Polarized Reflectance at Oblique Incidence on Single Crystal (TTF)(TCNQ) in the Range 3000Å-5μ

P. M. Grant, R. L. Greene and G. Castro

Some question exists as to the intra- or extra- molecular origins of transitions observed in normal incidence reflectance and transmittance of (TTF)(TCNQ) crystals and films in their visible and near-IR spectra. We have performed polarized reflectance measurements on the ab face of large single crystals (a:b:c* = 3:7:0.05 mm) of (TTF)(TCNQ) as one approach to providing answers to this question. Incidence angles used varied from 19-54° with the E-vector of the light always in the plane of incidence, and runs made with either E∥a or E∥b with respect to the monoclinic unit cell. An oriented gas model is used to treat the data and sort local allowed intra-molecular transitions from extra-molecular states.

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temperature and energy dependence of the scattering time indicates a similar conductivity and relaxation process throughout the series.

*Research at UCLA supported by National Science Foundation under Grant #37250.

HK 6 Contact Effects on Conductivity Measurements of Anisotropic Organic Crystals. L. R. BICKFORD and K. K. KANAZAWA, IBM Research Lab, San Jose.--Since current flow across metal-organic interfaces is inhibited by a relatively large contact resistance, conductivity in organics is usually measured by four-probe methods. Attempts to account for the giant conductivity peak at T≈70° in TTF-TCNQ in terms of an error introduced by contact geometry were not entirely successful. They did underscore the vulnerability of conductivity measurements in highly anisotropic materials to geometry and contact placement. We further pursued this area of investigation at 300°K in TTF-TCNQ, by plotting electrical potential in two dimensions over crystal surfaces under various known conditions of contact geometry and current flow. The potential probe was a movable mercury-coated fine wire. Our results verify in detail the existence of a spreading resistance due to the combination of large anisotropy and poor geometry. We also demonstrate the importance of inhomogeneities in the contact resistance at the current-carrying contacts. The resistance is neither easily reproducible nor generally uniform across a given contact. A judicious choice of sample geometry can sometimes virtually eliminate this problem.

HK 7 Magnetic Susceptibility and Low Temperature d.c. Conductivity of TSeF-TCNQ. S. ETEMAD, T. PENNEY, and E. M. ENGLER, IBM Research Center.--Measurement of d.c. conductivity below the metal-semiconductor transition in the isostructural family of organic metals TTF-TCNQ, DSeDTF-TCNQ, and TSeF-TCNQ, together with magnetic susceptibility of TSeF-TCNQ are presented. In addition to the conductivity peak at 59K, the TTF-TCNQ data shows an anomaly at ∿ 38K indicative of a second transition, which is absent in TSeF-TCNQ. At lower temperatures the conductivity exhibits a 250K activation energy in TTF-TCNQ which differs from the reported activation energy ∿ 80K of the magnetic susceptibility.[1] The paramagnetic susceptibility of TSeF-TCNQ has a similar temperature dependence to that of TTF-TCNQ, but is smaller by a factor of two in magnitude. The similarity in conductivity and magnetic susceptibility of TTF-TCNQ and TSeF-TCNQ indicates a common mechanism responsible for their metallic properties.

[1] J. C. Scott, A. F. Garito, A. J. Heeger, Phys. Rev. B Oct. 74.

HK 8 Polarized Reflectance at Oblique Incidence on Single Crystal (TTF)(TCNQ) in the Range 3000Å-5μ. P. M. GRANT, R. L. GREENE and G. CASTRO, IBM San Jose.- Some question exists as to the intra- or extra- molecular origins of transitions observed in normal incidence reflectance and transmittance of (TTF)(TCNQ) crystals and films in their visible and near-IR spectra. We have performed polarized reflectance measurements on the ab face of large single crystals (a:b:c* = 3:7:0.05 mm) of (TTF)(TCNQ) as one approach to providing answers to this question. Incidence angles used varied from 19-54° with the E-vector of the light always in the plane of incidence, and runs made with either E∥a or E∥b with respect to the monoclinic unit cell. An oriented gas model is used to treat the data and sort local allowed intra-molecular transitions from extra-molecular states.

