

Thermoelectric-Power Studies of (N-Methylphenazinium)_x(Phenazine)_{1-x}- (Tetracyanoquinodimethanide), 0.5 ≤ x ≤ 1.0

A. J. Epstein and J. S. Miller^(a)

Xerox Webster Research Center, Rochester, New York 14644

and

P. M. Chaikin

Department of Physics, University of California, Los Angeles, California 90024

(Received 20 April 1979)

Temperature-dependent thermoelectric-power (S) studies of (N-methylphenazinium)_x-(phenazine)_{1-x}(tetracyanoquinodimethanide) [(NMP)_x(phen)_{1-x}(TCNQ)] show that for $x=0.5$, $S(T)$ is identical to that of (quinolinium)(TCNQ)₂. $S(T)$ for $0.5 < x < 1.0$ is intermediate between that of (NMP)(TCNQ) and (quinolinium)(TCNQ)₂. Our results show strong Coulomb correlations are important in these salts and that their transport properties are determined by semiconducting gaps with disorder having only secondary importance for $T > 70$ K.

The conducting salts of the organic compound tetracyanoquinodimethane (TCNQ) have been widely studied and are the basis for examination of the relevance of a variety of models.^{1,2} The proper description of the electronic ground state of quasi-one-dimensional molecular conductors remains one of the central issues of the field. In particular, the role of on-site Coulomb interactions (U) and whether or not there exist extended electronic states with or without semiconducting gaps at room temperature continues to be of importance. We have performed experiments to distinguish between the dominance of semiconducting gaps and disorder, and to determine the role of U .

We report here the measurement of the temperature (T) dependence of the thermoelectric power (S) in an isomorphous series of materials as a function of the number of excess electrons per site and of disorder.³ Our results are the first unequivocal demonstration that the two prototype systems, (N-methylphenazinium)(TCNQ) [(NMP)(TCNQ)] and (quinolinium)(TCNQ)₂ [Qn(TCNQ)₂], are part of the same family of compounds, with a semiconducting gap at the Fermi energy and weak disorder.

The systems studied are based upon (NMP)-(TCNQ), and are achieved by substituting neutral phenazine, phen⁰, for up to 50% of the nontotally symmetric NMP.⁴ The phen⁰ is of similar size, shape, and polarizability to NMP⁺ but is neutral, closed shell, and symmetric. Detailed analysis has shown that the overall (NMP)(TCNQ) crystal structure remains unchanged even with replacement of NMP by up to 50% phen⁰.⁴ Consequently, the number of excess electrons per TCNQ de-

creases as a function of phen⁰ doping. In addition, replacing NMP⁺ with phen⁰ increases the randomness in the potential at TCNQ sites. Conductivity, σ , studies have shown these materials to have a $\sigma(T)$ similar to that of (NMP)(TCNQ) with a maximum in $\sigma(T)$ at a temperature lower than that of (NMP)(TCNQ).⁵

We have measured $S(T)$ of (NMP)_x(phen)_{1-x}-(TCNQ) along the stack direction (a axis) as a function of x for $0.5 \leq x \leq 1.0$ using an apparatus designed for needle-shaped crystals.⁶ Measurements were performed on small single crystals ($\sim 1 \times 0.02 \times 0.02$ mm³) at both the Xerox Webster Research Center and the University of California at Los Angeles with essentially identical results. Measurements of up to five crystals randomly chosen from the same synthetic batch gave very similar results. Figure 1 shows $S(T)$ as a function of x for representative samples. The data for $x=0.54$ is indistinguishable from that of the previously studied^{6,7} Qn(TCNQ)₂.⁷ It is readily seen that the experimental results for (NMP)_x-(phen)_{1-x}(TCNQ) form a continuous family of curves intermediate between those previously reported for (NMP)(TCNQ) and Qn(TCNQ)₂.

