SUPERCONDUCTING FLUCTUATIONS AND THE PEIERLS INSTABILITY IN AN ORGANIC SOLID


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The discovery of extraordinary conductivity maxima in a class of organic charge transfer salts is reported. The data are interpreted as resulting from superconducting fluctuations at high temperatures. A possible mechanism for achieving high temperature superconductivity is suggested based on the electron–phonon interaction, in the strong-coupling limit, and the Peierls soft-mode instability in pseudo-one-dimensional systems. Procedures are suggested for the possible eventual stabilization of the superconducting state.

WE REPORT in this letter the discovery of extraordinary electrical conductivity maxima in a class of organic charge transfer salts. We interpret these data as arising from superconducting fluctuations (i.e. paraconductivity) associated with a tendency toward high temperature superconductivity in these pseudo-one-dimensional solids. The ground state of the compounds thus far studied is, however, that of a Peierls insulator, we have not yet been able to stabilize the superconducting state. We propose a possible mechanism for achieving such high temperature superconductivity based on the electron–phonon interaction and the Peierls instability; and then outline procedures for the possible eventual stabilization of the superconducting state in such systems.

The organic charge transfer salts based on tetracyanoquinodimethane (TCNQ) with a metal–insulator transition to a magnetic semi-conducting low temperature phase occurring at about 200K. The critical role of cation polarizability in reducing the electron–electron Coulomb repulsion so as to make possible the achievement of the metallic state in such narrow band systems was first demonstrated in the (NMP) (TCNQ) work. As part of a continuing effort to stabilize the metallic phase, other donor cations have been considered. There are two basic requirements: (1) large cation polarizability, and (2) relatively small size. The former has been thoroughly discussed, the latter follows from the fact that the interaction between the conducting electron and the induced polarization dipole varies as $r^{-4}$. Consequently, upon the report of the initial characterization of tetrathiofulvalene (TTF) by Wedl et al., it seemed clear that systems of this general kind were prime candidates for stabilizing the metallic state, being both relatively small and possessing a large molecular polarizability as a result of the low energy electronic transitions arising from the sulfur heteroatoms. That the resultant TTF cations are also open-shell systems and thus potentially metallic provided an additional attractive feature.

The question of superconductivity in organic salts in the strong coupling polaron limit was considered

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previously, wherein it was concluded that superconductivity via an excitonic mechanism was unlikely. Superconductivity via the usual phonon mechanism appeared possible if the metallic state could be stabilized.

The room temperature conductivity of the sample of Fig. 1 was measured as \( \sigma_{RT} = 1837 (\Omega \text{cm})^{-1} \), the absolute accuracy being limited to about \( \pm 10 \text{ per cent due to uncertainties in sample dimensions as measured by reticle and microscope} \). The maximum conductivity observed at 58K thus has the extraordinary value of \( \sigma_{\text{max}} > 10^6 (\Omega \text{cm})^{-1} \) with a slope \( (d\sigma/dT) \) which appears to be divergent.

A conductivity of this magnitude simply cannot be understood on the basis of conventional metallic conduction. The unit cell volume of (TTF)(TCNQ) is approximately \( 220 \text{Å}^3 \). Allowing for two carriers per unit cell (one electron on TCNQ\(^+\) and a mobile hole on TTF\(^-\)), the resulting carrier density is \( 8 \times 10^{21} \text{ cm}^{-3} \), or roughly a factor of ten times smaller than that of copper metal. For comparison, the room temperature conductivity of Cu is \( 6 \times 10^6 (\Omega \text{cm})^{-1} \), and the mean free path has been determined as \( \lambda_{\text{Cu}} = 420 \text{Å} \). Thus, if the bandwidth were the same as in Cu, a maximum mean free path greater than one micron would be implied. The actual bandwidth is almost certainly much less than that of a nearly free electron metal, and the structure is highly anisotropic. Detailed studies of the tight-binding system (NMP)(TCNQ) yielded \( \lambda \approx 0.1 \text{eV} \). Similar numbers are relevant to (TTF)(TCNQ) as evidenced by the magnitude of the room temperature spin susceptibility\(^{12,13}\) and nuclear relaxation rates.\(^{14}\) For the tight-binding one-dimensional limit, the mean free path is given by\(^3\)

