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ABSTRACT The energy gap and charge conduction mechanism of $(NMP)_x(Phen)_{1-x}(TCNQ)$ with x between 0.5 and 0.6, a range where this large U system evolves from a commensurate ($x \lesssim 0.57$) to an incommensurate ($x \gtrsim 0.57$) Peierls insulator, have been studied with infrared and transport measurements. The conductivity and infrared absorption studies show that the low temperature gap is 0.1 to 0.15 eV. The weak T-dependence of this gap reflects contributions from both the Peierls order parameter and an external periodic potential due to ordering of the NMP^+ and $Phen^\circ$ in the donor stack, Δ_e. The oscillator strengths of the low frequency phonon modes provide a measure of the T-dependence of the order parameter, $\Delta(T)$. The results are in agreement with a calculation of Conwell and Howard of the Peierls distortion $\Delta(T)$ in the presence of a small Δ_e. The T-dependent thermopower S(T) varies markedly with x. This behavior implies an important hole type conduction despite the presence of excess electrons, in accord with charge conduction at the soliton level, though a large asymmetry in electron and hole mobilities may have a role.

I. INTRODUCTION

The $(N\text{-methylphenazinium})_x(phenazine)_{1-x}$(tetracyanoquinodimethane) system [1], Fig. 1, has been a model system for the study of a variety of unusual phenomena[2]. Through control of the chemical composition, x, the number of conduction electrons per unit cell can be varied from ~0.5 to 1.0. This series of one-dimensional conductors is then a nearly ideal system in which to test the numerous physical concepts. Earlier x-ray diffuse scattering[3,4,5], optical[6,7] and magnetic studies[2,8] demonstrated that for $x \gtrsim 0.67$ this system has conduction electrons on both donor and acceptor chains and coulomb repulsion (U) less than the bandwidth (W). In contrast, for $x \lesssim 0.67$ nearly all the conduction electrons are on the TCNQ stack and the system is in a large U ($U/W > 1$) regime. Structural studies[4,5] have shown that the $x = 0.5$ system is an ordered crystalline segregated stack charge transfer salt with 0.5 excess electrons per TCNQ. The sysem has a commensurate Peierls distortion at $4k_f = a^*/2$ where a^* is the reciprocal lattice vector in the TCNQ stacking direction. Thermally generated solitons have been shown[9,10,11] to have a large role in this system. Addition of up to seven percent extra NMP

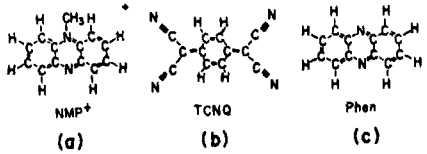

FIGURE 1. (a) NMP^+, (b) TCNQ, (c) *Phenazine*°.

(i.e., $0.50 \lesssim x \lesssim 0.57$) leads to the excess charge being accommodated in soliton states on the TCNQ stack. The theoretical studies[12] of highly correlated one-dimensional salts near the one-quarter filled band limit predicted that the solitons in this system have charge $\pm e/2$. For $x \gtrsim 0.58$, these studies show a crossover to an incommensurate Peierls distortion. The conductivity of $(NMP)_x(Phen)_{1-x}(TCNQ)$ system has been analyzed as that of a Peierls semiconductor[13].

We have carried out temperature-dependent infrared absorption studies of the $(NMP)_x(Phen)_{1-x}(TCNQ)$ system. We report the first direct detection of the Peierls gap in these systems, in contradiction to the disorder models[14-17] which predict a finite density of states at the fermi level. The anomalously strong and temperature (T) dependent a_g modes demonstrates that the semiconducting gaps in these materials are indeed Peierls gaps. The detailed analysis of this data supports that the interchain potential due to the alternation of NMP^+ and $Phen^\circ$ leads to a potential which is commensurate with the Peierls distortion and results in shifting the insulator-metal transition to higher temperatures and confinement of the solitons into bipolaron units. Temperature dependent thermopower of this system confirms the commensurate-incommensurate transition and implies an important contribution of holes to the dc conductivity, in accord with charge conduction at the soliton level, although asymmetry in electron and hole mobilities may have a role.

II. EXPERIMENTAL TECHNIQUES

The small crystals were grown from solution. Generally, the values of x, which are determined by solution absorption spectra, are accurate to ± 0.02. In cases where solution analysis yields $x = (0.50-\delta)$ with $\delta \sim 0.01$, concerted studies suggest that for these samples, x is equal to or slightly larger than 0.50, that is, very close to stoichoimetric. An example of such a composition is an $x = 0.49$ sample.