The two end points of the series, (NMP)(TCNQ) (Ref. 6) and Qn(TCNQ)₂, have apparently different behaviors. (NMP)(TCNQ) features an $S(T)$ which monotonically decreases as T increases from 80 to 300 K. In contrast, $S(T)$ for Qn(TCNQ)₂ is nearly T independent for $70 \text{ K} < T < 300 \text{ K}$ and then turns abruptly less negative for $T < 70 \text{ K}$. With increasing levels of phenazine doping, $S(300 \text{ K})$ becomes progressively more negative and the T dependence weaker. At the 37% phenazine level ($x=0.63$) S has become T independent

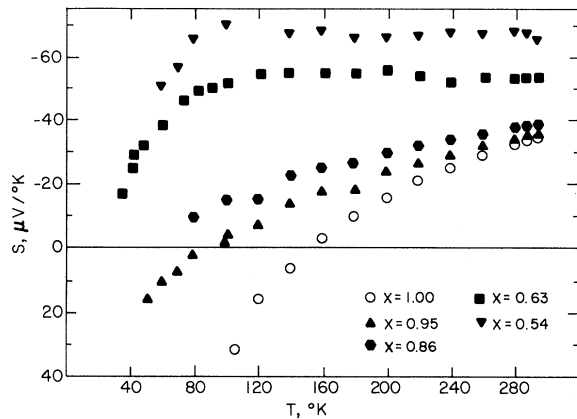


FIG. 1. Thermoelectric power vs temperature for $(\text{NMP})_x(\text{phen})_{1-x}(\text{TCNQ})$ of five different stoichiometries. The data for $x=0.54$ are indistinguishable from that of $\text{Qn}(\text{TCNQ})_2$.

for $T > 80$ K. Further doping (decreasing x) leads only to increasingly negative value for S and does not significantly change the T dependence.

The $S(T)$ for $(\text{NMP})_{0.54}(\text{phen})_{0.46}(\text{TCNQ})$ is nearly identical to that of $\text{Qn}(\text{TCNQ})_2$ as well as that of (acridinium) TCNQ_2 (Ref. 7) and $(\text{NMP})(\text{TCNQ})_2$.⁸ Assuming that there is one electron transferred from each NMP^+ to the TCNQ stacks in $(\text{NMP})_{0.5}(\text{phen})_{0.5}(\text{TCNQ})$, this system has the same number of charges per TCNQ as $\text{Qn}(\text{TCNQ})_2$ (one-quarter-filled band in a $U=0$ picture). The $\text{Qn}(\text{TCNQ})_2$ (Ref. 9) and (acridinium) TCNQ_2 (Ref. 10) materials have two acceptor stacks for each donor stack. The $(\text{NMP})_{0.5}(\text{phen})_{0.5}(\text{TCNQ})$ has one acceptor stack for each donor stack as well as increased disorder. These results demonstrate that for a large family of one-quarter-filled band systems the thermoelectric properties are nearly identical despite very different crystal structures, donors, and degree of disorder. $S(T)$ depends only upon the number of electrons per TCNQ at this band filling.

A plot of the data in Fig. 1 as $-S(T)$ vs T^{-1} reveals a systematic behavior, Fig. 2. In the high-temperature regime ($T > 100$ K), S is fit by a linear function with the slope monotonically decreasing with decreasing x . In addition, all samples studied have an intercept (constant term b) of $S \approx -60 \mu\text{V}/^\circ\text{K}$.

The value $S \approx -60 \mu\text{V}/^\circ\text{K}$ ($= -|k_B/e| \ln 2$) for a large number of quarter-filled-band materials has been understood as the effect of spin entropy (statistics), reflecting the role of strong Coulomb correlations (large U) in these materials.¹¹⁻¹³

