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Proposed model of a high-temperature excitonic superconductor*

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We present a detailed calculation of the transition temperature of a model filamentary excitonic superconductor. The proposed structure consists of a linear chain of transition-metal atoms to which is complexed a ligand system of highly polarizable dyelike molecules. Calculations of the electronic properties and experimental data on related materials are used to estimate the strength of the excitonic interaction, Coulomb repulsion, and band structure. From this the superconducting transition temperature was calculated by numerical integration of the gap equation. For the particular structure proposed, transition temperatures of several hundred degrees are calculated. However, we find superconductivity only in those systems where the excitonic medium is within a covalent bond length of, and completely surrounds, the conductive spine. This imposes severe constraints on the structure of any excitonic superconductor. We show that for the structure proposed the momentum dependence of the exciton interaction results in the superconducting state being favored over the Peierls state and in vertex corrections to the electron-exciton interaction which are small.

I. INTRODUCTION

The phonon-exchange mechanism is generally believed to be responsible for superconductivity in all the presently known superconductors. The possible existence of an alternative mechanism, the so-called exciton mechanism, was suggested by Little[1] in polymeric systems and extended by Ginzburg[2] to sandwich structures. The term "exciton" applies here broadly to any electronic excitation. In this new mechanism the effective attraction between electrons on the Fermi surface is induced by the exchange of an exciton. The common feature of the models proposed by Ginzburg and Little for the realization of this mechanism is the distinction between the electrons which are expected to form Cooper pairs and those which participate in the virtually excited excitons. These two types of electrons are confined to two spatially separated regions in close contact with each other. Little proposed a one-dimensional spine of conducting electrons with organic dye molecules chemically bound to this spine at regular distances, while Ginzburg discussed thin metallic films sandwiched between, or coated on one side by, layers of a highly polarizable material.

One of the main attractions of the proposed exciton mechanism is the apparent possibility of higher transition temperatures. This follows from the BCS formula for T_c:

$$T_c = \Theta e^{-1/(\lambda - \mu^*)}, \tag{1}$$

where λ characterizes the strength of the attractive interaction necessary for the formation of Cooper pairs and μ^* the repulsive Coulomb interaction. In the case of the phonon mechanism Θ is approximately the Debye temperature which is of the order of several hundred degrees. In analogy, for the exciton mechanism Θ is expected to be a typical electronic excitation temperature of the order of 10^4–10^5 °K, thus leading to much higher values of T_c. This argument is oversimplified and the conclusion is not correct in general but depends upon the details of the system. While it appears that under special conditions the exciton mechanism may lead to higher values of T_c than those obtained with the phonon mechanism, the high temperature of an electronic excitation is by itself not sufficient to yield unusually high values of T_c. This point will be discussed later in greater detail. The original proposal of the exciton mechanism was followed by a series of critical arguments and counter arguments, most of which are discussed in review articles by Ginzburg.[3]

We believe that of all the systems suggested for the realization of the exciton mechanism of superconductivity, the one-dimensional structure has the best prospects for success. The arguments for this opinion will be made clear in Sec. VIII. In the present paper we discuss in detail a particularly favorable metal-organic system consisting of a linear chain of platinum atoms closely similar to the structure of the much studied KCP system[4] [$K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$], but with the cyano-ligands replaced by polarizable cyanine-dye-like ligands. The most favorable system seems to be the disclike structure illustrated in Fig. 1. Compounds of this general type can be expected to stack so that in the solid state the platinum atoms would form a conductive linear chain. However, it is not clear whether this particular compound will stack, but means are known for inducing stacking between aromatic moieties by the addition of suitable substituents.[5] This may be difficult but is not expected to be impossible. The chemical properties of such systems and the dif-

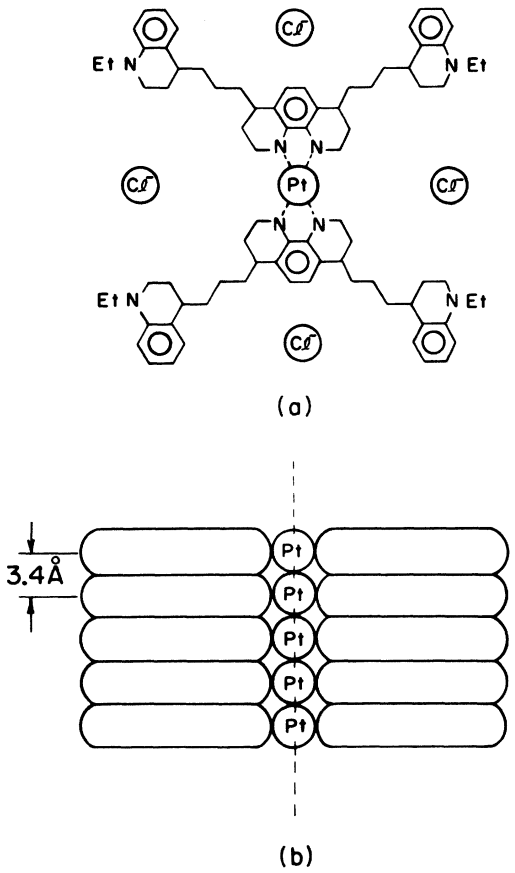

FIG. 1. Proposed model of the structure of an excitonic superconductor. (a) Top view of square planar phenanthroline-dye ligands complexed to Pt. Double bonds in the chromophore are omitted for simplicity. Et stands for ethyl. (b) Side view of chain.

ficulties associated with their preparation are discussed in Sec. II.

In the bulk of the paper we describe the procedure and details of a calculation of the superconducting transition temperature in such a system. The purpose of this calculation is to see whether in the most favorable, but conceivably realizable system, an excitonic interaction of sufficient strength to yield high-temperature superconductivity is obtainable at all. Our conclusion is that it is possible, but the requirements are rather exacting and not easily met. In particular, the distance between the dye molecule and the conductive spine has to be of the order of a chemical bond length and several dye molecules appear to be needed for each atom of the spine.

In addition to a detailed calculation it is also necessary to justify the applicability of the conventional theory of superconductivity which works so well for the electron-phonon system to the completely different electron-exciton system. One difficulty which arises from the replacement of phonons by excitons is that of vertex corrections, another is that of exchange. There are other difficulties associated with the one dimensionality of the proposed system such as the role of fluctuations and the competition between the superconducting and the Peierls instability. All these questions are discussed in Sec. VIII. Of particular significance are the conclusions that for the specific model systems discussed here the vertex corrections are small and that the pairing instability is favored over other possible types of order.

Although there is at present no experimental evidence for the exciton mechanism, it seems that it does not violate any physical principle and its existence or nonexistence will depend on the specific properties of the system under consideration.

II. SPECIFICATION OF THE MODEL SYSTEM

In this section we describe some of the chemical details of a proposed structure illustrated in Fig. 1 and the simplified model system of Fig. 2 upon which calculations were done. For those more interested in the physics of the model and less interested in these important but chemical details, this section may be omitted.

