Microwave Response of Confined Soliton Pairs (Bipolarons) in (N-Methylphenazinium)$_x$ (Phenazine)$_{1-x}$ (Tetracyanoquinodimethanide)

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The temperature-dependent dielectric response and conductivity at $\simeq 10^{10}$ Hz is reported for the title compound, $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}(\mathrm{TCNQ})$, in the regime $0.50 \leq x \leq 0.59$, spanning commensurate, bipolaron, and incommensurate regimes. The large and strongly temperature-dependent dielectric constant and $\sigma(10^{10}\ \mathrm{Hz})$ are accounted for by a model based on the dynamics of pinned charge-density waves and the presence of relatively mobile charged bipolarons (confined soliton pairs) in the commensurate phase.

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Anomalously large and often strongly temperature-dependent microwave dielectric constants have been reported for many 1D TCNQ salts of conduction-electron charge density of one electron per two TCNQ. For example, Buravov *et al.* and Shchegolev report[1,2] that the dielectric permeability, ϵ, measured at 1.0×10^{10} Hz of acridinium$(\mathrm{TCNQ})_2$ was $\simeq 700$ at 4 K, increasing to $\simeq 3000$ at 60 K. At higher frequencies, e.g., 3.84×10^{10} Hz, ϵ was reduced somewhat (for example, $\simeq 700$ and 1500 at 4 and 60 K, respectively, for this compound). A localized-electron model based upon the electric-field–induced admixture of an excited state was proposed[2] to explain the data. The conductivity, σ, at microwave frequencies was shown to be nearly identical to σ_{dc} for temperatures $T \gtrsim 100$ K and larger than σ_{dc} for lower T. The crossover temperature was dependent upon the compound studied. A similar model was applied to dielectric data for $\mathrm{Qn(TCNQ)_2}$ (Qn for quinolinium).[3] It was independently proposed[4] that randomness in the orientation of the asymmetric donors would lead to localization in these 1D systems. A $T=0$ dielectric constant was calculated by Bush[5] in the limit of strong localization (to less than three sites). However, this model cannot account for the temperature dependence of ϵ.[6,7] It was alternatively noted[8] that a model of linear metallic strands interrupted by insulating lattice defects could account for a dielectric constant of several thousand in the microwave regime. A generalization of this model to include a random barrier height between conducting segments was successful at fitting the real and imaginary parts of the conductivity of $\mathrm{Qn(TCNQ)_2}$ over a wide range of frequencies and temperatures.[9] A common perspective in all of these studies is that disorder localization and barriers dominate the physics of these materials.

An alternative approach to these systems is based on the suggestion[10] that these systems are (Peierls) semiconductors. It was later shown that $\mathrm{Qn(TCNQ)_2}$ and the related $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}(\mathrm{TCNQ})$ ($0.50 \leq x \lesssim 0.64$) undergo a structural instability with one-dimensional $4k_{\mathrm{F}}$ precursor effects.[11,12] For the latter compound, the number of conduction electrons per TCNQ is determined by the fraction of sites in the donor chain occupied by the NMP^+ molecule.[12,13] The temperature-dependent Peierls gaps of $\mathrm{Qn(TCNQ)_2}$[13] and $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}(\mathrm{TCNQ})$[14] were later directly observed via optical techniques. NMR studies[15] of $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}(\mathrm{TCNQ})$ demonstrated that $\sigma_{\mathrm{dc}}(T)$ was not solely determined by temperature-dependent electron mobility in contrast to the earlier conclusion of the $\mathrm{Qn(TCNQ)_2}$ NMR experiments.[16,17] It was predicted[18,19] and shown[13,14,20] that addition of a small number of conduction electrons to the commensurate $(\mathrm{NMP})_{0.5}(\mathrm{Phen})_{0.5}\mathrm{TCNQ}$ (for $0.50 < x \lesssim 0.56$) resulted in the formation of pairs of solitons of charge $-e/2$ (confined by the cation potential to form bipolarons[20] of charge $-e$ for each electron added. For $x \gtrsim 0.58$, an incommensurate Peierls semiconducting ground state is formed.[12,13]

