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Conductivity Studies on High-Purity *N*-Methylphenazinium Tetracyanoquinodimethan*

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An experimental study of the electrical conductivity in high-purity single crystals of *N*-methylphenazinium tetracyanoquinodimethan (NMP)(TCNQ) is presented. The conductivity at high temperature is larger than that previously reported while the low-temperature conductivity (below 100 °K) is more than a factor of 10 smaller than that of earlier data. Both regimes are consistent with considerably improved sample purity. The data are analyzed from the point of view of a continuous metal-to-insulator transition with fluctuations playing a central role. The low-temperature results indicate that for (NMP) (TCNQ) the curvature in $\log_{10}\sigma$ vs T^{-1} observed in earlier data arises from impurity contributions with the intrinsic behavior being exponential in T^{-1}. The exponential behavior is consistent with the magnetic data which indicate that (NMP) (TCNQ) is a magnetic Mott–Hubbard insulator at low temperature.

I. INTRODUCTION

The charge-transfer salts of tetracyanoquinodimethan (TCNQ) have been of considerable interest because of their novel electronic and magnetic properties. Of these, *N*-methylphenazinium (NMP) TCNQ is particularly important for it possesses the highest conductivity of any organic solid.[1] This is a 1 : 1 salt with each NMP molecule donating a single electron to form the $(TCNQ)^-$ anion. The crystal structure consists of linear chains of $(TCNQ)^-$ anions and parallel chains of NMP cations.[2] Within a simple noninteracting-particle approximation, such a system would possess a single half-filled band and therefore would be metallic. However, it is obvious from the outset that electron-electron interactions must play an important role in such narrow-band conductors. If the electron-electron Coulomb repulsion is sufficiently large compared to the energy bandwidth, the electrons localize (one per site) to form a magnetic insulator, and a Mott metal-insulator transition takes place. The physical properties of NMP TCNQ have been analyzed in detail from this point of view in a series of papers.[3–6] The temperature dependences of the electrical conductivity, magnetic susceptibility, specific heat, electron-spin resonance, and proton-spin–lattice relaxation rates can be understood on the basis of a Mott transition from metal to small-band-gap magnetic insulator in a one-dimensional (1-d) system as the temperature is lowered below 200 °K.[4] The low-temperature 1-d antiferromagnetic (AF) state was shown experimentally to have properties consistent with the exact numerical results of Ovchinnikov[7] and Takahashi[8] for the 1-d half-filled-band Hubbard model.[3,4] The linear temperature dependence of the specific heat[3,4] and the finite nuclear relaxation rate predicted for the 1-d spin-$\frac{1}{2}$ AF at low temperatures were observed.[9] The enhanced susceptibility at $q = 2k_F$ predicted for a 1-d metal has been confirmed by nuclear relaxation studies at high temperatures.[5]

The metal-insulator boundary occurs in the vicinity of 200 °K; the transition is not sharp, for a true phase transition cannot occur in a 1-d system. Moreover, recent theoretical studies of the half-filled band Hubbard model[10] demonstrate that fluctuation effects are of such importance in considering the thermodynamic transition from insulator to metal that a sharp phase transition is unlikely in a Hubbard system even in three dimensions.

An alternative explanation of the electrical conductivity of NMP TCNQ and related salts was proposed by Bloch *et al.*,[11] who emphasized the role of cation disorder in 1-d systems. Based on the published resistivity of Shchegolev *et al.*,[12] an argument was constructed which attributed the conductivity to variable range hopping[13,14] in a disordered system at low temperature and classical diffusion through random potentials at high temperatures. The 1-d variable range-hopping theory was founded on the experimental observation of a curvature in the plot of $\log_{10}\sigma$ vs T^{-1} as presented by Shchegolev *et al.*,[12] and was applied generally to the entire class of the highly conducting TCNQ salts.[11] However, the existence of a metallic state above 130 °K in quinolinium $Q(TCNQ)_2$ has been verified by observation of a Korringa relaxation rate for protons with a magnitude in reasonable agreement with simple band theory.[6,15] Moreover, conductivity measurements on high-purity NMP TCNQ, presented in detail in this paper, indicate that the curvature in $\ln\sigma$ vs T^{-1}, seen in earlier data, was the result of impurities; the purer samples showing straight-line behavior over nearly six orders of magnitude change in σ. These data together with the demonstrated effect of small amounts of added disorder[6] confirm that the electronic properties of NMP TCNQ are dominated by band and

