it must be quite weak, no more than a few tenths of a percent of the peak main band intensity. An effect as large as 0.6% would have been easily detectable at the present noise level. A sharper edge of the experimentally indicated magnitude would also have been easily established. Hence further work on the light alkali metals (where the predicted edge width is much smaller and adequate intensity is available) seems indicated, in spite of the considerable experimental difficulty involved in securing reliable data from such highly reactive materials.

We would like to express our thanks to Dr. S. Lundqvist, Dr. L. Hedin, Dr. A. J. Glick, and Dr. S. M. Bose for communication of their results prior to publication. We also thank Dr. R. E. Watson for several instructive conversations.

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Possible Cooperative Phase for Electrons in Double-Stranded DNA

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The possibility of a superfluid phase occurring in macromolecules such as double-stranded DNA is discussed. The restricted geometry for electron states in macromolecules is probably more propitious for the excitonic insulator than for superconductivity. The excitonic insulator in restricted geometry is discussed, and some qualitative comments are made on the band structure of double-stranded DNA.

I. INTRODUCTION

In 1964, Little[1] examined in detail an earlier suggestion by London[2] that a superfluid state might occur in macromolecules. One of the motivations for this proposal is that the stability of the genetic code could indicate a highly stable cooperative state for electrons in, for example, double-stranded DNA (Watson-Crick double helix). It was recently suggested that a Cooper-pair condensation in DNA might be important in biology, since it would increase order at the expense of free energy and provide an "amplification of quantum phenomena to the 'classical level'."[3] We shall not discuss here the manner in which a macroscopic quantum state for electrons in DNA may be important biologically, but shall confine our discussion to the possibility that such a state might actually occur. And, of necessity, our remarks will be qualitative.

Several discussions and critiques of Little's model for an organic superconductor have been published.[4-8] We shall discuss the more important of these briefly. However, our main purpose in this discussion is to argue that another cooperative state for electrons, the excitonic insulator, may occur in macromolecules such as double-stranded DNA. The excitonic insulator is a supercurrent of excitons. Many characteristics of the excitonic-insulator phase are similar to those of an ideal Bardeen-Cooper-Schrieffer (BCS) superconductor, for example, the energy gap and single-particle excitation spectrum. However, the total charge of the basic group is zero, and this phase displays neither charge transport nor the Meissner effect. Moreover, the excitonic insulator is characterized by diagonal rather than off-diagonal long-range order. These characteristics are theoretical predictions,[9] since the excitonic insulator has not yet been experimentally observed.

It appears that the restricted geometry for electron states in macromolecules is considerably less propitious for superconductivity than the nonrestricted geometry of an idealized bulk solid. We suggest, and will support by some qualitative arguments, that the reverse may be true for the excitonic insulator, and that this phase is more likely to occur than superconductivity in macromolecules such as double-stranded DNA.

II. OBJECTIONS TO LITTLE'S PROPOSAL

We shall not discuss in detail the Little model for an organic superconductor,[1] but shall only comment that

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

[2] F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950).

[3] Robert M. Pearlstein, Phys. Rev. Letters **20**, 594 (1968).

[4] Richard A. Ferrell, Phys. Rev. Letters **13**, 330 (1964).

[5] T. M. Rice, Phys. Rev. **140**, A1889 (1965).

[6] C. G. Kuper, Phys. Rev. **150**, 189 (1966).

[7] David A. Krueger, Phys. Rev. Letters **19**, 563 (1967).

[8] W. L. McCubbin, Phys. Letters **19**, 461 (1965).