The possibility of using a stacked array of square planar transition-metal complexes as the spine of a one-dimensional superconductor was first suggested by Collman.[6] This suggestion was based on the work of Krogmann,[7] who showed that many Pt complexes could be oxidized to give highly conductive quasi-one-dimensional metals. Of these the compound KCP $[K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O]$ has been studied most extensively by many groups. Our approach has been to attempt to replace the simple ligands (CN in KCP) with other more polar-

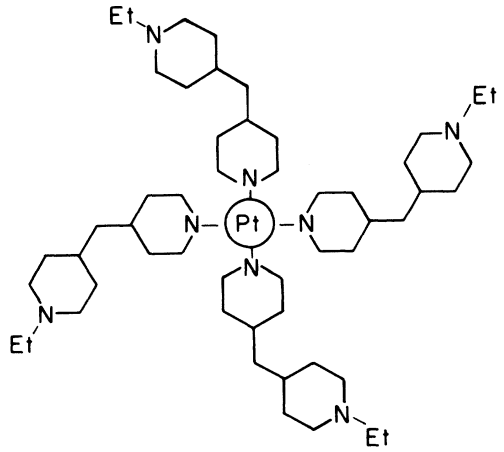

FIG. 2. Simplified version of structure of Fig. 1 for which detailed calculations are presented in this paper.

izable structures so as to satisfy the theoretical criteria for an *excitonic* superconductor. Preliminary calculations on structures based on a glyoxime ligand system[8] indicated that any polarizable groups which might be attached to this ligand would be held at a distance too far from the spine for the excitonic interaction to be sufficiently attractive to lead to superconductivity. Winkler and Mayer[9] in our laboratory then showed that it was possible to complex certain cyanine-dye bases directly to a transition metal such a Pt and so bring the exciton system into much closer proximity to the spine. The metal effectively quarternizes the nitrogen and transforms the dye base to the dye. Based on this result we proposed the structure illustrated in Fig. 1. Each unit of the chain consists of a platinum complex of two, 1-10 phenanthroline ligand systems with cyanine-dye chromophoric units attached to each phenanthroline at the 4 and 7 positions.

In the proposed structure the polarization of the chromophore results in the movement of a positive hole between one nitrogen atom remote from the Pt site and the nitrogen adjacent to the Pt. Because of this large movement of charge a strong electron-exciton interaction can be expected. For the proposed structure one would require four negatively charged counterions (Cl^-), one for each of the chromophore units plus two additional negatively charged ions to yield Pt in the Pt (II) oxidation state. Then the Pt chain needs to be oxidized to give a partially filled d_{z^2} conduction band. Virtual excitation of the chromophoric units provide the excitonic interaction.

The d_{z^2} orbitals of the Pt atoms of the chain overlap with one another creating a linear conductive pathway. It is expected from the geometry that only a weak overlap will occur between these orbitals and the orbitals of the phenanthroline ligands so that the two sets of orbitals may be treated as essentially orthogonal to one another. Because of this the Coulomb interaction between the d_{z^2} electrons and the electrons on the ligands will be much greater than any exchange interaction.

Because of the van der Waals repulsion between the π electrons of the proposed bulky ligands the Pt atoms along the chain could be no closer than about 3.4 Å. We assume here that even at this relatively large metal-metal separation a partially oxidized salt of this general type can form a highly conductive spine. This has yet to be established. We also assume that the proposed ligand system will stack in the manner indicated. Prior to synthesis this is not known of course. However, the point of our calculation is to see whether, given these favorable conditions and this favorable structure—a highly conductive spine in intimate contact with a highly polarizable excitonic medium—can one expect superconductivity or not.

We believe that the proposed structure or a closely related one has a reasonably good chance of being synthesized. Some work has been done on some closely related structures. In particular, Lorentz[10] in our laboratory has prepared a merocyanine version of the ligands illustrated in Fig. 1. This is an important step forward, first, because the merocyanines can be prepared with a polarizability as large as that of the cyanines.[11] To do this one requires the appropriate choice of terminal groups on the chromophore unit so as to make the electronic environment effectively symmetric about the center of the dye as in the cyanines. Second, the merocyanines are electrically neutral so that the ligand system would not carry the large positive charge as it does in the cyanine dye case of Fig. 1. The presence of the large charge on the latter may well inhibit the formation of a stacked array but the merocyanines would not have this problem.

Whether or not the proposed system would form the stacked array is impossible to predict at present. However, enough is known about stacking forces to guess that the proposed stacked array has some chance of occurring. The reasons for believing this are as follows: First, models of the structure show that the disclike ligand system with its counter ions is a relatively tightly packed structure filling all the available space and without large holes in it. Because of this the van der Waals energy would be at a minimum. Second, the large transition dipole moments of the individual polarizable dyelike groups on the ligands would favor a face-to-face arrangement of the planar ligands because of the attractive contribution to the van der Waals energy from the dye-dye interaction. A small rotation of the ligand system from one Pt atom to the next could be expected to avoid direct contact between the nitrogen atoms on the phenanthroline, each of which carry a net positive charge. The metal-metal interaction is probably too weak to contribute significantly to the packing forces except perhaps after oxidation of the Pt chain.

In this paper we present detailed calculations on a simplified version of the system illustrated in Fig. 1. Instead of working with the large phenanthroline groups we use a skeletonlike structure of the chromophore units alone as illustrated in Fig. 2. This simplifies the description of the system and illustrates more clearly the physical points. A full calculation on the system of Fig. 1 and several related cyanine, carbocyanine, and dicarbocyanine structures have been done.[12] They

show that the results reported here for the model system (Fig. 2) are typical of the results obtained for the full system with similar size of the chromophore structures. The carbo- and dicarbocyanines give higher T_c's but would make more difficult the chemical problems of synthesis, complexation, and oxidation.

One additional point should be made in regard to the complexation of the dye base to the Pt atom. In our calculation of the cyanine moieties of Fig. 2 we have treated as equivalent the two ends of the dye—one attached to an ethyl group and the other to the Pt. This is not strictly valid, but there is evidence[10] that by modifying the half of the dye remote from the spine the electronic environment at each end can be made essentially symmetric as can be done for the merocyanines. In that case the polarizability is found to be essentially the same as for the model system proposed.

In Sec. III we discuss how the superconducting T_c is calculated for this system and in Secs. IV, V, and VI how the exciton band, exciton-electron interaction, and Coulomb interaction are calculated.

III. EQUATION FOR T_c

To calculate the transition temperature T_c we have adopted the method developed by Kirzhnits, Maximov, and Khomskii[13] (to be referred to as KMK). This method applies to a weak coupling superconductor and it results in a simple BCS-like equation for the gap function and for T_c. Its merit is that it brings out explicitly and in a convenient form the relationship between the kernel of this equation and the microscopic properties of the system such as the electron band energies, the exciton band energies, and the electron-exciton coupling matrix elements.

We shall now summarize briefly the KMK method and discuss it with regard to the system under consideration. The starting point is the integral equation for the anomalous Green's function F, which at $T = T_c$ reads

$$F(\vec{p}, i\omega_n) = -G(\vec{p}, i\omega_n)G(-\vec{p}, -i\omega_n) \times \sum_m \int \frac{d^3k}{(2\pi)^3} V(\vec{p}-\vec{k}, i(\omega_n-\omega_m)) \times F(\vec{k}, i\omega_m), \quad (2)$$

where $\omega_n = (2n+1)\pi T_c$. This equation is already an approximation in that it neglects vertex corrections. In the case of the phonon-mechanism this is justified by Migdal's theorem, which asserts that these corrections are small in view of the ratio ω_D/ϵ_F (ω_D—Debye energy, ϵ_F—Fermi energy) being much smaller than unity. When the Debye energy is replaced by a characteristic exciton energy this is no longer the case. We shall return to discuss the question of vertex corrections in Sec. VIII, where we show that the special properties of the exciton system proposed here do indeed keep these corrections small, but at present we proceed from Eq. (2). At T_c the "imaginary time" Green's functions G of the superconducting state are replaced by their counterpart in the normal state and approximated by the unperturbed functions G_0,

$$G_0(\vec{p}, i\omega_n) = 1/[i\omega_n - \xi(\vec{p})], \quad (3)$$

where $\xi(\vec{p}) = \epsilon(\vec{p}) - \epsilon_F$ is the single electron energy measured with respect to ϵ_F. It is this approximation which restricts the present treatment to weak coupling superconductors.

