45, 2065 (1974).

[12] R. C. Hughes, Appl. Phys. Lett. 26, 436 (1974).

Differences in Charge Transfer between Surface and Bulk Species in Tetrathiafulvalene-Tetracyanoquinodimethane

R. S. Swingle, II, R. P. Groff, and B. M. Monroe
Central Research and Development Department, E. I. du Pont de Nemours and Company,
Wilmington, Delaware 19898
(Received 24 March 1975)

The charge-transfer complex tetrathiafulvalene-tetracyanoquinodimethane has been studied by x-ray-photoelectron spectroscopy at both normal and grazing electron take-off angles. Changes in the N_{1s} and S_{2p} spectra with angle show that a discrete layer exists at the surface of the *a-b* plane. Essentially zero electron transfer takes place in this layer versus $\sim 0.8\pm0.2$ in the bulk. The surface layer is ca. 1 to 5 layers of complex thick and appears to be intrinsic to "good" organic conductors.

Unusual multiplet structure in the N_{1s} and S_{2p} core-electron spectra of the charge-transfer complex tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) has been reported.[1-3] Both discrete intrinsic energy-loss phenomena[1] and chemical shifts due to neutral and singly charged molecules coexisting in the solid on the time scale of bond vibrations[2] have been mentioned as possible causes of the structure. To date, however, neither explanation has been demonstrated and, consequently, conclusions based on core-level or valence-band photoemission spectra concerning the amount of charge transfer and the localization of conducting electrons in solid TTF-TCNQ are open to question.

We find from grazing-angle[4,5] x-ray-photoelectron spectroscopy (ESCA) that the core-level multiplet structure is due to a discrete layer of

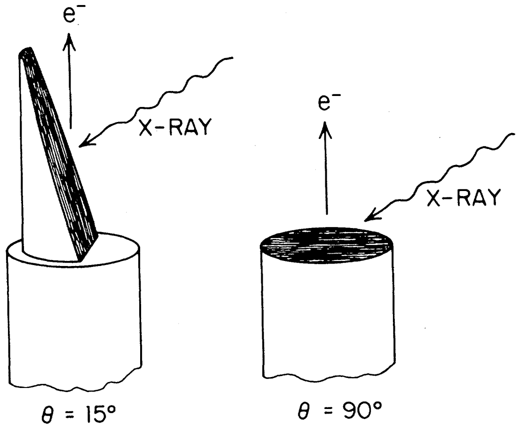

FIG. 1. Sample configuration for grazing-angle experiments.

complex, distinguishable from the bulk material, at the *a*-*b* surface. Empirical evidence indicates this surface layer is characteristic of "good" organic conductors. Of the 24 organic conductor candidates examined, only one (TTF-TCNQCl_2) which showed clear evidence of the surface layer gave a powder-compaction resistivity greater than 1 Ω cm.

For samples with specular surfaces, it is possible to decrease the effective sampling depth by lowering the electron take-off angle, θ, between the electron-analyzer entrance and the plane of the sample surface. Grazing-angle spectra for TTF-TCNQ were taken on a DuPont 650B electron spectrometer by mounting 20–50 solution-grown crystals[6] on stubs specially machined for 90° and 15° take-off angles (see Fig. 1). The crystals were closely packed so as to cover the entire surface of the holder and were aligned with their needle axis parallel to one another (*a*-*b* plane exposed). Other compounds, prepared by literature procedures,[7,8] were studied as powders using a Varian IEE-15 spectrometer and an instrument previously described.[9,10] An analog curve resolver was used to deconvolute overlapping peaks.

Figure 2 compares typical background corrected N_{1s} spectra from TTF-TCNQ taken at $\theta = 90°$ and $\theta = 15°$. The $\theta = 90°$ spectrum exhibits the doublet structure characteristic of TTF-TCNQ, while the $\theta = 15°$ spectrum is dominated by the single peak at 399.9-eV binding energy (E_B). Enhancement of this higher E_B peak is observed at $\theta = 15°$ when the crystals are mounted with the high-conductivity direction both perpendicular to and nearly parallel to the photoelectron take-off direction. Thus it is unlikely that an anisotropic, discrete energy loss with unit cross section in one direction could be responsible for the changes evident in Fig. 2.

