Superconductivity and charge-density waves

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A theory of two competing order parameters — superconductivity and charge-density waves — as applied to layered compounds is presented. Both effects are caused by the phonon-mediated attractive interaction between itinerant electrons in narrow-band materials. The interplay between superconductivity and charge-density waves is analyzed. The main results of our model calculation are: (i) all metallic charge-density systems should be superconducting at low temperatures; (ii) the presence of superconductivity tends to reduce the charge-density wave and *vice versa;* (iii) under some conditions it is possible to have a charge-density-wave–induced semiconductor which, at low temperatures, makes a transition to a superconducting state. This last case is examined in detail.

I. INTRODUCTION

Among the states of broken symmetry in a solid, charge-density waves (CDW) and superconductivity (SC) are the two most prominent ones which require an effective attractive electron-electron interaction[1–6] mediated by phonons. It is therefore not surprising that systems in which CDW's have been experimentally observed[4] are also superconducting at very low temperatures.[7]

The tendencies toward the formation of SC and CDW are to a certain degree opposing one another: While the SC state has infinite conductivity and a Meissner effect, the CDW state, for large enough interactions, produces a semiconductor gap in the spectrum and a nonconducting state. From the microscopic point of view on the other hand the SC state arises from electron-electron coupling into Cooper pairs, the CDW state from electron-hole coupling and charge redistribution: two effects which are in principle independent of one another.

Although considerable uncertainty exists, it has been mentioned in the literature[8] that some CDW layered compounds, e.g., 1*T*-TaS_2, despite the apparent lack of metallic properties are reported to be superconducting below a given temperature T_{SC} ($T_{SC} \sim 0.8$ K for 1*T*-TaS_2).

It is the purpose of this work to study the interdependence of the SC and CDW states. In particular we are interested in setting up a model Hamiltonian which allows us to test both effects on the same footing. We thus expect to clarify several points: (a) the difference in order of magnitude of T_{CDW}, the CDW transition temperature, and T_{SC}, the SC transition temperature; (b) the range of relevant parameters over which a CDW exists; (c) the nature of the competition between SC and CDW's; and (d) the possibility of coexistence of both effects, i.e., a nonuniform charge distribution with its attendant CDW gap and a superconducting state also with its characteristic gap. A similar study for one-dimensional systems is reported in the work of Levin *et al.*[9] and similarities can also be found in the article by Bilbro and McMillan.[5]

In Sec. II we set a model Hamiltonian and discuss its validity. Section III studies the existence and properties of the CDW state within this model. Section IV is concerned with the competition and coexistence of CDW and SC states. Section V examines in more detail the semiconductor-to-superconductor transition. Section VI contains a discussion and conclusions.

II. THE MODEL HAMILTONIAN

Our starting point is a collection of crystalline electrons moving in a single band and interacting with lattice phonons

$$H_0 = H_e + H_p + H_{ep} \ , \tag{2.1}$$

where

$$H_e = \sum_{k\sigma} \epsilon_k a_{k\sigma}^\dagger a_{k\sigma} \ , \tag{2.2}$$

ϵ_k is the band energy of a state k in the Brillouin zone, σ is the spin index, and $a_{k\sigma}^\dagger$ ($a_{k\sigma}$) is the fermion creation (destruction) operator. The phonon Hamiltonian

$$H_p = \sum_q \hbar\omega_q b_q^\dagger b_q \tag{2.3}$$

corresponds to a single-branch phonon spectrum, the phonons being identified by a wave vector $\vec{q}$ and a creation (destruction) operator $b_q^\dagger$ (b_q). Finally H_{ep}

describes the electron-phonon interaction

$$H_{ep} = i \sum_{kq\sigma} D_q a^{\dagger}_{(k+q)\sigma} a_{k\sigma} (b_q - b^{\dagger}_{-q}) \ , \tag{2.4}$$

with an interaction D_q which, for convenience, we take to be a constant D.

The standard procedure in studying the SC state[1] at this point is to produce an effective electron-electron interaction mediated by phonons, and replace it by an approximate expression which leads to the BCS reduced Hamiltonian. The well-known canonical transformation leads to an effective Hamiltonian

$$H_{\text{eff}} = H_e + H_i \ , \tag{2.5}$$

where H_e is given by Eq. (2.2) and the interaction term is

$$H_i = \tfrac{1}{2} D^2 \sum_{\substack{kk'q \\ \sigma\sigma'}} [(\epsilon_k - \epsilon_{k-q} - \hbar\omega_q)^{-1} - (\epsilon_{k'} - \epsilon_{k'+q} + \hbar\omega_q)^{-1}] \times a^{\dagger}_{(k+q)\sigma'} a_{k'\sigma'} a^{\dagger}_{(k'-q)\sigma} a_{k\sigma} \ . \tag{2.6}$$

Among the many terms in Eq. (2.6), the relevant ones for the SC state are those which scatter coherently a pair $[k\uparrow, -k\downarrow]$ into another pair $[(k+q)\uparrow, (-k-q)\downarrow]$, i.e., only those terms for which $k' = -k$ and $\sigma' = -\sigma$. The retention of only those terms yields

$$H_i^{\text{SC}} = \sum_{kq} V_{kq} a^{\dagger}_{(k+q)\uparrow} a^{\dagger}_{(-k-q)\downarrow} a_{-k\downarrow} a_{k\uparrow} \ , \tag{2.7}$$

where

$$V_{kq} = \frac{2D^2 \hbar\omega_q}{(\epsilon_k - \epsilon_{k+q})^2 - (\hbar\omega_q)^2} \ . \tag{2.8}$$