The essential feature of the KMK method is the use of the Lehmann representation for the effective electron-electron interaction. The latter can be written in the form

$$V(\vec{q}, \omega) = V_0(\vec{q}, \omega)/\epsilon(\vec{q}, \omega) \quad (4)$$

and the finite temperature analog of the Kramers-Kronig relation for the reciprocal of the dielectric function[14] leads to the spectral representation

$$V(\vec{q}, i\omega_n) = V_0(\vec{q})\left(1 - 2\int_0^\infty \frac{\omega'\rho(\vec{q}, \omega')\,d\omega'}{\omega_n^2 + \omega'^2}\right). \quad (5)$$

The spectral density $\rho(\vec{q}, \omega)$ is relat' to the dielectric function by

$$\rho(\vec{q}, \omega) = -(1/\pi)\,\mathrm{Im}[1/\epsilon(\vec{q}, \omega)]. \quad (6)$$

It is also convenient to write the anomalous Green's function in the spectral representation

$$F(\vec{p}, i\omega_n) = \int_{-\infty}^{\infty} \frac{f(\vec{p}, x)dx}{i\omega_n - x}. \quad (7)$$

Substituting Eqs. (5) and (7) into Eq. (2) one can perform the frequency sum explicitly and after some manipulations and plausible approximations, described in Ref. 13, one obtains the equation

$$\phi(\vec{p}) = -\int \frac{d^3k}{(2\pi)^3} \frac{U(\vec{p}, \vec{k})\tanh(|\xi(\vec{k})|/2T_c)}{2\xi(\vec{k})}\phi(\vec{k}), \quad (8)$$

where

$$\phi(\vec{p}) = 2|\xi(\vec{k})| \int_0^\infty F(\vec{p}, x)dx, \quad (9)$$

and

$$U(\vec{p}, \vec{k}) = V_0(\vec{p}-\vec{k})\left(1 - 2\int_0^\infty \frac{\rho(\vec{p}-\vec{k}, \omega)d\omega}{\omega + |\xi(\vec{p})| + |\xi(\vec{k})|}\right).$$

Before confining the discussion to the one-dimensional electron-exciton system, let us mention briefly how one proceeds in the conventional case from Eq. (8) to obtain an equation similar to the BCS equation. One assumes that the material is either isotropic or that the "dirty" limit approximation is valid.[15] This allows one to replace the three-dimensional momentum integral by an integral over the energy variable ξ' and over the "angle" variables in momentum space, leading to an integral equation in a single energy variable

$$\phi(\xi) = -\int d\xi' \frac{U(\xi, \xi')\tanh(\xi'/2T_c)\phi(\xi')}{2\xi'}, \qquad (10)$$

where $U(\xi, \xi')$ is essentially $U(\vec{p}, \vec{k})$ integrated over the angle variables of $\vec{k}$ in momentum space. Comparison with BCS theory shows that $\phi(\xi) = \mathrm{Re}\Delta(\omega = |\xi_{p_F}|)$. Without discussing in detail the form of $U(\xi, \xi')$ in the general case, we point out its two most important properties: (a) the kernel $U(\xi, \xi')$ is a smooth function of the variables ξ, ξ', unlike the interaction itself, which has a complicated resonant structure; (b) the magnitude of $U(\xi, \xi')$ decreases when either one of the variables ξ, ξ' departs from the Fermi energy. To make the analogy with the BCS equation complete, one has to separate the contributions of the phonon and the Coulomb interactions. The first has an effective cutoff at ω_D. The latter extends over a much larger energy range, however, it may be replaced by a reduced pseudointeraction[16] which is also cut off at an energy ω_D from the Fermi energy, so that one finally gets the finite-temperature BCS-like Eq. (10) with the ξ' integration from $-\omega_D$ to $+\omega_D$.

Let us now return to Eq. (8). In the one-dimensional case there is only one integration variable, so that we shall gain nothing by transforming to an energy variable. Also, the concept of the Coulomb pseudopotential is not useful in our case because the exciton interaction extends over an energy range of the same order as the Coulomb. We therefore prefer to leave Eq. (8) as an equation in the momentum variable and we shall extend the integration over the entire Brillouin zone:

$$\phi(p) = -\int_{-\pi/\alpha}^{\pi/\alpha} \frac{dk}{2\pi} \frac{U(p,k)\tanh(|\xi(k)|/2T_c)}{2\xi(k)}\phi(k). \qquad (11)$$

Let us now be more specific about the kernel $U(p, k)$. The spectral density $\rho(q, \omega)$ in Eq. (9) may be separated into the contribution of the exciton-induced interaction ρ_{ex} and the contribution of the Coulomb interaction ρ_C. We can similarly separate $U(p, k)$ into its two components

$$U_{ex}(p, k) = -2\int_0^\infty \frac{V_0(p-k)\rho_{ex}(p-k, \omega)d\omega}{\omega + |\xi(p)| + |\xi(k)|} \qquad (12)$$

and

$$U_C(p, k) = V_0(p-k)\left(1 - 2\int_0^\infty \frac{\rho_c(p-k, \omega)d\omega}{\omega + |\xi(p)| + |\xi(k)|}\right). \qquad (13)$$

The numerator in the integrand in Eq. (12) is related to the imaginary part of the effective exciton-exchange interaction. We write the latter in the form

$$V_{ex}(q, \omega) = \sum_\alpha |Q_\alpha(q)|^2 D_\alpha(q, \omega), \qquad (14)$$

where $Q_\alpha(q)$ is the electron-exciton coupling to be discussed in Sec. IV and $D_\alpha(q, \omega)$ is the propagator of an exciton of momentum q and energy ω, which is assumed to be a boson Green's function

$$D_\alpha(q, \omega) = 2E_\alpha(q)/[\omega^2 - E_\alpha^2(q) + i\delta], \qquad (15)$$

where $E_\alpha(q)$ is the exciton energy and α is a band index in the case where there are several types of excitons. On account of Eqs. (6) and (15), we obtain

$$V_0(q)\rho_{ex}(q, \omega) = \sum_\alpha |Q_\alpha(q)|^2 \delta(\omega - E_\alpha(q)), \qquad (16)$$

and the exciton-exchange contribution to the kernel becomes

$$U_{ex}(p, k) = -2\sum_\alpha \frac{|Q_\alpha(p-k)|^2}{E_\alpha(p-k) + |\xi(p)| + |\xi(k)|}. \qquad (17)$$

The calculation of $U_{ex}(p, k)$ thus requires a knowledge of the electron-band energies $\xi(p)$, the exciton-band energies $E_\alpha(q)$, and the coupling constants $Q_\alpha(q)$. The calculation of the latter two quantities is described in Secs. IV and V. The Coulomb part of the kernel will then be discussed separately in Sec. V.

IV. CALCULATION OF THE EXCITON-BAND ENERGIES

We consider first an electronically excited state of the array of polarizable molecules such as that of Fig. 1 in which the molecule in the mth unit cell at the lth site in this cell is in the excited state $\chi_\nu(R_{ml})$, and all the rest of the molecules are in their ground state $\psi_0(R_{11})$, $\psi_0(R_{12})$, ... Let this excited configuration be given as

$$\Psi_\nu(R_{ml}) = \psi_0(R_{11})\cdots\chi_\nu(R_{ml})\cdots\psi_0(R_{Nz}). \qquad (18)$$

We assume we have z different sites in the unit cell and that there is a total of N unit cells. Due to interactions between the molecules, delocalized exciton states can be formed from the set of functions $\Psi_\nu(R_{ml})$. These we take of the form

$$\Psi_\alpha(q)=\frac{1}{\sqrt{N}}\sum_{m,l,\nu}[u^\nu_{\alpha,l}(q)+iv^\nu_{\alpha,l}(q)]\,e^{iqR_m}\Psi_\nu(R_{ml}), \tag{19}$$

where u and v are real. Given the energy of the excited state ν of an isolated molecule we obtain the secular equations for $u_\alpha(q)$ and $v_\alpha(q)$ for the exciton state of energy $E_\alpha(q)$ from

$$\int\Psi^*_\mu(R_{st})[H-E_\alpha(q)]\Psi_\alpha(q)\,d\tau=0, \tag{20}$$

where H is the total Hamiltonian. We shall neglect any exchange contribution to the matrix elements resulting from the overlap of electron distributions of neighboring molecules because the electron wave functions of the organic molecules of interest to us are relatively well localized on each molecule. We obtain thus the secular equations

$$\begin{aligned}u^\mu_{\alpha s}(q)[E_\mu-E_\alpha(q)]+\sum_{\nu,l,t}u^\nu_{\alpha l}(q)M^{\mu\nu t}_{sl}\cos qR_t\\ -\sum_{\nu,l,t}v^\nu_{\alpha l}(q)M^{\mu\nu t}_{s,l}\sin qR_t=0,\end{aligned} \tag{21}$$

$$\begin{aligned}v^\mu_{\alpha s}(q)[E_\mu-E_\alpha(q)]+\sum_{\nu,l,t}v^\nu_{\alpha l}(q)M^{\mu\nu t}_{sl}\cos qR_t\\ +\sum_{\nu,l,t}u^\nu_{\alpha l}(q)M^{\mu\nu t}_{sl}\sin qR_t=0.\end{aligned}$$