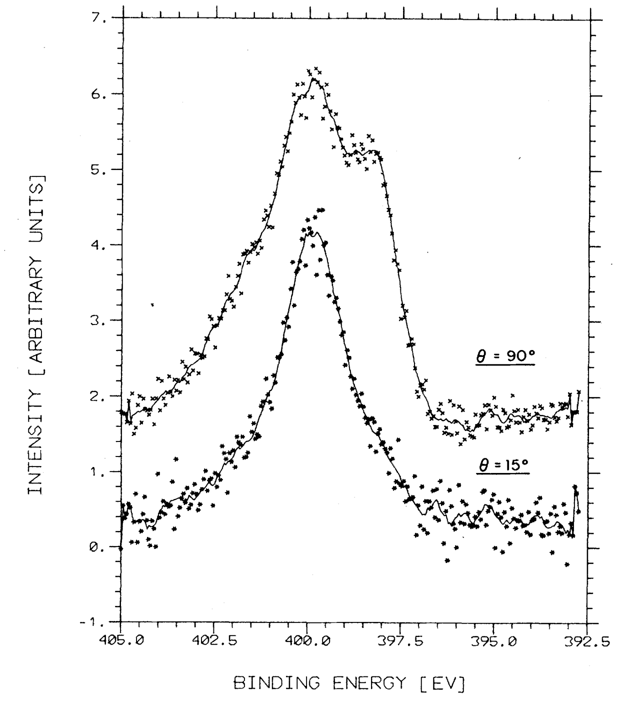

FIG. 2. N_{1s} grazing-angle spectra for TTF-TCNQ.

Similar changes with θ are also evident in the S_{2p} spectra. At $\theta = 15°$ the full width at half-maximum of the total S_{2p} envelope decreases by 0.3 to 0.5 eV and the position shifts by 0.2 to 0.4 eV toward lower E_B. These changes in the S_{2p} spectra are more subtle because the S_{2p} peak has a greater natural linewidth (~0.5 eV) because of spin-orbit coupling, and consequently the surface-bulk doublet is not as easily resolved. In addition, the kinetic energy of the S_{2p} photoelectron (~1090 eV) is 25% greater than that of the N_{1s} photoelectron (~855 eV) and the inelastic mean free path of the S_{2p} photoelectron ($\lambda_{S_{2p}}$) will be greater than $\lambda_{N_{1s}}$.[11] This should result in relatively more bulk species contributing to the S_{2p} spectrum than to the N_{1s} spectrum, particularly at lower take-off angles.

Thus it appears that, at the *a*-*b* surface, there is a thin layer of TTF-TCNQ which is distinguishable from the bulk. (This layer may or may not be present at the surfaces of other exposed crystal planes.) In order to ensure that our spectra were not impurity dominated, we sublimed away ca. 50% of our starting material by heating *in situ* and obtained the same spectrum. Furthermore, our spectra did not change with time (over a period < 6 h in the spectrometer versus several weeks out of the spectrometer) provided the samples were not simultaneously exposed to light and air. Consequently we feel that this surface layer is an intrinsic property of TTF-TCNQ.

The thickness of this layer can be estimated from $I(x)=I(\infty)\,[1-\exp(-x/\lambda\sin\theta)]$, where $I(x)$ is the photoelectron intensity from a layer of thickness x, and $I(\infty)$ is the intensity that would be observed if the layer were infinitely thick. From the relative area of the surface peak, $I(x)$, and the area of the total N_{1s} envelope, $I(\infty)$, the thickness of the layer was estimated to be $(0.5 \pm 0.25)\lambda_{N_{1s}}$.[12] If we assume a value of 50 Å for $\lambda_{N_{1s}}$,[13] then x will be ca. 10–40 Å. In these experiments the photoelectrons eminate from the a-b surface plane; the normal axis is the c^* crystal axis. The long axes of both TTF and TCNQ lie generally in the c^* direction (herringbone stacking)[14] and, for both donor and acceptor, the projection of the long axes on the c^* axis is ~8 Å. Hence the thickness of the surface layer is probably not more than five and possibly only one layer of complex thick.