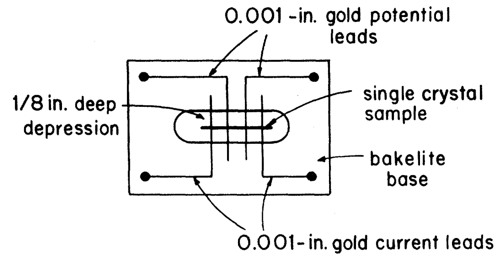

FIG. 1. Schematic diagram of the sample holder for four-probe conductivity measurements on single crystals.

interaction effects with disorder playing only a peripheral role.

Nevertheless, it is clear that in such 1-d systems structural defects or cation disorder will surely limit the effective chain length to a finite value, implying that the conducting TCNQ salts should be viewed as collections of long but finite chains in which the microscopic electronic structure is determined by the competition between band and interaction effects.[4]

In this paper we present an experimental study and analysis of the conductivity results taken from high-purity single crystals of NMP TCNQ. The conductivity at high temperatures is larger than that previously published, while the low-temperature conductivity (below 100 °K) is more than a factor of 10 smaller than that of the earlier data; both regimes are consistent with considerably improved purity of the samples. The data are analyzed from the point of view of a continuous insulator-to-metal transition with fluctuations playing a central role.

II. EXPERIMENTAL TECHNIQUES AND SAMPLE PREPARATION

N-methylphenazinum tetracynanoquinodimethan single crystals are black lathes (needle shaped with long axis parallel to the crystallographic *a* axis) with well-defined faces giving good optical reflections. Four-probe resistance measurements were made on single crystals (2.5–3.5 mm long and 0.05–0.10 mm in diameter) along the needle axis parallel to the TCNQ stacks.

Due to the difference in thermal expansion between the crystals and any substrate used, a sample mounting was needed which would allow the crystal to expand and contract as freely as possible. The sample-mounting configuration is shown in Fig. 1. The crystal is suspended by four 0.001-in. gold wires over a depression machined into the bakelite base. Electrical contact was made by wetting the gold wires with a silver-paste paint. Using this arrangement the crystals could be thermally cycled without damage. Contact resistances, measured by three-probe methods, were approximately 50 Ω per contact on all samples. This is due both to the silver-paint–sample boundary and to the anisotropy of the conductivity. With no sample mounted, the resistance of the sample holder between any two leads was greater than 10^{12} Ω, roughly two orders of magnitude larger than the highest measured sample resistance.

Two sample holders were mounted on a copper block surrounded by a copper can which in turn was placed in a glass vacuum can. The temperature drift rate was adjusted by controlling the amount of exchange gas in the vacuum can. From room temperature to 77 °K the temperature was lowered at a rate of 1 °K every 5 min, and from 77 to 4 °K the temperature was lowered at a slower rate of between 10 and 15 min per deg. This slow cooling (and corresponding warming) rate kept the samples in thermal equilibrium with the exchange gas and the thermometers.

The temperature was measured by two methods: a copper-constantan thermocouple (with one junction suspended over the depression in the bakelite mount and with the reference junction at either 195 or 77 °K, depending upon the temperature region studied), and a platinum resistance thermometer mounted on a bakelite base and secured to the copper block. The relative temperature error was less than 1% over the entire temperature range.