In the BCS reduced Hamiltonian the matrix element V_{kq} is replaced by a simpler form

$$V_{kq}^{\text{BCS}} = \begin{cases} -\lambda, & \text{if } |\epsilon_k - \epsilon_F| < \hbar\omega_D \ , \\ & |\epsilon_{k+q} - \epsilon_F| < \hbar\omega_D \ , \\ 0, & \text{otherwise} \ , \end{cases} \tag{2.9}$$

where ϵ_F is the Fermi energy and ω_D is a characteristic (Debye) frequency. The use of the mean-field approximation now yields

$$H_{\text{BCS}} = H_e - \Delta \sum_k{}' (a^{\dagger}_{k\uparrow} a^{\dagger}_{-k\downarrow} + a_{-k\downarrow} a_{k\uparrow}) + \Delta^2/\lambda \ , \tag{2.10}$$

where the superconducting order parameter Δ is defined by

$$\Delta \equiv \lambda \sum_k{}' \langle a_{-k\downarrow} a_{k\uparrow} \rangle \ , \tag{2.11}$$

the primed summation is over all states $\vec{k}$ such that $|\epsilon_k - \epsilon_F| < \hbar\omega_D$, and $\langle \cdots \rangle$ indicates thermodynamic mean values.

The terms in Eq. (2.6) responsible for the formation of a CDW are completely different. We restrict ourselves to the case of a single wave vector Q and choose a commensurable Q of special value such that $2Q$ is a vector of the reciprocal lattice, i.e., $k + 2Q = k$. The terms in Eq. (2.6) which contribute to this CDW are those for which $q = Q$, i.e.,

$$H_i^{\text{CDW}} = \sum_{\substack{kk' \\ \sigma\sigma'}} \tfrac{1}{4} (V_{kQ} + V_{k'Q}) a^{\dagger}_{(k+Q)\sigma} a_{k\sigma} a^{\dagger}_{(k'+Q)\sigma'} a_{k'\sigma'} \ , \tag{2.12}$$

where V_{kQ} is given by Eq. (2.8).

In the same spirit of the BCS model we replace V_{kQ} by the simpler form (2.9). The use of the mean-field approximation now yields

$$H_{\text{CDW}} = H_e - G_0 \sum_{k\sigma} a^{\dagger}_{(k+Q)\sigma} a_{k\sigma} - G_1 \sum_{k\sigma}{}'' a^{\dagger}_{(k+Q)\sigma} a_{k\sigma} + G_0 G_1/\lambda \ . \tag{2.13}$$

In Eq. (2.13) the doubly primed summation is over states which satisfy the two conditions $|\epsilon_k - \epsilon_F| < \hbar\omega_D$ and $|\epsilon_{k+Q} - \epsilon_F| < \hbar\omega_D$, and

$$G_0 \equiv \lambda \sum_k{}'' \langle a^{\dagger}_{(k+Q)\uparrow} a_{k\uparrow} \rangle \ , \tag{2.14}$$

$$G_1 \equiv \lambda \sum_k{}'' \langle a^{\dagger}_{(k+Q)\uparrow} a_{k\uparrow} \rangle \ . \tag{2.15}$$

In addition we have assumed that there are no unusual spin arrangements and

$$\langle a^{\dagger}_{(k+Q)\uparrow} a_{k\uparrow} \rangle - \langle a^{\dagger}_{(k+Q)\downarrow} a_{k\downarrow} \rangle = \langle a^{\dagger}_{(k+Q)\uparrow} a_{k\downarrow} \rangle = 0 \ . \tag{2.16}$$

Finally our total Hamiltonian which includes both SC and CDW states is now given by[10]

$$H = H_{\text{BCS}} + H_{\text{CDW}} - H_e \ . \tag{2.17}$$

The values of the SC parameter Δ and the CDW parameters G_0 and G_1, as well as all the transition temperatures and stability conditions, depend crucially on the details of the band structure and Fermi surface of the electronic system, i.e., on the form of ϵ_k and the number of electrons. For the sake of definiteness we now restrict ourselves to a well-defined model. We choose a two-dimensional structure in a square lattice of constant a with first- and second-neighbor couplings, where the band energies are given by

$$\epsilon_k = -2t_0(\cos k_x a + \cos k_y a) - 4t_1 \cos k_x a \cos k_y a \ . \tag{2.18}$$

Band structures and Fermi surfaces for this model for a half-filled band and various values of (t_1/t_0) are shown in Fig. 1. The structure given by Eq. (2.18) has two degenerate saddle points of energy $\epsilon_{sp}=4t_1$ and located at the X points of the square Brillouin zone. For $t_1=0$ the saddle-point energy coincides with the Fermi level of the half-filled band. We choose our Q vector to be that which connects the two saddle points, i.e., $Q=M=(\pi/a,\pi/a)$.