Siegbahn has demonstrated a linear relationship between the S_{2p} binding energy and the calculated initial-state charge on the sulfur atom.[15] Using the S_{2p} binding energies for TTF and TTFCl as "standards,"[16] the S_{2p} binding energies from TTF-TCNQ (Table I) indicate essentially zero and 0.8 ± 0.2 electron transfer in the surface layer and bulk, respectively.[1,3] In addition to the statistical uncertainty, parameters other than initial-state charges are known to affect core-level binding energies[17] and it is not possible to calculate the effect of these parameters in the TTF-TCNQ system. However, the same amount of charge transfer is indicated using the N_{1s} binding energies from the standards[18] TCNQ and KTCNQ. This partly justifies the assumptions inherent in this simple treatment of the S_{2p} binding energies because any large extra-molecular relaxation of electrons toward the photohole during ionization would probably decrease the measured binding energies of both the S_{2p} and N_{1s} photoelectrons and would lead to values for electron transfer that are too small based on S_{2p} measurements and too large based on N_{1s} measurements.

The logarithm of the powder-compaction resistivities ρ (measured at room temperature under 5 kbar) and the ratio of height of the N_{1s} satellite structure at maximum intensity divided by the height of the main or bulk N_{1s} peak (A/B ratio) for 24 compounds (studied as powders) are listed in Table II. (Figure 3 shows the structures and corresponding abbreviations for these com-

TABLE I. S_{2p} binding energies for TTF, TTF-TCNQ, and TTFCl.

Compound	E_B (eV)
TTF	163.65 ± 0.20
TTF-TCNQ	163.70 ± 0.10; 164.90 ± 0.10
TTFCl [a]	164.00 ± 0.10; 165.30 ± 0.10

[a] See Ref. 16.

TABLE II. Resistivities (Ref. 8) and A/B ratios for various complexes. All data are taken on powered samples.

Compound	$\log_{10}\rho$ (ohm-cm)	A/B
TTF-TCNQ	−1.2	1.16
TTF-TCNQ	−1.2	0.83
TTF-TCNQBr	−1.0	1.00
TTF-TCNQBrCH$_3$	−1.0	0.94
TTF-TCNQEt$_2$	−1.0	0.95
NMP$^+$TCNQ$^-$ [a]	−1.0	1.11
TTF-TCNQCl	−0.7	1.00
TTF-TCNQClCH$_3$	−0.5	1.10
TTF-TCNQBr$_2$	−0.4	1.18
TTN-TCNQ	−0.2	0.94
TTN-TCNQ	+0.5	0.91
Tl$^+$TCNQ$^-$ [b]	+1.8	0.45
TTF-TCNQCl$_2$	+2.9	0.90
TTF-TCNQF$_4$	+2.9	0.54
K$^+$TCNQ$^-$	+3.7	0.42
Cs$^+$TCNQ$^-$	+4.5	0.40
Na$^+$TCNQ$^-$	+4.5	0.30
TMDSA-TCNQF$_4$	+5.0	0.40
Li$^+$TCNQ$^-$	+5.3	0.30
S-Se-TCNQ	+5.6	0.21
S-Se-TCNQF$_4$	+5.6	0.44
Ag$^+$TCNQ$^-$	+5.9	0.30
TTF-DDQ [c]	+6.8	0.29
TMDSA-TCNQCl$_2$	+7.0	0.26
TMDSA-TCNQ	+9.3	0.18
$(\emptyset_3PCH_3)^+$TCNQ$^-$	+10.0	0.40

[a] A/B uncertain due to overlap of N_{1s} from donor and acceptor.

[b] A/B uncertain due to partial N_{1s}-$Tl_{4d\,3/2}$ overlap.

[c] A/B uncertain due to small, if any, ΔE_B between N_{1s} main line and satellite structure.

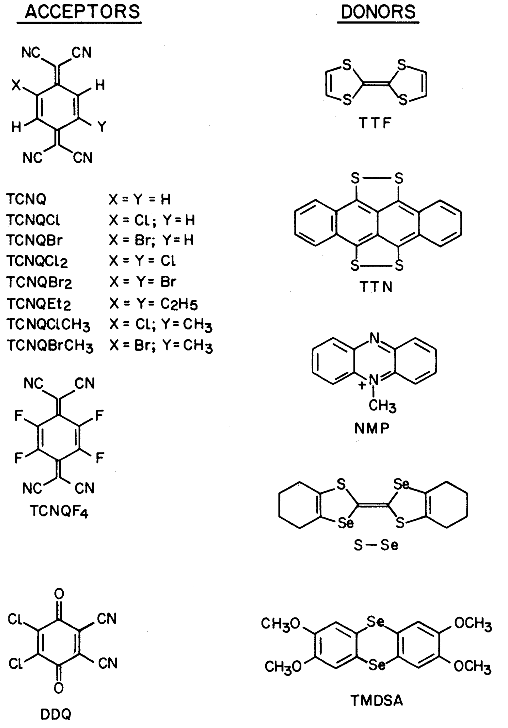

FIG. 3. Molecular structures for compounds in Table II.