The applied test current was 1 μA at room temperature decreasing to 2 nA at 4.2 °K. The voltage was measured by two methods. From room temperature to approximately 25 °K a nulling dc voltmeter was used. Below 25 °K, where the sample resistance is large, the potential was measured with an electrometer with input impedance greater than 10^{14} Ω. At all temperatures, checks were made to ensure that the measured current was in fact passing through the sample. The relative error of the resistance measurements was less than 2%.

For absolute values of the conductivity, the diameter and length of the crystal between the potential contacts were measured by using a reticle and microscope. The error introduced by the uncertainty of the sample dimensions is of order 10%. The absolute value of the conductivity depends critically on crystal perfection, since internal microcracks or microscopic structural defects can significantly reduce the effective cross-sectional area. The room-temperature value discussed below [$\sigma = 380$ $(\Omega\,\mathrm{cm})^{-1}$] is the highest obtained from a freshly prepared crystal batch of highest purity.

Tetracyanoquinodimethan was prepared according to the procedure of Acker *et al.*,[16] but under careful experimental conditions. All syntheses and handling of materials were carried out in a Labcon glove box filled with Matheson 99.999% argon, using freshly washed oven-baked glassware.

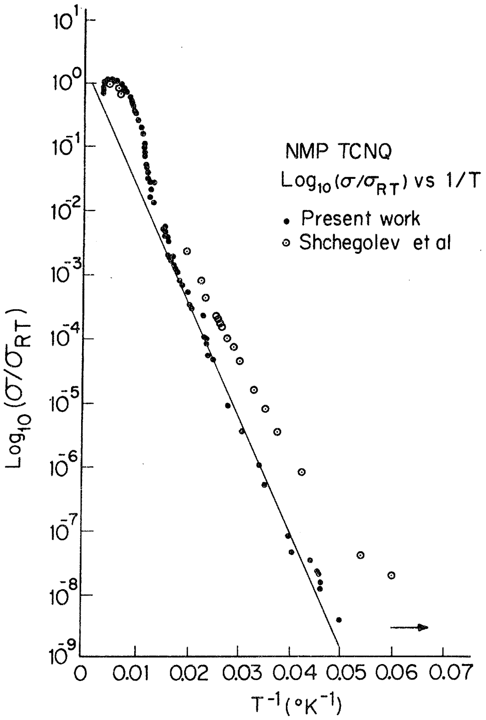

FIG. 2. Temperature dependence of the conductivity of NMP TCNQ. The solid points represent the data presented in this paper. The arrow indicates the constant value found below 10 °K. The circled points are previous data taken from Ref. 12. σ_{RT} denotes the room-temperature value of σ.

All solvents and reactant liquids were thoroughly bubbled with argon, vacuum pumped, and back flushed with argon repeatedly before being placed in the glove box. The starting materials, cyclohexane-1, 4-dione (Aldrich), and malononitrile (Aldrich) were twice recrystallized before use. The acetonitrile solvent (Matteson–Coleman–Bell chromatoquality) was refluxed for 24–48 h over BaO and P_2O_5 and then distilled over P_2O_5. As originally reported in our earlier work, the resultant TCNQ is a brilliant yellow-orange crystalline material giving yellow-orange solutions when dissolved in acetonitrile and not a rust-brown power yielding yellow-to-yellow-green solutions as previously reported. The TCNQ crystalline material was recrystallized twice from acetonitrile giving large well-formed crystals. These were placed in a gradient sublimator lined with an inert DuPont "Kapton" sleeve, and the sublimator was pumped and back flushed with argon several times. Upon completion of sublimation at 130 °C and 1-Torr pressure, only brilliant yellow-orange TCNQ crystals from the center zone were collected for further use.

