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OVERHAUSER PHASE AND BOND ALTERNATION IN LONG-CHAIN MOLECULES

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It is suggested that bond alternation in long conjugated carbon chains is due to an Overhauser charge-density wave in the π-electron assembly.

A number of recent papers have discussed the excitonic insulator, expected to occur in solids with an even number of electrons per unit cell.[1,2] The band gap or band overlap in semiconductors or semimetals, respectively, must be less than the exciton binding energy E_B. When the number of electrons per unit cell is odd, the static charge-density or spin-density waves discussed first by Overhauser constitute a similar phase.[3] The oscillations are characterized by a wavelength π/k_F and may occur in the presence of a uniform positive-charge background as well as an ion lattice. In a one-dimensional ion lattice the Overhauser condensation is characterized by a wavelength which is twice as great as the ion spacing.

Overhauser showed that the usually assumed Hartree-Fock ground state is unstable in the presence of interactions. For a gas of spinless fermions in one dimension, consider a Hartree-Fock state

$$\Phi = \prod_{k=-k_F}^{k_F} c_k^{\dagger}|vac\rangle. \tag{1}$$

Here

$$c_k = u_k a_k + v_k a_{k+2k_F}, \quad k<0;$$
$$c_k = u_k a_k + v_k a_{k-2k_F}, \quad k>0. \tag{2}$$

$a_k^{\dagger}$ creates a particle in a Bloch state $\psi(k)$ with kinetic energy given approximately by an effective-mass expression

$$\epsilon_k = k^2/2m^* \tag{3}$$

($\hbar = 1$). When we have a one-dimensional Brillouin-zone scheme due to an ion lattice, and one electron per unit cell, the product in Eq. (1) is complete within the first Brillouin zone.

When the particles interact via an effective Coulomb potential $V(q)$ (including a dielectric function which reflects screening and the static dielectric constant), a nontrivial $v_k \neq 0$ solution exists. The corresponding gap equation is

$$\Delta_{k'} = \sum_{p'} V(k'-p')[\Delta_{p'}/2(\epsilon_{p'}^2 + |\Delta_{p'}|^2)^{1/2}] \times \tanh[(\epsilon_{p'}^2 + |\Delta_{p'}|^2)^{1/2}/2k_B T]. \tag{4}$$

Here we have introduced a new variable to express the gap function in the most symmetrical form:

$$k' = k - k_F, \quad k>0; \quad k' = k + k_F, \quad k<0. \tag{5}$$

Equation (4) can also be written, at zero temperature,

$$[(k'^2/m^*)^2 + 4|\Delta_{k'}|^2]^{1/2}\varphi_{k'} = \sum_{p'} V(k'-p')\varphi_{p'}, \tag{6}$$

where

$$\varphi_{k'} = \Delta_{k'}/2[\epsilon_{k'}{}^2 + |\Delta_{k'}|^2]^{1/2}. \quad (7)$$

Comparison of (6) with the one-dimensional exciton wave equation shows that[4] $\Delta_k = k_F \simeq E_B$. When the Fermi energy is not close to zero, E_B is a function of E_F. However in one dimension $E_B > 0$ for all E_F, since at least one bound state exists for any one-dimensional attractive potential. We will be interested in the amplitude of the charge-density wave, and clearly when $\Delta_k = k_F > E_F$, all particles are included in the wave. This requires $E_B(E_F) > E_F$.

As we have discussed previously,[5] there are no general arguments regarding long-range order in one dimension which would exclude long-range order in the π-orbital-electron assembly of a long carbon chain. In the Bogoliubov inequality,[6-8] compressional mode,[9] or similar discussions in the literature,[10] long-range order in one dimension has been ruled out. Actual physical situations involve three-dimensional quasifree-electron assemblies in which coordinates in two dimensions are severely restricted. A zero-point energy and discrete series of energy eigenvalues result from the kinetic-energy operator for the corresponding directions. These discrete eigenvalues must be included along with the continuous spectrum from the remaining dimension. In the Bogoliubov inequality, for example, it can easily be verified that when eigenvalues of the kinetic-energy operator are taken in the proper manner, long-range order in restricted geometry is not condemned. We emphasize that the transverse degrees of freedom remove the divergence appearing in the one-dimensional formulation for arbitrary geometry, and the magnitude of the zero-point energy or separation of eigenvalues is not important in this regard.

