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Vibronic Structure in the Reflection Spectrum of the TCNQ<sup>o</sup> Crystal. J. M. TURLET, P. GRANT and M. R. PHILPOTT, IBM Research Laboratory, San Jose.--Polarized reflection spectra of the first singlet transition  $1B_{2u} + 1A_{1g}$  of TCNQ<sup>o</sup> crystal off the (010) face has been measured at room and liquid He temperatures. The spectrum consists of a massive block of high reflectivity spanning 1.5 eV with well defined lower and upper edges at 2.79 and 4.18 eV respectively. Considerable structure appears upon cooling to low temperatures, most of which seems to be vibrational in nature and is located on the low energy side between 2.79 and 3.10 eV. Some of the structure can be correlated with the known vibrational modes of the Raman spectrum of the crystal thereby providing the first confirmation of the basic notions of the theory of strong vibronic coupling in crystals with transitions of dye-like intensity.

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# bulletin

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**EL 2 Polaronic Effects on the Transport Coefficients of the Narrow Band Hubbard Chain.** GERARDO BENI, Bell Labs., and CORNELIUS F. COLL, III, Sandia Labs. --- We have considered the effects on the electrical conductivity and the thermoelectric power (TEP) of a narrow band electronic system due to coupling to a set of vibrational modes. The electronic system is described by a Hubbard Hamiltonian and the vibrational coupling is chosen to correspond either to modulation of the single site energy or modulation of the Coulomb interaction. The calculations are presented for the limit of a very narrow half-filled band. Particularly interesting is the behavior of the TEP when the coupling corresponds to vibrational modulation of the on-site Coulomb repulsion. Including the coupling gives a non-zero TEP which vanishes only at very low and very high temperature. The results are discussed with reference to the organic conductors based on the acceptor molecule TCNQ.

**EL 3 Vibronic Structure in the Reflection Spectrum of the TCNQ<sup>0</sup> Crystal.** J. M. TURLET, P. M. GRANT and M. R. PHILPOTT, IBM Research Laboratory, San Jose. --- Polarized reflection spectra of the first singlet transition  ${}^1B_{2u} \leftarrow {}^1A_{1g}$  of TCNQ<sup>0</sup> crystal off the (010) face has been measured at room and liquid He temperatures. The spectrum consists of a massive block of high reflectivity spanning 1.5 eV with well defined lower and upper edges at 2.79 and 4.18 eV respectively. Considerable structure appears upon cooling to low temperatures, most of which seems to be vibrational in nature and is located on the low energy side between 2.79 and 3.10 eV. Some of the structure can be correlated with the known vibrational modes of the Raman spectrum of the crystal thereby providing the first confirmation of the basic notions of the theory of strong vibronic coupling in crystals with transitions of dye-like intensity.

**EL 4 Electron Escape Depth and Temperature-Dependent Photoemission from TTF-TCNQ and Related Compounds.** S.F. LIN and W.E. SPICER, Stanford U. and B.H. SCHECHTMAN, IBM San Jose Research Lab. --- The electron escape lengths of organic charge transfer salts TTF-TCNQ, Cs<sub>2</sub>(TCNQ)<sub>3</sub> and neutral TCNQ have been studied by UV-photoemission from threshold energy up to 11.8 eV. Estimation made from quantum yields and energy distribution curves (EDCs) of thin films of different thickness suggests that the average electron escape lengths for these solids are less than 10 Å in the range of energy involved. The EDCs of TTF-TCNQ are found to be strongly dependent on the substrate temperature during film deposition and the subsequent thermal history of the film. It is found that as the films are allowed to warm slowly, the EDCs from films deposited onto 77° K Au substrates transform irreversibly into EDCs from films deposited onto 295° K substrate. Low temperature (77° K to 295° K) differential thermal analyses performed on TTF-TCNQ formed at 77° K also showed irreversible changes as the samples were warmed. A model involving molecular rearrangements and qualitative surface composition of TTF-TCNQ will be discussed in interpreting the above phenomena.