Analysis. Calculated for $C_{12}H_4N_4$: C, 70.57; H, 1.98; N, 27.44; found: C, 70.62; H, 1.91; N, 27.52. The lithium salt, Li (TCNQ), was prepared[17] using ultrapure anhydrous LiI (Alfa Inorganics). Contrary to all previous reports, solid pure Li (TCNQ) is not a purple powder but a glistening red microcyrstalline material much like K (TCNQ) and Rb (TCNQ). These Li (TCNQ) crystals are obtained only under these preparative conditions, whereas the purple powder results directly using any less careful procedure, for example, using hydrated LiI ($LiI \cdot 3H_2O$).

Analysis. Calculated for $C_{12}H_4N_4Li$: C, 68.26; H, 1.91; N, 26.55; Li, 3.29; found: C, 68.32; H, 1.91; N, 26.59; and Li, 3.27.

N-methylphenazinium TCNQ was prepared following Melby[1] from twice-recrystallized NMP methosulfate (Aldrich). The resultant black (NMP TCNQ) crystalline material was dissolved and recrystallized twice from acetonitrile. Single crystals were grown from saturated acetonitrile solutions by slow recrystallization under argon atmosphere. The largest crystals obtained measured 0.5×5 mm.

Analysis. Calculated for $C_{25}H_{15}N_6$: C, 75.16; H, 3.79; N, 21.04; found C, 75.18; H, 3.79; N, 21.00.

An immediate consequence of this higher-purity material is that ESR measurements at low temperatures show the paramagnetic impurity contribution to be diminished by about a factor of 3 compared to that in our previously reported studies.[4]

III. EXPERIMENTAL RESULTS

The conductivity data are presented in Fig. 2, where $\log_{10}(\sigma/\sigma_0)$ is plotted as a function of T^{-1}. The data consist of a compilation of results from many samples and were taken over a period of several months. The results are reproducible from sample to sample and from run to run on a given sample. The higher-temperature data are shown in more detail in Fig. 3. The room-temperature conductivity $[\sigma = 380\ (\Omega\,\mathrm{cm})^{-1}]$ has a magnitude more than twice as large as compared with previously published data $[170\ (\Omega\,\mathrm{cm})^{-1}$ at room temperature$]$ on samples prepared in our laboratory or elsewhere. The larger value indicates higher sample purity and/or more nearly perfect crystals. The temperature dependence in the high-temperature regime does not follow a simple power law; certainly the conductivity *does not* vary as T^{-1} above 300 °K, as suggested by diffusion theory.[11] Analysis of the *resistivity* vs temperature in the limited range from 300 to 400 °K suggests a dependence of the form $A + BT^4$. The samples cycle well at temperatures below 400 °K with reproducible results.

The plot of $\log_{10}(\sigma/\sigma_0)$ vs $1/T$ shows straight-line behavior 70 °K, indicating a well-defined and temperature-independent activation energy. From this low-temperature slope, one obtains the value of 0.037 eV for the activation energy, indicating an

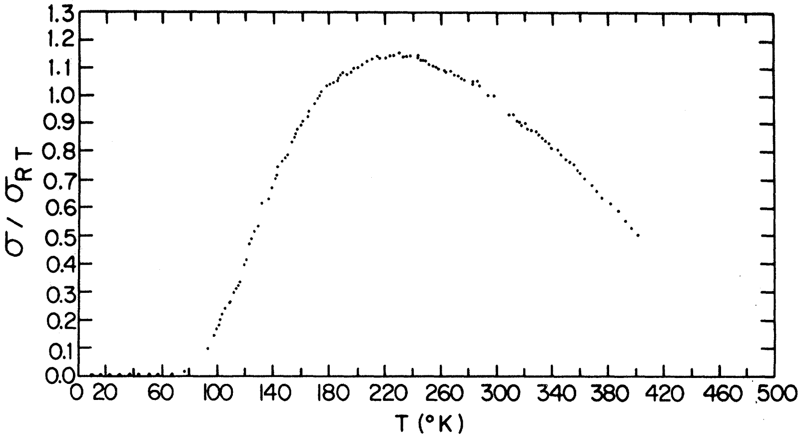

FIG. 3. Normalized conductivity of NMP TCNQ showing the high-temperature regime in detail.

