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Elastic properties of $(N(CH_3)_3\,H)(I)(TCNQ)$

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We present the results of a study of the temperature dependence of the Young's modulus and internal friction of $(N(CH_3)_3H)(I)(TCNQ)$. The Young's modulus was measured in a direction parallel to the TCNQ (tetracyanoquinodimethane) stacking axis using a vibrating reed technique. The results confirmed a transition observed via transport measurements at 150 K and predicted a transition (later observed) at 89 K. The data support the model that this system is a semiconductor at temperatures above 150 K despite the "metal-like" dc conductivity.

I. INTRODUCTION

The study of linear-chain organic and inorganic anisotropic compounds has emphasized those systems with high "metal-like" conductivity.[1–4] 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 $N(CH_3)_3H^+I^-$ to form a novel ternary material of $(N(CH_3)_3H)(I)(TCNQ)$ stoichiometry with one cation and two different segregated acceptor chains, presumably only one of which, TCNQ, is conducting. X-ray studies[5–7] have shown that the $(N(CH_3)_3H)(I)(TCNQ)$ system consists of two interpenetrating lattices, one associated with the $(N(CH_3)_3H)(TCNQ)$, and the other with the iodine lattice. The chemical composition and crystal structure of this system are unusual and hence provide an opportunity to explore the range of phenomena that are present in quasi-one-dimensional molecular conductors.

The $(N(CH_3)_3H)(I)(TCNQ)$ system forms lustrous green needlelike crystals with the flat planar TCNQ molecules and iodine both forming segregated stacks parallel to the needle (b) axis. The TCNQ molecules form a uniformly spaced atypical zigzag structure. That is, the TCNQ molecules, while having the "typical" ring over exterior double bond overlap,[8] are also perpendicular to the stacking axis. This is in contrast to the more common canted chain structure for highly conducting TCNQ salts.[8] The only other highly conducting TCNQ compound with this detailed zigzag structure is tetramethyl-*p*-phenylenediamine-$(TCNQ)_2$.[9]

We previously reported[10–12] the initial results of extensive physical studies undertaken on this system. These studies include elemental analysis, x-ray diffraction, thermal gravimetric analysis, differential scanning calorimetry, Raman scattering, polarized reflectance, anisotropic dc conductivity, microwave conductivity, dielectric constant, electron-spin resonance (ESR), proton magnetic resonance (^{1}H NMR), anisotropic thermoelectric power (TEP), and Young's modulus (E). These results show the large highly conducting metallic green-appearing crystals to be $(N(CH_3)_3H^+)(I_3^-)_{1/3}(TCNQ)^{2/3-}$, a thermally stable compound which undergoes semiconductor-semiconductor transitions at 150 and 89 K. Thus there is a $\frac{1}{3}$ 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[10,11,13] $\sigma_{RT} \simeq 20\ (\Omega\ \text{cm})^{-1}$. The temperature, T, dependence of σ features[10,11,13] "metal-like" behavior between 300 and 240 K at which temperature ($T = T_M$) it achieves its maximum value, $\sigma = 1.08\sigma_{RT}$. There is a maximum in $-d\ln\sigma(T)/d(1/T)$ at 150 K, indicating a transition at this temperature.

Recently, Epstein *et al.*[14–16] 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 in large part 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 in triethylammonium-$(TCNQ)_2$,[17] and in K(TCNQ).[18] The model predicts the existence of a semiconducting energy gap of $E_g \sim 0.14$ eV for (N(CH$_3$)$_3$H)(I)(TCNQ) 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. Below the 150 K transition, the dc conductivity is activated with a semiconducting energy gap of $E_g \sim 0.17$ eV.[13] These energy gaps may be due to the periodic potential on the TCNQ chains caused by the triiodide (I_3^-) chains.

The thermoelectric power, S, measurement[11] for $T > 150$ K is fit by $S = |k_B/e|(-\ln 2 + 110/T)$ in agreement with semiconducting behavior[19] in a system with large on site Coulomb repulsions.[20] Polarized reflectance measurements have been made on room-temperature lustrous metallic green specimens using conventional techniques.[21] A Kramers-Kronig integral of the reflectance gives the frequency dependent conductivity, $\sigma_1(\omega)$ and the real part of the dielectric function, $\epsilon_1(\omega)$. (N(CH$_3$)$_3$H)(I)(TCNQ) is the first conducting TCNQ system in which there is agreement between the dc and far-infrared conductivities.[21] The implications of both the Drude-Lorentz 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. An optical gap of 0.10–0.14 eV is both in agreement with, and experimental evidence for, an analysis within the dc conductivity model[13–16] described above ($E_g \sim 0.14$ eV at 300 K).[13] The conductivity for frequencies $\omega < E_g/\hbar$ is then due to carriers thermally excited across the gap. These "free carriers" in turn drive the dielectric function negative below 40 cm^{-1}.