[9] D. Jerome, T. M. Rice, and W. Kohn, Phys. Rev. **158**, 462 (1967).

it involves substituting dynamic polarization of bound electrons for the Frohlich electron-lattice interaction basic to the BCS model.[10] The supercurrent is intended to flow along a central spine with the polarizable electrons in side chains. In accordance with the isotope effect,[10] the transition temperature is expected to be considerably higher than room temperature because of the small mass of the polarizable electrons. It is noteworthy that Frohlich recently proposed a similar mechanism for room-temperature superconductivity in modified transition metals.[11]

It has often been inferred in the literature that superconductivity is not possible in the restricted geometry of electron states in organic molecules.[4–7] Unfortunately, "dimensionality" and boundary conditions have sometimes been confused. The question of long-range order in one dimension is not relevant to the boundary conditions in macromolecules. The dimensions in which coordinates become small (because of the confining potential of the lattice) do not decrease in importance. A pragmatic application of the Heisenberg uncertainty principle leads to large zero-point energies in the severely restricted dimensions, and this is nontrivial. (This factor cannot, in general, be described by a change in the reference potential.) Discussions in the literature which show that long-range order cannot exist in a one-dimensional formulation are not relevant to a cooperative assembly of electrons in macromolecules. There is no inviolate recipe by which we can proceed from such a model to conclusions about the fully quantum-mechanical regime. And if this in itself were not sufficient, it cannot be inferred that interactions which are of short range in a geometrically nonrestricted assembly will remain of short range when one or two dimensions are severely restricted. Any meaningful discussion of long-range order for an electron assembly in restricted geometry must include the effects of physical boundary conditions in all three dimensions.

To support the preceding remarks, consider the argument that compressional modes of vibration of the superconducting state smear out any possible long-range order in an organic superconductor.[4] This conclusion depends upon divergence of an integral occurring in a Debye-Waller type of parameter. In nonrestricted geometry the integral is $\int_0^{k_{\max}} d\mathbf{k}/k$, which, of course, is well defined, since an additional factor k^2 appears in the numerator of the integrand after the angular integration has been done. In the one-dimensional calculation the corresponding integral $\int_0^{k_{\max}} dk/k$ diverges logarithmically at $k=0$ [Eq. (11) of Ref. 4]. Since in this case the Debye-Waller factor is zero, the discussion concludes that long-range order in one dimension cannot occur. This is true; however, it does not relate to superconductivity with coordinates in two dimensions severely restricted. The proper integral in restricted geometry is $\int_0^{k_{\max}} dk/(k^2+K^2)^{1/2}$, where K^2 expresses the zero-point energy in the restricted dimensions. When the maximum coordinates in these dimensions become very small, K becomes very large, and the integral tends to $\ln[(k_{\max}+K)/K]$. Compressional modes should, in fact, be less important in smearing out long-range order in a macromolecule than in a bulk superconductor. Similar arguments apply to Eqs. (19), (32), and (33) of Ref. 12 (Bogoliubov inequality) and Eq. (9) of Ref. 5.

Long-range order of interacting Bose or Fermi systems is discussed in a recent paper by Krueger.[7] The calculations show that no condensation can occur in partially finite geometry. However, the derivation uses periodic rather than box boundary conditions, with zero-momentum components allowed in all dimensions. By the previous arguments, this discussion is valid only for a one- or two-dimensional model, but not for a three-dimensional model in which coordinates in one or two dimensions are severely restricted.

Criticism of Little's proposal which we regard as more to the point concerns the electron-electron interaction in the actual circumstances. The relevant question is whether or not an attractive interaction sufficient for superconductivity exists in macromolecules. Kuper has shown that when two dimensions are restricted to a few angstroms,[6] the repulsive component of the electron-electron interaction is much stronger than Little's calculations indicate.[1] (This circumstance is, of course, highly favorable for the electron-hole interaction required for the excitonic-insulator phase.) There will be no corresponding increase in the attractive part of the electron-electron interaction. McCubbin has discussed the electron-electron interaction in macromolecules with regard to known experimental parameters,[8] and suggests that an attractive interaction will not occur in the specific model proposed by Little but may possibly occur in some other manner.