energy gap of 0.074 eV. At the very lowest temperatures (below 10 °K) the conductivity levels off to a constant value. The residual value is more than an order of magnitude larger than that of the sample holder wired in the usual fashion but without the sample. The origin of this residual conductivity is not presently understood; however, the sharp turnover from exponential dependence to a constant value indicates that the *intrinsic* low-temperature data are of the form

$$\sigma=\sigma_0 e^{-\Delta/kT} . \tag{1}$$

It is unlikely that the constant term is in any sense fundamental or intrinsic. It may arise from a slight bulk nonstoichiometry or even from surface states. In this respect we note that although the samples studied in this work are the purest yet synthesized by any group, the residual impurity level is still in the range of 0.1% as evidenced by the low-temperature spin resonance. Hopefully, continued attempts at higher purity will clarify the origin of this very small ($10^{-9}\sigma_{RT}$) residual contribution to the lowest-temperature conductivity.

At intermediate temperatures (above 70 °K) the plot of $\log_{10}(\sigma/\sigma_0)$ vs T^{-1} deviates *above* the extrapolated straight line, suggesting a temperature-dependent activation energy which goes continuously to zero at about 200 °K where the system becomes metallic. The temperature dependence of the slope $d[\log_{10}(\sigma/\sigma_0)]/d(T^{-1})$ is given in Fig. 4, having been obtained by computer fitting the data of Fig. 2 and then differentiating the digitized curve.

The low-temperature data may be compared with the results of Shchegolev *et al.*,[12] as shown in Fig. 2. The comparison shows two features of particular importance. First, the low-temperature curvature away from the straight line (the $T^{-1/2}$ behavior?[11]), which was evident in the earlier data,[12] is completely absent in the present work. Second, the low-temperature resistance in the present work is larger by more than an order of magnitude, indicating higher sample purity (in agreement with the inference from the high-temperature data). We thus conclude *that for* NMP TCNQ *the curvature* $\ln(\sigma/\sigma_0)$ vs T^{-1} *arises from impurity contributions with the intrinsic behavior being exponential in* T^{-1}. The impurity contributions may have a more complicated temperature dependence, suggesting hopping mechanisms, but the intrinsic conductivity is dominated by the temperature-dependent energy gap.

It should be noted that the intrinsic conductivity mechanisms can dominate the bulk measurements in pseudo-1-d systems even though the uninter-

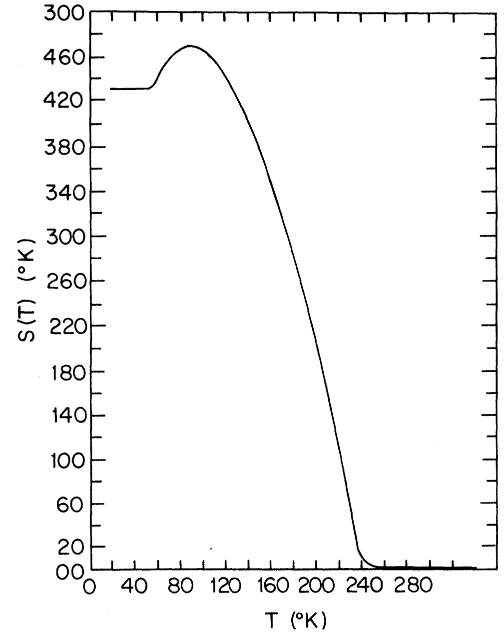

FIG. 4. Slope $S(T)$ of $\ln(\sigma/\sigma_0)$ vs T^{-1} as a function of temperature. The curve was obtained by computer fitting the data of Fig. 2 and then differentiating the digitized curve.

rupted chain length is much less than the sample dimension. For this to be the case, it is necessary that the resistance of a typical strand be greater than the equivalent resistance associated with interstrand hopping. This condition is easily satisfied at high temperatures where the thermally activated interstrand hopping takes place with relative ease. At lower temperatures one might expect the opposite limit to be appropriate. However, if a metal-insulator transition occurs in the microscopic electronic structure, the intrinsic conductivity will dominate the bulk measurements at all temperatures. This is evidently the case for NMP TCNQ.