In this Letter we report the temperature and microwave frequency behavior of dielectric constant and conductivity of $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}(\mathrm{TCNQ})$ for $0.50 \lesssim x \lesssim 0.59$. This range of samples allows the study of the real and imaginary dielectric responses as a quasi one-dimensional system is varied from commensurate ($x=0.50$), to commensurate with bipolarons added through chemical doping ($0.50 < x \lesssim 0.56$), to incommensurate ($x \gtrsim 0.58$). At low temperature, $T < 40$ K, the real part of the dielectric constant, ϵ, is $\simeq 200-300$

near commensurability, increasing to $\simeq 600$ for $x \simeq 0.53$, then decreasing to $\simeq 300$ for $x > 0.56$. For all samples, ϵ increases with increasing T, tending to level off or decrease at high T. The $\sigma_{\mu w}(T)$ is similar in magnitude and temperature dependence to the dc conductivity for samples with $x \simeq 0.50$ and $x > 0.58$ for $T > 100$ K, and $\sigma_{\mu w} > \sigma_{dc}$ below $\simeq 100$ K. An excess contribution to $\sigma_{\mu w}$ is observed to room temperature for samples of $x \simeq 0.53$ (the composition with the larger dc conductivity). We suggest that these data reflect the peculiarities of the evolution of a charge-density wave (CDW) system from that of a pinned commensurate CDW with thermally generated bipolarons ($x \simeq 0.50$), to that of a pinned commensurate CDW system with chemically doped and thermally generated bipolarons ($0.50 < x \lesssim 0.56$), to that of a pinned incommensurate CDW system. The large and strongly T-dependent dielectric constant for compositions that are commensurate with thermally generated (and chemically doped) dipolarons is proposed to originate from the polarization of these charged bipolarons within the confines of the coherence length of the CDW, similar to the origin of the high dielectric constant within the interrupted-strand model. The generalization of these concepts to the dielectric properties of other charge-transfer salts is indicated.

Samples were prepared by the previously described method.[21] The relative NMP composition is accurate to ±0.015, so that the composition with minimum NMP prepared, i.e., $x = 0.49$, is most likely $x = 0.50$. The real and imaginary components of the dielectric constant were measured with the cavity perturbation technique of Buravov and Shchegolev.[22] The data were acquired with a Hewlett-Packard model 8350B sweep generator and 6.5-GHz (TM_{010}) and 10.5-GHz (TE_{011}) cavities, with a Janis Supervaritemp Dewar for T control. Measurement of change of cavity frequency and Q, together with an estimated depolarization factor, allows the calculation of ϵ and σ.[22] Potential error bars are indicated in the figures.

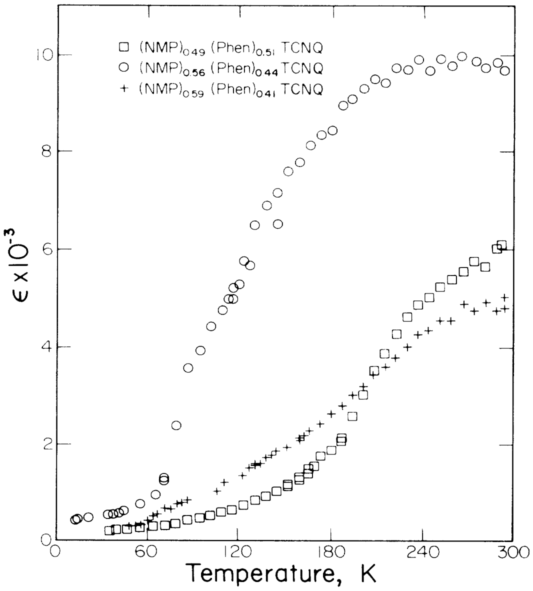

FIG. 1. $\epsilon(T)$ at 6.5×10^9 Hz for representative $(NMP)_x$-$(Phen)_{1-x}(TCNQ)$ compounds.

The real part of ϵ vs T for representative samples is shown in Fig. 1, with the variation of ϵ at low temperature with composition, x, given in Fig. 2. It is observed that at low T, $\epsilon \approx 200$ for $x = 0.50$, increasing with x to nearly 600 for $x \simeq 0.53$ then decreasing to $\simeq 300$ for $x > 0.56$. The ratio ϵ_{max} [the maximum value of $\epsilon(T)$ measured] to ϵ_L (the value of ϵ at low T) has its largest value at $x = 0.50$, decreasing with increasing x.

The microwave conductivity, at 6.5 GHz, normalized to the dc value at room temperature is shown in Fig. 3(a) together with the dc conductivity[13,19] (uncertainties in the depolarization factor prevent determination of a more accurate absolute value for $\sigma_{\mu w}$), for a sample representative of the intermediate regimes. A plot of $\log\sigma$ vs T^{-1} of a typical commensurate CDW ($x \simeq 0.50$) as well as an incommensurate CDW ($x > 0.59$) is in Fig. 3(b). In all cases the $\sigma_{\mu w}$ is larger than σ_{dc} for $T < 100$ K, the largest $\sigma_{\mu w}/\sigma_{dc}$ for samples in the intermediate ($x \simeq 0.53$–0.56) regime. As T increases toward room temperature, the $\sigma_{\mu w}(T)$ is the same as $\sigma_{dc}(T)$ within experimental error, except for samples in the intermediate regime, where $\sigma_{\mu w}$ indicates the presence of an additional conduction mechanism.

