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Evidence for Strong Coulomb Correlations in an Organic Conductor

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The thermopower of highly conducting quarter-filled–band TCNQ (tetracyanoquinodimethane) salts corresponds to an entropy per carrier of $k\ln 2$. We have measured the change of the thermoelectric power upon application of a magnetic field for quinolinium ditetracyanoquinodimethane. We find an isotropic shift which agrees with the entropy change of a free-spin system. Coupled with the observation of a negligibly small magnetoresistance, this provides definite evidence that the conducting electrons are correlated as in the strong-coupling Hubbard model.

One of the most lingering questions which has concerned researchers in the area of quasi–one-dimensional conductors is the role played by the Coulomb interaction between electrons as compared with the electronic bandwidth.[1] Several authors have analyzed susceptibility,[2-4] nuclear magnetic resonance,[5,6] and x-ray[7] data in a number of TCNQ (tetracyanoquinodimethane) salts and conclude that the Coulomb interaction is either dominant, comparable to bandwidth, or small.

In this Letter, we present the results of our study of magnetoresistance and magnetothermopower of quinolinium ditetracyanoquinodimethane [denoted hereafter as $Q(TCNQ)_2$]. These results show that the electrons involved in transport retain their spin degrees of freedom. This is the first hard evidence that in at least one compound, $Q(TCNQ)_2$, the Coulomb interaction is sufficiently strong to correlate the electrons apart so that they behave as free spins. We also believe this system to be the first compound (organic or not) in which this strong correlation has been experimentally demonstrated. A strong-coupling Hubbard model therefore seems appropriate.[8]

Buravov, Fedutin, and Schegolev[9] were the first to point out the similarity between the thermoelectric power (TEP) of a number of 1:2 TCNQ salts. As temperature was increased toward 300 K, the thermopower tended to saturate to a value of ~ -60 μV/K. More recently it has become apparent that the saturation toward -60 μV/K is a more general phenomenon for 1:2 TCNQ salts than was originally envisioned. A compilation of data from several authors is shown in Fig. 1.[9-12]

To date all quarter-filled–band (one electron per two sites on the conducting chain) TCNQ salts which exhibit "metallike" conductivity at room temperature have a thermopower of -60 μV/K. In this context we take "metallike conductivity" to merely signify that the conductivity is not apparently strongly activated. Note that Fig. 1 also contains data from (N-methylphenozinium)$_{0.54}$-(phenozine)$_{0.46}$-TCHQ, [abbreviated as (NMP)$_{0.54}$-(Phen)$_{0.46}$-TCNQ],[13] which achieve a quarter-filled–band situation by partial substitution of a poor donor (Phen) for a good donor (NMP) in the cation chain.

Buravov, Fedutin, and Schegolev[9] were able to fit their data on three of the 1:2 salts by a model in which the spin degrees of freedom were quenched and the thermopower was due to the motion of bonds formed between near-neighbor and next-near-neighbor molecules along the conducting chain. An alternative approach was suggested in several papers by Beni[14] and by Kwak

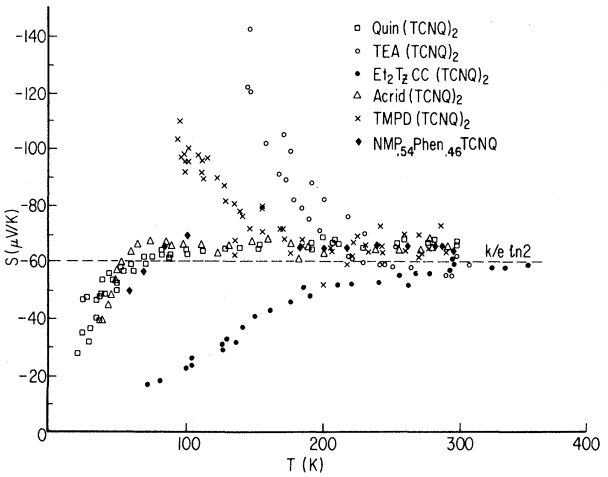

FIG. 1. Absolute thermoelectric power as a function of temperature for a number of TCNQ salts with a charge density of approximately one electron per two TCNQ molecules. References from top to bottom are Refs. 12, 11, 9, 9, 10, and 13.

and Beni.[15] They pointed out that in the case of the strong-coupling Hubbard model the thermopower contains two terms corresponding to the separation of spin and orbital motion. The first term is merely the entropy per carrier associated with the spin degeneracy of electrons which cannot doubly occupy a single site. This contribution is the spin entropy $k\ln 2$ divided by the electronic charge and has a value of -59.8 μV/K. The orbital motion would also make a contribution, but in the case of electron-hole symmetry this would be identically zero. For 1:2 salts the singly occupied states are close to half filled and we would expect approximate electron-hole symmetry independent of the nature of these states (i.e., whether they are localized, or extended, metallic, or simiconducting with finite electron and hole bandwidths[16]).