Because the crystals were too small for reflectance studies, absorption measurements were made on composite samples prepared by grinding and mixing many small crystals with an insulating host and compressing the mixture into a pellet. The typical crystal size in these samples was several microns and the volume fraction in the mixture was below 0.01. Thus, the crystals were isolated in the host; the absorption coefficient of the TCNQ salts could be determined after correcting for the absorption and reflection of the host. In the frequency range studied (below 4000 cm^{-1}) this absorption is mostly from the TCNQ chain direction. Measurements were made in two overlapping frequency regions. From 50 to 800 cm^{-1} a homebuilt Michelson interferometer was used to study paraffin-host samples. Low-temperature measurements were made by putting the samples in the detector cryostat. Between 600 and 4000 cm^{-1}, a Digilab rapid-scanning interferometer was used to study KCl-host specimens. Use of a Helitran continuous-flow refrigerator enabled the low-temperature measurements.

The thermopower (S) was measured for at least a half dozen crystals of each composition. Measurements were taken with the temperature gradient of less than 1K along the stacking axis using a technique designed for use with these small single crystals[18]. The results for crystals from the same batch were reproduceable with small variation in the maximum value of -S observed. The variation between batches of the same "x" values reflected the uncertainty in x.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Infrared Studies

The far infrared results for samples of the various compositions were similar for all compositions studied and similar to the results for Quinolinium $(TCNQ)_2$[19]. Figure 2 presents typical absorption data for $(NMP)_{0.55}(Phen)_{0.45}(TCNQ)$ at 25K. Figure 3 shows the temperature dependence of the $(NMP)_{0.55}(Phen)_{0.45}$ (TCNQ) absorption data over a broader frequency range and as a function of temperature. Three features are of particular importance:

(i) $\alpha \simeq 0$ for frequencies less than 100 cm^{-1}.

(ii) Nine of the ten TCNQ a_g modes display anomalously strong infrared activity. The modes with frequencies below ~1000 cm^{-1} are resonances while those above 1000 cm^{-1} are antiresonances.

(iii) Broad absorption is observed, increasing above 150 cm^{-1}.

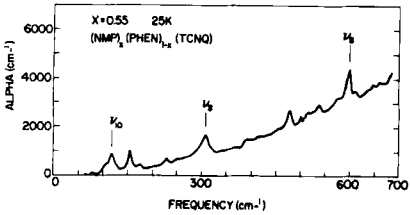

FIGURE 2. Absorption coefficient vs. frequency for $(NMP)_{0.55}(Phen)_{0.45}(TCNQ)$ at 25K. Note the linear scales. The arrows indicate the a_g modes.

The lack of absorption below 100 cm^{-1} demonstrates that there is a gap in the density of states at the Fermi level. The presence of a gap demonstrates that earlier models [14-17] which focused on disorder localization of conduction electrons are not appropriate for these systems. In contrast, the presence of the TCNQ a_g modes is strong evidence for the description of these materials as Peierls semiconductors. These modes were normally infrared inactive because they are totally symmetric oscillators. However, they become strongly infrared active in the presence of the phase oscillators of a charge density wave [20]. The crossover from resonance to antiresonance for these modes allow an estimation of the bandgap of this material of 2Δ in the range of 950 to 1200 cm^{-1}. This is in reasonable agreement with numbers estimated from the conductivity data [9-11,21]. The temperature dependence of the oscillator strength of these a_g is a measure of the temperature dependence of the Peierls gap, Δ_p. The data in Fig. 3 show that Δ_p does not go to zero near the mean field transition temperature of ~150K. It has been shown that

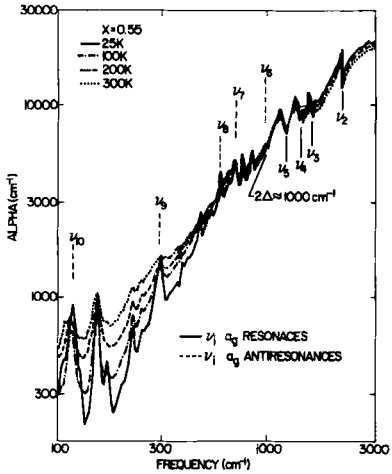

FIGURE 3. Absorption coefficient vs. frequency for $(NMP)_{0.55}(Phen)_{0.45}(TCNQ)$ at 25K, 100K, 200K and 300K. The arrows indicate the a_g modes. Note the logarithmic scales.

the persistance of the Peierls gap to higher temperatures is a result of the presence of a small (~20K) interchain potential with the same periodicity as the Peierls distortion[19,22].

The increase in absorption beginning at ~150 cm^{-1} is similar to that reported for moderately doped polyacetylene [23] and polypyrrole [24] although the scale of energies is reduced by an order of magnitude. The data suggest a broad absorption by the solitons in this system. The presence of an interchain potential is expected to lend to the formation of two bipolaron levels in the gap [22,25]. In addition, overlap of the bipolarons, and the presence of the excess donor charges should cause the bipolaron levels to spread across the gap. This absorption increases with temperature as expected due to the thermal nucleation of additional bipolarons.