To summarize, there is no general statement regarding long-range order in restricted geometry which rules out superconductivity or any other cooperative phase for electrons in macromolecules. The relevant question of whether or not an attractive electron-electron interaction sufficient for superconductivity exists in any organic molecule has not been fully resolved. The increase in the direct Coulomb electron-electron interaction in restricted geometry reduces the possibility that superconductivity will occur, but increases the likelihood that the excitonic insulator will occur. In the following sections, we shall discuss the possibility that the excitonic insulator occurs in macromolecules, for example, double-stranded DNA.

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[10] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[11] H. Frohlich, Phys. Letters **26A**, 169 (1968).

[12] P. C. Hohenberg, Phys. Rev. **158**, 383 (1967).

III. ENERGY BANDS IN RESTRICTED GEOMETRY

We shall now discuss the energy-band structure of macromolecules. Consider, first, a nearly free-electron Brillouin-zone model. We choose a cylinder of radius $a_\perp$ and length L, with constant potential in the interior and bounded by an infinite potential. This is intended as a low-order approximation to the confining potential due to the atoms of a long-chain molecule. Assuming for this crude model that the electrons which might condense into a cooperative phase do not affect the potential distribution because of these more massive bodies, the free-electron wave functions, neglecting spin, are

$$\Psi_\alpha(\mathbf{x}) \equiv \Psi_{k_z,n,m}(z,\rho,\phi) = A\exp[i(k_z z+m\phi)]J_m(q_{nm}\rho). \tag{1}$$

Here $J_m(q_{nm}\rho)$ is the Bessel function of the first kind and $q_{nm}a$ is the nth root. The energy levels are

$$W_{k_z,n,m} = (\hbar^2 k_z^2/2m_z)+(\hbar^2 q_{nm}^2/2m_\perp) \tag{2}$$

and

$$k_z = n\pi/L, \qquad n=1,2,3,\cdots,$$

$$q_{nm} = l_{nm}\pi/a_\perp.$$

We let L become very large so that the k_z eigenvalues are quasicontinuous. A few of the lower l_{nm}^2 eigenvalues are shown in Table I. The first three energy levels arising from the restricted dimensions are similar to those of a two-dimensional harmonic oscillator with the same characteristic radius.

If we impose a small periodic potential along the z axis, characterized by a length a_z, then we arrive at a nearly free-electron Brillouin-zone model as shown in Fig. 1. This diagram is interesting in that it illustrates the possibility that in restricted geometry a small band gap G (or band overlap for negative values) may occur between a full valence band and empty conduction band (or nearly full and nearly empty). (Of course, the band parameters and number of electrons per unit cell in Fig. 1 do not correspond to any real macromolecule.) The band structure with restricted geometry in two dimensions is qualitatively similar to the Landau-level scheme that large magnetic fields introduce into the band theory of solids.[13] We emphasize that in both cases, the "boundary conditions" are introduced by means that we can regard as external to the electron assembly we are discussing. An in both cases, screening of the Coulomb interaction by free carriers is greatly reduced from the bulk-solid regime.[6,14]

TABLE I. Eigenvalues l_{nm}^2 for low n, m.

(n, m)	$n=1$	$n=2$	$n=3$
$m=0$	0.59	3.09	7.56
$m=1$	1.49	4.97	10.49
$m=2$	2.66	7.18	13.62
$m=3$	4.12	9.67	17.16

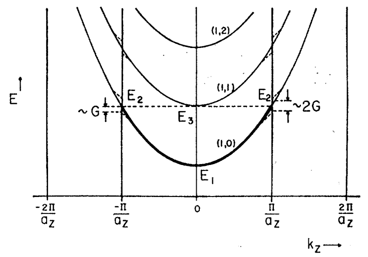

FIG. 1. Band structure for free electrons confined to a cylinder. $a_z = a_\perp$, $m_z = m_\perp$, and there are two electrons per unit cell.