\[
\lambda = \nu_F \tau = \frac{\sigma \hbar}{2N e^2 a}
\]

where \( N \) is the carrier density, \( a \) the lattice constant along the chain, \( e \) the electronic charge, and \( \sigma \) the measured conductivity. Note that the band parameter, i.e. the tight-binding transfer integral, cancels out of equation (1). Taking \( a = 3.8 \text{Å} \), one estimates \( \lambda_{\text{max}} > 2100 \text{Å} \). Such enormous scattering lengths are not possible in systems such as these at the temperatures in question. The Debye temperature of (TTF)(TCNQ) as obtained from the \( T^3 \) term in the low temperature
heat capacity is 90K. Thus, the strong electron—phonon scattering that limits the room temperature conductivity would still be operative at 60K (witness the variation of $\sigma(T)$ for Cu or any other simple metal in the vicinity of its Debye temperature). These quantitative arguments, together with the qualitative sharpness of the $\sigma$ vs. $T$ anomaly, suggest that the excess conductivity is to be interpreted as arising from superconducting fluctuations above $T_c$, i.e. paraconductivity.

The behavior shown in Figs. 1 and 2 is not typical for (TTF) (TCNQ). This apparently divergent conductivity has been observed in only three single crystals out of approximately seventy which have been measured. These particular crystals had excellent morphology with exceptionally smooth faces. The 'typical' conductivity behavior exhibited by the other crystals is shown in Fig. 3 for comparison. The typical curve follows the divergent curve at high temperatures, but breaks away as the temperature is lowered, exhibiting a weaker maximum at or very near the divergence temperature. It appears that extreme microscopic perfection is required to obtain the data of Fig. 1. There is in addition some indication of strain sensitivity with characteristically higher values found with smaller diameter gold wires and smaller silver paint contact areas. However, taken at face value, the data indicate that the divergent behavior is characteristic of only rare microscopically perfect crystals of (TTF) (TCNQ). It is to be noted that for a given crystal the data are reproducible on successive runs, and no discontinuity or significant hysteresis is observed. Since it appears that the ground state of (TTF) (TCNQ) is that of a Peierls insulator (see below), the break-away and weak maximum typically observed might result from imperfections in the crystal. The

$$\frac{\sigma - \sigma_N}{\sigma_N} = \left(\frac{\pi e^2}{16\hbar}\right) \frac{R_N}{L} \xi(0)$$ (3)

where $\epsilon = (T - T_c)/T_c$ and $f_1(\epsilon)$ is a slowly varying function of $\epsilon$ with magnitude of order unity in the strong pairbreaking limit appropriate to the materials in question. In the above expression, $R_N/L$ is the resistance per unit length of the $1 - d$ chains (cross-sectional area determined by the molecular dimensions of TTF and TCNQ), and $\xi(0)$ is the superconducting coherence length evaluated at $T = 0K$. The single unknown in equation (3) is the coherence length $\xi(0)$ ($R_N/L$ is estimated from the normal state conductivity which is taken as approximately $10^5 \, (\Omega cm)^{-1}$ or half of the room temperature value). From the experimental data as shown in Fig. 2, one finds $\epsilon^{3/2} \approx 7.3$. A simple calculation then leads to the estimated value of $\xi(0) \approx 50\,\text{Å}$ as inferred from the paraconductivity through equations (2) and (3). Although certainly a rough estimate, it is noteworthy that this value is of the correct magnitude. The BCS value would be $\xi(0) = \frac{2h \nu_F}{n(3.5 \, kT_c)} = \frac{2h \nu_F}{3.5 \, kT_c}$, for a $1 - d$ tight binding band. Using the values for $E_F \approx 0.2eV^{13}$ and $T_c \approx 60K$, one estimates $\xi(0) \approx 50\,\text{Å}$. The