SUPPLEMENTARY PROGRAM

HK 12 Variation in D.C. Conductivity of an Organic Alloy; $(TTF)_x(TSeF)_{1-x}(TCNQ)$. S. ETEMAD, E. M. ENGLER, B. A. SCOTT, AND T. PENNEY, IBM Research Center.--The isomorphism of TTF-TCNQ and its selenium analogue TSeF-TCNQ has been used in making organic crystalline alloys. We report the unit cell constants and the d.c.

HK 9 Interpretation of Optical Properties of TCNQ Compounds, J.B. TORRANCE, B.A. SCOTT, and F.B. KAUFMAN, IBM Research (Yorktown)--The infrared and visible spectra of several TCNQ compounds which exhibit a wide variety of physical properties are discussed. The spectra of simple and complex salts are interpreted in a unified way in terms of inter- and intra-molecular excitations in the TCNQ chains, which are distinguished by single crystal polarization measurements. It is concluded that:

1) The electron-electron interactions are not appreciably screened by the electronic polarizability of the cations and the correlation energy, U, is ∿ 1eV for all TCNQ compounds;

2) most simple TCNQ salts, eg. K-TCNQ, have half filled bands and are Mott insulators;

3) both TTF- and NMP-TCNQ have incomplete charge transfer and hence less than half filled bands; and

4) this lack of complete charge transfer accounts for the greater conductivities of these salts compared to that of K-TCNQ, for example.

HK 10 Mixed Valence Interactions in the TTF-Halide Systems. B. A. SCOTT, J. B. TORRANCE, S. J. LA PLACA, P. CORFIELD*, D. C. GREEN and S. ETEMAD, IBM Research Center.--The TTF-halide systems $(TTF)X_n$, where X = Cl, Br, I, have been studied by chemical and physical methods. In addition to the insulating n=1 and n=2 compounds, we have found mixed valence (MV) phases in all of these systems, with homogeneity ranges contained within the limits n=0.7 to 0.8. For example, $(TTF)Br_n$ occurs in a MV, segregated stack structure having a stability range $0.72 \leq n \leq 0.78$. The mixed valence compound in this range exhibits semiconducting behavior with $\sigma(RT) \approx 500$ $(ohm\text{-}cm)^{-1}$, comparable to "metallic" (TTF)(TCNQ). The MV nature of these compounds is also evidenced by the existence of two charge transfer bands observed in the infrared at 0.65 and 1.6 eV. In contrast, $(TTF)Br_{1.0}$, which cannot be easily prepared by the usual methods, is essentially an insulator containing non-segregated stacks. Since the requirement of a stable lattice energy determines the composition of the MV phase, we will discuss how the stoichiometry relates to the degree of charge transfer in the TCNQ salts.
*The Kings College, Briarcliff Manor, NY.

HK 11 Effect of Valency Changes on the Crystal and Molecular Structure of TTF and Its Salts. S.J. LA PLACA, J.E. WEIDENBORNER, B.A. SCOTT and P. CORFIELD*, IBM Research Center (Yorktown).--For neutral TTF and its salts, correlations will be presented between the degree of oxidation of the TTF molecule and structural features drawn from the literature and from our x-ray studies on: $(TTF)X_2$ - a new uniform, segregated stacking moiety for TTF cations (pseudo-tetragonal ($I4_1/acd$:Z=8); X=Br; a=13.78, c=10.56Å, X=Cl; a=13.56, c=10.10Å). (TTF)Br - The orthorhombic (Pbca, Z=8, a=11.235, b=11.357, c=14.133Å) crystal structure contains well isolated, dimeric "twisted" TTF molecules which are eclipsed and ∿3.34Å apart. $(TTF)Br_{.72-.78}$ - The monoclinic structure is comprised of distinct cation and anion sublattices which are translationally non-integral (incommensurate) with respect to each other in one direction. The nonvariable cation sublattice contains stacks of eclipsed TTF molecules 3.57Å apart while the compositionally variable anion sublattice contains rows of Br ions 4.4-4.7Å apart. The detailed molecular architecture, including the incommensurability effect, reflects the anion sublattice periodically modulating the TTF sublattice. β-TTF - A tri-clinic modification currently under investigation.
*The Kings College, Briarcliff manor, N.Y.