The presence of the Peierls gap is in agreement with the observed [26] decoupling of the spin diffusion and charge conduction in this system.

B. Thermopower Studies

Figure 4 summarizes the results of the temperature dependence of the thermopower of $(NMP)_x(Phen)_{1-x}(TCNQ)$ for representative compositions. Generally all compositions studied have $S \approx -65\mu V/K$ at room temperature. As the temperature is lowered, S becomes increasingly negative for samples with $x \lesssim 0.53$. At the lowest temperature ($T < 100K$) $|S|$ begins to decrease again. In contrast for $0.54 \lesssim x \lesssim 0.56$, S is nearly T independent above 100K, a behavior similar to that of $Quinolinium(TCNQ)_2$[11,27]. For $x > 0.57$, S(T) changes again, becoming more T-dependent. Figure 5 summarizes this variation in S(T,x) with a plot of minimum thermopower observed, S^{min}, vs. x.

The decrease in S^{min} as x increases from ~0.50 to ~0.56 corresponds to the regime where increasing numbers of soliton pairs are being introduced in the gap of $(NMP)_x(Phen)_{1-x}(TCNQ)$ through doping. The sudden change in S^{min} for $x \gtrsim 0.57$ corresponds to the crossover to the incommensurate regime.

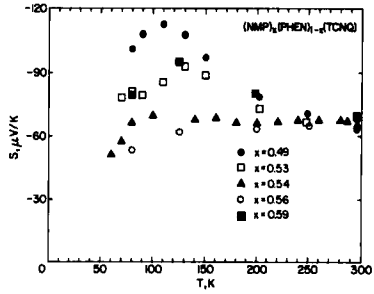

FIGURE 4. Representative temperature dependent thermopower data for $(NMP)_x(Phen)_{1-x}(TCNQ)$.

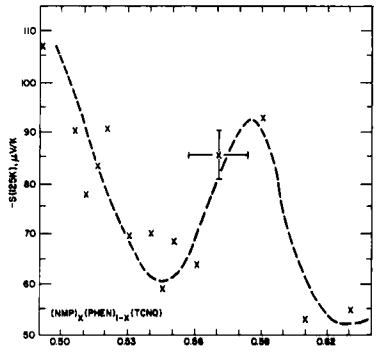

FIGURE 5. Variation of the thermopower at ~125K ($\approx S^{min}$) with composition x.

The value of $S \approx -60\mu V/K$ ($= -|k_B/e|\ln 2$) was early on suggested to reflect the effect of the role of strong Coulomb correlations (large U) in these materials[18,28]. It was later demonstrated that this value could be obtained in the infinite U limit for a semiconductor with 0.5 electrons per site and finite bandwidths[29]. The S(T) may be evaluated as a sum of the contributions of the individual carriers, S_i, weighed by their conductivities, σ_i:

$$S = (\Sigma_i S_i\sigma_i)/(\Sigma_i \sigma_i) \qquad (1)$$

For the symmetric large U quarter filled band semiconductor ($x = 0.50$) these leads to $S = -60\mu V/K$[29]. For high temperatures (~300K) the number of electrons and holes excited becomes increasingly similar for all x [10] in moderate agreement with the observed $S \sim -65\mu V/K$. However, at lower temperatures (e.g., ~100K) and $x > 0.50$, more electrons are excited than holes [10].

With increasing doping (x) (and greater number of defect states in the gap) the Fermi energy becomes increasingly larger so that there are greater numbers of electrons in the conduction band than holes in the valence band. Utilizing Eq. 1, S is predicted to become increasingly more negative as x goes from 0.50 to ~0.56. This is in contrast to the data in Fig. 5. These data can, however, be understood if a significant contribution to the total conductivity is from charge conduction through the defect states in the gap. Since these

states are below the Fermi level, their contribution to S through Eq. 1 is as a positive term, leading to a predicted decrease in S with increasing x in accord with Fig. 5. It has also been pointed out [22] that these defect states in the gap may lead to an asymmetry in the scattering of electrons and holes, and hence, could account for the measured decrease in $|S^{min}|$ with increasing x.

IV. SUMMARY

We have shown that the $(NMP)_x(Phen)_{1-x}(TCNQ)$ $(0.50 \lesssim x \lesssim 0.60)$ system and analogous materials such as Quinolinium$(TCNQ)_2$ are spinless fermion analogues of polyacetylene. The infrared studies have given a direct measure of the Peierls gap. The measured variation of thermopower with composition and temperature demonstrate that the presence of the defect state in the gap affect the transport in this system.

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