III. CDW INSTABILITY

We first study the CDW instability in the absence of superconductivity, i.e., we study Eq. (2.13) or equivalently set $\Delta=0$ in Eq. (2.17). In particular if $t_1=0$ in Eq. (2.18), most of the calculation can be carried out analytically. For $t_1=0$ we have

$$\epsilon_{k+Q}=-\epsilon_k \tag{3.1}$$

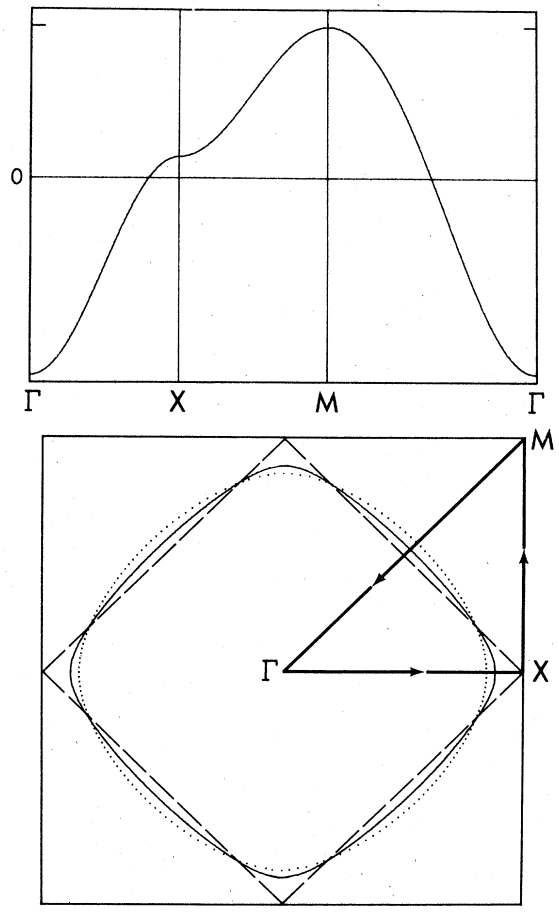

FIG. 1. (a) Band structure of the two-dimensional square lattice for $t_1/t_0=0.25$. (b) The Fermi surface for the two-dimensional square lattice and a half-filled band. The dashed line is for $t_1/t_0=0$, the full line for $t_1/t_0=0.125$, and the dotted line for $t_1/t_0=0.25$.

and the quasiparticle energies of Eq. (2.17) for $\Delta=0$ are given by[1,11]

$$E_{1k}=-(\epsilon_k^2+G_k^2)^{1/2};\quad E_{2k}=+(\epsilon_k^2+G_k^2)^{1/2}\ ; \tag{3.2}$$

where

$$G_k=\begin{cases}G_0+G_1, & \text{if } |\epsilon_k-\epsilon_F|<\hbar\omega_D\ ,\\ G_0, & \text{otherwise}\ .\end{cases} \tag{3.3}$$

Evaluation of the relevant expectation values in Eqs. (2.14) and (2.15) yields, in terms of the usual Fermi-Dirac functions $f(E)$,

$$G_0=-\lambda(G_0+G_1)\sum_k{}'' \frac{f(E_{1k})-f(E_{2k})}{E_{1k}-E_{2k}}\ , \tag{3.4}$$

$$G_1=-\lambda\sum_k G_k\frac{f(E_{1k})-f(E_{2k})}{E_{1k}-E_{2k}}\ , \tag{3.5}$$

which are the self-consistent equations for G_0 and G_1. A CDW instability sets in whenever Eqs. (3.4) and (3.5) yield nonvanishing values for G_0 and G_1. The onset of this instability can be obtained from the linearized form of these equations

$$1=\lambda\left(1+\frac{G_1}{G_0}\right)\int_{-\hbar\omega_D}^{\hbar\omega_D}\rho(\epsilon)\chi(\epsilon)\,d\epsilon\ , \tag{3.6}$$

$$\frac{G_1}{G_0}=1+\lambda\left(\int_{-4t_0}^{-\hbar\omega_D}+\int_{\hbar\omega_D}^{4t_0}\rho(\epsilon)\chi(\epsilon)\,d\epsilon\right)\ ; \tag{3.7}$$

here $\rho(\epsilon)$ is the electronic density of states, and the temperature-dependent susceptibility $\chi(\epsilon)$ is defined by

$$\chi(\epsilon)\equiv\{\tanh[(\epsilon-\epsilon_F)/2k_BT]+\tanh[(\epsilon+\epsilon_F)/2k_BT]\}/4\epsilon\ . \tag{3.8}$$

At $T=0$ and half-band occupation, $\epsilon_F=\epsilon_{sp}=0$, the integral (3.6) diverges, indicating a stable CDW at all positive values of λ. This is easily understood in terms of the features of the Fermi surface: for $t_1=0$ and $\epsilon_F=0$, as seen in Fig. 1, the Fermi surface is a perfect square with perfect nesting,[11–13] and even an infinitesimal perturbation is sufficient to open a complete gap in the spectrum and stabilize the CDW.

For $t_1=0,\epsilon_F\neq 0$ a minimum value of λ is required to stabilize the CDW. This value is shown in Fig. 2.