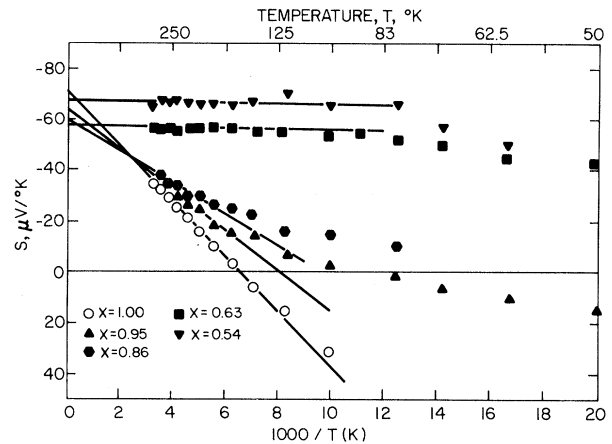


FIG. 2. Thermoelectric power vs T^{-1} for $(\text{NMP})_x(\text{phen})_{1-x}(\text{TCNQ})$ samples of Fig. 1. The straight lines are a fit of Eq. (1) to the data points using the parameters of Table I.

Recent experimental measurement of the magnetothermopower of $\text{Qn}(\text{TCNQ})_2$ has verified this assignment.¹⁴ This large- U model for $S(T)$ has been explicitly demonstrated theoretically for semiconductors with 0.5 electrons per site and finite bandwidths.¹⁵

The presence of a constant contribution of $\sim -60 \mu\text{V}/^\circ\text{K}$ for the $(\text{NMP})_x(\text{phen})_{1-x}(\text{TCNQ})$ family supports the central role of strong Coulomb correlations in these materials. Noting the linear behavior in Fig. 2, we have

$$S = -|k_B/e|(\ln 2 + A/T + \epsilon), \quad (1)$$

where the third term accounts for the small deviation of the constant term from $-60 \mu\text{V}/^\circ\text{K}$. Such a simple parametrization of $S(T)$ is unusual. Separate spin and orbital contributions will occur only in a strong-coupling Hubbard model.

A model previously developed for $\sigma(T)$ of $(\text{NMP})_x(\text{phen})_{1-x}(\text{TCNQ})$ treats these materials as semiconductors for all values of x studied.^{5,16,17} That is, an energy gap, 2Δ , occurs at the Fermi energy for all phenazine levels (the system cannot be doped metallic as for traditional semiconductors) which decreases with decreasing NMP content as $\Delta = (900 \text{ K})x^2$. Charge carriers are activated to extended states with a large, strongly T -dependent mobility. This model has also been applied to $\text{Qn}(\text{TCNQ})_2$.^{16,18}

In light of the conductivity analysis, it is appropriate to analyze the second and third terms in Eq. (1) in terms of a simplified qualitative

semiconductor model wherein the semiconducting energy gap occurs in the lower Hubbard band.¹⁸ Figure 3 schematically shows our model. Only the lower Hubbard band is shown (1 state/ k). The empty upper Hubbard band is at higher energies and is unimportant in this analysis. An energy gap, 2Δ , is shown at the Fermi wave vector, k_F . The gap at k_F divides the lower Hubbard band into two subbands. As the number of excess electrons per TCNQ decreases (x decreases), k_F moves to lower values; the gap 2Δ continues to occur at k_F but with lower magnitude. The charge carriers in the $k > k_F$ region are electronlike, and those with $k < k_F$ are holelike.

Using results for three-dimensional intrinsic semiconductors ignoring spin effects,¹⁹ $S = -|k_B/e| \ln(A/T + \epsilon)$ with

$$A = [(b-1)/(b+1)]\Delta, \quad b = \mu_e/\mu_h \quad (2)$$

and

$$\epsilon = \frac{3}{4} \ln(m_e/m_h) + \frac{b}{b+1} Q_e^* - \frac{1}{b+1} Q_h^*. \quad (3)$$

Here μ_e and μ_h and m_e and m_h are, respectively, the electron and hole mobilities and masses. Q_e^* and Q_h^* are the heats of carrier transport for electrons and holes given by

$$Q_{e,h}^* = \frac{\langle \tau_{e,h} E_{e,h}^2 \rangle}{\langle \tau_{e,h} E_{e,h} \rangle}$$

with τ and E the appropriate scattering times and normalized energies for the carriers.¹⁹ This simple model can be applied to the second and third terms on the right-hand side of Eq. (1).