IV. ANALYSIS OF DATA

As indicated in Sec. III, the low-temperature behavior indicates a Hubbard gap of magnitude $E_H(0) = 0.074$ eV. This value is somewhat smaller than the 0.1 eV inferred from the earlier data[12] and implies a reduced value of the effective Coulomb interaction U_F.[3,4] Use of the measured low-temperature magnetic susceptibility[3,4] and the corrected value for $E_H(0)$ leads to values of $U_F \simeq 0.14$ eV and the transfer integral $t = 0.02$ eV. Although slightly smaller, these more accurate values confirm the conclusions of our earlier work.[4] As emphasized there, the small magnitude of U_F explicitly demonstrates the important role of the cation polarizability in achieving the metallic state.

From the slope $S(T)$ of $\ln(\sigma/\sigma_0)$ vs T^{-1}, as given in Fig. 4, one can obtain information on the temperature dependence of the Hubbard gap. Assuming a temperature dependence for the conductivity of the form

$$\ln(\sigma/\sigma_0) = \Delta(T)/kT \, , \tag{2}$$

it follows that the slope may be written

$$S(T) = \frac{d \ln(\sigma/\sigma_0)}{d(T^{-1})} = \Delta(T) - T\frac{d\Delta(T)}{dT} \, . \tag{3}$$

Equation (3) is a simple differential equation for $\Delta(T)$ which demonstrates that the apparent activation energy cannot be taken simply from the slope of $\ln(\sigma/\sigma_0)$ vs T^{-1}. $\Delta(T)$ can be obtained by solving Eq. (3) numerically using Fig. 4 as the experimental input, or equivalently, directly from Eq. (2). The normalized result $\Delta(T)/\Delta(0)$ is shown in Fig. 5. There are two features of particular interest. First, the apparent gap begins to show deviations from the asymptotic ($T \rightarrow 0$) value at relatively low temperatures ($T \sim 60$ °K). This is well below the metal-insulator (MI) transition region as indicated by the magnetism and conductivity turnover (~200 °K). Second, the gap goes smoothly to zero, without discontinuity, and appears to approach zero with nearly zero slope. This is to be contrasted with the behavior in a conventional second-order phase transition, where the order parameter approaches zero, at least in mean-field theory, with infinite slope. The fluctuations involved in the MI transition evidently are dominant, again emphasizing the fact that the MI transition (in absence of a large accompanying lattice distortion) is a local phenomenon.

It is of interest to compare the magnetic properties with the inferred temperature dependence of the Hubbard gap. Examination of the magnetic susceptibility data shows, as emphasized in our earlier work,[4] that local moments persist in the insulating state essentially without change in magnitude right up to 200 °K, whereas the apparent Hubbard gap begins to decrease at much lower temperatures. This again emphasizes the important role of the fluctuations. At intermediate temperatures the Hubbard model can be viewed as a disordered system in which the random potentials, experienced by a given electron, arise from the electron-electron interaction as a result of the finite number of single-particle excitations and the magnetic spin disorder. On general grounds one expects this disorder to be reflected in a smearing of the density of states with band tailing into the Hubbard gap. From this point of view the experimentally determined temperature dependence of the Hubbard gap has only qualitative meaning. The gap does not simply renormalize. There is in addition a significant change in the shape of the density-of-states curve arising from the fluctuating electron-electron potentials, with the result that a significant state density appears in the gap with an