Equations (3.6) and (3.7) also yield the transition temperature T_{CDW} at which the CDW becomes unstable. In the particular case of a half-filled band the expression for T_{CDW} becomes identical to the expression of Bardeen, Cooper, and Schrieffer for the SC transition temperature

$$T_{CDW}(t_1=0,\epsilon_F=0)=1.14\,\hbar\omega_D\exp(-1/\lambda_{eff}\rho_0)\ , \tag{3.9}$$

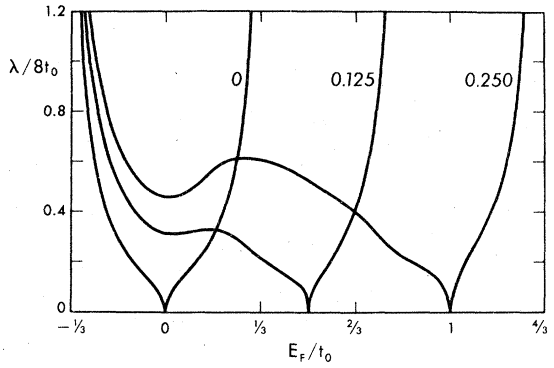

FIG. 2. Phase diagrams (interaction strength λ versus Fermi energy ϵ_F) for CDW formation. Various values of t_1/t_0 are shown. For ϵ_F at the saddle point of the band structure (point X) a CDW is stable at any value of λ.

where, to a very good approximation,

$$\rho_0 \equiv (8t_0)^{-1} \tag{3.10}$$

and

$$\lambda_{\text{eff}} \equiv \lambda[2 - \lambda\rho_0 \ln(2\rho_0 \hbar\omega_D)] \ . \tag{3.11}$$

This is to be compared with the ordinary SC transition temperature T_{SC}

$$T_{\text{SC}} = 1.14\, \hbar\omega_D \exp(-1/\lambda\rho_0) \ . \tag{3.12}$$

An examination of Eqs. (3.9) and (3.12) gives us a clear understanding of orders of magnitude. If in temperature-energy units we choose $t_0 = 1500$ K (a bandwidth of 1.2×10^4 K ~ 1 eV), $\hbar\omega_D = 300$ K, and $\lambda = 2000$ K we obtain $T_{\text{CDW}} \sim 31$ K, $T_{\text{SC}} \sim 0.8$ K. If we increase λ to 3000 K we obtain $T_{\text{CDW}} \sim 80$ K and $T_{\text{SC}} \sim 6.3$ K. In both cases T_{CDW} is more than one order of magnitude larger than T_{SC}.

For the general case $t_1 \neq 0$ the Fermi surface changes shape and even for the half-filled band situation there is no perfect nesting (see Fig. 1). Even though the Fermi surface is no longer a perfect square, there are large regions of good if not perfect nesting, and CDW's may occur. However in this case, and for low enough values of $G_0 + G_1$, the system is always metallic. It is therefore a much better model to describe the physical properties of layered compounds to consider the general case of $t_1 \neq 0$. The expressions for the CDW order parameters G_0 and G_1 are still given by Eqs. (3.4) and (3.5), but the expression for the quasiparticle energies E_{1k} and E_{2k} are now given by

$$E_{\nu k} = \tfrac{1}{2}(\epsilon_k + \epsilon_{k+Q}) \mp \tfrac{1}{2}[(\epsilon_k - \epsilon_{k+Q})^2 + 4G_k^2]^{1/2} \ , \tag{3.13}$$