We use the above real representation to simplify the subsequent machine computation. The matrix element $M^{\mu\nu t}_{sl}$ is defined as

$$M^{\mu\nu t}_{sl}=2\int\rho_\mu(r_1,R_{0s})\,V(r_1,r_2)\,\rho_\nu(r_2,R_{tl})\,d^3r_1d^3r_2, \tag{22}$$

where $\rho_\mu(r_1,R_{tl})$ is the transition density for the excited state μ of a molecule at site R_{tl} and E_μ is the excitation energy of that state. These were calculated using the extended Pariser-Parr-Pople method and parameters as described in Refs. 17 and 18. The factor of 2 arises from the assumed singlet nature of the excited state[19] and $V(r_1,r_2)$ is the interaction between an electron at r_1 in the molecule at site $R_{0,s}$ and an electron at r_2 in the molecule at site $R_{t,l}$. Using standard matrix-diagonalization techniques we obtain from Eqs. (21) the exciton-band energies $E_\alpha(q)$ and the coefficients $u_\alpha(q)$ and $v_\alpha(q)$ which describe the exciton states.

For the system illustrated in Fig. 1 one finds a dispersion curve for $E_\alpha(q)$ of the general form shown in Fig. 3. In this case with four polarizable groups per unit cell each excited state of an individual ligand gives rise to four exciton bands. Due to the high symmetry of the structure some of these are degenerate or near degenerate as shown.

V. ELECTRON-EXCITON COUPLING PARAMETER

The electron-exciton coupling parameter in Eq. (17) has the form $Q_\alpha(q)=\langle 1_\alpha q,k-q|V|0,k\rangle$, which corresponds to the scattering of an electron from k to $k-q$ with the creation of an exciton of wave vector q and band index α. We use the tight-binding approximation for the electron states on the spine

$$\phi_k(r)=\frac{1}{\sqrt{N}}\sum_j\phi(r-R_j)e^{ikR_j}, \tag{23}$$

where $\phi(r-R_j)$ is an atomic orbital located at site R_j. For simplicity we assume one atom per unit cell on the spine and neglect the overlap of atomic orbitals between neighboring cells. Our matrix element Q is thus given by

$$Q_\alpha(q)=\frac{1}{N^{3/2}}\int\sum_{j,k}\phi^*(r_1-R_j)\,\phi(r_1-R_k)e^{i[kR_k-(k-q)R_j]}V(r_1r_2)\sum_{m,l,\nu}[u^\nu_{\alpha l}(q)+iv^\nu_{\alpha l}(q)]\,e^{-iqR_l}\,\Psi^*_\nu(R_{ml})\Psi_{00}\,d^3r_1d^3\tau, \tag{24}$$

where Ψ_{00} is the ground state of the array of polarizable molecules.

Using the assumption of zero differential overlap[20] and the orthogonality of the molecular orbitals on different molecules we find for Q,

$$Q_\alpha(q)=\frac{1}{N^{3/2}}\int\sum_j|\phi(r_1-R_j)|^2\,V(r_1,r_2)e^{iqR_j}\sum_{m,l,\nu}[u^\nu_{\alpha l}(q)+iv^\nu_{\alpha l}(q)]^*\,\chi^*_\nu(R_{ml})\,\psi_0(R_{ml})\,d^3r_1d^3\tau. \tag{25}$$

Using [see Eq. (10) of Ref. 20],

$$\int\chi^*_\nu(R_{ml})\,\psi_0(R_{ml})\,d^3r_3\,d^3r_4\ldots=\sqrt{2}\;\rho_\nu(r_2,R_{ml}), \tag{26}$$

and the invariance of $V(r_1,r_2)$ under a translation of both r_1 and r_2 by a unit cell, and setting $R_l=R+R_j$, we

obtain finally that

$$Q_\alpha(q) = (2/N)^{1/2} \int \sum_{t,l,\nu} |\phi(r_1)|^2 V(r_1, r_2)[u^\nu_{\alpha l}(q) - i v^\nu_{\alpha l}(q)]\, e^{iqR_t} \rho_\nu(r_2, R_{lt})\, d^3r_1\, d^3r_2 . \tag{27}$$

The terms $u^\nu_{\alpha l}(q)$ and $v^\nu_{\alpha l}(q)$ are the normalization terms and fix the phase of the contributions from the dyes at each site, l within the unit cell. The exponential term e^{iqR_t} defines the phase relationship of the transition densities of dyes in different unit cells. The factor $\sqrt{2}\,|\phi(r_1)|^2 V(r_1 r_2) \times \rho_\nu(r_2, R_{lt})$ represents the interaction between an electron on the spine and the transition charge $\sqrt{2}\,\rho(r_2, R_{lt})$ at r_2 of a dye at site, l in unit cell t. For r_1 and r_2 in the same unit cell for the structure illustrated in Fig. 1 this term yields a contribution of about 1 eV/dye as can be estimated from Fig. 6.

Because the interaction between $|\phi(r_1)|^2$ and $\rho(r, R_{lt})$ (i.e., the electron at site r_1 in the conductive system and the transition density on the dye at site $R_{l,t}$) falls off as a dipole interaction with distance $(r_1 - r_2)$, one can truncate the sum over the sites after a small number of terms without a serious error. The finite sums can then be done easily on a computer.

In Fig. 4 the typical dependence of $|Q_\alpha(q)|^2$ upon q is illustrated for a mode α which couples most strongly to the spine. Its most distinctive characteristic is the sharp fall off in $|Q_\alpha(q)|^2$ with increasing q. In this it differs in an essential way from the phonon-electron interaction. In conventional superconductor the electron-ion interaction is strongly screened and this gives the phonon-electron interaction a very short-range character. For this reason the phonon-electron coupling constant is only weakly dependent upon momentum. On the other hand, in our proposed exciton system the bulky polarizable ligands make it impossible for the charges in the ligands to be very close to the charges in the spine and this together with reduced screening in such filamentary compounds makes the exciton-electron interaction one of long range. The drop off in $|Q_\alpha(q)|^2$ occurs at values of $q \sim 1/b$, where b is of the order of the distance of the nearest terminal group of the dye from the spine. We shall see that this strong momentum dependence of $|Q_\alpha(q)|^2$ plays an important role in the structural stability of the proposed system and in reducing vertex corrections to the coupling constant.

VI. CALCULATION OF THE COULOMB INTERACTION

The bare Coulomb interaction between the electrons in the conductive spine is treated in the tight-binding approximation with the assumption of zero differential overlap. In this case the Coulomb interaction is represented by the parameters γ_n which correspond to the interaction between electrons on two atoms on the spine separated by a distance $r_n = na$, where a is the interatomic spacing in the spine. Of particular importance is the parameter γ_0 which measures the Coulomb interaction between two electrons on the same atom. This parameter may be evaluated from the ionization energy I, and the affinity A of the atoms on the spine,[21]

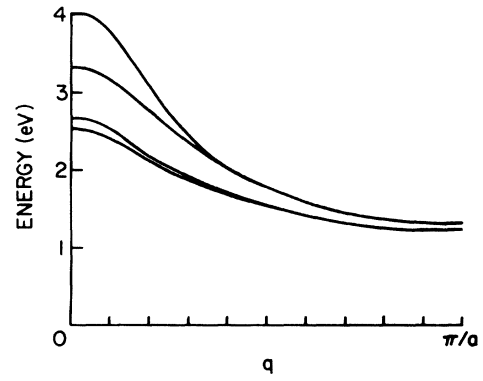

FIG. 3. Calculated exciton-band energies for the structure of Fig. 2.