pounds.) Compounds with $A/B < 0.8$ are generally "good" conductors ($\rho < 1\ \Omega$ cm) while those with $A/B < 0.6$ are poorer conductors. It is probable that compounds in the latter group do not have a discrete surface layer and that the additional structure in their N_{1s} spectra is due to shake-up satellites.[19] The presence of this surface layer appears to be a necessary but not sufficient characteristic of a good organic conductor. Perhaps the charge transfer is sufficiently weak in "good" conductors that it can be altered significantly either by changes in the Madelung energy[20] at the surface or by absorbed impurities.

The presence of a surface layer in TTF-TCNQ suggests caution when using valence-band photoemission spectra to discern the electronic properties of organic conductors. Particularly when using uv light for photoexcitation, the surface layer will make a significant contribution to the observed valence-band spectrum and possibly result in an erroneous assignment of orbital positions. For example, in previous photoemission work on TTF-TCNQ,[2,21] the observed broadening of orbitals in the valence band might be due to overlap in the spectrum of states from the surface and bulk species, and the highest lying peak at -1.0 eV could be due to neutral TTF on the surface of the complex rather than a localized affinity electron on TCNQ. Also, these grazing-angle measurements do not support Coulomb potential differences in bulk TTF-TCNQ[22] as the cause of the multiplet structure.

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[1] C. R. Ginnard, R. S. Swingle, II, and B. M. Monroe, J. Electron Spectrosc. Relat. Phenom. 6, 77 (1975).

[2] W. D. Grobman *et al.*, Phys. Rev. Lett. 32, 534 (1974).

[3] M. A. Butler *et al.*, Chem. Phys. Lett. 24, 600 (1974).

[4] C. S. Fadley *et al.*, J. Electron Spectrosc. Relat. Phenom. 4, 93 (1973).

[5] W. A. Fraser *et al.*, Surface Sci. 36, 661 (1973).

[6] R. P. Groff, A. Suna, and R. E. Merrifield, Phys. Rev. Lett. 33, 418 (1974).

[7] L. R. Melby *et al.*, J. Am. Chem. Soc. 84, 3373 (1962); L. R. Melby *et al.*, J. Org. Chem. 39, 2456 (1974).

[8] R. C. Wheland and J. L. Gillson, to be published.

[9] R. D. Davies *et al.*, Adv. X-Ray Anal. 16, 90 (1973).

[10] J. D. Lee, Rev. Sci. Instrum. 43, 1291 (1972).

[11] C. J. Powell, Surface Sci. 44, 29 (1974).

[12] The large uncertainty in this calculation is due to the energy-loss structure which overlaps the surface N_{1s} peak (see Fig. 2). One cannot tell how to allocate the area from this structure between the surface and bulk peaks.

[13] 50 Å is likely too large for $\lambda_{N_{1s}}$ and should be considered as an approximate upper limit. Typical values for conductors range from ~ 5 to 20 Å. Although λ values of ~ 100 Å have been measured for organic material, the systems studied were not conductors and were considerably less dense than TTF-TCNQ (see Ref. 11).

[14] T. E. Phillips *et al.*, J. Chem. Soc., Chem. Commun. 1973, 471.

[15] K. Siegbahn *et al.*, *ESCA Atomic, Molecular and Solid State Structure Studies by Means of Electron Spectroscopy* (Almqvist and Wiksells, Uppsala, Sweden, 1967).

[16] The S_{2p} spectrum of TTFCl also exhibits a doublet structure (see Ref. 1). In this form the TTF cation is readily reduced to neutral TTF in air. We feel that the observed doublet is due to the presence of both species on the sample surface. The observed low Cl_{2p} intensity supports this argument.

[17] See, for example, P. H. Citrin and D. R. Hamann, Phys. Rev. B 10, 4948 (1974); D. W. Davis, M. S. Banna, and D. A. Shirley, J. Chem. Phys. 60, 237 (1974).

[18] Determination of charge transfer from the N_{1s} bind-

ing energies gives a larger error because of the additional satellite structure (Refs. 1–3).