For (NMP)(TCNQ) and the systems with low

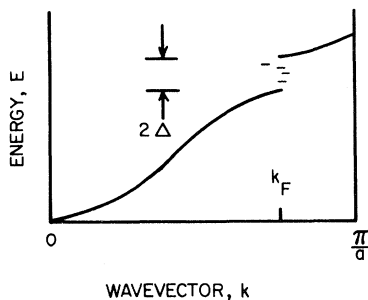


FIG. 3. Schematic model for $(\text{NMP})_x(\text{phen})_{1-x}(\text{TCNQ})$ energy band. Only the lower Hubbard band is shown. An energy gap, 2Δ , occurs at k_F for all x , decreasing for decreasing x . The dashed lines in the energy gap region symbolize the presence of a small number of localized states induced by disorder, defects, and/or impurities.

levels of phenazine doping, $k_F \gg \pi/2a$ and the two subbands are asymmetric. Thus μ_e and μ_h should differ significantly, resulting in b considerably different than one, and $A \sim [(b-1)/(b+1)]\Delta$ as well as ϵ should be large. In fact, these samples feature the largest slopes in the $-S$ vs T^{-1} plots. For $k_F \sim \pi/2a$ [materials with large amounts of phenazine doping as well as all "one-quarter-filled" band systems with large U (half-filled lower Hubbard band)], the two subbands of Fig. 3 are nearly symmetric and A should be near zero. For $x \sim 0.5$ as well as $\text{Qn}(\text{TCNQ})_2$ and similar materials, the S vs T^{-1} curves feature near zero slope in agreement with this model. The variation in ϵ with x is less systematic, suggesting that a more sophisticated analysis is necessary for this term. The deviation of $S(T)$ from this model prediction for $T < 100^\circ\text{K}$ is attributed to the roles of defects and impurities, which lead to a significant contribution due to excess carriers (extrinsic behavior) at low temperatures. This low- T behavior varies from sample to sample as expected for defect and impurity contributions. A similar analysis can be performed for other systems with strong Coulomb correlations and other than 0.5 excess electrons per site.⁸

Table I summarizes the results obtained in applying Eq. (1) to these materials using Δ obtained from previous analysis of conductivity data⁵ and Eq. (2). The values of $b < 1$ for large x demonstrate that the hole mobilities are larger than the electron mobilities, consistent with the wider bandwidths for holes for an energy gap in the upper half of the lower Hubbard band. Because of the strong disorder and poor overlap, it is assumed that the charges remaining on the donor stack²⁰ do not significantly contribute to the transport properties of the $(\text{NMP})_x(\text{phen})_{1-x}(\text{TCNQ})$ system, although they would contribute to the magnetic behavior.²¹

The $S(T)$ results presented here for $(\text{NMP})_x-$

TABLE I. Thermoelectric-power parameters for $(\text{NMP})_x(\text{phen})_{1-x}(\text{TCNQ})$, $S = -|k_B/e| \ln(2 + A/T + \epsilon)$.

x	A ($^\circ\text{K}$)	Δ ($^\circ\text{K}$) ^a	b	ϵ
1.00	-126	900	0.75	0.14
0.95	-92	812	0.80	0.047
0.86	-72	666	0.81	0.012
0.63	0	357	1.00	0.035
0.54	0	262	1.00	0.093

^aFrom $\Delta = (900 \text{ K})x^2$; see Ref. 5.

(phen)_{1-x}(TCNQ) rule out disorder as the dominant factor in transport for $T > 70$ °K. If U were less than or on the order of ϵ_D [variation in site energies (disorder bandwidth)] then some carriers would be in doubly occupied sites. These sites would have no spin-entropy contribution and hence would result in a high-temperature thermoelectric power of less than $-60 \mu\text{V}/^\circ\text{K}$. In contrast, all of the samples studied gave an extrapolated value of $\sim -60 \mu\text{V}/^\circ\text{K}$ at infinite temperature. In addition, if $2\Delta \approx \epsilon_D$, then the T^{-1} behavior of $S(T)$ for $T > 100$ °K would not be expected to occur. It is possible, however, that the decrease in the apparent magnitude of the gap 2Δ with increasing phenazine loading may be due in part to the smearing out of the gap and introduction of localized states into the gap by the increasing disorder.