Since there is not exact electron-hole symmetry the orbital contribution is not negligible. However, as temperature is increased the orbital contribution for a nearly half-filled system should tend to a small constant value[15] (which depends on the asymetry) and the spin term will dominate. In Fig. 1 it is seen that samples with quite different low-temperature behavior saturate to about -60 μV/K near room temperature.

Of course, any physical situation in which the conduction electrons are in twofold-degenerate states will also produce a thermopower of $(k/e)\ln 2$. Considering the continuing controversy over the strength of the Coulomb interaction in TCNQ, it was necessary to find a way to distinguish the degeneracy as being spin or orbital in nature. The most direct way to proceed is to see the effect of a magnetic field in changing the thermopower. If the change is anisotropic with field direction, it is an orbital effect. If it agrees with the entropy change of spins in a field, it is a spin effect.

The experiments were performed on a conventional apparatus used for TEP measurements on organic crystals.[12] Two single-crystal quartz blocks with Evanohm heaters were placed in weak thermal contact with a copper block which was part of a copper vacuum can. The samples were mounted on 1-mil gold wires which were thermally anchored to the quartz blocks. The temperature difference was monitored by a Chromel-Constantan thermocouple attached to the quartz blocks. The temperature was periodically modulated at one cycle per two minutes by alternately heating the two blocks.

In one set of runs at the Francis Bitter National Magnet Laboratory (NML) the copper sample can was placed in a sealed exchange-gas tube with approximately 10 mm of nitrogen gas. The entire apparatus was immersed in liquid nitrogen. The temperature was controlled by a capacitance temperature controller, or allowed to reach equilibrium with the nitrogen bath. The temperature was measured with a silicon diode in zero field. Any changes in temperature upon application of the field were measured with a capacitance temperature thermometer. Many temperature swings of the quartz blocks were monitored, recording both the voltage across the Chromel-Constantan and across the sample. When steady state was reached, the temperature drift of the can was less than 0.1 K/h and the voltage swings changed by less their 0.2%/h. The magnetic field was then increased to 18.5 T and several temperature swings were again recorded. Finally, the field was returned to zero and the process repeated.

The temperature change over the entire field off-on-off period was less than 0.1 K (as measured with both the silicon diode and capacitor), the center of the voltage readings from the thermocouple and sample remained fixed (indicating no additional thermals) and the measured thermopower of the sample before and after application of the field reproduced to better than 0.3%. Data were taken on four samples, one parallel and one perpendicular to the applied magnetic field at NML and a separate set at the University of California at Los Angeles (UCLA). These results

are shown in Fig. 2.

Although the absolute thermopower of a particular compound can only be determined to ≈5% by this technique (because of the differences in sample contacts) the sensitivity to changes (with magnetic field or temperature) and the reproducibility for a single sample are ~0.2%. In measuring the temperature dependence of each sample used in this study, we found $dS/dT \approx 0.07$ μV/K at 80 K and $dS/dT \approx 0.4$ μV/K at 50 K so that temperature stability produced a negligible error at ~80 K and a small error at ~50 K.

The main source of error in the data taken at 18.5 T involves the possible change in the thermopower of the Chromel-Constantan thermocouple used to measure the temperature difference. The magnetothermopower of Chromel-Constantan has only been reported up to 60 kG.[17] In monitoring the temperature swing of our blocks with this thermocouple, we were not able to rule out a change of from 0.4% to 0.6% on different runs. (Some of this may be due to the magnetoresistance of the Evanohm heaters which has been reported as 0.2% to 0.8% at 4.2 K and 18.5 T).[18]

Experiments performed at UCLA used a superconducting magnet with a maximum field of 8.0 T. The techniques were identical with the exception that the exchange can contained ~5 μTorr of He gas and temperature stability required a longer period due to the large temperature difference between the sample can and the 4.2-K bath. The main source of error in these data involved temperature stability at 80 K and the uncertainty in extrapolating the magnetothermopower of the Au leads for the 50-K data.[19] These data are also shown in Fig. 2.