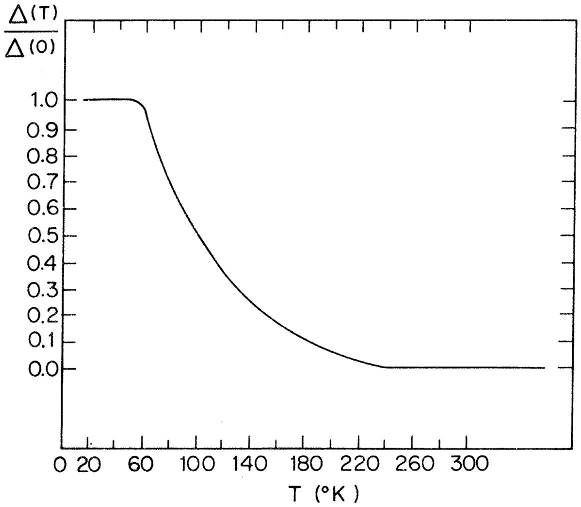

FIG. 5. Apparent activation energy as a function of temperature showing deviations from the asymptotic ($T \rightarrow 0$) value for $T > 60$ °K. Comparison with the persistence of localized moments to much higher temperatures demonstrates the importance of fluctuations in the metal-insulator transition.

associated contribution to the conductivity. This kind of a self-consistent change in the density of states has been identified theoretically in the functional integral approach to the Hubbard model of Kimball and Schrieffer,[10] as well as in Pleischke's[18] improved theory of the Falicov–Kimball two-band model.[19] The importance of fluctuations and the associated buildup of Coulomb hole correlations in the MI transition were emphasized in our earlier paper.[4] The detailed analysis of the high-purity conductivity data presented here brings this even more clearly into focus.

V. SUMMARY AND CONCLUSION

The high-temperature conductivity reported here for high-purity crystals is larger than previously reported, indicating higher-quality samples. The absolute value of the conductivity is evidently limited by crystalline imperfection. It seems likely that the imperfections involved are microcracks or other large-scale defects which limit the effective cross-sectional area of the samples. The major evidence in support of this is that the normalized conductivites agree to within a few percent from sample to sample even though the absolute values at room temperature may vary by more than a factor of 2. As indicated above, the highest room-temperature conductivity attained thus far is 380 $(\Omega\,\mathrm{cm})^{-1}$. The intrinsic conductivity for NMP TCNQ at room temperature must be equal to or greater than this value.

Even with the improved purity, an estimate of the mean free path based on a tight-binding structure[4] leads to values of about one lattice constant,

$$\lambda = \tau v_F = \left(\frac{\sigma_M \pi \hbar}{2Ne^2a^2}\right) a \simeq a\ , \tag{4}$$

where a is the lattice constant and σ_M is the conductivity in the metallic state. Equation (4) is of course based on simple band theory and completely neglects the fact that the metallic state is highly correlated so as to minimize double occupancy. The effect of correlation on the transport properties has been recently discussed by Rice and Brinkman[20] from the point of view of Fermi liquid theory and the Gutzwiller variational approach.[21] It appears that the dominant effect is in the effective number of carriers [note that the band parameters cancel out in Eq. (4)]. The actual number of carriers is reduced in the correlated electron gas as a result of the small fractional double occupancy. Thus the true mean free path for the correlated metallic state of NMP TCNQ must be in the range of several lattice constants.

In our earlier paper[4] we discussed the question of conductivity in metallic systems with very short mean free path. When the scattering time τ becomes sufficiently short such that $\tau E_F \lesssim h$, the usual approximations break down and simple scattering theory is inappropriate. In this limit the proper view must go over continuously to a diffusion transport of the electrons through the random (in space and time) potential arising from thermal disorder in the lattice. Evidently, this is not the case in NMP TCNQ in the experimental range studied, where the mean free path is a few lattice constants. It would seem in principle possible to cross over into the diffusion regime by extending the measurements to higher temperature. Unfortunately, thermal decomposition sets in at about 100 °C, so that such experiments cannot be carried out. The general theoretical question of the crossover from band propagation to diffusion with increasing electron-phonon coupling is worthy of study, for it would appear that this interesting intermediate regime could be experimentally accessible in organic molecular crystals of this kind.