The relationship of the transition observed at 150 K in (N(CH$_3$)$_3$H)(I)(TCNQ) to structural changes is as yet uncertain. Near phase transitions, the elastic constants usually undergo a perturbation in their temperature dependence, reflecting structural change. In several materials (such as [22]TaSe$_2$ and [23]NbSe$_3$) undergoing charge-density wave transitions with corresponding lattice distortions, anomalies (minima) in the Young's modulus have appeared at the transition temperature, usually accompanied by maxima in the internal friction. In TTF-TCNQ (TTF≡tetrathiafulvalene) on the other hand, the Young's modulus has been observed[24–26] to increase rapidly[25,26] at temperatures below the 53-K Peierls distortion.

In order to shed light on the nature of the transition observed in (N(CH$_3$)$_3$H)(I)(TCNQ) at 150 K, we have examined the Young's modulus for the b axis as a function of temperature. In contrast with TTF-TCNQ, only a weak anomaly is observed in the neighborhood of the 150 K transition. This qualitatively different behavior is related to the differences in electronic state of these materials above their respective transition temperatures.

II. EXPERIMENTAL

The Young's modulus and internal friction of (N(CH$_3$)$_3$H)(I)(TCNQ) were measured using the vibrating reed technique of Barmatz.[22,27–29] The frequency f_0 of the fundamental flexural resonance of a cantilevered reed is given by[27]:

$$f_0 \approx \frac{1}{6.19}\left(\frac{t}{l^2}\right)\left(\frac{E}{\rho}\right)^{1/2}, \tag{1}$$

where t is the reed thickness, l the length, ρ the density, and E the Young's modulus in the axial (b) direction. Corrections to Equation (1) are of order $(t^2/l^2)E/C$, where C is the effective shear modulus,[30] and are negligible ($<< 1\%$) for the crystals measured.[31]

A long thin crystal was mounted on the end of a copper rod with low-temperature solder,[32] and placed so that the free end was between two copper electrodes approximately 1 mm apart. An ac voltage applied to one unbiased electrode electrostatically excited flexural vibrations in the reed at twice the applied frequency. The resulting vibration was detected at the biased second electrode, and the signal fed into a lock-in amplifier, the output of which was used to phaselock the drive signal to the reed resonance.[22,23,31] This technique allows continuous monitoring of the resonance frequency, and therefore the Young's modulus, as the sample is cooled. {For simplicity, the effects of thermal contraction on the resonance frequency [see Eq. (1)] were neglected, and it was assumed that $f_0 \propto (E)^{1/2}$.} The internal friction was found by measuring the relative width of the resonance, $1/Q$, either by introducing ±45° phase shifts into the phaselock loop or by cutting the loop and measuring the amplitude of the detected signal as a function of frequency.[31] The crystal strain ϵ was kept sufficiently small ($\epsilon \sim 10^{-5}$) so that the Q was strain independent.

The sample was cooled with a Cryodyne 350 refrigerator.[33] The temperature was measured with a copper wire thermometer while a thermistor controlled heater kept temperature fluctuations to less than 0.1 K during internal friction measurements.[31]

The Young's moduli of two crystals were measured at room temperature, with $E = (1.4 \pm 0.5) \times 10^{11}$ dynes/cm^2 and $E = (1.7 \pm 1.2) \times 10^{11}$ dynes/cm^2, respectively. The room-temperature Young's modulus is approximately 50% larger than that of (TTF)-(TCNQ).[25] Only the second, thinner crystal (approximate dimensions $3.0 \times 0.2 \times 0.04$ mm^3 with an ambient resonance frequency of 2.8 kHz) was cooled. It was cycled to 17 K several times with small (less than two percent) offsets in the resonance frequency observed, probably due to thermal creep in the clamp. For the final runs, the low-temperature signal to noise was improved by evaporating ~ 250 Å of gold onto each broad crystal surface. This increased the internal friction ($Q^{-1} \sim 2.5\times10^{-3}$) by three percent and resonance frequency by two percent, with the temperature dependence of the frequency changing negligibly from earlier runs.

