THE PHYSICAL AND CHEMICAL PROPERTIES OF THE REACTION PRODUCT BETWEEN TRIMETHYLAMMONIUM IODIDE AND TCNQ. A TERNARY 1-D SEMICONDUCTOR WITH 'METAL-LIKE' CONDUCTIVITY.

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Abstract

New results on an extensive series of physical and chemical measurements on $(NMe_3H^+)(I_3^-)_{1/3}(TCNQ)$ are reported. The data, including transverse conductivity and thermoelectric power, reflectivity and X-ray studies, indicate that this system is a semiconductor at high temperatures (>240K) with a strongly temperature dependent mobility despite its 'metal-like' conductivity. A semiconductor-semiconductor transition is observed at 150K with a second transition suggested at 89K. The role of large on site coulomb repulsion (U) is indicated. An unusual variation in the degree of disorder among the iodine stacks is reported, with no change observed in the iodine order at the 150K transition.

The study of linear chain organic and inorganic anisotropic compounds has emphasized those systems with high 'metal-like' conductivity.[1,2,3,4] Such systems typically have one donor and one acceptor. Cougrand et al.[5] were the first to report that 7,7,8,8-tetracyano-p-quinodimethane, TCNQ, reacts with $NMe_3H^+I^-$ (Me=CH_3) to form a novel ternary component material of $(NMe_3H)(I)(TCNQ)$ stoichiometry with one cation and two different segregated acceptor chains, presumably only one of which, TCNQ, is conducting.

We previously reported[6,7] the initial results of extensive physical studies undertaken on this system. These studies include elemental analysis, x-ray

diffraction, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), Raman scattering, polarized reflectance, anisotropic dc conductivity, microwave conductivity, dielectric constant, electron spin resonance (ESR), proton magnetic resonance (^{1}H NMR), thermoelectric power (TEP), and Young's Modulus (E). These results show the large highly conducting metallic green-appearing crystals to be $(NMe_3H^+)(I_3^-)_{1/3}(TCNQ)^{2/3-}$, a thermally stable compound which undergoes a semiconductor-semiconductor transition at 150K, with a second transition at 89K. Thus there is a 1/3 filled band in the TCNQ chains in a one-electron picture.

The room temperature dc electrical conductivity measured (4-probe) parallel to the TCNQ stacking axis is[6-8] $\sigma_{RT} \simeq 20(\Omega\text{-cm})^{-1}$. The temperature, T, dependence of σ[7,8] features 'metal-like'behavior between 300K and 240K at which temperature ($T=T_M$) it achieves its maximum value, $\sigma = 1.08\ \sigma_{RT}$. There is a maximum in $-d\ell n\sigma(T)/d(1/T)$ at 150K, indicating a transition at this temperature.

Recently, Epstein et al.[9-11] have proposed a model for conduction in many TCNQ salts with broad maxima in $\sigma(T)$ which postulates a semiconducting state at all temperatures. For $T > T_M$, σ is dominated by a strongly temperature dependent mobility determined by interactions between the conduction electrons and molecular vibrations. For $T < T_M$ $\sigma(T)$ is dominated by the thermal activation of carriers across the gap. The model requires significant coupling of the conduction electrons to molecular vibrational modes of TCNQ, an effect which has been observed (triethylammonium)(TCNQ)[12] and in (K)(TCNQ).[13] The model predicts the existence of a semiconducting energy gap of $E_g \sim 0.14$ eV even at room temperature where the $\sigma(T)$ is 'metal-like' ($d\sigma/dT < 0$). The conductivity in the directions perpendicular to the TCNQ chain axis seems to be governed only by the T-dependent carrier concentration.

The thermoelectric power, S, measurement[7] for T >150K fit $S=|\frac{K}{e}|(-\ell n2 + \frac{110}{T})$ in agreement with semiconducting behavior[14] in a system with large on site coulomb repulsions.[15] The effective gap obtained, is consistent with the semiconductor model for conductivity results with nearly equal electron and hole mobilities.[14] The T-dependence of the thermoelectric power in the directions perpendicular to the TCNQ stacking axis was measured to be small and nearly T-independent for T >150K, with considerable variation among samples.