where the negative (positive) sign corresponds to $\nu = 1 (\nu = 2)$, and

$$\epsilon_{k+Q} = -\epsilon_k - 8t_1 \cos k_x a \cos k_y a \ . \tag{3.14}$$

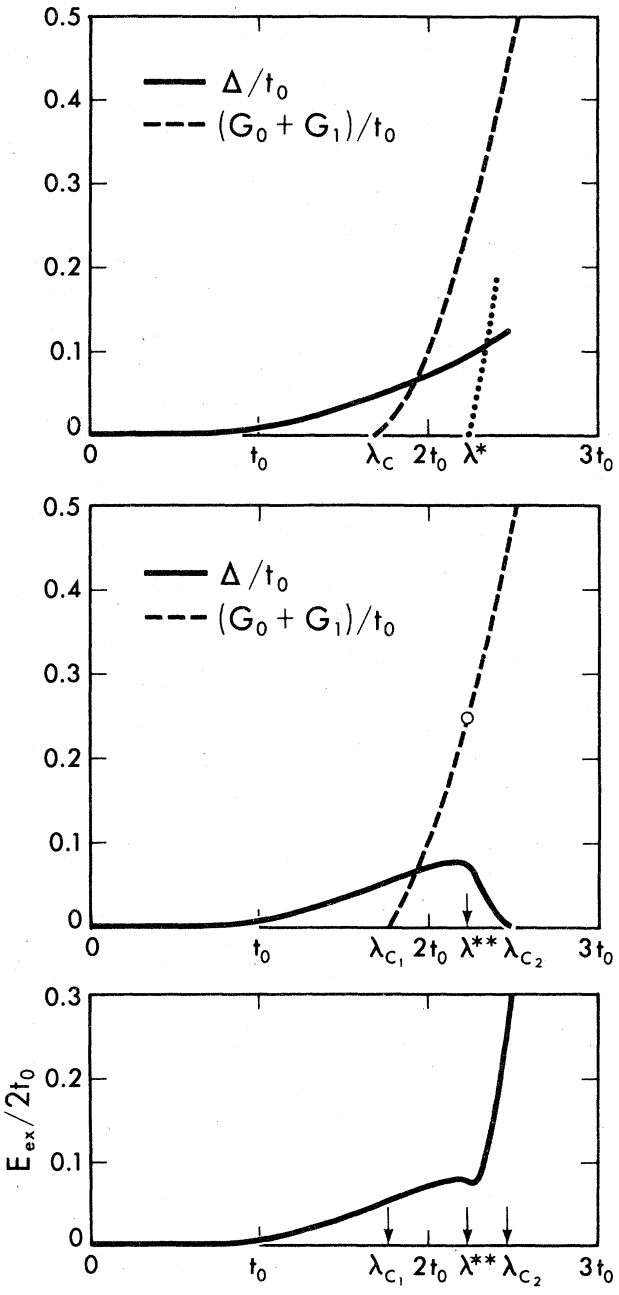

FIG. 3. Various order parameters for the square lattice and a half-filled band as a function of the interaction strength λ for $t_1/t_0 = 0.125$. (a) The CDW parameter $(G_0 + G_1)$ in the absence of SC for $\lambda > \lambda_c$ (dashed line); the semiconducting half-gap for $\lambda > \lambda^*$ (dotted line); and the SC order parameter Δ in the absence of CDW's (full line). (b) The CDW order parameter $(G_0 + G_1)$ (dashed line) and the SC order parameter Δ (full line) when the two effects are considered; $G_0 + G_1 = 0$ for $\lambda < \lambda_{c1}$ and $\Delta = 0$ for $\lambda > \lambda_{c2}$. Coexistence occurs for $\lambda_{c1} < \lambda < \lambda_{c2}$. (c) The excitation half-gap (half the excitation energy of a pair) for the case shown in (b). All order parameters are energies in units of t_0.

The results for this model can now be summarized as follows: (i) If the Fermi level is at the saddle point $\epsilon_F = \epsilon_{sp} = 4t_1$, the CDW is stable for any positive value of λ (see Fig. 2). (ii) For $t_1 > 0$, there is no stable CDW state if the Fermi level falls *outside* of the interval $-\hbar\omega_D < \epsilon_F < \epsilon_{sp} + \hbar\omega_D$; for ϵ_F outside this interval there are no states such that $|\epsilon_k - \epsilon_F| < \hbar\omega_D$ and $|\epsilon_{k+Q} - \epsilon_F| < \hbar\omega_D$ simultaneously, and therefore there is no effective interaction.

The solution of Eqs. (3.4) and (3.5) must be found, in the general case, numerically. In Fig. 3(a) we show the value of $G = G_0 + G_1$ as a function of λ for $T = 0$, $t_1/t_0 = 0.125$, $\hbar\omega_D/t_0 = \frac{1}{3}$ and a half-filled band (the bandwidth is in this case $8t_0$, independent of t_1). The CDW is stable only for values of $\lambda > \lambda_c$; in our example $\lambda_c = 1.67t_0$. As λ increases beyond λ_c, G increases rapidly. For $\lambda_c < \lambda < \lambda^*$, where $\lambda^* = 2.23t_0$ in the example of Fig. 3(a), a CDW state is stable, but the system exhibits no gap in the quasiparticle spectrum, i.e., we have a metallic CDW state. For $\lambda > \lambda^*$, the two quasiparticle bands, E_{1k} and E_{2k}, have no overlap and a gap appears in the spectrum; for a half-filled band the system now becomes a semiconductor. The value of the gap in the spectrum is also shown in Fig. 3(a) for $\lambda > \lambda^*$. For the sake of completeness we also show in Fig. 3(a) the value of the SC parameter Δ corresponding to the same model and to the Hamiltonian (2.10). It should be noted that $\Delta \neq 0$ for any value of λ, and that the SC and CDW gaps are of the same order of magnitude for $\lambda \sim \lambda^*$.

IV. SUPERCONDUCTIVITY AND CHARGE-DENSITY WAVES

The self-consistent solution of Eqs. (2.17), (2.11), (2.14), and (2.15) involves as a first step the solution of a (4×4) secular equation.[14]

$$\begin{vmatrix} \epsilon_k - \epsilon_F - E & -G_k & -\Delta_k & 0 \\ -G_k & \epsilon_{k+Q} - \epsilon_F - E & 0 & -\Delta_{k+Q} \\ -\Delta_k & 0 & -\epsilon_k + \epsilon_F - E & G_k \\ 0 & -\Delta_{k+Q} & G_k & -\epsilon_{k+Q} + \epsilon_F - E \end{vmatrix} = 0 \ , \tag{4.1}$$

where G_k is given by Eq. (3.3) and Δ_k is defined by

$$\Delta_k = \begin{cases} \Delta, & \text{if } |\epsilon_k - \epsilon_F| < \hbar\omega_D \ , \\ 0, & \text{otherwise} \ . \end{cases} \tag{4.2}$$