III. RESULTS AND DISCUSSION

The relative change in the Young's modulus from its room-temperature value (E_0), $\Delta E \equiv E - E_0$, during a cooling run is shown in Fig. 1. The ambient value of the temperature derivative, $d\ln E/dT \approx -2\times10^{-3}$ K^{-1}, is intermediate between values of ionic salts and molecular solids, as expected. A weak anomaly in the modulus was observed just above the 150 K transition, at 157 K, Fig. 2. The discontinuity in modulus, assuming that the transition is broadened over 3 K, is $\Delta E/E \approx -4\times10^{-3}$. No significant peak in the internal friction Q^{-1} is observed ($\Delta Q^{-1} < 2\times10^{-5}$). Also, no discontinuity in the derivative of the modulus with temperature is observed at the transition.

The difference in behavior of the Young's modulus and internal friction of $(N(CH_3)_3H)(I)(TCNQ)$ and that of (TTF)-(TCNQ) is particularly striking in the regions of their electronic transitions, 150 and 53 K, respectively. There is a marked increase in the Young's modulus of (TTF)-(TCNQ) below 53 K,[25,26] with a quantitatively different temperature dependence above and below 53 K. In contrast, the Young's modulus of $(N(CH_3)_3H)(I)(TCNQ)$ exhibits only a small discontinuity at 157 K, and the same linear temperature dependence above and below this discontinuity, Fig. 2. Tiedje *et al.* proposed[26] that the change in behavior of the Young's modulus of (TTF)-(TCNQ) below the transition was due to a stiffening of the modulus caused by a freezing out of the electronic contribution to elastic constants caused by the opening of an energy gap at the transition temperature. Above the transition temperature, the electronic contribution to the Young's modulus was proposed[26] to arise through a strain-dependent Fermi wave vector and hence a strain-dependent charge transfer.

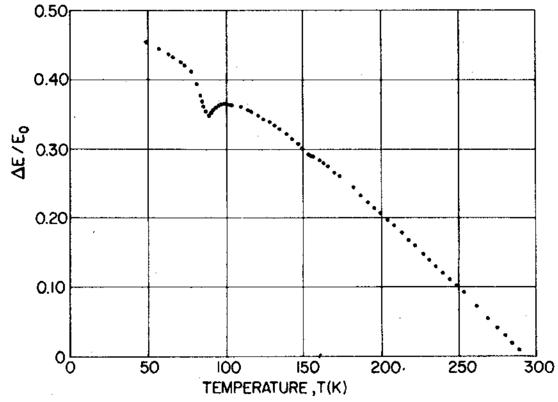

FIG. 1. Relative change in Young's modulus of $(N(CH_3)_3H)(I)(TCNQ)$ when cooling from room temperature.

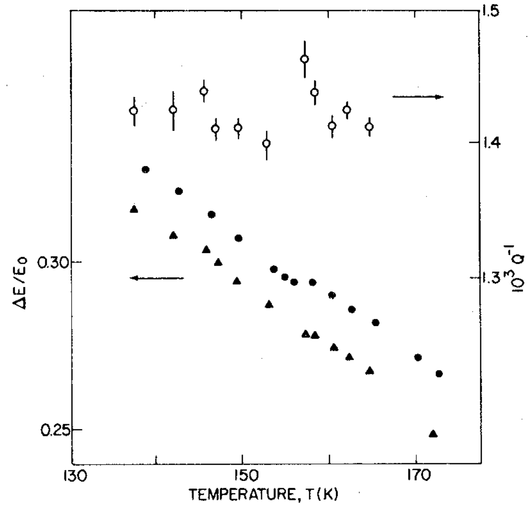

FIG. 2. Internal friction (Q^{-1}) (ϕ) and Young's modulus (cooling ●, warming ▲) in the region of the 150 K transition. The offset between warming and cooling data is probably due to the crystal loosening in the clamp (thermal creep).

Assuming that the $(N(CH_3)_3H^+)$ molecule remains fully ionized, strain-dependent charge transfer can still occur in this system through charge exchange between the TCNQ and iodine chains. The only chemical constraint is that the average charge per TCNQ plus the average charge per iodine must sum to minus one. Results of extensive studies[10–12] show this system to be well represented by $(N(CH_3)_3H^+)(I_3^-)_{1/3}(TCNQ)^{2/3-}$. Small variations of charge distribution about this value may be energetically unfavorable because of the commensurate nature of two-thirds charge per TCNQ. If such strain-dependent charge transfer were occurring, then following the viewpoint of Epstein *et al.*[10–13] that this system is a semiconductor both above and below the 150 K transition, and utilizing the proposed model of Tiedje *et al.*,[26] only a minimal change in the electronic contribution to the Young's modulus is expected for $(N(CH_3)_3H)(I)(TCNQ)$ at 150 K. This is because there is a gap in the density of states at the Fermi energy both above and below this transition. Thus the $(N(CH_3)_3H)(I)(TCNQ)$ Young modulus results are in agreement with the applicability of the semiconductor model[14–16,34] for many of the "metal-like" conductors.