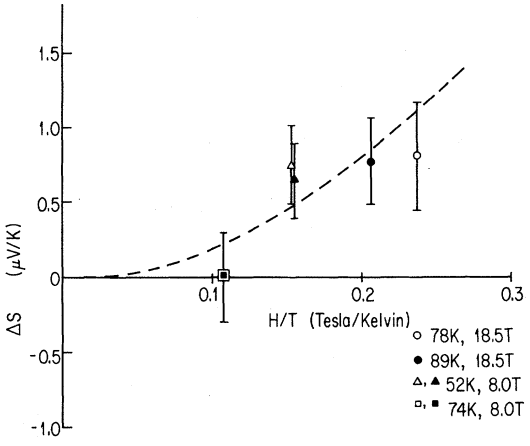

FIG. 2. Change of the absolute thermoelectric power upon application of a magnetic field. Solid points correspond to magnetic field perpendicular to the highly conducting axis, open points to a parallel field. The dashed line is the predicted change due to lowering the spin entropy [Eq. (3)], and contains no adjustable parameters.

The magnetoresistance of $Q(TCNQ)_2$ was also measured at 80 K and 18.5 T. With the magnetic field perpendicular to the conducting axis a positive magnetoresistance of 0.2 ± 0.1% was observed. With the field parallel to the conducting axis, a 0.1 ± 0.1% positive magnetoresistance was observed. Both obeyed a roughly quadratic field dependence.

The fact that the change in the thermopower is independent of the field orientation indicates that the effect is related to spin rather than orbital motion. It should be noted that the isotropy is known to better than the error bars in Fig. 2 by a factor of 2, as the main errors occur in analysis rather than measurement. The conclusion that the magnetothermopower is a spin effect is also supported by noting that the magnetoresistance changes by at most 0.3% under conditions where the magnetothermopower has a 1.5% change. This result also indicates a decoupling of spin and orbital motion as would be expected for a system in the strong-coupling limit of the Hubbard model.

The spin entropy (Σ) of a single electron in a magnetic field is given by

$$\Sigma = k_B[\ln(e^{-\mu_0 H\beta} + e^{\mu_0 H\beta}) - \mu_0 H\beta \tanh(\mu_0 H\beta)], \quad (1)$$

where k_B is Boltzmann's constant, μ_0 is the electronic magnetic moment, and β is reciprocal temperature ($1/k_B T$), If the spin entropy is the dominant contribution to the thermopower (S) then we would have

$$S(H/T) = \Sigma/(-|e|) \quad (2)$$

(where e is the electron charge) which produces a value of -59.8 μV/K at $H = 0$. As seen in Fig. 1, $Q(TCNQ)_2$ remains at this value in zero field down to temperatures of ~50 K. We are interested in small deviations from this value caused by the application of a field. If the thermopower is described by Eq. (2), then the change should go as

$$\Delta S = [\Sigma(H/T) - \Sigma(0)]/(-|e|). \quad (3)$$

The magnitude of the entropy decreases with increasing field. Since the zero-field thermopower [Eq. (2)] is negative, the result is a positive shift. Equation (3), which, of course, contains no ad-

justable parameters, appears as the dashed line in Fig. 2.

We see that the experimental points agree both in sign and in magnitude with the expected behavior for a free-spin system. It is very unlikely that any orbital effects would show the isotropy, sign, and magnitude of the changes which we have observed. Combined with the zero-field thermopower, the magnetothermopower confirms that the electronic carriers in $Q(TCNQ)_2$ behave as free spins.

Although the available field constrains us to use $Q(TCNQ)_2$ and in a region where it is somewhat temperature dependent, the thermopower remains within ~5% of -60 μV/K, and hence we believe our model is applicable. The model should also be applicable to the *spin* contribution to the thermopower of the other salts shown in Fig. 1.

Since this result leads us directly to the conclusion that the Coulomb interaction dominates in $Q(TCNQ)_2$ it is worth discussing some of the contradictory evidence. For a free-spin system the susceptibility should obey a Curie law, whereas the susceptibility of $Q(TCNQ)_2$ has usually been interpreted in terms of a Bonner-Fischer-type behavior with an exchange interaction of ~300 K.[20] This would imply an almost complete quenching of the spin entropy and a reduction of the magnetothermopower by more than an order of magnitude.