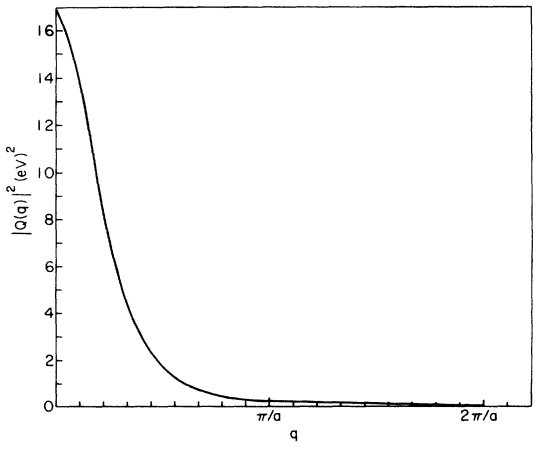

FIG. 4. Calculated electron-exciton interaction $|Q(q)|^2$ as a function of momentum transfer q.

$$\gamma_0 = I - A . \tag{28}$$

For the case of platinum $I = 8.88$ eV and $A = 2.85$ eV, giving $\gamma_0 = 6.03$ eV. This value of A was derived using Pauling's relation[22] between the work function ϕ of a metal and its electronegativity x, $\phi = 2.27x + 0.3$ (eV), and his expression for the average of the ionization energy and electron affinity, $(I + A)/5.36 = x$. The above values were obtained from properties of metallic platinum, but we expect them to give a rough estimate of the properties of the metal atoms of the chain. For simplicity, we use the Nishimoto-Mataga[23] expression for the parameters γ_n

$$\gamma_n = e^2/(r_n + b) . \tag{29}$$

This defines a characteristic length b, which is the effective "distance" between two electron clouds on one and the same atom. From the above value of γ_0 we get for platinum $b = 2.4$ Å.

The bare interaction is modified by the screening of the electrons in the same filament and in neighboring filaments. In addition, it is also screened by the dielectric constant of the surrounding organic medium. Let us first consider the first of these two contributions to screening. Davis[24] has calculated the screening of the Coulomb field in filamentary compounds such as KCP $[K_2Pt(CN)_4Br_{0.3} \cdot H_2O]$, using the Thomas-Fermi approximation. He found that the screening was approximately isotropic, but with a screening constant about ten times that of platinum metal. Our compounds are closely similar to KCP except that the ligands are larger than in KCP. We use his approximate expression to obtain the screened parameters γ_n

$$\bar{\gamma}_n = e^2 \exp[-\lambda(r_n + b)]/(r_n + b) , \tag{30}$$

with $\lambda = 0.14$ Å^{-1}. The Fourier transform of the screened Coulomb interaction is

$$V(q) = \bar{\gamma}_0 + 2 \sum_{n=1}^{\frac{1}{2}N-1} \bar{\gamma}_n \cos(q r_n) , \tag{31}$$

where N is the number (odd, for simplicity) of atoms in the chain. Equation (31) is used to compute $V(q)$ for sufficiently small q, such that the wavelength exceeds the interatomic distance. The higher momentum components are obtained from the Fourier integral

$$V(q) = \frac{2e^2}{a} \int_0^{L/2} \frac{\cos(qr) e^{-\lambda(r+\bar{b})}}{r + \bar{b}} dr , \tag{32}$$

where the set of the interaction parameters γ_n at the discrete points r_n are replaced by a continuous interaction. The parameter b is modified to $\bar{b}$ to correct for the error made, in particular for small r, by the transition from the discrete to the continuous representation. The value of $\bar{b}$ is adjusted so that for small q Eq. (32) gives the same result as Eq. (30). In our case $\bar{b} = 1.8$ Å. The function $V(q)$ obtained in this manner is plotted in Fig. 5 (upper curve). We assume that the unperturbed interaction $V_0(q)$, which appears in Eqs. (12) and (13) already contains the screening effect of the conducting electrons in all the filaments.

Let us now discuss the screening effects of the organic medium. The interaction of the spine electrons with the low-lying highly polarizable states of the dyelike ligands was singled out in Eq. (12) and is referred to as the exciton interaction. There still remains the interaction with the higher excited states. In the cyanine dyes these states lie at substantially higher energies (5–15 eV) and are well separated from the low-lying states (2–4 eV). In view of this separation it is convenient to include the interaction with the higher excitations in the Coulomb part of the interaction kernel, because they simply contribute to the overall static dielectric constant, while the interaction with the low-lying states is treated dynamically in the exciton part of the kernel, exactly as the electron-phonon interaction in conventional superconductors. Thus, $V_0\rho_c$ in Eq. (13) is the spectral density of the electron-electron interaction due to the high excitations of the organic ligands, namely,

$$V_0(q)\rho_c(q,\omega) = \sum_{E > E_{ex}} |Q_E(q)|^2 \delta(E - \omega) , \tag{33}$$

where E_{ex} is the energy of the lowest exciton band.

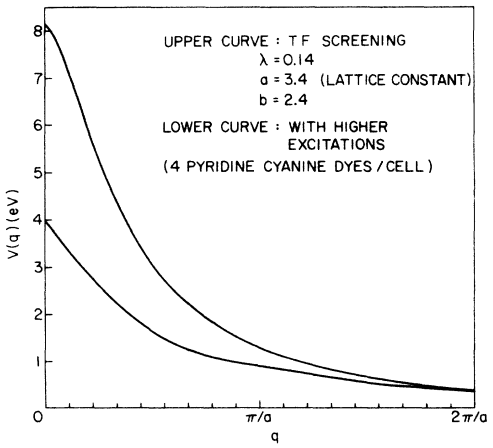

FIG. 5. Screened Coulomb interaction calculated using Thomas-Fermi screening due to electrons in the same and neighboring filaments (upper curve), and with the addition of dielectric screening from the neighboring organic environment (lower curve).

The higher excitation bands are generally relatively narrow and one can therefore neglect the momentum dependence of their energies. One can also neglect the much lower electron excitation energies $\xi(p)$. Therefore, Eq. (13) becomes

$$U_c(p-k) = V_0(p-k) - 2\sum_{E>E_{ex}} \frac{|Q_E(p-k)|^2}{E}. \quad (34)$$

The contribution of screening by higher excitations to the interaction between electrons at r_1 and r_2 on the spine can also be conveniently expressed in coordinate space in the form

$$V_{hex}(r_1-r_2) = \sum_{n,R_1^n,R_2^n} V_0(r_1,R_1^n)\,\Pi_0(R_1^n,R_2^n)\,V_0(R_2^n,r_2), \quad (35)$$

where R_1^n, R_2^n are atomic coordinates of the nth polarizable ligand and Π_0 is the lowest-order contribution to the proper polarization of the dye molecule in the static ($\omega=0$) approximation [see Refs. 17 and 18]. The expression in Eq. (34) was evaluated numerically. It drops off rapidly with increasing values of (r_1-r_2) and summation over 11 unit cells was found to give adequate accuracy. The Fourier transform of this expression, for the particular organic medium to be described in Sec. VII, is subtracted from $V_0(q)$ to give the lower curve of Fig. 5, which represents the Coulomb part of the kernel used in subsequent calculations of T_c.

Note that the total Coulomb interaction $V_C(r) = V_0(r) + V_{hex}(r)$ can be written in the form

$$V_C(r) = \frac{V_0(r)}{1 - V_{hex}(r)/V_C(r)}, \quad (36)$$

the denominator playing the role of an effective dielectric constant ϵ. We found that the numerical value of this dielectric constant came out to be of the order 2, which is close to the value found for the electronic contribution to ϵ of nonpolar organic compounds.[25] This is reasonable, for the electrons in the spine may be considered as buried in an organic environment whose dielectric constant would be of this order of magnitude. It should be noted that our expression for the electron-exciton coupling [Eq. (27)] contains a similar reduction in its effective strength through the π screening of the transition density ρ_ν which as described in Ref. 17 [Eq. (10)] is reduced precisely by a term of the form (36).

