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Evidence for Solitons in Conducting Organic Charge-Transfer Crystals

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Magnetic susceptibility of (N-methylphenazinium)_x(phenazine)_{1-x}(tetracyanoquinodimethanide) [(NMP)_x(Phen)_{1-x}(TCNQ)] shows the formation of defect states for $0.5 \lesssim x \lesssim 0.54$. Diffuse x-ray scattering and *g*-value studies indicate that these defects are solitons formed in the highly correlated quasi-one-dimensional system that occurs near the quarter-filled-band limit. A model for the decrease in the energy gap in the presence of large numbers of solitons is proposed to explain the excess conductivity.

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Quasi-one-dimensional (1D) conductors have been widely studied, both as crystalline charge-transfer salts, e.g., salts of TCNQ, and (doped) polymers, e.g., polyacetylene, (CH)_x.¹ The proper description of the electronic ground state of 1D conductors with nearly commensurate charge concentration (i.e., number of charges per unit cell close to a rational fraction) has been a central issue in the field. The suggestion^{2,3} that a small excess or deficit of charge relative to the commensurate state is accommodated in (CH)_x by the formation of solitons with charge $\pm e$, where *e* is the charge on the electron, is now well supported by experimental evidence.¹ Recent theoretical studies of highly correlated 1D charge-transfer salts near the quarter-filled-band limit have predicted the existence of solitons

with fractional charge $\pm e/2$.⁴ We report here the results of an experimental and theoretical study of such a salt, (NMP)_x(Phen)_{1-x}TCNQ with $x \approx 0.5$, as a function of the concentration of conduction electrons. Our magnetic and diffuse x-ray scattering results are a direct demonstration that solitons are experimentally realized in charge-transfer salts. Effects of these solitons upon the temperature-dependent conductivity, $\sigma(T)$, are observed and can be understood within a model of a decreased gap caused by the presence of the solitons. The concentration regime for soliton formation is identified.

The system studied is based upon (NMP)(TCNQ), and is achieved by substituting neutral phenazine, Phen⁰, for up to 50% of the NMP.^{5,6} The Phen⁰ is of similar size, shape, and polarizability to

NMP⁺ but unlike NMP contributes no carriers. The overall (NMP)(TCNQ) crystal structure⁷ remains unchanged even with replacement of NMP by up to 50% Phen^{0,5,8,9}. The number of conduction electrons per unit cell to be shared among the donors and TCNQ is equal to the fraction, x , of NMP in the alloy (NMP) _{x} (Phen) _{$1-x$} (TCNQ).⁵ Note that the values of x are accurate to ± 0.01 . The distribution between donor and acceptor chains has been determined both by x-ray diffuse scattering⁷⁻⁹ and by resonance Raman scattering.¹⁰ Detailed x-ray diffuse scattering,⁷⁻⁹ optical,¹¹ thermoelectric power,¹² and magnetic¹³ studies have demonstrated that the Coulomb repulsion, U , is greater than the energy bandwidth, $W (=4t)$, for $x \lesssim 0.67$.

The calculations of Rice and Mele⁴ were carried out for a Peierls-distorted (dimerized) Hubbard chain in the limit $U/W \rightarrow \infty$. In that limit, they point out, a quarter-filled-band 1D material becomes a spinless analog of (CH) _{x} . For small departures from the quarter-filled band the creation of solitons to accommodate the excess of carriers over the commensurate value is favored over the excess electrons going into the conduction band (or holes into the valence band) since the energy of formation of a soliton for this case is $1/2\pi$ times the Peierls energy gap, 2Δ .⁴ For a concentration of solitons, c , greater than the value $c^* = \Delta/\pi W$ an incommensurate lattice distortion occurs.¹⁴ Similar concepts have been proposed for n -fold commensurate systems.¹⁵⁻¹⁷

Earlier^{6,8} studies have established that (NMP) _{0.5} (Phen) _{0.5} (TCNQ) is a large- U quarter-filled-band system with a dimerized lattice ground state. As x is increased to 0.54, the x-ray diffuse scattering for the TCNQ chain^{8,9} remains pinned at the commensurate value of $a^*/2$, where a^* is the reciprocal lattice vector parallel to the TCNQ stacking axis. This suggests that the extra electrons go into defect states whose properties fit the predictions for solitons.² Further increase in x (the number of conduction electrons per unit cell) to 0.59 results in a shift of the x-ray diffuse scattering from the commensurate $0.5a^*$.