[19] I. Ikemoto, J. M. Thomas, and H. Kuroda, J. Chem. Soc., Faraday Trans. 54, 208 (1972), and Bull. Chem. Soc. Jpn. 46, 2237 (1973); L. A. Aarons *et al.*, J. Chem. Soc., Faraday Trans. 2 69, 270 (1973).

[20] R. E. Merrifield, Phys. Rev. Lett. 34, 877 (1975).

[21] P. Nielsen, A. J. Epstein, and D. J. Sandman, Solid State Commun. 15, 53 (1974).

[22] A. J. Epstein *et al.*, Phys. Rev. Lett. 34, 914 (1975).

Implications on the Band Structure of the Isostructural Family Tetrathiafulvalene Tetracyanoquinodimethane (TTF-TCNQ), Tetraselenafulvalene Tetracyanoquinodimethane (TSeF-TCNQ), and Their Solid Solutions from Spin-Resonance Measurements

Y. Tomkiewicz, E. M. Engler, and T. D. Schultz
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 31 March 1975)

We show that electron-phonon coupling plays a major role in the spin relaxation of the isostructural family of organic metals, $(\mathrm{TSeF})_x(\mathrm{TTF})_{1-x}\mathrm{TCNQ}$ (tetraselenafulvalene tetrathiafulvalene tetracyanoquinodimethane). The dependence of this relaxation on the fraction of TSeF in the donor chain suggests a picture of hybridized donor-acceptor bands for TSeF-TCNQ in contrast to the nonhybridized bands of TTF-TCNQ.

The origin of the EPR absorption linewidth in organic metals is presently unknown. An early attempt was made[1] to assign the linewidth of *N*-methyl-phenazinium–tetracyanoquinodimethane (NMP-TCNQ) in its metallic phase to spin-lattice relaxation (T_1), produced by the scattering of conduction electrons with the acoustic modes of the lattice vibrations. However, this contribution has been found[2] to be of relatively small importance for NMP-TCNQ, probably because of the small spin-orbit coupling of the atomic constituents.

Recently the synthesis of organic metals with larger spin-orbit couplings, as tetrathiafulvalene (TTF) TCNQ[3] and its isostructural selenium analog, tetraselenafulvalene (TSeF) TCNQ,[4] has opened new possibilities for observing spin-lattice relaxation involving spin-orbit interaction. The free cations of these salts have large, yet significantly different, spin-orbit couplings as indicated by g measurements in solution. We have measured the g value of TSeF and found it to be 2.027, while the g value of TTF was reported[5] to be 2.0084. Moreover, the isostructurality of the compounds makes feasible the preparation of the solid solutions $(\mathrm{TSeF})_x(\mathrm{TTF})_{1-x}\mathrm{TCNQ}$ where $0 \leqslant x \leqslant 1$. These solid solutions provide a system in which the effective spin-orbit coupling of the donor stack can be varied continuously while the structure is maintained.[6]

In the temperature range of metallic conductivity, the parent compounds and their solid solutions show a single EPR absorption line with a width that depends strongly on the relative fraction of TSeF in the donor chain, as is shown in Fig. 1. At room temperature the linewidth varies from 5 to 500 G over the range from $x=0$ to $x=1$. The origin of the linewidth appears to be similar for the different compositions, a conclusion that we infer from having observed marked insensitivity of linewidth anisotropy to composition.

The observed dependence of the linewidth on x indicates that the donor chain participates in the spin resonance. Moreover, the enormous rate of increase in the linewidth with increasing concentration of TSeF suggests that spin-orbit coupling plays a dominant role in the spin relaxation, because the most significant spin-related difference between TTF and TSeF is the much larger

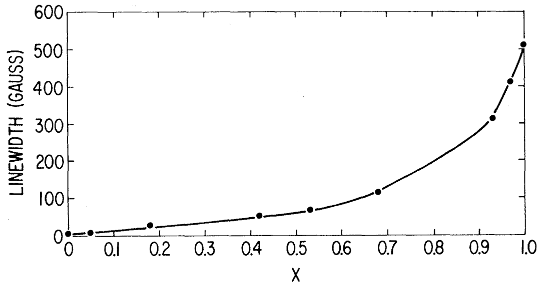

FIG. 1. Linewidth dependence for $H_{\mathrm{dc}} \parallel c^*$ direction, on x—the fraction of TSeF in the donor chain. The measurements were taken at 300°K.