Now consider the dielectric function for quasifree π-orbital electrons in long conjugated carbon chains. This function can be estimated using Thomas-Fermi screening theory. A calculation by Kuper shows that the screening length is greater than $\sim 15a_0$, where a_0 is an effective Bohr radius with regard to the dielectric constant and electron effective mass.[11] A screening length of this magnitude decreases the exciton binding energy from $E_B(E_F = 0)$ by only a small increment. (In contrast, the same density of free electrons in the nonrestricted geometry of a bulk solid yields a very small screening length.)

The Fermi energy for the π-orbital-electron density in carbon chains is $\lesssim 5$ eV, the maximum value corresponding to completely free electrons. $E_B(E_F) \simeq E_B(0)$ is somewhat difficult to evaluate in restricted geometry. With regard to the reduced mass of the exciton and the restricted transverse coordinates, we estimate the exciton binding energy as approximately 1 Ry, or ~10 eV. (Here we have taken the dielectric constant as unity.) The Fermi energy is thus less than the exciton binding energy for a quasifree one-electron band structure, and of course, in a tight-binding band structure as well. In long-chain molecules, values of the dielectric constant and the effective mass may in some cases combine to yield values for E_B much smaller than 1 Ry. However, in many cases E_B is comparable with or larger than E_F, and in the other cases, an appreciable fraction. Either all or a large fraction of the π electrons would contribute to a charge-density wave.

We think it fair to state that no satisfactory theory has been developed to date for the alternating single and double bonds of long carbon chains such as the polyenes. Previous attempts have not given a proper emphasis to electron-electron interactions.[12] We suggest that the alternating bonds are the result of an Overhauser condensation in the π-orbital-electron assembly, and do not arise directly from interactions between π electrons and the ions. The first Brillouin zone for the π electrons is half filled, and $k_F = \pi/2d$, where d is the spacing between carbon nuclei, ~1.4 Å. Wavelength of the charge-density oscillations of the Overhauser phase is therefore $2d$. (We have restricted this discussion to long chains with one quasifree π electron per carbon atom. In situations where there is one such electron for every 1.5 carbon atoms, the double bond occurs after two single bonds, and the Overhauser theory also applies.)

To this point we have considered only spinless fermions. It is well known, of course, that the Overhauser phase may be a spin-density rather than a charge-density wave. In fact, if the lattice were perfectly rigid, the ground state would certainly be the spin-density wave. For a nonrigid lattice in the presence of a charge-density wave, an effect similar to the Jahn-Teller effect occurs, breaking the symmetry of the lattice. The resulting reduction in total energy makes the charge-density wave the ground state when the lattice is sufficiently soft. Halperin and Rice[2] have discussed a simple parameter for determining which wave is the ground state if a condensa-

tion occurs:

$$\gamma = \omega_I^2 F^2(2k_F)/\nu^2(2k_F). \quad (8)$$

Here ω_I is the ion plasma frequency, $F(2k_F)$ is the ionic form factor, and $\nu(2k_F)$ is the relevant phonon frequency. When γ is less than $\frac{1}{2}$, the spin-density wave is expected to occur. In chromium, for example, with a value of $F(2k_F)$ close to unity,[13] γ is somewhat less than $\frac{1}{2}$, favoring the spin-density wave. For long conjugated carbon chains the square of the velocity of sound is an order of magnitude or more smaller than in transition metals,[14] and the square of the ion plasma frequency greater by a factor of 5 or more. These factors combine with an ionic form factor of order unity[15] to yield values for γ of order 10. Assuming validity of Eq. (8) for long carbon chains, the charge-density wave is lower in energy than the spin-density wave. It is unlikely that the assumptions implicit in Eq. (8)[2] are sufficiently violated to reverse this prediction. And of course, alternation of bond lengths in long carbon chains is observed in x-ray and infrared analysis.[16]

When the number of atoms in open or cyclic carbon chains is small, the k values are no longer quasicontinuous. The discrete nature of the k spectrum, the presence or absence of a zero-point k for box or cyclic boundary conditions, and an odd or even number of carbon atoms will all affect the solution of the gap equation. Screening in the long-wavelength limit will also decrease since momentum exchange must then be finite in all dimensions. Qualitatively, since phase and particle number are conjugate variables satisfying the uncertainty principle, resonance may occur between equivalent ground states in chains where the number of carbon atoms is less than approximately ten (e.g., benzene). And in some cases, the Overhauser charge-density wave may be higher in energy than the spin-density wave, or both may be higher than the normal state. The Overhauser phase for three restricted dimensions is considerably more complicated than when the chain length may be regarded as infinite, and we will not discuss that topic in detail here.