The four roots of Eq. (4.1), labeled $E_{\nu k} (\nu = 1, 2, 3, 4)$ in order of increasing energy, are such that

$$E_{1k} = -E_{4k}, \quad E_{2k} = -E_{3k} \ . \tag{4.3}$$

When the eigenstates of Eq. (4.1) are determined and included in Eqs. (2.11), (2.14), and (2.15), three integral equations are obtained for Δ, G_1, and G_2. These are

$$\Delta = \lambda\Delta \sum_k{}' \frac{1}{E_{4k}^2 - E_{3k}^2} \left(\frac{E_{4k}^2 - \epsilon_{k+Q}^2}{2E_{4k}} - \frac{E_{3k}^2 - \epsilon_{k+Q}^2}{2E_{3k}} \right) - \lambda\Delta \sum_k{}'' \frac{\Delta^2 + (G_0 + G_1)^2}{E_{4k}^2 - E_{3k}^2} \left(\frac{1}{2E_{4k}} - \frac{1}{2E_{3k}} \right) \ , \tag{4.4}$$

$$G_0 = \lambda(G_0 + G_1) \sum_k{}'' \frac{1}{E_{4k}^2 - E_{3k}^2} \left(\frac{E_{4k}^2 + \epsilon_k\epsilon_{k+Q} - \Delta^2 - (G_0 + G_1)^2}{2E_{4k}} - \frac{E_{3k}^2 + \epsilon_k\epsilon_{k+Q} - \Delta^2 - (G_0 + G_1)^2}{2E_{3k}} \right) \tag{4.5}$$

and

$$G_1 = \lambda \sum_k \frac{G_k}{E_{4k}^2 - E_{3k}^2} \left(\frac{E_{4k}^2 + \epsilon_k\epsilon_{k+Q} - \Delta_k^2 - G_k^2}{2E_{4k}} - \frac{E_{3k}^2 + \epsilon_k\epsilon_{k+Q} - \Delta_k^2 - G_k^2}{2E_{3k}} \right) \ . \tag{4.6}$$

These equations must be solved numerically. Some results follow.

(a) If $t_1 = 0$ and $\epsilon_F = \epsilon_{sp} = 0$ the summations in Eqs. (4.4) and (4.5) become identical. This implies three possibilities $\Delta = 0$; $G_0 = G_1 = 0$; or $\Delta = G_0$ and $G_1 = 0$. However it can be easily seen that Eq. (4.6) [or equivalently Eqs. (2.14) and (2.15)] requires that if $G_0 \neq 0$ then $G_1 \neq 0$. Therefore the third possibility is unacceptable and there can be no coexistence of SC and CDW. It can be seen in addition that the stable

solution is $\Delta=0$ at all temperatures, i.e., the semiconductor CDW state is the stable phase for $T<T_{\mathrm{CDW}}$ and the results of Sec. III apply.

(b) For $t_1\neq 0$, even when CDW's are stable, if the nonsuperconducting state is metallic then a SC state is always present and stable at low enough temperatures.

(c) In Fig. 3(b) we show the results for the same parameters of Fig. 3(a), i.e., $T=0$, $t_1/t_0=0.125$, $\hbar\omega_D/t_0=\frac{1}{3}$ and a half-filled band.

(d) For $\lambda<\lambda_{c1}$ ($\lambda_{c1}=1.75t_0$ in the example of Fig. 3) the CDW is not stable and an ordinary BCS superconductor[1] appears, with its characteristic gap parameter Δ and transition temperature T_{SC}. It should be noted that λ_{c1} is larger than the value λ_c obtained in Sec. III when SC correlations were not included.

(e) For $\lambda_{c1}<\lambda<\lambda^{**}$ ($\lambda^{**}\sim\lambda^{*}=2.23t_0$ in Fig. 3) the ground state of the system is a state in which SC and CDW coexist, i.e., both order parameters are nonvanishing; the value of Δ remains practically unchanged throughout the interval because of the competing effects of increasing λ and decreasing density of states at the Fermi level. It should be mentioned that the pure CDW state is metallic in this range.

(f) For $\lambda^{**}<\lambda<\lambda_{c2}$ ($\lambda_{c2}=2.46t_0$ in Fig. 3) the CDW induces a (semiconductor) gap in the quasiparticle spectrum, but superconductivity does exist and the ground state of the system is SC. In this range of λ values, Δ decreases drastically with increasing λ. We expect in this case to have a transition as a function of increasing temperature between a SC and a semiconducting CDW state; this is discussed in Sec. V.

(g) For $\lambda_{c2}<\lambda$ no SC state is stable, and the ground state of the system is an insulating CDW state.

(h) In Fig. 3(c) we give the minimum quasiparticle excitation energy (one half of the pair excitation energy) as a function of λ. For $\lambda<\lambda^{**}$ this energy corresponds to the breaking up of a Cooper pair; for $\lambda>\lambda_{c2}$ it is the excitation across the CDW gap; at intermediate values $\lambda^{**}<\lambda<\lambda_{c2}$ it is a combined effect. Comparison of the gaps in Fig. 3(c) with the various gaps in Fig. 3(a) is instructive.

V. SUPERCONDUCTOR TO SEMICONDUCTOR TRANSITION

Of the cases reported in Sec. V, the most interesting one is that corresponding to large enough values of λ, very close to the values where the SC state becomes unstable: $\lambda^{**}<\lambda<\lambda_{c2}$. In this range, in the absence of SC, the system is a semiconductor of electron-hole pair excitation gap $2G$. At first sight it might seem unlikely that a system with no electron states at the Fermi level can produce a SC state with infinite conductivity and a Meissner effect. We explore this situation here in greater detail.