For a second-order phase transition, the anomaly in the modulus in the *i* th crystallographic direction

ΔE_i is related to the discontinuity in specific heat (at constant stress) ΔC_σ by[35]

$$\frac{\Delta E_i}{E_i} = -E_i \frac{\Delta C_\sigma}{T_c}\left(\frac{\partial T_c}{\partial \sigma_i}\right)^2 . \qquad (2)$$

The specific-heat anomaly has been measured as ~50 joules/mole K at 150 K.[36] Using $\Delta E_b/E_b = -4\times10^{-3}$, and E_b (150 K) $=1.9\times10^{11}$ dynes/cm^2, we find

$$\left|\frac{\partial T_c}{\partial \sigma_b}\right| \sim 2 \text{ K/kbar} , \qquad (3)$$

a value comparable to the pressure dependence of the transition temperatures in the quasi-one-dimensional conductors (TTF)-(TCNQ)[37] and $\mathrm{NbSe_3}$.[38]

A second, much larger, hysteretic anomaly was observed at approximately 90 K (see Fig. 3). The data shown were taken during three cycles through the transition with no significant changes in results. A hysteresis of approximately 5 K was observed during temperature cycling, near 90 K. Any offsets between the temperature of the peaks in internal friction and Young's modulus is less than 1 K. The observation of this low-temperature anomaly in the Young's modulus led to a re-examination of other data. A corresponding small increase in the microwave dielectric constant is observed[39] as the temperature increases above 89 K. Further, the proton-spin-lattice relaxation is reported[40] to be thermally activated for $T > 100$ K. These results together suggest that the 89 K anomaly may be associated with the freezing out of methyl group rotations below this temperature.

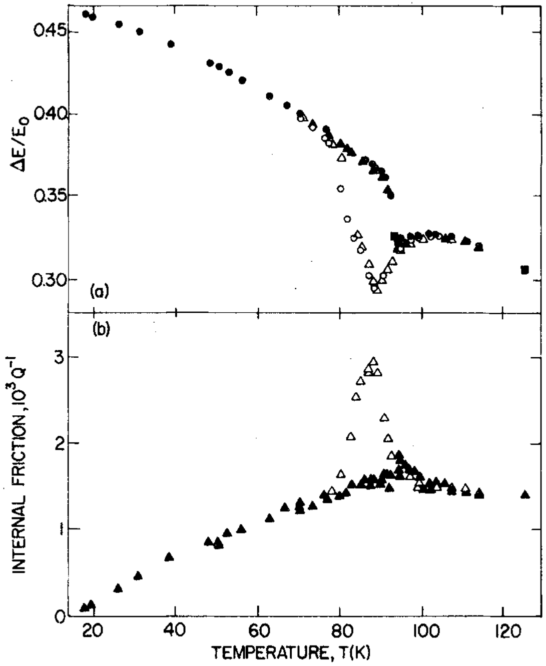

FIG. 3. (a) Low-temperature Young's modulus of $(\mathrm{N(CH_3)_3H})(\mathrm{I})(\mathrm{TCNQ})$. Solid points taken during warming sweeps; open points taken during cooling sweeps. (b) Low-temperature internal friction Q^{-1} of $(\mathrm{N(CH_3)_3H})(\mathrm{I})(\mathrm{TCNQ})$. Solid points taken during warming sweeps; open points taken during cooling sweeps.

IV. SUMMARY

The temperature dependence of the Young's modulus and internal friction of $(\mathrm{N(CH_3)_3H})(\mathrm{I})(\mathrm{TCNQ})$ is seen to be qualitatively different from that of (TTF)-(TCNQ). The experimental results show two anomalies, one at 157 K associated with the transition observed in the dc conductivity at 150 K, and one at 90 K, associated with the freeze out of methyl-group rotations. These experimental results are in agreement with and evidence for a model of $(\mathrm{N(CH_3)_3H})(\mathrm{I})(\mathrm{TCNQ})$ as a semiconductor both above and below the 150 K transition.

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