VII. NUMERICAL RESULTS FOR T_c

In this section we summarize the results of calculations of T_c for a model system consisting of a spine of platinum atoms, each of which is surrounded by four molecules of the pyridine cyanine dye lying in the plane perpendicular to the spine, as shown in Fig. 2. The nitrogen atoms of the dye are located 2.0 Å from the metal atom. The lowest excited state of the pyridine cyanine molecule is calculated to be at $E = 2.7$ eV and the transition density at the various atomic sites, showing a strong oscillating dipole pattern, is represented in Fig. 6. The spacing between the platinum atoms is taken to be 3.4 Å, which is sufficiently large to accomodate parallel layers of the dye molecules. The platinum atoms are assumed to be oxidized by the presence of Cl or Br atoms, as in KCP.

Instead of solving the finite-temperature BCS-like Eq. (13), we shall solve the zero-temperature equation for the gap

$$\phi(p) = -\int_{-\pi/\alpha}^{\pi/\alpha} \frac{dk}{2\pi} \frac{U(p,k)\,\phi(k)}{[\xi^2(k)+\phi^2(k)]^{1/2}}, \quad (37)$$

and use the relation between T_c and the gap at $T=0$.

$$kT_c = 3.5\phi(k_F)_{T=0}, \quad (38)$$

where k is Boltzman's constant. This relation is found emprically to be very well satisfied for weak coupling superconductors.[26] Due to the reflection symmetry in a plane parallel to the chains, we have $\xi(k)=\xi(-k)$, $U(p,k)=U(-p,-k)$, which implies $\phi(k)=\phi(-k)$, so Eq. (37) may be written as

$$\phi(p) = \frac{-1}{4\pi}\int_0^{\pi/\alpha} dk \frac{\phi(k)}{[\xi^2(k)+\phi^2(k)]^{1/2}} \times [U_1(p,k)+U_2(p,k)], \quad (39)$$

where

$$U_1(p,k) = V(p+k) - \frac{2|Q(p+k)|^2}{E(p+k)+|\xi(p)|+|\xi(k)|}, \quad (40)$$

$$U_2(p,k) = V(p-k) - \frac{2|Q(p-k)|^2}{E(p-k)+|\xi(p)|+|\xi(k)|}. \quad (41)$$

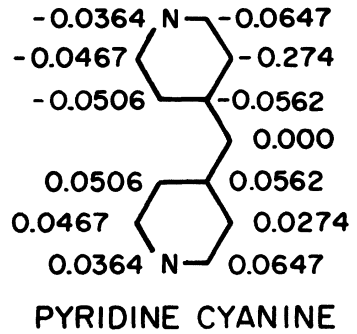

FIG. 6. Linear combination of atomic orbitals calculated values of the transition density for the principal low-lying absorption band for the pyridine cyanine.

The calculation of $E(q)$, $|Q(q)|^2$, and $V(q)$ was described in the preceding sections and the results for the system under consideration are plotted in Figs. 3, 4, and 5. It remains to specify the conduction electron's excitation energies $\xi(p)$. We performed calculations for a tight-binding electron band

$$\xi(p) = \tfrac{1}{2}E_0[\cos(ap_F) - \cos(ap)], \tag{42}$$

and for a free-electron band

$$\xi(p) = \alpha(p^2 - p_F^2). \tag{43}$$

The parameters for the tight-binding case were taken from the d_{z^2} band calculations of Arbarbanel[27] and Whitmore[28] on Pt compounds of the unoxidized Pt square planar structures. These calculations give a value for the bandwidth E_0 in the range 1–2 eV at a lattice constant of 3.4 Å.

Zeller[29] has shown from optical data that in the oxidized salt KCP the electrons behave as if they are in a simple parabolic band of total width 17 eV extending from $k = 0$ to $2\pi/a$. This corresponds to an energy of 4.25 eV at the first zone boundary. In this case the metal-metal distance is 2.88 Å. If in our case, where we have a metal-metal distance of 3.4 Å, a similar parabolic band could occur then we estimate from the variation of the bandwidth with distance obtained by Whitmore that this parabolic band would be about 8.5 eV in width. Thus $\alpha = 8.5(a/2\pi)^2$ eV Å^2.

The transition temperature T_c depends on two quantities: the strength of the electron-exciton interaction and the density of states at the Fermi energy. The first quantity, which can be roughly characterized by the value of $U(p_F, p_F)$ determines whether or not one gets a superconducting transition. The value of T_c is then strongly influenced by the density of states $N(0)$. Strictly speaking, such a separation of these two factors is not exact because the electron-exciton interaction itself depends on the electron band and hence on $N(0)$. However, this dependence is much weaker than the dependence of T_c on $\xi(p)$ in Eq. (33). The electron-exciton interaction $|Q(q)|^2$ was calculated for a tight-binding electron band. The bandwidth was taken as 3.0 eV and the Fermi momentum as $\frac{5}{6}(\pi/a)$, as it is in KCP. With this $|Q(q)|^2$ we have calculated T_c for several alternative forms of $\xi(p)$. The results for typical parameters are summarized in Table I. The changes in T_c follow the changes in $N(0)$. The gap function for the tight-binding case with $E_0 = 3.0$ is shown in Fig. 7 for $k_F = \frac{5}{6}(\pi/a)$ and $k_F = \frac{1}{2}(\pi/a)$.

In addition, we computed the exciton and Coulomb interaction for a configuration with two dyes per unit cell instead of four. We also considered a configuration where the polarizable dyes of Fig. 2 were moved a little further away from the spine. They were moved so that the nitrogen atoms of the terminal groups of the dyes were at a distance of 3 Å from the platinum atom instead of at 2 Å. In both of these cases the kernel $U(p, k)$ was found to be positive everywhere and no superconducting solution was found. This shows how important it is to have the excitonic medium in essentially atomic contact with the conductive spine and filling and whole region around it. Because of this it appears most unlikely that excitonic superconductivity could occur in a system like the tetracyanoquinodimethane (TCNQ) salts. Because in these the conduction electrons are distributed over a rather large molecule and therefore would not be at an average distance of less than 3 Å from any polarizable neighbors.

TABLE I. Calculated transition temperatures T_c, for various values of the bandwidth E_0, and Fermi momentum k_F.

	E_0 [a] (eV)	k_F (a/π)	T_c (°K)
Tight-binding band	2.0	$\frac{5}{6}$	1282
	3.0	$\frac{5}{6}$	946
	4.0	$\frac{5}{6}$	128
	3.0	$\frac{1}{2}$	186
Free-electron band	2.1	$\frac{5}{6}$	538
	3.5	$\frac{5}{6}$	129
	4.2	$\frac{5}{6}$	15
	2.1	$\frac{1}{2}$	844

[a] For the free electron band: $E_0 = \alpha(\pi/a)^2$, the energy at the Brillouin-zone boundary.

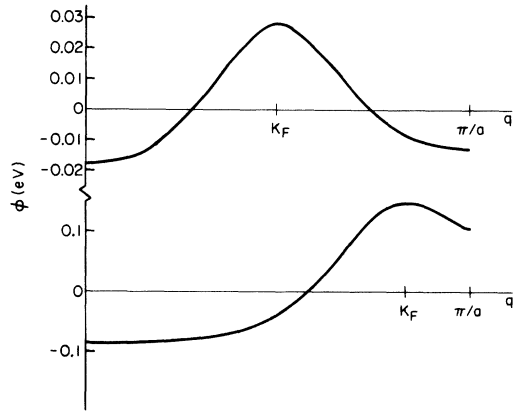

FIG. 7. Plot of the calculated superconducting gap function for the proposed excitonic superconductor for two values of the Fermi momentum k_F corresponding to a half filled and $\frac{5}{6}$ filled bands.