With $|E_3-E_2| \ll E_2-E_1$, we expect the exciton binding energy to exceed the band gap or band overlap, as required for the excitonic-insulator phase.[9] With an effective mass equal to the free-electron mass for both valence-band holes and conduction-band electrons, and with a dielectric constant ~3,[15] in the hydrogen-atom model the exciton binding energy is ~0.5 eV. And for this case, $E_2-E_1 \sim 5$ eV.

Following Pearlstein,[3] we might expect 14 quasifree π-orbital electrons for each base pair in double-stranded DNA. The double-helix structure repeats along the z axis after 10 base pairs, and thus there are 140 relatively mobile electrons in the unit cell. If we consider the double-helix structure as a simple cylinder with a periodic potential along the z axis, $a_\perp \simeq 6$ and $a_z \simeq 34.6$ Å. X-ray reflections along the z axis occur at ~3.4 and 34.6 Å.

We shall not, of course, produce here the 70-band nearly free-electron band structure of double-stranded DNA which would be analogous to Fig. 1. However, it can easily be verified that many of the band edges are grouped in energy in a similar manner to E_3 and E_2 in Fig. 1. This description is, of course, arbitrary with the limited information available. However, when we consider that departure from the nearly free-electron model toward the tight-binding case will decrease bandwidths and increase band gaps, in the actual band structure of double-stranded DNA almost 70 bands will be completely filled, and at most only a few bands will be partially filled. The bandwidths will be $\lesssim 0.1$ eV and the Fermi energy $\lesssim 5$ eV. Band overlap between

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[13] E. W. Fenton, Phys. Rev. **170**, 816 (1968).

[14] E. W. Fenton and R. R. Haering, Phys. Rev. **159**, 593 (1967).

[15] C. T. O'Konski, P. Moser, and M. Shirai, Biopolymers Symp. **1**, 479 (1964).

any partially filled "conduction" bands and partially empty "valence" bands will be small in comparison with the Fermi energy. Almost all of the 140 electrons per unit cell will not contribute to screening of the Coulomb interaction required for exciton states, by application of the exclusion principle to the completely filled bands. The feature peculiar to this band structure is that we can expect energy gaps due to the 34.6 Å periodicity at most of the points where (n, m) levels would otherwise intersect the Fermi surface. In addition, any free carriers due to partially filled bands will not be as effective in screening the Coulomb interaction as electrons in a bulk solid, since small energy and momentum transfer can occur only through changes in k_z. As discussed in detail by Kuper,[6] with restricted geometry the electron assembly becomes more rigid than in a bulk solid, and the charge density is less able to distribute in a manner which would reduce Coulomb interactions.

We conclude that exciton states cannot be ruled out in the π-orbital-electron assembly of double-stranded DNA, even though the density of these electrons is high, $\sim 10^{22}$ cm^{-3}. In the absence of detailed energy-band information, we cannot say whether the normal phase of double-stranded DNA is a semiconductor or a semimetal.

IV. EXCITONIC INSULATOR IN RESTRICTED GEOMETRY

In this section, we shall make frequent reference to calculations in the literature which are very similar, particularly to the case for the excitonic insulator in large magnetic fields.[13] We consider the most simple model which will illustrate characteristics of the excitonic insulator in restricted geometry, the band structure shown in Fig. 1. With $|k_z|$ less than π/a_z, the (1, 0) level will be referred to as the valence band and the (1, 1) level as the conduction band. We assume that the periodic potential along the z axis yields an effective mass near the valence-band maximum and that the direct gap at the zone boundary is appreciably greater than any band gap between valence and conduction bands.

Using the basis functions for single particles of Eq. (1), the single-particle energies are

$$\epsilon_a(\alpha) \equiv \epsilon_a(k_{az}, n, m) = -\tfrac{1}{2}G - (2m_a)^{-1}k_{az}^2,$$
$$\epsilon_b(k_{bz}, n, m) = \tfrac{1}{2}G + (2m_b)^{-1}k_{bz}^2, \qquad (3)$$

where $\hbar = c = 1$. The quantum numbers (n_a, m_a) and (n_b, m_b) appear implicitly in G. Although the band extrema in Fig. 1 are denoted by a separation of $\pm\pi/a_z$, we shall call this separation w_z. In general, w_z will not be equal to $\pm\pi/a_z$, although we expect a multiple or submultiple of this value. k_{az} and k_{bz} are measured from the band extrema, whatever the separation.