Summarizing, we have demonstrated that the (NMP)_x(phen)_{1-x}(TCNQ) system constitutes a continuous series in thermoelectric-power properties. We have seen that all one-quarter-filled band systems with strong Coulomb correlations have nearly identical thermoelectric powers despite different crystal structure and donors. We have shown that the $S(T)$ data for all (NMP)_x(phen)_{1-x}(TCNQ) $0.5 \leq x \leq 1.0$ as well as many other highly conducting quasi-one-dimensional conductors can be fitted by Eq. (1) and understood in terms of a model of two additive contributions, that due to spin entropy and that due to an intrinsic band semiconductor.

The authors are grateful for useful discussions with E. M. Conwell. This work was supported in part by the National Science Foundation under Grant No. DMR76-83421. One of us (P.M.C.) is in receipt of an A. P. Sloan Foundation Fellowship.

^(a)Present address: Occidental Research Center,

P. O. Box 19601, Irvine, Cal. 92713.

¹See, for example, *Proceedings of the International Conference on Organic Conductors and Semiconductors, Siofok, Hungary, 1976*, edited by L. Pal *et al.* (Springer, Berlin, 1977); *Chemistry and Physics of One-Dimensional Metals*, edited by H. J. Keller (Plenum, New York, 1977), Vol. 25B.

²See, e.g., Ann. N. Y. Acad. Sci. **313** (1978).

³A preliminary account was given by A. J. Epstein, J. S. Miller, and P. M. Chaikin, Bull. Am. Phys. Soc. **23**, 382 (1978).

⁴J. S. Miller and A. J. Epstein, J. Am. Chem. Soc. **100**, 1639 (1978).

⁵A. J. Epstein and J. S. Miller, Solid State Commun. **27**, 325 (1978).

⁶J. F. Kwak, G. Beni, and P. M. Chaikin, Phys. Rev. B **13**, 641 (1976).

⁷L. I. Buravov, D. N. Fedutin, and I. F. Shchegolev, Zh. Eksp. Teor. Fiz. **59**, 1125 (1971) [Sov. Phys. JETP **32**, 612 (1971)].

⁸A. J. Epstein, J. S. Miller, and P. M. Chaikin, to be published.

⁹H. Kobayashi, F. Marumo, and Y. Saito, Acta Crystallogr. **B27**, 373 (1971).

¹⁰H. Kobayashi, Bull. Chem. Soc. Jpn. **47**, 1346 (1974).

¹¹G. Beni, Phys. Rev. B **10**, 2186 (1974).

¹²J. F. Kwak and G. Beni, Phys. Rev. B **13**, 652 (1976).

¹³P. M. Chaikin, in *Proceedings of the International Conference on Thermoelectric Properties of Metallic Conductors, East Lansing, Michigan, 1977*, edited by F. J. Blatt and P. A. Schroeder (Plenum, New York, 1978), p. 359.

¹⁴P. M. Chaikin, J. F. Kwak, and A. J. Epstein, Phys. Rev. Lett. **42**, 1178 (1979).

¹⁵E. M. Conwell, Phys. Rev. B **18**, 1818 (1978).

¹⁶A. J. Epstein, E. M. Conwell, and J. S. Miller, Ann. N. Y. Acad. Sci. **313**, 183 (1978).

¹⁷A. J. Epstein, E. M. Conwell, D. J. Sandman, and J. S. Miller, Solid State Commun. **23**, 355 (1977).

¹⁸A. J. Epstein and E. M. Conwell, Solid State Commun. **24**, 627 (1977).

¹⁹J. Tauc, *Photo and Thermoelectric Effects in Semiconductors* (Pergamon, New York, 1962).

²⁰J. P. Pouget, S. Megtert, R. Comès, and A. J. Epstein, Phys. Rev. B (to be published).

²¹A. J. Epstein and J. S. Miller, to be published.