Long-chain organic semiconductors appear to present an enigma at the present time. The thermal activation energies for electronic conduction are usually much smaller than the values indicated by optical data.[17] (We cannot be certain about this, however, since the experimental data are quite uncertain.) Perhaps in these cases the materials are not semiconductors in the usual sense. The temperature dependence of the number of quasiparticle excitations from the Overhauser phase (or the excitonic insulator) simulates semiconductor behavior when $T \ll T_C$,[5] the critical temperature for transition to the normal state, approximately E_B/k_B, which is $\gtrsim 1000°K$. Direct optical transitions cannot occur from the charge-density wave condensate since the propagation vector of the basic group (exciton) is neither zero nor a reciprocal lattice vector, but $2k_F$. We suggest that in many cases at least, thermal-activation energies in long-chain organic semiconductors (e.g., polyenes) may correspond to excitations from an Overhauser condensate, with an energy gap 2Δ. In this case, optical-activation energies correspond to excitations from low-lying bands to the quasiparticle states in the conduction band, and may be much larger than 2Δ. Electron-tunneling experiments of the same type as those first performed on superconductors by Giaever would be diagnostic[18] if the required junction could be constructed. The quasiparticle density of states for the Overhauser or excitonic-insulator condensation is similar to that of an ideal superconductor.[19]

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BAND-GAP EFFECTS IN THE STOPPING OF Ge^{72*} ATOMS IN GERMANIUM*

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Measurements of the ionization losses of 10.0- to 30-keV Ge^{72*} atoms in germanium show no evidence for a cutoff for particle energies less than 23 keV, as might be expected from adiabatic arguments concerning the effect of an energy gap in germanium. The ionization loss is consistent with Lindhard's conjecture that the electronic stopping power of heavy particles is proportional to the particle velocity even at energies far less than this cutoff energy. Any effective energy gap encountered by the germanium atoms moving in a germanium crystal is less than ~0.1-0.2 eV.

We report on a search for the effect of the energy gap on the ionization produced in a semiconductor by slow heavy particles. The results bear on the important practical question as to the inherent lower limits of resolution in solid-state particle detectors. They also resolve, at least for germanium, a basic question of long standing concerning the energy-loss processes of slow particles in insulators and semiconductors, as will be summarized presently.

It is known from the work of Fermi and Teller[1] and of Lindhard and Winther[2] that in a free-electron gas the energy-loss cross section of slow particles approaches zero linearly with the particle velocity. Brandt and Reinheimer[3] studied the theory of the slowing down of a heavy point charge in a uniform electron gas with an energy gap. They found, as did Schweinler[4] who considered the band structure of specific insulators, that the electronic energy loss of a moving point charge has a threshold. It drops to zero as the particle velocity v becomes smaller than a critical value, v_C, which is determined by the energy gap of the material. Bohr[5] and Seitz[6] have argued from adiabatic considerations that heavy ions of mass M moving with an energy $E < E_C$ also encounter a cutoff in the electronic energy loss, with a critical energy $E_C \simeq ME_g/4m$, where m is the band-gap energy. This implies that, for example, Ge atoms moving in a germanium detector cannot be detected if the particle energy has fallen significantly below $E_C = \simeq 23$ keV.

The total energy-loss cross section of heavy atoms in this low-energy range is dominated by the momentum transfer in atomic collisions, and electrons are excited in these processes because of the exclusion principle. Lindhard[7] has argued that these collisions, although slow and practically elastic with regard to momentum transfer, are actually quasielastic in the sense that the electron clouds interpenetrate during the collisions, in effect setting the outer electrons free. If one nevertheless maintains a description of the total energy loss in terms of independent contributions from elastic atomic collisions and from inelastic electronic excitations, the electronic stopping-power component must be nearly the same as that in a free-electron gas, and approach zero linearly with v even for $v \ll v_C$, or $E \ll E_C$.

Our measurements of the ionization yield produced by Ge atoms moving in germanium detectors give no evidence for a cutoff near $E \sim E_C$. They support Lindhard's conjecture of an electronic stopping power proportional to v for particle energies at least down to $(0.1\text{-}0.2)E_C$.

Previous experiments[8-10] determined the ionization yield produced by the stopping of Ge atoms in germanium for energies $\gtrsim E = 23$ keV. There is satisfactory agreement with the theory of Lindhard et al.[11] on the fractions of the initial particle energy lost in electronic excitations and in atomic collisions. In the present experiments the