The dielectric response on $(NMP)_x(Phen)_{1-x}$-(TCNQ) and the related $Qn(TCNQ)_2$ (earlier shown[11,20,23] to be similar to the subject compounds with $x = 0.54$) can be understood in the context of a Peierls ground state and bipolarons/solitons. It is assumed that the dielectric constant can be decomposed into a sum of

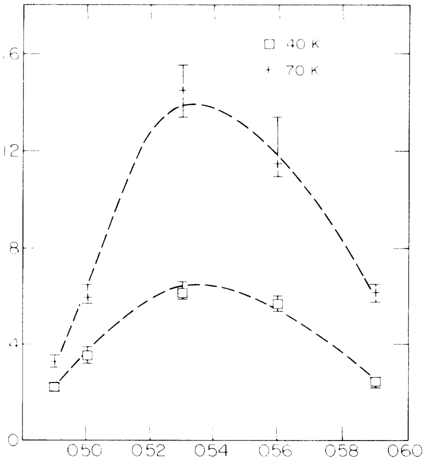

FIG. 2. ϵ vs x for $T = 40$ K and $T = 70$ K (the dashed curves are guides to the eye).

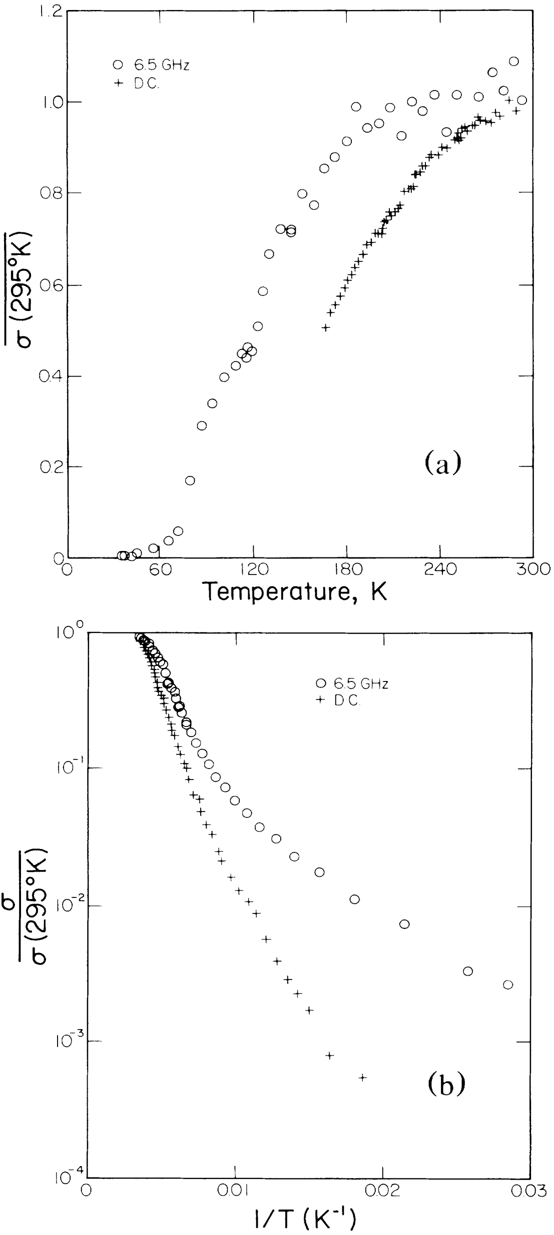

FIG. 3. dc and 6.5-GHz conductivity for representative $(NMP)_x(Phen)_{1-x}(TCNQ)$ samples. The microwave data are normalized to their dc counterparts. (a) σ vs T, $x=0.56$; (b) $\log\sigma$ vs T^{-1}, $x=0.49$.

contributions:

$$\epsilon = 1 + \epsilon_{sc} + \epsilon_b(n_b,T,\omega) + \epsilon_{CDW}, \qquad (1)$$

where ϵ_{sc} is the contribution due to activation across the energy gap $(\hbar\omega_g)$ of the 1D semiconductor, $\epsilon_{sc} \simeq \frac{2}{3}(\omega_p^2/\omega_g^2)$,[24,25] ϵ_{CDW} that due to the pinned charge-density wave,[24] $\epsilon_{CDW} \simeq \Omega_p^2/(\omega_t^2-\omega^2)$ (Ω_p^2 is the pinned-mode oscillator strength and ω_t the pinning frequency), and $\epsilon_b(n_b,T,\omega)$ is that due to n_b bipolarons (see below). For $x<0.60$, the plasma frequency $\hbar\omega_p \simeq 0.7$ eV,[26] and $\hbar\omega_g \simeq 0.1$ eV,[14] yielding $\epsilon_{sc}=33$, too small to account for the measured dielectric constants.