VIII. DISCUSSION

In this paper we present calculations which were performed to check whether the exciton mediated interaction could be strong enough to overcome the Coulomb repulsion and lead to high-temperature superconductivity. We saw that this was the case of the particular system considered here. We believe that the overall procedure adopted above to calculate $U(p,k)$ is fairly reliable. This belief is supported by the success of the general method used in computing the excitation energies and the oscillator strengths for single dye molecules, in reasonable agreement with experiment.[30] This same method should give reliable values for the excitonic properties. The spatial separation between the spine electrons and the exciton medium allows us to neglect the exchange interaction between the electrons in the two regions. This also adds to the credibility of our procedure, because it is free of the uncertainties and complications involved with the inclusion of exchange. There remains, however, the uncertainties with regard to the assumptions made on the values of the various parameters describing the details of the structure and the interactions. It is therefore necessary to discuss the sensitivity of the results to these parameters. It seems to us that the quantity which is the hardest to estimate is the Coulomb interaction. We have therefore investigated the effect of possible changes in $V_c(q)$ for low q on T_c. For example, if we have underestimated $V(q)$ for low q by 2.0 eV, then T_c for the case of the tight-binding band with $E_0 = 3.0$ eV and $k_F = \frac{5}{6}(\pi/a)$ would drop from 944 to 102 °K.

Of particular note is the extreme sensitivity of T_c to the distance between the excitonic system and the spine. Movement of the dyelike structure from 2 to 3 Å from the spine destroys the superconductivity. In addition the calculation of two dyes per unit cell likewise shows that T_c is reduced to a negligible value. Together these impose a severe constraint on the acceptable structures for the excitonic system. Only those structures with the excitonic system bonded chemically to the conductive spine and containing three or four dyes per atom of the spine appear to have any chance of exhibiting superconductivity due to the exciton mechanism. This appears to rule out excitonic superconductivity in systems of higher dimensionality unless one can obtain a comparable density of the polarizable medium in intimate contact with the conductive system. No scheme has been devised in these two- or three-dimensional systems to realize such a high exciton density; on the contrary, all estimates to date show the interaction is much too weak to lead to superconductivity.[31,32]

Our calculation shows that for the very special system considered above the interactions do appear to be strong enough to lead to superconductivity at high temperatures. However, the system is quasi-one-dimensional or at least filamentary, and as such is subject to certain instabilities and to the effects of fluctuations. In addition it is designed to use a nonphonon mechanism, different from that of known superconductors. In attempting to extrapolate and make predictions beyond the known area of validity of the BCS theory as we are attempting to do, these, and problems which are unique to the exciton mechanism, need to be considered.

First, our calculation is a mean-field calculation and has not considered the effects of fluctuations. However, it is known[33] that a small degree of interchain coupling is sufficient to bring the actual transition temperature close to the mean-field value. Moreover, we are not claiming any great precision for the accuracy of the calculated values of T_c but seek only to point out that for these systems one is getting into an interesting region where some manifestation of superconductivity or at least of superconducting fluctuations can be expected. The bulk properties of these compounds would clearly depend rather strongly on material properties such as the strand lengths, the degree of cross-linking of the filaments, etc., which affect the fluctuation amplitudes. We feel however, that it would be premature to attempt to estimate these effects at this time.

Problems of a more general nature which we can address relate to the stability of the system and to the unique properties of the proposed exciton mechanism. We consider each of these here.

All the properties characteristic of a particular system are contained in the kernel $U(p,k)$. Of special significance for the present discussion are the values of $U_1(p_F,p_F)$ and $U_2(p_F,p_F)$. Let us define the interaction parameters $g_1 = N(0)U_1(p_F,p_F)$ and $g_2 = N(0)U_2(p_F,p_F)$, where $N(0)$ is the density of states at the Fermi energy. These parameters measure the static effective interaction between two spine electrons on opposite sides of the Fermi surface with momentum transfer $q = 0$ (g_2) and $q = 2p_F$ (g_1). As mentioned before, the basic feature of the proposed system is the spatial separation between the electrons in the spine and the excitonic medium which results in electron-exciton coupling constants decreasing rapidly with increasing momentum. Thus, g_1 is dominated by the Coulomb interaction at $2p_F$ and is therefore positive (and small). Under favorable conditions, as is the case for the specific system discussed above, g_2 may be negative.

One of the basic properties of one-dimensional electron systems is that they possess two inherent instabilities which show up as divergences in the two-particle vertex function. One of them occurs in the particle-particle channel (Cooper channel) and it indicates the onset of superconductivity. The other divergence occurs in the particle-hole channel ("zero sound" channel) and it indicates the onset of the Peierls or Overhauser instabilities leading to an insulating state with a charge or spin-density wave. There is a competition between these instabilities and any discussion of a phase transition in such systems should treat them simultaneously. This was first done in the mean-field approximation by Bychkov *et al.*[34] who found that in the logarithmic approximation $T_c = T_p$ (T_P—transition temperature to the Peierls state). Recently, there has been extensive work on this problem which goes beyond mean-field theory.[35] Our present understanding of the problem may be summarized as follows. Each system is represented by a point in the (g_1, g_2) plane, where g_1 and g_2 are the parameters defined above. In the upper half plane ($g_1 > 0$) corresponding to our case, every point to the left of the line $g_1 = 2g_2$ describes a system with a superconducting ground state. The typical electron-exciton systems discussed here are indeed characterized by values of g_1, g_2 to the left of and quite remote from this line. This assures us that the superconducting instability will dominate and for this reason, we feel that we are justified in treating this instability separately as is done in the present paper.

We should, however, point out that the interaction of the conducting electrons with the lattice vibrations of the spine might lead to a doubling of the period and consequently to a gap in the single electron spectrum. In this case it is still possible to get superconductivity provided that the attraction induced by the excitons is sufficiently strong so that it pays to create Cooper pairs above the gap. This was discussed in Ref. 1 and the argument applies to our case because the pairing interaction and the possible gap in the single-particle spectrum result from different mechanisms.

The formulation of the theory of superconductivity, both in the weak and strong coupling regimes, depends on the validity of Migdal's theorem[36] which asserts that vertex corrections are small and may be neglected. The lowest-order correction to the electron-phonon vertex is shown in Fig. 8. For an incoming phonon of a phase velocity ω/q, much smaller than the Fermi velocity v_F, this correction is of the order of $\omega_D/E_F \approx 10^{-2}$. Most of the phonons involved in conventional superconductivity have momentum $q \simeq p_F$ and, therefore, a very small phase velocity. This is the basis of

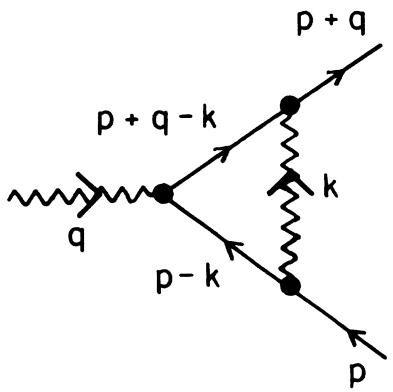

FIG. 8. First vertex correction to the Migdal approximation which we show is small for the particular model proposed here.