It is important to emphasize the difference between these two measurements. Thermopower probes the carriers which are responsible for conductivity and which occupy states in the direct vicinity of the Fermi surface. Susceptibility probes all of the electrons. If the interpretation of the susceptibility is correct, then our measurements would indicate that the exchange interaction is an increasing function of distance from the Fermi energy.

Another source of controversy is the NMR study of $Q(TCNQ)_2$ which shows an unenhanced Koringa relaxation.[9] Although the NMR data do not fit a theory with relatively large Coulomb interaction in a system where the bandwidth is dominant, there has been no attempt to develop a theory of the relaxation processes for a system with a large Coulomb interaction and smaller yet sizable bandwidth.

In conclusion, the thermopower, magnetothermopower, and magnetoresistance definitely indicate that the conducting electrons in $Q(TCNQ)_2$ have free spins and hence a strong electron-electron correlation. To the best of our knowledge, this is the only system where a strong-coupling Hubbard model has been demonstrated as applicable.

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Fermi Surface of Incommensurate Mercury-Chain Compounds

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Measurement of the de Haas–van Alphen effect at 1.1 K in the linear-chain mercury compound $Hg_{3-\delta}AsF_6$ shows that the Fermi surface consists of a set of straight or nearly straight cylinders with axes along the $\vec{c}$ direction. The cylinders are formed from one-dimensional Fermi-surface sheets by the interaction of mutually perpendicular mercury chains and by translation by superlattice vectors resulting from the periodicity of the incommensurate mercury chains.

The linear-chain mercury compounds, $Hg_{3-\delta}AsF_6$ and $Hg_{3-\delta}SbF_6$, exhibit anisotropic electrical[1,2] and optical[3,4] properties. These compounds contain infinite, nonintersecting chains of mercury atoms running along $\vec{a}$ and $\vec{b}$ directions of the tetragonal structure.[5] The separation between mercury atoms is incommensurate with the tetragonal host lattice. Direct measurements of the Fermi surface of these compounds would be highly desirable to determine the Fermi surface of one-dimensional, nonintersecting conducting chains. We report the results of a de Haas–van Alphen (dHvA) experiment on $Hg_{3-\delta}AsF_6$ which explain the anisotropic electrical conduction and support a model of the Fermi surface formed from one-dimensional bands.

The dHvA effect was observed at 1.1 K in a magnetic field range 3–5.5 T with the low-frequency modulation technique.[6] Single-crystal samples of $Hg_{3-\delta}AsF_6$ with dimensions $2\times2\times1$ mm^3 contained in a sealed sample holder were mounted in a sensitive modulation-pickup–coil assembly. Measurements were made for magnetic field directions between the $\vec{c}$ axis and the (001) plane which were determined optically. Directions in the isotropic (001) plane could not be determined optically so that it was not known where the plane that was studied intersected the (001) plane. The data were collected on magnetic tape and analyzed by computer.

dHvA frequencies of $Hg_{3-\delta}AsF_6$ shown in Fig. 1 consist of six branches with minima along the $\vec{c}$ axis. Five branches, α, β, δ, and ϵ, extend 64 $\pm$ 10° from the $\vec{c}$ axis toward the (001) plane. Branch μ is over a smaller angular range of $\pm$ 20° from the $\vec{c}$ axis and is not observed below a magnetic field of 4.6 T. Table I shows the values of the dHvA frequencies and corresponding cross-sectional areas of the Fermi surface measured with the magnetic field along the $\vec{c}$ axis. A low frequency with a value of approximately 48 T, which is not shown in Table I and Fig. 1, was observed over a very small angular range about the $\vec{c}$ axis. No dHvA frequencies were found in a careful search with magnetic-field directions in the (001) plane, indicating that no closed Fermi-surface pieces exist.

Cyclotron masses were determined from the temperature dependence of the dHvA amplitude in a crystal where the magnetic field was oriented 20° from the $\vec{c}$ axis. The cyclotron masses of the branches with sufficient amplitude for the mass determination (the γ, δ, and ϵ branches) are the same to within experimental error and have a value of $(0.35\pm0.05)m_0$.

The angular dependence of the dHvA frequencies suggests pieces of Fermi surface which are cylinders along the $\vec{c}$ axis in k space. The cross-sectional area of a straight cylinder varies as $A_0\sec\theta$, where A_0 is the cross-sectional area perpendicular to the axis of the cylinder and θ is the angle between the magnetic field direction and the cylinder axis. The dHvA frequencies in Fig. 1 follow this $\sec\theta$ dependence closely for values of