A semiconductor of energy gap $2G$ is such that each electron-hole pair requires an energy of the order of and greater than $2G$. Since in order to produce a current $\vec{j}$ we must excite approximately n_j pairs ($n_j\approx 2|\vec{j}|/|e||\vec{v}|$, where $\vec{v}$ is a typical band velocity), the minimum excitation energy necessary to produce a current $\vec{j}$ is $\sim 2n_jG$, i.e., the total energy of the system is a linear function of $|\vec{j}|$ and therefore has a cusplike behavior at $\vec{j}\to 0$. The energy gap $2G$ is a consequence of the self-consistent lattice (or CDW) potential which couples two points in k space separated by a vector of the reciprocal lattice Q and opens gaps wherever $\epsilon_k=\epsilon_{k+Q}$, the equation for the generalized Bragg surfaces (planes).

In a superconductor, on the other hand, a supercurrent is established by forming Cooper pairs of wave-vector 2κ, i.e., by coupling states $(k+\kappa)\uparrow$ with $(-k+\kappa)\downarrow$ in the BCS ground state. The state thus obtained yields a supercurrent $\vec{j}_s(\kappa)$ such that the total energy of the system is proportional to $(\vec{j}_s\cdot\vec{j}_s)$ and gaps in the quasiparticle spectrum appear at points on the displaced Fermi surface k such that

$$\epsilon_{k-\kappa}=\epsilon_F \ .$$

The resulting "supercurrent" state is metastable as long as quasiparticle energies inside and outside the Fermi distribution have no overlapping range, i.e., as long as the two branches of the quasiparticle spectrum

$$E_{\nu k}(\kappa)=\tfrac{1}{2}(2\epsilon_F+\epsilon_{k+\kappa}-\epsilon_{k-\kappa}) \pm\tfrac{1}{2}[(\epsilon_{k+\kappa}+\epsilon_{k-\kappa}-2\epsilon_F)^2+4\Delta^2]^{1/2} \qquad (5.1)$$

have no common values.

The anomalous situation we want to examine has four states coupled by two different mechanisms: $(\vec{k}+\vec{\kappa})\uparrow$, $(\vec{k}+\vec{\kappa}+\vec{Q})\uparrow$, $(-k+\kappa)\downarrow$, and $(-k+\kappa+Q)\downarrow$. The relevant Hamiltonian for a given κ is

$$H(\kappa)=\sum_{k\sigma}\epsilon_k a^{\dagger}_{k\sigma}a_{k\sigma}-G\sum_{k\sigma}a^{\dagger}_{(k+Q)\sigma}a_{k\sigma} -\Delta(\kappa)\sum_{k}{}'(a^{\dagger}_{(k+\kappa)\uparrow}a^{\dagger}_{(-k+\kappa)\downarrow} +a_{(-k+\kappa)\downarrow}a_{(k+\kappa)\uparrow}) \ . \qquad (5.2)$$

Here we have taken G to be a fixed parameter, since the fact that it originates from a CDW correlation is of no relevance for the present purposes. We also take $\epsilon_F=0$, $\epsilon_{k+Q}=-\epsilon_k$, and

$$\Delta(\kappa)\equiv\lambda\sum_{k}{}'\langle a_{(-k+\kappa)\downarrow}a_{(k+\kappa)\uparrow}\rangle \qquad (5.3)$$

in agreement with Eq. (2.11). For $\kappa=0$ we find that

the quasiparticle energies are given by

$$E_k = \pm(\epsilon_k^2 + \Delta_m^2)^{1/2} \ , \tag{5.4}$$

valid for

$$G < \Delta_m \tag{5.5}$$

and where Δ_m is the BCS gap parameter for Eq. (5.2) *when G is put equal to zero,* i.e., in the metallic case

$$\Delta_m = 2\,\hbar\omega_D e^{-1/\lambda\rho} \ . \tag{5.6}$$

The energy gap parameter Δ, defined in Eq. (5.3), is given by

$$\Delta(\kappa=0) = (\Delta_m^2 - G^2)^{1/2} \ . \tag{5.7}$$

For $G > \Delta_m$ there is no superconducting solution, $\Delta(\kappa=0)=0$, and the quasiparticle spectrum is that typical of a semiconductor

$$E_k = \pm(\epsilon_k^2 + G^2)^{1/2} \ . \tag{5.8}$$

For $\kappa \neq 0$ the equation that determines the energy gap parameter is

$$\Delta(\kappa) = \lambda\Delta(\kappa) \sum_k{}' [2(E_{4k}^2 - E_{3k}^2)]^{-1} \{[E_{4k}^2 - \epsilon_{k+\kappa}\epsilon_{k-\kappa} - G^2 - \Delta^2(\kappa)]E_{4k}^{-1} - [E_{3k}^2 - \epsilon_{k+\kappa}\epsilon_{k-\kappa} - G^2 - \Delta^2(\kappa)]E_{3k}^{-1}\} \ , \tag{5.9}$$

where the quasiparticle energies $E_{\nu k}(\nu = 1, 2, 3, 4$ in order of increasing energy $E_{1k} \leq E_{2k} \leq E_{3k} \leq E_{4k})$ are

$$E_{\nu k}(\kappa) = \pm\{\tfrac{1}{2}\epsilon_{k+\kappa}^2 + \tfrac{1}{2}\epsilon_{k-\kappa}^2 + \Delta^2(\kappa) + G^2 \pm |\epsilon_{k+\kappa} - \epsilon_{k-\kappa}|[\tfrac{1}{4}(\epsilon_{k+\kappa} - \epsilon_{k-\kappa})^2 + \Delta^2(\kappa)]^{1/2}\}^{1/2} \ . \tag{5.10}$$