To determine the type of state into which the extra electrons go, we performed several experiments. The spin susceptibility χ , obtained with a Faraday technique, is plotted in Fig. 1. The data can be decomposed into two contributions,^{13,18} (1) a Bonner-Fisher susceptibility associated with a 1D antiferromagnetic (AFM) system, and (2) a contribution proportional to $T^{-\alpha}$, with α a

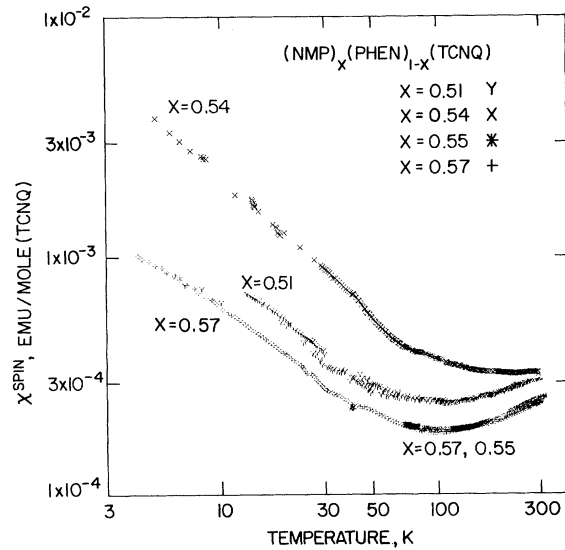


FIG. 1. Molar spin susceptibility vs temperature for (NMP) _{x} (Phen) _{$1-x$} (TCNQ), $0.50 < x < 0.60$. Note that the data for $x = 0.55$ are nearly indistinguishable from those for $x = 0.57$.

constant, $0.6 \lesssim \alpha \lesssim 1$. Table I summarizes $\eta(T)$, the number of spins per TCNQ, observed at 300 and 4 K, and α between 4 and 60 K for each sample. The data for $T > 100$ K are generally in agreement with 1D AFM with an exchange interaction $J(=2t^2/U) \approx 300$ K, consistent with other highly correlated quarter-filled-band TCNQ salts.¹⁸ For $T < 100$ K there is an additional contribution to $\chi(T)$ beyond that of the 1D AFM¹⁸ which is largest for $x = 0.54$. As the bulk of the TCNQ spins are coupled in the 1D AFM array, this low- T χ arises from spins not coupled to this electronic ground state. T -dependent g -value measurements for $x = 0.51$ and $x = 0.54$ verify that these spins are associated with states on the TCNQ stacks.

For $x = 0.51$ and $x = 0.54$ $\eta(4$ K) correlates closely with N_d , the number of chemically added carriers per TCNQ in excess of 0.5 ($N_d \equiv x - 0.50$). For $x = 0.54$, $\alpha = 0.81$ implies that these spins are nearly completely decoupled (Curie spins).¹⁸ For $x = 0.55$ and $x = 0.57$, the smaller $\eta(300$ K) implies that the spins are now more strongly coupled (J is larger) and $\eta(4$ K) shows that there are now fewer defect (uncoupled or weakly coupled) spins. Together, the $\chi(T)$, g -value, and diffuse x-ray scattering studies demonstrate that increasing N_d from zero to 0.04 increases the number of defect states observed on the TCNQ chain with the lattice distortion remaining commensurate. The

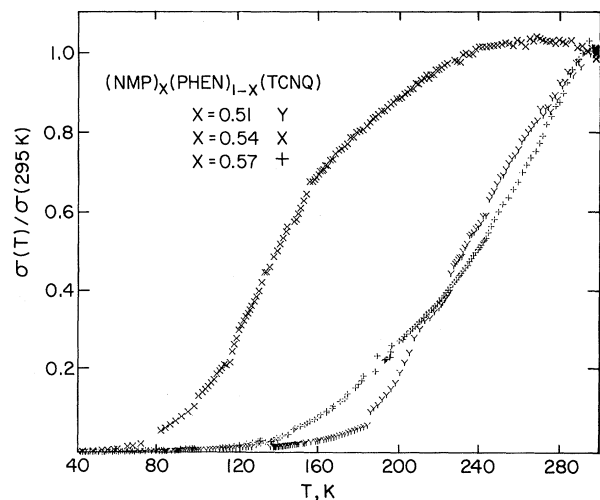
TABLE I. Spin susceptibility parameters for $(\text{NMP})_x(\text{Phen})_{1-x}(\text{TCNQ})$.

x	$\eta(300 \text{ K})^a$	$\eta(4 \text{ K})^a$	α
0.51	0.245	0.017	0.67
0.54	0.263	0.048	0.81
0.55	0.196	0.008 ^b	...
0.57	0.205	0.011	0.65

^a $\eta \equiv$ spins per unit cell.^bExtrapolated from $70 \text{ K} < T < 90 \text{ K}$.

magnetic defects may be described in terms of formation of kinks in the AFM system.¹³ For $x > 0.55$ the number of defect states decreases rapidly. Hence the defects are associated with the formation of solitons at midgap with the addition of charge below a critical excess electron concentration above $x = 0.5$ of 0.05. The latter number may be compared with the characteristic excess electron concentration $c^* = \Delta/\pi W$,¹⁴ below which solitons may exist, with Δ taken as 900 K (from the slope of $\ln \sigma$ vs T^{-1}) and a reasonable bandwidth for TCNQ of 4500 K. This leads to $c^* = 0.06$, in fair agreement with experiment.