\* Work at Stanford supported by NSF through CMR at Stanford

**EL 5 Energy Levels of TCNQ<sup>-</sup> and TTF<sup>+</sup> in Charge Transfer Salts from Photoemission Studies.** B. H. SCHECHTMAN, IBM San Jose Research Lab, S. F. LIN and W. E. SPICER, Stanford Univ. --- The energy level structure of the radical anion TCNQ<sup>-</sup> has been determined using photoemission observations of the changes in the occupied and unoccupied valence orbitals of neutral TCNQ<sup>0</sup> upon its chemical reaction with Cs vapor to form the complex salt Cs<sub>2</sub><sup>+</sup>(TCNQ<sup>-</sup>)<sub>2</sub>TCNQ<sup>0</sup>. The energy levels of TCNQ<sup>0</sup> and TCNQ<sup>-</sup> are found to be completely independent of the anion's concentration in the solid, emphasizing the strong molecular localization of the excess electronic charge on TCNQ<sup>-</sup>. The localization of the anionic charge also causes a large relaxation (by about 2 eV) of the  $b_{1u} - b_{2g}$

energy gap in going from TCNQ<sup>0</sup> to TCNQ<sup>-</sup>. Comparison of results from Cs<sub>2</sub>(TCNQ)<sub>3</sub> and TTF-TCNQ confirm the presence of some TCNQ<sup>0</sup> near the surface of TTF-TCNQ, allow assignment of the TTF energy levels in the conducting salt, and suggest the presence of a partially occupied TTF<sup>+</sup> orbital in the same region near the Fermi energy as the TCNQ<sup>-</sup>  $b_{2g}$  level. Comparisons are made between our experimental cation and anion energy levels and electronic structures available from Hückel, scattered-wave and *ab initio* calculations.

\*Work at Stanford supported by NSF through CMR at Stanford.

**EL 6 Reflectance of TTF-I<sub>2</sub> Single Crystals.** R. J. WARMACK, T. A. CALLCOTT, University of Tennessee, C. R. WATSON and C. K. JOHNSON, Oak Ridge National Laboratory. --- The polarized reflectance of TTF-I<sub>2</sub> single crystals has been measured in the spectral region 0.7 eV to 5 eV for two crystalline forms, monoclinic and orthorhombic, at room temperature and at liquid nitrogen temperature. The electrical conductivity along the needle axis of the monoclinic crystals was high at room temperature (ca. 300 ohm<sup>-1</sup> cm<sup>-1</sup>) and the reflection polarized along that axis was typical of a Drude-like free electron gas with the edge occurring at 1.15 eV. The reflectance perpendicular to the needle axis showed structure which is interpreted as electron transitions in the plane of the TTF molecule. The reflectance of the orthorhombic form of TTF-I<sub>2</sub> will also be discussed.

\* Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corp.

<sup>1</sup> Consultant, Oak Ridge National Laboratory, Oak Ridge, TN

**EL 7 Thermoelectric Power of an Extended Hubbard Model Chain in the Strong-Coupling Limit.** J. F. KWAKT, Univ. of Calif., Los Angeles and G. BENT, Bell Telephone Laboratories, Murray Hill, N. J. --- We have studied the thermoelectric power of an infinite linear chain with an arbitrary electron density in the strong coupling limit of an extended Hubbard model. The calculations were carried out for two distinct cases. The first is the simple Hubbard chain with arbitrary transfer integral; the second is the atomic limit of an extended Hubbard model having an arbitrary nearest neighbor repulsion. We apply the results to the high-conductivity complex salts of tetracyanoquinodimethan (TCNQ).

\*Submitted by Philip A. Pincus

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**EL 8 New NMR Results in NMP-TCNQ.** M. A. Butler, F. Wudl, Bell Laboratories and Z. G. Soos, Princeton U. --- The proton NMR second moment ( $M_2$ ) in NMP-TCNQ has been measured in the temperature range 1.5-300°K and a field range 2-13.5 kOe.  $M_2$  has the form  $M_2(T,H) = M_2(T,0) + A(T)H^2$  with both  $M_2(T,0)$ ,  $A(T)$  and their first derivatives increasing monotonically with lower temperature. Calculations indicate that the methyl group (CH<sub>3</sub>) must be rapidly rotating at 300°K where  $M_2$  is quantitatively given by internuclear dipolar interactions. The increase in  $M_2(T,0)$  at lower temperature cannot be ascribed to the slowing of this motion as the same behavior is observed in a sample in which the CH<sub>3</sub> group is deuterated. We believe this temperature dependence to arise from dynamic coupling to the electronic spins. The field dependence of  $M_2$  may be explained by the static broadening caused by the electronic spins. We also observe in all samples at 300°K superimposed on the main resonance a narrow (FWHM < 0.5 G) resonance which indicates ~1% of the protons must undergo rapid motion.

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