Conductivity studies on high-purity NMP TCNQ single crystals have demonstrated that the curvature in $\log_{10}\sigma$ vs $1/T$, seen at low temperatures in earlier data, is the result of impurities. The intrinsic behavior is exponential in T^{-1} and is consistent with NMP TCNQ being a magnetic Mott–Hubbard insulator below 200 °K. As we have shown, this conclusion, although valid for NMP TCNQ, should not be generally applied to the entire class of highly conducting TCNQ salts. Thus far only the NMP salt shows the magnetic properties characteristic of a Mott transition. The Q(TCNQ)$_2$ compound, on the contrary, remains microscopically metallic at least down to 130 °K,[6,15] i.e., well below the temperature at which the conductivity is maximum. Evidently in this quarter-filled band case, an interrupted metallic strand model[22] may be appropriate with the low-temperature conductivity being limited by interstrand hopping. However, we emphasize the need for studies on high-purity samples to avoid application of sophisticated theoretical models to impurity-related effects.

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Superconductivity, Ferroelectricity, and the Mott Insulator*

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It is shown that Mott-insulator (or semiconductor) state can become unstable to the formation of Cooper pairs. The transition between the states can be either first or second order. The ferroelectric instability of the Mott insulator is also discussed and a spin-analog model is presented that can account for all three thermodynamic states.

I. INTRODUCTION

The strong correlation effects that appear to be present among electrons in partially filled orbitals in certain organic substances [e.g., those containing tetracyanoquinodimethan (TCNQ)] suggest a description in terms of a Hubbard model.[1,2] An advantage of this description is that it incorporates the Mott insulator[3] as a possible ground state for certain organic semiconductors. The simple model does not allow for electron-phonon or electron-exciton interactions which may be important in describing the equilibrium and transport properties of a particular material. A novel feature of the organic systems is that thermal promotion of polar states may occur at reasonable temperatures,[2] quite unlike the situation in the transition-metal and rare-earth compounds.

Given that the Mott insulator represents the normal state of the electronic system (i.e., the Coulomb repulsion is much greater than the bandwidth in the half-filled-band Hubbard model), we investigate the instability of this normal state in the presence of interactions extraneous to the Hubbard model. These include indirect interactions via phonons or excitons, as well as electron-electron interactions not included in the Hubbard model. A consideration of these interactions is important in attaining an understanding of the complex behavior of these substances, as is indicated by experiment. Further, the theoretical investigation represents the first in which the short-ranged Coulomb interaction is treated exactly in a model superconductor. The principal result is that the Mott insulator (or semiconductor) can become unstable to Cooper-pair[4] formation below a certain transition temperature. It is also found that the phase transition can be either first or second order, depending on the parameters. The possibility of a ferroelectric instability has also been considered, and it has been found that, within the molecular-field scheme, the phase boundary between the ferroelectric and superconductor is independent of temperature. It is also seen that the competing interactions that lead to ferroelectricity, or superconductivity in a strongly correlated electron system, can be represented in terms of a spin-analog model.

II. INSTABILITY TO THE SUPERCONDUCTOR

The Hubbard model[5] can be written

$$H_1 = I_1 \sum_i C^\dagger_{i\uparrow} C_{i\uparrow} C^\dagger_{i\downarrow} C_{i\downarrow} + \sum_{i,j} t_{ij} C^\dagger_{i\sigma} C_{j\sigma} , \qquad (1)$$

where $C_{i\sigma}$ destroys an electron on site R_i and spin σ and I_1 and t_{ij} are the intrasite repulsion and hop-