Further confidence in this interpretation can be found in the log $\sigma$ vs. log$(T - T_c)$ plot shown in Fig. 2. The straight line behavior indicates a $(T - T_c)^{-n}$ dependence with $n = 1.5$ and $T_c = 58K$. In Fig. 2, we plot the total conductivity, not $\sigma - \sigma_N$, since the true value for $\sigma_N$ cannot be determined from the data. The $n = 1.5$ power law is suggestive of fluctuations in a one-dimensional system where $n = 3/2$ would be expected. Note that subtracting $\sigma_N$ would tend to bring the data onto the $n = 1.5$ straight line over the entire temperature range. In plotting the data as in Fig. 2, we implicitly neglect the temperature dependence of $\sigma_N$. This will not be misleading as long as $\sigma_N$ varies slowly compared to the total conductivity. With these qualifications, one can attempt a comparison with the theoretical expression of Patton

$$\frac{\sigma - \sigma_N}{\sigma_N} = (\frac{\pi e^2}{16\hbar}) \frac{R_N}{L} \xi(0)$$ (2)
Peierls instability then occurs non-uniformly over the sample whereas the rare divergent behavior signifies a uniform Peierls soft-mode transition over macroscopic regions.

FIG. 3. Temperature dependence of the conductivity of (TTF) (TCNQ) single crystal (— • — • ) and of (TTF) (TCNQ) typical crystals (— ○ — ○ ).

As a first attempt to stabilize the crystal structure, we have synthesized the related cation\textsuperscript{18}cis\textsc{(trans)}-dimethyltetraphthiofulvalene (ATTF) shown in Fig. 4. The motivation is straightforward. The Peierls instability ultimately arises from the divergence in the temperature dependent Lindhard function in one dimension. To stabilize the structure, we add a small amount of residual disorder, in addition to the thermal disorder, through the random orientation of the asymmetric cation. The disorder is a small effect; much smaller than that present in (NMP)(TCNQ). Having demonstrated that the electronic properties of the NMP compound are not dominated by disorder,\textsuperscript{19} there is little doubt that the added methyl groups (Fig. 4) represent a small perturbation which might, however, be sufficiently large compared to $k_B T$ to aid in the stabilization of the structure. The results on (ATTF) (TCNQ) are reproducible with $T_c$ decreased somewhat, qualitatively as expected.

Despite considerable effort over a three month period, we have not yet been successful in obtaining single crystals of (ATTF) (TCNQ) of a size suitable for four-probe conductivity measurements. As a result, we have devised an experimental technique for obtaining information on the bulk properties from compaction of samples. The voltage-shorted compaction (VSC) device is shown schematically in Fig. 5. Compaction conductivity measurements of metallic organic salts typically show an exponentially activated behavior with the activation arising from inter-particle contact resistance. The essence of the voltage-shorted compaction is to allow current paths between particles near the compaction surface via the conducting silver paint short and thereby to wipe-out the interparticle resistance.

FIG. 4. Molecular structure of ATTF.
activation effect. The result is a complicated series-parallel network which has been modeled and analyzed, and will be presented in detail in a subsequent paper. For our purposes here, it is sufficient to note that we have verified the qualitative behavior experimentally by studying compactions of (NMP) (TCNQ). Whereas regular compactions of (NMP) (TCNQ) show an exponentially small and thermally activated conductivity ($\Delta \approx 0.07eV$), a voltage-shorted compaction of this compound clearly reflected the weak and broad maximum well-known in single crystal studies of this compound.1,3 VSC data on the symmetric (TTF) (TCNQ) show a very weak maximum, with $\sigma_{\text{max}} / \sigma_{RT} \sim 2$, i.e. comparable to the non-shorted compaction data for this compound. Thus, no evidence of the divergent paraconductivity is seen in the polycrystalline data in agreement with the frequency of occurrence in single crystals. On the contrary, typical voltage-shorted compaction data on (ATTF) (TCNQ) are shown in Fig. 6. The voltage-short was adjusted to give room temperature values of about 0.1$\Omega$ for the four-probed effective resistance, although the precise value was not crucial. In every case, the VSC data show a large and relatively narrow maximum centered at about 50K, as shown in Fig. 6. This characteristic behavior is all the more remarkable on recalling that the compaction is shorted by a highly conducting silver paint and that only those current lines passing through the layer of particles adjacent to the surface can avoid the inter-particle contact problem, so that a small thickness of the actual material is involved. The device conductivity does not diverge since the limiting conductivity (i.e. with $\sigma_{\text{bulk}}$ infinite) is determined by the inter-particle contact through the silver paint. In the region where $\sigma / \sigma_{RT} \gg 1$, log-log plots indicate $(T - T_c)^n$ behavior with $n = 1.5 \pm 0.3$ and $T_c \approx 50K$. The asymmetric TTF cation, therefore, has solved the reproducibility problem. Single crystal data are clearly needed, and continued attempts are in progress. However, the voltage-shorted compaction device should prove a valuable technique for evaluation of new systems.