The dielectric constants of pinned incommensurate CDW systems such as (TTF)(TCNQ)[25] and related compounds[27] are 4000 ± 2000 for $T<20$ K, often increasing at higher temperatures as the pinning frequency decreases.[27] The $\epsilon(T)$ we report for the incommensurate $(NMP)_{0.59}(Phen)_{0.41}(TCNQ)$ is consistent with this behavior.

The much larger pinning frequencies expected for the commensurability-2 $(NMP)_{0.5}(Phen)_{0.5}(TCNQ)$ implies that the ϵ_{CDW} for this system should be much less than that for the incommensurate $x=0.59$ system. However, for $0.50 \le x < 0.56$, a substantial contribution due to chemical-doped and thermally generated confined soliton-antisoliton pairs (bipolarons) is possible:

$$\epsilon_b(n_b,T,\omega) = n_b\epsilon_b^0 + \epsilon_b^p(n_b,T,\omega). \qquad (2)$$

Here ϵ_b^0 represents the electronic polarizability of bipolarons and ϵ_b^p the dielectric response of bipolarons diffusing a length L ($<$ coherence length of pinned commensurate CDW) in the presence of the applied oscillating electric field. An upper bound on ϵ_b^0 can be estimated if we assume a (field-induced) dipole moment of $(e)l_b$, where l_b is the length of each bipolaron ($\simeq 11$ TCNQ-TCNQ spacings or[20] $\simeq 42$ Å) and an excitation energy of $\hbar\omega_g/2$. This yields $n_b\epsilon_b^0 \approx 150$ for a concentration of one bipolaron per 100 TCNQ molecules. This ϵ_b^0 is too small to account for the magnitude, frequency, and T dependence of the experimental ϵ at all but the lowest temperatures.

Disorder prevents 3D ordering of the CDW's and leads to a finite coherence length L of the CDW's.[12] Bipolarons, especially thermally generated bipolarons,[20,28] are expected to be only weakly pinned within the coherence length L of a CDW, because of the large dielectric constants and the bipolaron's large spatial extent along the chain.[20,29] For $x>0.51$, the effective pinning will be dramatically reduced as the average separation of the pinning sites (excess NMP^+ beyond the ordered $x=0.50$ composition) on the four donor chains surrounding each TCNQ chain is less than the bipolaron length. The rapid increase in ϵ for $T \simeq 180$ K for the $x=0.49$ samples suggests that this is the pinning energy for the commensurate system in excellent agreement with theoretical estimates.[29] The rapid rise in $\epsilon(T)$ at 70 K for $x=0.56$ may reflect the reduction in pinning energy with x indicated above. If we assume a classical model for a rotating dipole to represent the motion of unpinned bipolaron within L, the dielectric response for n_b bipolarons per unit length confined to the length L is

$$\epsilon_b^p \approx \frac{4\pi}{\epsilon_0}\left(\frac{n_b}{A}\right)e^2\frac{(L-n_bLl_b)^2}{k_BT}\left(\frac{1}{1+\omega^2\tau^2}\right), \qquad (3)$$

where A is the cross sectional area per TCNQ chain, and τ represents the time to polarize the bipolarons within L. If $\omega\tau \ll 1$, $L \simeq 100$ A,[30] and $T = 100$ K, if we assume two bipolarons per L (as a result of thermal generation[20] or doping) then $\epsilon_b^p \approx 50\,000$, larger than that measured at 10^{10} Hz for these materials but approximately equal to that reported[9] for Qn(TCNQ)$_2$ at 100 K for $\omega/2\pi < 1.25 \times 10^8$ Hz. As ω is increased to $\omega/2\pi = 9 \times 10^9$ Hz, ϵ decreases, suggesting that the $(1+\omega^2\tau^2)^{-1}$ term is important at higher frequencies. These earlier lower-frequency $\epsilon(\omega,T)$ results[9] for Qn(TCNQ)$_2$ are likely representative for (NMP)$_x$(Phen)$_{1-x}$(TCNQ) in the bipolaron regime $(0.50 \le x \le 0.56)$ as well. Hence, the model of moving bipolarons can readily account for the T-dependent high dielectric constants.

The $\sigma(10^{10}$ Hz) exceeds σ_{dc} for $T < 100$ K in all compositions. This result for the incommensurate (NMP)$_{0.59}$(Phen)$_{0.41}$(TCNQ) is in accord with similar experiments on other incommensurate CDW systems[25,27] and may be related to charge hopping among coherent CDW regions. The larger $n_b(T)$ and shorter L for the samples of $0.53 < x < 0.56$ may lead to more pronounced frequency behavior even as T approaches room temperature.

In summary, the variation of dielectric response as a function of commensurability, bipolaron concentration, and temperature reveal a systematic variation of ϵ and $\sigma_{\mu\text{w}}$ with x. A proposed model based on the dynamics of pinned charge-density waves and relatively mobile bipolarons in the commensurate phases can account for the data.

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