Consider a Hamiltonian as in Refs. 9 and 13 and a Hartree-Fock trial wave function for the ground state:

$$|\Psi\rangle = \prod_\alpha c_\alpha^* \,|\, vac\rangle. \qquad (4)$$

c_α^* creates an electron in a linear normalized combination of band-a and band-b states:

$$c_\alpha = u_\alpha a_\alpha - v_\alpha b_\alpha, \qquad (5)$$

where a_α and b_α are annihilation operators for electrons in bands a and b. Using a variational calculation which minimizes the free energy as a function of u_α and v_α,[10] a gap function is obtained:

$$\Delta_\alpha = \sum_\alpha V_{\alpha\alpha'}(\Delta_{\alpha'}/2E_{\alpha'}), \qquad (6)$$

where

$$V_{\alpha\alpha'} = \int V(|\mathbf{x}-\mathbf{x}'|)\Psi_\alpha^*(\mathbf{x})\Psi_\alpha(\mathbf{x}')\Psi_{\alpha'}^*(\mathbf{x}')\Psi_{\alpha'}(\mathbf{x})\,d\mathbf{x}d\mathbf{x}' \qquad (7)$$

and

$$E_\alpha^2 = [\tfrac{1}{2}(\epsilon_b - \epsilon_a)]^2 + |\Delta_\alpha|^2. \qquad (8)$$

$V(|\mathbf{x}-\mathbf{x}'|)$ is an effective Coulomb interaction between electrons. (When $G<0$, V is reduced in range because of screening by free carriers.) Using temperature-dependent Green's functions in the identical manner to Ref. 13, the temperature-dependent gap function can be obtained:

$$\Delta_\alpha = \sum_{\alpha'} V_{\alpha\alpha'} \frac{\Delta_{\alpha'}}{E_{\alpha'}} \tanh\frac{E_{\alpha'}}{2kT}. \qquad (9)$$

A phase diagram for the excitonic insulator is obtained similar to those of Refs. 9, 13, and 16, shown here in Fig. 2. As in the high-magnetic-field regime of Ref. 13, the phase boundary in the band-overlap region is not well determined because of the fact that there is at the present time no satisfactory theory for screening by free carriers in either restricted geometry or high magnetic fields.

We shall present here only the result of a calculation

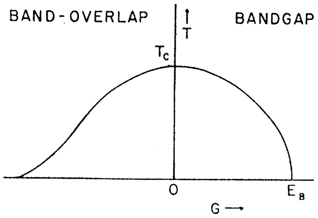

Fig. 2. Phase diagram for the excitonic insulator.

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[16] A. N. Kozlov and L. A. Maksimov, Zh. Eksperim. i Teor. Fiz. **49**, 1284 (1965) [English transl.: Soviet Phys.—JETP **22**, 889 (1966)].

of the number of single particles in the band-overlap regime as a function of temperature. This derivation is closely similar to the calculation of Ref. 13, Eqs. (20)–(43). When the number of electrons and holes in the normal phase is the same and $m_a = m_b$, the effective number of single particles is

$$n_{\mathrm{eff}} = 2n_c \int_0^\infty \frac{d\nu}{(\nu^2+1)^{3/2}} \left\{ \exp\left[\frac{\Delta(\nu^2+1)^{1/2}}{kT} \right] + 1 \right\}^{-1}, \qquad (10)$$

where n_c is the number of either electrons or holes of the normal phase. The number of single particles as a function of temperature is shown in Fig. 3. As commented earlier, for an organic molecule we expect $T_c \gtrsim 10^3$ °K, since $kT_c \sim \Delta \sim E_B \gtrsim 0.1$ eV.[9,16] For $T \ll T_c$, temperature dependence of the number of free carriers is similar to the number of excitations in a semiconductor with band gap equal to the gap function Δ.