We have suggested that although the divergent conductivity results from superconducting fluctuations, the phase transition is a Peierls instability to a non-magnetic insulating ground state. The experimental evidence leading to this conclusion is summarized in the following facts. At low temperature, $T < < 60K$, the single crystal conductivity becomes exponentially small [1,2] $[\sigma(T) \approx 10^{-8} (\Omega \text{cm})^{-1}]$. The spin susceptibility is small and shows a monotonic decrease with decreasing temperature. The limiting low temperature behavior indicates a non-magnetic ground state. Nuclear spin–lattice relaxation studies (40MHz) on protons in the metallic state of (TTF) (TCNQ) show a single relaxation time with no evidence of significant electron–electron interactions ($\chi^2 T_1 = \text{const.}$), as further confirmation that only the electron–lattice interaction is involved. Finally, the fact that the substitution of the disordered asymmetric cation lowers the transition temperature is consistent with a rounding of the peak at $q = 2k_F$ in the temperature dependent Lindhard function.

Given this interpretation, the obvious question to be answered is why do the fluctuations toward superconductivity appear just as the electron–lattice system approaches the Peierls instability? We suggest that the answer lies in the nature of the Peierls instability itself. As $T \to T_p$ (the Peierls transition temperature), the phonon spectrum goes soft near the zone boundary which is located at $2k_F$ for the
half-filled band in \( \mathbb{1} - d \). A straightforward analysis of the idealized one-dimensional system yield

\[
\omega_a = 2 \sqrt{\frac{K - \gamma^2 F(q, T)}{m}} \sin \frac{1}{2} qa
\]

where \( K \) is the spring constant, \( m \) the molecular mass, \( F(q, T) \) the \( \mathbb{1} - d \) tight-binding Lindhard function and \( \gamma \) is the electron–phonon coupling constant. For a detailed numerical analysis of \( F(q, T) \), see reference 2. Thus, as \( T \to T_p \) and \( \omega(2k_F) \to 0 \), the lattice response diverges and an anomalously large indirect attractive electron–electron interaction might be expected. This is particularly significant for a \( \mathbb{1} - d \) system because \( 2k_F \) spans the Fermi surface, and would thus lead to pair–pair scattering near \( \epsilon_F \) as required for superconductivity. The conventional argument, however, would indicate that as the system approaches strong-coupling, the renormalization effect dominates \((\lambda_p + \lambda_p(1 + \lambda_p))\) and \( T_c \) is thereby limited. The data presented here indicate superconductivity at temperatures comparable with, but somewhat greater than, the maximum estimates of strong-coupling theory. However, the strong-coupling limitation may not be general. For instance, in the true strong-coupling limit, the problem may be approached from the point of view of small polaron theory. Using the results of Chaikin et al.\(^5\) for the degenerate polaron problem (equation (5) of reference 5), the indirect attractive interaction may be written

\[
H'' = -\frac{1}{2N} \sum_{\mathbf{i}, \mathbf{k}, \mathbf{k}', \sigma, \sigma'} (\Gamma_{\mathbf{k}}/\hbar \omega_0) n_{\mathbf{i} \sigma} n_{\mathbf{i}' \sigma'} [\exp (i \mathbf{k} \cdot (\mathbf{r}_\mathbf{i} - \mathbf{r}_{\mathbf{i}'})) + \exp (-i \mathbf{k} \cdot (\mathbf{r}_\mathbf{i} - \mathbf{r}_{\mathbf{i}'})] + W(\mathbf{k}, \mathbf{k}')
\]