Polarized reflectance measurements have been made on room temperature lustrous metallic green specimens using conventional techniques.[16] For $\underline{E} \parallel \underline{a}$ polarization, R is nearly flat. In the chain direction, $\underline{E} \parallel \underline{b}$, a strong peak in the visible is responsible for the green color.[7,16] As is characteristic of many TCNQ salts, for $\underline{E} \parallel \underline{b}$ there is a weak structure in the near infrared including a minimum at 4820 cm^{-1}, and a broad reflectance maximum. Below 150 cm^{-1} the reflectance rises rapidly, reaching nearly unity at 20 cm^{-1}. Between 1000 cm^{-1} and 2300 cm^{-1} there

are four clear minima, associated with symmetric stretching modes of the TCNQ ion.[16]

A least squares fit to R for $\underline{E} \parallel \underline{b}$ was made for reflectance calculated from a Drude-Lorentz dielectric function of the form

$$\varepsilon(\omega) = \frac{\omega_p^2}{\omega_g^2 - \omega^2 - i\omega/\tau} + \frac{\omega_L^2}{\omega_0^2 - \omega^2 - i\omega\Gamma} + \varepsilon_\infty \qquad [1]$$

The first term in Eq. [1] describes the reflectance maximum below 4800 cm^{-1}, the second term includes the weak structure around 10,000 cm^{-1}, and the third term is the contribution of all higher frequency contributions to the static dielectric constant. The fit was made to the data between 2400 cm^{-1} and 8000 cm^{-1} and the best results were obtained with the following parameters: strength of the first transition, ω_p = 0.66 eV; center frequency, ω_g = 0.22 eV; and relaxation rate, $1/\tau$ = 0.32 eV. For the second transition, ω_L = 0.62 eV, ω_0 = 1.2 eV, and Γ=0.56eV. The high frequency dielectric constant is ε_∞ = 2.65.

Because of the wide frequency range studied, a Kramers-Kronig integral of the reflectance should yield accurate values for the phase shift in the center of the experimental region. Figure 1a gives the frequency dependent conductivity, $\sigma_1(\omega)$ and Figure 1b the real part of the dielectric function, $\varepsilon_1(\omega)$. Below 200 cm^{-1} the average value of the conductivity is σ_1 = 19 ± 1 $(\Omega\text{-cm})^{-1}$, in excellent agreement with the dc value of 20 $(\Omega\text{-cm})^{-1}$.[6-8] $(NMe_3H)(I)(TCNQ)$ is the first conducting TCNQ system in which there is agreement between the dc and far infrared conductivities! There is a strong peak in $\sigma_1(\omega)$ centered near ω_g = 1770 cm^{-1} (0.22 eV). The full width at half maximum observed in Figure 1a is approximately equal to the relaxation rate obtained from the fit above 0.32 eV. The maximum value of the conductivity is 180 $(\Omega\text{-cm})^{-1}$ as expected from the Drude-Lorentz parameter, $\omega_p^2\tau/4\pi$.

The dielectric function is negative below 40 cm^{-1}, characteristic of free carriers, and has a maximum of 10 in the far infrared. This value is comparable to the static value calculated from Eq. [1], $\varepsilon_1(0)$ = 12, but is considerably lower than the measured[7] microwave value at 4.2K of ε_1 = 30. The transition in the infrared is not quite strong enough to drive $\varepsilon_1(\omega)$ negative between ω_g and ω_p, in part because of the relatively large value of ε_∞. The transition in the visible is sufficiently strong; $\varepsilon_1(\omega)$ is negative between 19,000 cm^{-1} (2.4 eV) and 21,700 cm^{-1} (2.7 eV).