To summarize, the excitonic insulator in restricted geometry is similar to the high-magnetic-field regime, and both are similar to the bulk-solid zero-field regime.

V. DISCUSSION

The excitonic insulator is expected to exhibit microscopic charge-density oscillations which are correlated over macroscopic dimensions, and apart from the long-range order of the lattice. This postulated phase is an assembly of electrons which propagate over macroscopic dimensions and at the same time occupy a cooperative, highly stable state. The excitonic insulator is a superfluid of excitons, although no net charge, mass, or thermal flow occurs. Biological significance attached to superconductivity in macromolecules[1,3,17,18] can also be attributed to the excitonic insulator if it were to occur.

The cylindrical boundary conditions discussed in Sec. III may not be as crude as they might first appear. Field-emission electrons from metallic surfaces on which molecules or molecular complexes are adsorbed exhibit cylindrical mode patterns to high-order numbers.[19] Although the electrons traversing the molecules are "low energy," they may nevertheless occupy states in bands much higher than the Fermi energy. This result shows that electron states in at least some energy bands are well described by the wave functions of Eq. (1), although not necessarily in the energy bands with which we are here concerned.

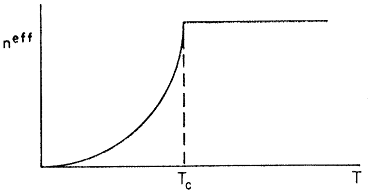

FIG. 3. Number of free carriers as a function of temperature for the excitonic insulator.

Experimental confirmation of the excitonic-insulator phase in macromolecules such as double-stranded DNA would be exceedingly difficult to achieve. The temperature dependence of the free-carrier density with $T \ll T_c$ is similar to a semiconductor in which a band gap replaces the gap function. In addition, with a transition temperature which is probably higher than the stable regime for macromolecules, the semiconductor-excitonic-insulator phase transition cannot be a distinguishing feature experimentally. The difference between the two phases is important, however, no matter how subtle the differences between transport properties may be for $T \ll T_c$. The excitonic-insulator phase introduces an additional long-range order not present in semiconductors (or in semimetals),[9] and because of this, a highly stable state.

Very low conductivity has been observed in DNA, less than 10^{-12} $(\Omega\ \mathrm{cm})^{-1}$ at room temperature, with a semiconductor type of temperature dependence.[15] [For comparison, the conductivity of silicon at room temperature is ~ 1 $(\Omega\ \mathrm{cm})^{-1}$.] The activation energy is ~ 1 eV, which compares with our crude estimate in Sec. III of 0.5 eV for the exciton binding energy. With regard to the experimental conditions,[15] it can not be fully concluded that this transport behavior is an intrinsic characteristic of DNA.

When and if experimental and theoretical results for the excitonic insulator in bulk solids become detailed and well established, a simple and definite criterion may exist for this phase which can be applied experimentally to macromolecules at room temperature.

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[17] T. A. Hoffman and J. Ladik, Cancer Res. **21**, 474 (1961).

[18] D. D. Eley, *Horizons in Biochemistry*, edited by M. Kasha and B. Pullman (Academic Press Inc., New York, 1962), p. 341.

[19] Robert Gomer and Donald A. Speer, J. Chem. Phys. **21**, 73 (1953); Allan J. Melmod and Erwin W. Muller, *ibid.* **29**, 1037 (1958); A. P. Komar and A. A. Komar, Zh. Tekhn. Fiz. **31**, 231 (1961) [English transl.: Soviet Phys.—Tech. Phys. **6**, 166 (1961)]. We thank Dr. R. A. Armstrong for bringing these three references to our attention.