where \( \Gamma_{\mathbf{k}} = 2\gamma(2\hbar/m \omega_0)^{1/2} \sin^{1/2} k a \) is of the form appropriate to the electron–phonon interaction. Note that equation (5) is valid when the polaron binding energy, \( E_B \), is greater than the tight-binding transfer integral. Under such circumstances, small polaron theory dictates that one must treat the electron–phonon interaction in zeroth order leaving the tight-binding transfer to be treated subsequently as a perturbation. The indirect interaction as written in equation (5) is appropriate in the true strong-coupling limit which suggests that the strong-coupling renormalization may not appear in \( T_c \). The physical origin lies in the fact that the indirect interaction [equation (5)] results from a site-diagonal electron–phonon coupling mechanism, i.e. the ionization potential is phonon modulated. We see no physical reason to expect the polaron orthogonality to affect such a mechanism. On the other hand, electron–phonon coupling via modulation of the tight-binding transfer integral, being site-non-diagonal, would be expected to renormalize just as the bandwidth itself is narrowed exponentially due to the polaron orthogonality. Thus, the usual strong-coupling renormalization can under the proper circumstances be avoided, thereby leading potentially to high temperature superconductivity via the conventional electron–phonon interaction coupled with the high density of states of the exponentially narrowed band.\(^25,26\) Note that the conditions for validity of the small polaron approach, \( E_B \gg \hbar \omega_0 \), appears to be a natural consequence of the soft-mode Peierls instability since the zone-boundary phonons approach zero as \( T \to T_p \). Obviously, many questions have been raised. However, these ideas appear attractive as a first attempt at an explanation of the data presented in this paper.

Procedurally, the important question is whether or not one can stabilize such a system just above the Peierls transition where \( \omega(2k_F) \geq 0 \), so that on lowering the temperature the superconducting state becomes truly stable. There are several possible avenues: (1) additional structural disorder carefully designed to limit \( F(q, T = 0) \); (2) steric hindrance of the Peierls dimerization; and (3) some weak two-dimensional coupling to limit \( F(q, T = 0) \). These are currently being pursued in our laboratory.

The Peierls instability–superconductivity connection suggested in this paper is a specific example of a general competition of \( k \)-space vs. real-space pairing. The ideas are more generally applicable (at least qualitatively) to three-dimensional systems with unstable crystalline structures such as the well-known \( A - 15 \) high temperature superconductors.\(^27\)

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9. All elemental analyses agreed with their calculated values well within experimental error.
15. WEI T., ETEMAD S., GARITO A.F. and HEEGER A.J., to be published.
26. In the strong-coupling limit described by Thouless, as in the original BCS theory in the same limit, $T_c$ is proportional to the strength of the indirect attractive interaction. However, from equations (4) and (5) of the text, one sees that the magnitude of the coupling in $H'$ is increasing as the zone-boundary phonon goes soft near $T_c$. Under such circumstances, the paraconductivity would not be expected to follow a simple power law. That the paraconductivity appears to follow equation (2) with fixed $T_c$ suggests that the interaction stabilizes at an approximately constant, large value. This might arise from a broadening of the phonon spectral weight as the mode goes soft or perhaps from the decrease in phonon density of states at $2\varepsilon_F$ as the mode softens. More detailed experimental results are required to clarify this point.
27. See for example, BARISIC S., Phys. Rev. B5, 932: 941 (1972) and references therein.
La découverte des maxima extraordinaires de conductivité dans une classe de sels chargés transférés est rapportée. Les données sont interprétées comme résultats des fluctuations supraconductivantes à haut temperature. On suggère un mécanisme possible pour achever la supraconductivité à haut temperature, fondée sur l'interaction électron-phonon, dans la limite d'accouplement fort, et sur l'instabilité de la mode douce de Peierls dans les systèmes pseudo-uni-dimensionnelles. On propose des méthodes pour la stabilisation possible et éventuelle de l'état supraconductant.