Samples for four-probe¹⁹ $\sigma(T)$ were from the same synthesis used for $\chi(T)$ and x-ray studies except for the 0.51 stoichiometry. Approximately a dozen samples of each stoichiometry were measured, with characteristic results found for each x . At 295 K $\sigma \approx 25\text{--}100 \Omega^{-1} \text{ cm}^{-1}$ for all x . The normalized a -axis conductivity $\sigma_n(T) [\equiv \sigma(T)/\sigma(295 \text{ K})]$ is shown in Fig. 2. The data have been

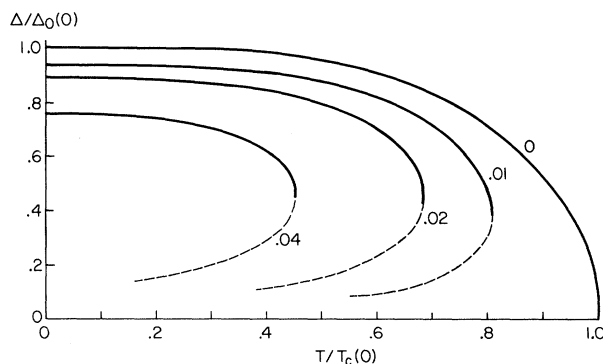
FIG. 2. Normalized a -axis conductivity vs temperature for $(\text{NMP})_x(\text{Phen})_{1-x}(\text{TCNQ})$, $0.50 < x < 0.60$.

renormalized to account for jumps in $\sigma_n(T)$ associated with formation of microcracks within these fragile crystals. A striking aspect of the data is the qualitatively different behavior of the $x = 0.54$ sample from the others. For both $x = 0.57$ and $x = 0.51$ $\sigma_n(T)$ is strongly activated up to and including 295 K. For $x = 0.54$, on the other hand, $\sigma_n(T)$ is strongly activated only up to $\sim 160 \text{ K}$ and $\sigma_n(T)$ is actually decreasing with increasing T above the broad maximum at 240 K.

We have shown that the increased conductivity in the $x = 0.54$ samples, as compared to those with $x = 0.51$ and 0.57, can be attributed to a decrease in gap caused by the large number of solitons. Solitons may contribute to σ but their contribution is expected to be negligible when there is a sizable concentration of electrons and holes, as is the case above perhaps 120 K. To obtain the gap equation we minimize the total free energy with respect to Δ . Since the gap on the TCNQ chain is mainly stabilized by internal rather than external lattice modes,²⁰ we may write the gap equation

$$(\pi t/mE_p) + (4N_d/m\Delta) = \int_0^\pi f(E_k, \mu)(1 - m^2 \sin^2 ka)^{-1/2} d(ka), \quad (1)$$

where t is the transfer integral, E_p is the so-called small polaron binding energy, $m^2 = 4t^2/(4t^2 + \Delta^2)$, $2N_d$ is the number of (half-integer charge) solitons per lattice site, a is the lattice constant, and $f(E_k, \mu)$ is the distribution function, E_k being the energy of an electron with wave vector k and μ the Fermi energy.²¹ In deriving (1) we have as-

FIG. 3. Ratio of the gap to its value $\Delta_0(0)$ at $T = 0 \text{ K}$ in the absence of solitons vs temperature in units of the critical temperature $T_c(0)$ in the absence of solitons. The numbers attached to each curve are $x - 0.5$, or $\frac{1}{2}$ the number of solitons per site. The parameters are $\Delta_0(0) = 900 \text{ K}$, $T_c(0) = 508 \text{ K}$.

sumed that the solitons are not on a lattice due to disorder on the neighboring chains. Equation (1) must be satisfied subject to the condition of conservation of charge:

$$2N_d + p_v = n_c + 2N_d f(\Delta), \quad (2)$$

where p_v and n_c are the densities of holes in the valence band and electrons in the conduction band, respectively. The latter number is much greater than the former, particularly at low temperatures, because electrons on the midgap soliton levels, $2N_d f(\Delta)$ in number, can get to the conduction band more readily than those from the valence band. For a given Δ Eq. (2) serves to locate μ . It should be noted that, for the case of large U but no solitons, μ lies below the center of the gap except at $T=0$.²²

The results of using Eqs. (1) and (2) to calculate Δ vs T for $4t=4500$ K, $E_p=1580$ K,²⁴ and different values of N_d are shown in Fig. 3. These values lead to $\Delta=900$ K at 0 K and a critical temperature T_c of 508 K in the absence of solitons. The presence of the solitons is seen to reduce the gap somewhat at $T=0$ K. The major decrease occurs at higher T , however, and is due to the excess number of electrons in the conduction band. For $N_d=0.04$, the change in gap at 150 K, for example, is sufficient to increase the number of conduction electrons and holes by a factor of 20. This could account for the excess σ observed in the $x=0.54$ samples.