The implications of both the fit to the reflectance and the Kramers-Kronig analysis is that there is an energy gap in the system at room temperature even though the dc conductivity is appreciable. The Drude-Lorentz dielectric function

probably overestimates the gap. The conductivity reaches half of its maximum value at 800 cm^{-1} (0.10 eV) while about 1/8 of the interband oscillator strength is used up by 1100 cm^{-1} (0.14 eV). Either of these criteria might be reasonably used to define the edge of a rather smeared band gap. A gap of 0.10 eV - 0.14 eV is both in agreement with, and experimental evidence for, an analysis within the dc conductivity model[8-11] described above ($E_g \sim 0.14$ eV at 300K).[8] The conductivity for $\omega < E_g$ is then due to carriers thermally excited across the gap. These "free carriers" in turn drive the dielectric function negative below 40 cm^{-1}.

Dark green needle-like crystals of $(NMe_3H^+)(I_3^-)_{1/3}(TCNQ)^{2/3-}$ have been found to consist of two interpenetrating lattices.[5,17] In contrast to earlier work in which one set of layer lines (attributed to the iodine atoms) was found to be diffuse,[5,17] several of the crystals showed discrete Bragg spots in all the layer lines of an oscillation photograph parallel to the needle axis.[18] The additional discrete layers (referred to here as B layers) do not have the mirror symmetry perpendicular to the oscillation axis which is evident for the A lattice. Further analysis of both oscillation and Weissenberg photographs indicates the iodine lattice to be triclinic with a pseudo mirror plane parallel to the iodine columns. Its b axis is parallel to the [104] direction of the trimethylammonium TCNQ lattice. While the c axis of the B lattice is parallel to b of A and along the direction of the columns, the a_B axis is inclined to a_A by 17.6°. Approximate cell dimensions of the B lattice are a = 10.68Å, b = 25.25Å, c = 9.70Å, α = 90°, β = 107.6°, γ = 97.3°. The relative orientation of the two lattices is such that the I_3^- molecule at 0,0,0 relates to one TCNQ molecule in the same way as the iodine at 100 (coordinates of B lattice) to an adjacent TCNQ molecule in the same stack.

Examination of the X-ray intensities leads to the conclusion that the I_3^- molecule at 1/2 1/2 z is at the height of a third TCNQ molecule in the same stack though it is too far away to be in contact with molecules in this stack. It is of interest that in the preparations studied so far smaller crystals tend to show diffuse streaks, while larger crystals generally give only discrete spots. Physical properties of both types of crystals are being examined in order to establish a possible correlation between these properties and the diffraction pattern.

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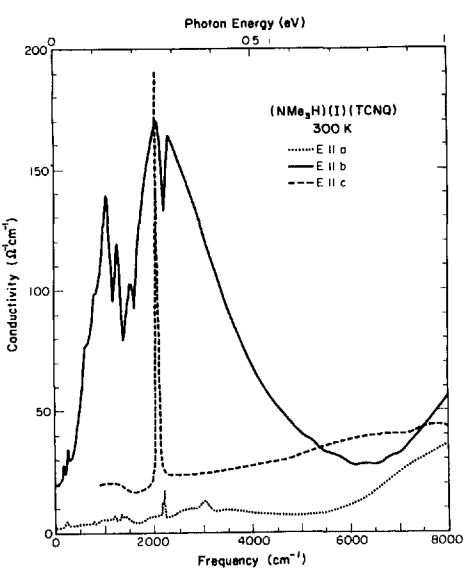

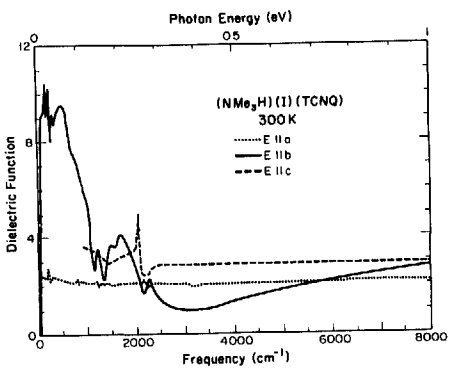

Figure 1. The frequency dependent conductivity (a) and real part of the dielectric function (b) determined by Kramers-Kronig analysis of the reflectance of $(NMe_3H)(I)(TCNQ)$ at room temperature. The dc conductivity is $\sigma_{RT} \sim 20\ (\Omega^{-1}cm^{-1})$.