Migdal's theorem. One of the essential differences between the phonon mechanism of superconductivity and the model discussed here is that in the present case only excitons with small momentum, and hence phase velocities much greater than v_F are involved in the conjectured superconducting transition. It was shown by Engelsburg and Schrieffer[37] that for phonons with a high phase velocity the vertex correction in Fig. 8 is of the order of $g^2N(0)/\omega_D$, where g is the electron-phonon coupling constant. This is a crude estimate of λ and can be of the order of unity for strong coupling superconductors. However, this result was obtained assuming that g^2 is momentum independent. This is certainly not the case in our model, since the coupling constant $Q(q)$ is strongly peaked around $q = 0$. Assuming that $Q(q)$ is constant for $q < q_c$ is an average width [of the order of $\frac{1}{5}(\pi/a)$] of $Q(q)$, we find that the lowest-order vertex correction is of the order of $[|Q^2|N(0)/E] \times (\Delta E/E)$, where E is a typical exciton energy and $\Delta E \sim \xi(p_F + q_c)$. In our case, $|Q^2|N(0)/E$ corresponding to λ is about 0.3 and this is further reduced by $\Delta E/E \sim 0.09$–0.18, to yield a net correction of order 0.06. Thus, the strong momentum dependence of the electron-exciton interaction, which as mentioned previously is due to the separation between the electrons in the spine and the excitons, is responsible for strongly reduced vertex corrections. We wish to point out that it is not so in some other models proposed for the realization of the exciton mechanism of superconductivity. For example, there has been extensive discussion[38] of the possibility of pairing in the s band of a transition metal induced by the interaction with d electrons. It is not clear that the vertex corrections in this case are small. Another model where this is expected to pose a difficulty is the model proposed by Allender, Bray, and

Bardeen.[39] These authors consider a thin metallic film coated on a semiconductor with a high dielectric constant. The electrons of the metal spend part of their time in the semiconducting region where they interact with electron excitations across the semiconducting gap.

In addition, in both the above models a strict spatial separation is not maintained between the electrons of the conductive system and those of the exciton system. This results in certain exchange contributions, which are expected to reduce substantially the effective coupling constant between the two system. In view of the delicate balance between the Coulomb repulsion and the exciton attraction this reduction of the latter could be disastrous. The importance of these exchanges term was pointed out by one of us previously.[40]

In conclusion, we believe that we have presented a plausible case for the possibility of the exciton mechanism of superconductivity in the particular model discussed here. Of course, it may turn out, once such systems are made, that they will not be superconducting. If that should be the case, it will happen for reasons which we cannot anticipate at present. It may also turn out that it is impossible to make systems which meet the requirements specified here. Matthias[41] believes that nature, as a matter of principle, conspires against high-temperature superconductivity. He argues that whenever there is good reason to believe that a particular compound will have a high T_c, then some instability will interfere and prevent it. The worst instability that can occur is that which makes it impossible even to make the material. There is ample empirical evidence in the field of conventional superconductors to support this point of view. In conventional superconductors, however, high transition temperatures are obtained when the coupling constant λ is large, whereas is our case λ is relatively small and the high T_c arises from the preexponential factor. Our system may thus be less subject to such a limitation than conventional high T_c superconductors. We are thus talking about a completely different regime and we feel that in view of the general arguments and the detailed calculations presented above, it is worth the effort to try and synthesize such systems as proposed here. We are saying it without underestimating the chemical difficulties and the problems posed by this goal.

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[1]W. A. Little, Phys. Rev. 134, A1416 (1964).

[2]V. L. Ginzburg, Zh. Eksp. Teor. Fiz. 47, 2318 (1964) [Sov. Phys.-JETP 20, 1549 (1965)].

[3]V. L. Ginzburg, Contemp. Phys. 9, 355 (1968); Usp. Fiz. Nauk 101, 185 (1970) [Sov. Phys.-Usp. 13, 335 (1970)]; Ann. Rev. Mater. Sci. 2, 663 (1972); V. L. Ginzburg and D. A. Kirzhnits, Phys. Rep. 4, 345 (1972).

[4]H. R. Zeller, Adv. Solid State Phys. 13, 31 (1973).

[5]M. D. Cohen and Bernard S. Green, Chem. Br. 9, 490 (1973).

[6]J. Collman, J. Polym. Chem. C 29, 138 (1970).

[7]K. Krogmann, Angew. Chem. 8, 35 (1969).

[8]T. Winkler and C. Mayer, technical report (Stanford University, 1972) (unpublished).

[9]T. W. Winkler and C. Meyer, Helv. Chem Acta 55, 2351 (1972).

[10]R. Lorentz (private communication).

[11]K. Mees, *Theory of the Photographic Process* (MacMillan, New York, 1966), p. 218.

[12]D. Davis, Ph.D. dissertation (Stanford University, 1974) (unpublished).

[13]D. A. Kirzhnits, E. G. Maximov, and D. I. Khomskii, J. Low Temp. Phys. 10, 79 (1973).

[14]J. R. Schrieffer, *Theory of Superconductivity* (Benjamin, New York, 1964).

[15]D. Scalapino, in *Superconductivity*, edited by R. Parks (Marcel Dekker, New York, 1969), Vol. 1, p. 449.

[16]P. Morel and P. W. Anderson, Phys. Rev. 125, 1263 (1962).

[17]H. Gutfreund and W. A. Little, J. Chem. Phys. 50, 4468 (1969).

[18]H. Gutfreund and W. A. Little, Phys. Rev. 183, 68 (1969).

[19]L. Salem, *Molecular Orbital Theory of Conjugated Systems* (Benjamin, New York, 1966), p. 359.

[20]See Ref. 19, p. 56.

[21]See Ref. 19, p. 419.

[22]L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell U.P., New York, 1960), p. 96.

[23]K. Nishimoto and N. Mataga, Z. Phys. Chem. (Frankf.) 13, 140 (1957).

[24]D. Davis, Phys. Rev. B 7, 129 (1973).

[25]*Handbook of Chemistry and Physics*, 48th ed. (Chemical Rubber, Cleveland, 1952), p. E58.

[26]R. Meservey and B. B. Schwartz, in *Superconductivity*, edited by R. Parks (Dekker, New York, 1969), Vol. 1, p. 144.

[27]A. Abarbanel, Ph.D. dissertation (Stanford University, 1973) (unpublished); Ann. Phys. 91, 356 (1975).

[28]D. Whitmore, Phys. Lett. 50 A, 55 (1974).

[29]H. R. Zeller, in *Low Dimensional Co-Operative Phenomena*, edited by H. J. Keller (Plenum, New York, 1974), p. 215.

[30]W. A. Little and H. Gutfreund, Phys. Rev. B 4, 817 (1971).

[31]L. N. Bulaevskii and Yu. A. Kukharenko, Zh. Eksp.

Teor. Fiz. 60, 1518 (1971) [Sov. Phys.-JETP 33, 821 (1971)].
[32]W. A. Little, J. Low Temp. Phys. 13, 365 (1973).
[33]T. Maniv and M. Weger, Phys. Chem. Solids 36, 367 (1975); for the Peierls transition this is discussed in B. Horovitz, H. Gutfreund, and M. Weger, Phys. Rev. B (to be published); interchain coupling in general is discussed in D. J. Scalapino, Y. Imry, and P. Pincus, Phys. Rev. B 11, 2042 (1975).
[34]Yu. Bychkov, L. P. Gor'kov, and I. E. Dzyaloshinskii, Zh. Eksp. Teor. Fiz. 50, 738 (1966) [Sov. Phys.-JETP 23, 489 (1966)].
[35]J. Solyom, J. Low Temp. Phys. 12, 529 (1973); H. Fukuyama, T. M. Rice, C. M. Varma, and B. I. Halperin, Phys. Rev. B 10, 3775 (1974); A. Luther and V. J. Emery, Phys. Rev. Lett. 33, 589 (1974); R. Klemm and H. Gutfreund (unpublished).
[36]A. B. Migdal, Zh. Eksp. Teor. Fiz. 34, 1438 (1958) [Sov. Phys.-JETP 7, 996 (1958)].
[37]S. Engelsberg and J. R. Schrieffer, Phys. Rev. 131, 993 (1963).
[38]B. T. Geilikman, Usp. Fiz. Nauk 109, 65 (1973) [Sov. Phys.-Usp. 16, 17 (1973)].
[39]D. Allender, J. Bray, and J. Bardeen, Phys. Rev. B 7, 1020 (1973).
[40]W. A. Little, J. Polym. Sci. 29 C, 17 (1970).
[41]For example, B. T. Matthias, in *Superconductivity in d- and f-Band Metals*, edited by D. H. Douglass (AIP, New York, 1972), p. 367.