It is a good approximation to take

$$\epsilon_{k\pm\kappa} = \epsilon_k \pm (\vec{\nabla}_k \epsilon_k) \cdot \vec{\kappa} \ , \tag{5.11}$$

from which we obtain a critical value of κ given by

$$\kappa_c \simeq \Delta(\kappa_c)/\hbar\bar{v}_F \ , \tag{5.12}$$

where $\bar{v}_F$ is the average value of the metallic Fermi velocity we would have obtained *if G is put equal to zero.*

In Fig. 4 we show the solution of Eq. (5.9) in units of Δ_m, given by Eq. (5.6), as a function of κ in units of $\Delta_m/\hbar\bar{v}_F$. The results can be summarized as follows:

(i) The condition for a critical current j_c or, equivalently, for a critical κ_c is given by Eq. (5.12), as in the metallic BCS-like SC state. However in this case Δ is a strong function of κ_c

$$\Delta(\kappa_c) < \Delta(\kappa=0) < \Delta_m \tag{5.13}$$

and therefore κ_c is smaller than the corresponding value for the metallic SC.

(ii) The critical κ_c decreases rapidly with increasing semiconducting gap G and vanishes for $G = \Delta_m$.

(iii) As a consequence of this a Meissner effect is present as long as $G < \Delta_m$ and the induced currents are smaller than the critical value.

(iv) A semiconductor to superconductor transition is possible for semiconductors of small enough gap; more explicitly the semiconductor gap G must be smaller than the energy gap Δ_m that the system would have in the superconducting state if it were metallic.

VI. DISCUSSION

The theory presented here treats SC and CDW's on the same footing. According to our model the phonon-mediated attractive electron-electron interaction leads to both CDW and SC states. There are four possible states: (i) a normal paramagnetic state

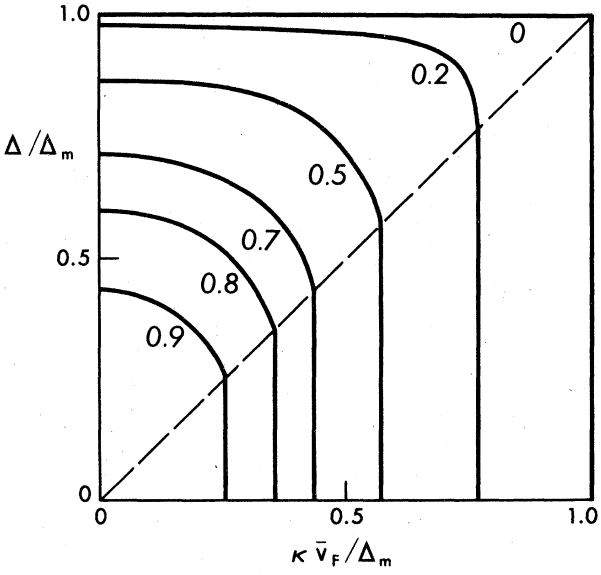

FIG. 4. The SC order parameter Δ as a function of $\kappa\bar{v}_F/\Delta_m$. This quantity is proportional to the intensity of the supercurrent. The various values of G/Δ_m in these semiconductor-superconductors are indicated. The values at which Δ drops discontinuously to zero correspond to critical currents.

$\Delta=0, G=0$; (ii) a SC state with uniform charge distribution $\Delta\neq 0, G=0$; (iii) a CDW state $\Delta=0, G\neq 0$ which may be either (a) metallic or (b) semiconducting; and (iv) a metallic SC and CDW state, with a modulated charge distribution $\Delta\neq 0, G\neq 0$. The stability of each of these states depends sensitively on the temperature, the strength of the interaction, and the details of the electronic spectrum and Fermi surface.

In general terms the order parameters interfere destructively, with CDW tending to suppress SC and *vice versa*. A large enough CDW which produces a semiconductor state may completely destroy SC. But all metallic CDW states become SC at low enough temperatures. Not all semiconducting CDW's on the other hand show a lack of SC at low temperature: if the CDW gap is small enough, smaller than an "ideal" SC gap, as the temperature decreases the system makes a transition from a nonuniform semiconductor to a nonuniform SC. This semiconducting-SC state shows persistent currents and a Meissner effect, but the dependence of the SC parameters on the total current is different and more pronounced than in the metallic SC state.

Experimental data[4,7,8] on the SC properties of the transition-metal dichalocogenides show that (i) all metallic CDW systems are SC at low enough temperature; (ii) those layered compounds which exhibit no SC show a nonlinear low-temperature specific heat, i.e., a lack of ordinary metallic properties; (iii) it has been reported,[8] although uncertainties still remain unsolved, that some systems which are SC at low enough temperature are probably semiconducting at temperatures higher than T_{SC}.

All these findings are in agreement with our theory.

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