Below ~ 240 K for $N_d=0.04$ the gap is double valued. As in the case of gap change due to injection,²³ the dashed portion is found to correspond to larger free energy and is thus unstable. Above ~ 240 K the metallic state ($\Delta=0$) is the only stable solution. The presence of a large concentration of chemically introduced solitons therefore causes the Peierls gap to be destroyed at much lower temperatures than in the absence of solitons. This can account for the disappearance of activated conductivity above ~ 200 – 240 K in the $x=0.54$ sample. The drop-off in activation energy beginning at ~ 280 K in the $x=0.51$ sample can also be accounted for by this effect (see Fig. 3).

In summary, we have shown experimental evidence for formation of solitons²⁴ near the quarter-filled-band limit below an experimentally determined critical concentration. An excess conductivity is observed in samples with large numbers of chemically induced solitons. To account for this a model is proposed based upon the decrease in the energy gap caused by the large num-

ber of solitons.

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²⁴It is unlikely that these defects are polarons since polaron formation would require the combination of two like-charged solitons, which would repel each other.

Spin Superlattice with Tunable Minigap

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A "spin superlattice" can be formed by periodical doping with paramagnetic ions, so that only the effective g factor of the conduction electrons is affected. An external magnetic field and temperature therefore provide a suitable control for the modulation amplitude of the potential and hence for the resulting minigap.

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Superlattices are periodically arranged layers of semiconductor materials having different energy-band parameters with a periodicity much greater than the fundamental lattice constant.¹ The superlattice periodicity leads to the formation of different subbands separated by minigaps. The energy position of the subbands and the width of the gaps depend directly on the effective superlattice potential. Up to now the parameters of this potential were essentially set during the growing process of the superlattice, usually by molecular-beam epitaxy. Afterwards only minor changes could be obtained by space-charge effects.

I propose now a completely novel kind of superlattice based on semimagnetic semiconductors. The effective superlattice potential can be tuned from zero to a saturation value depending on the external magnetic field, the temperature, and the "spin doping" of the material. In addition, the superlattice potential is approximately of the square-well type, so that from the theoretical point of view a corresponding simulation is most easily performed.

In a recent Letter we pointed out that spin doping by paramagnetic ions affects essentially the electronic g factor of a semiconductor, whereas all other energy-band parameters can be well approximated by the values of the undoped material.² Spin doping is easily achieved by substitution of only a very small amount of crystal constituents by paramagnetic ions. It is well known that for such a semiconductor $A_{1-x}M_xB$ — M indicating the paramagnetic substance—the effective

g factor is of the following form³:

$$g = g_0 + xJ\langle S_z \rangle / \mu_B H. \quad (1)$$

Here g_0 is the g factor of the undoped material, μ_B is the Bohr magneton, and H is the external magnetic field. J describes the s - d exchange coupling, and $\langle S_z \rangle$ is the thermal average of the localized spins of the paramagnetic dopant along the magnetic field axis. The quantity $\langle S_z \rangle$ is usually a very sensitive function of the temperature and therefore the temperature control provides a direct means of controlling the spin splitting. It should be noted that for very high temperatures the average polarization $\langle S_z \rangle$ vanishes, so that in this limit the band structure merges into that of the undoped material.

Actually the above assumption that the energy gaps are only negligibly affected by spin doping is not quite correct. This shortcoming, however, can be easily overcome by the combination of two different mixed crystals $A_{1-x}M_xB$ and $A_{1-y}D_yB$ in the superlattice, where the concentrations y of the nonmagnetic dopant D are chosen in such a way that the energy gaps of both materials are the same. Such complementary materials are, for example, $\text{Hg}_{0.99}\text{Mn}_{0.01}\text{Se}$ and $\text{Hg}_{0.976}\text{Cd}_{0.024}\text{Se}$, where only the manganese acts as "spin dopant," but the cadmium has no influence on the electronic g factor of the system.^{4,5}

Such a periodic arrangement of $A_{1-x}M_xB$ - $A_{1-y}D_yB$ double layers leads to a superlattice where only the electron g factor has a periodic spatial modulation, essentially a "spin super-