SUPERCONDUCTIVITY IN MACROSCOPIC ONE-DIMENSIONAL SYSTEMS

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Little[1] examined the possibility of superconductive phenomena in long-chain organic macromolecules within the framework of the BCS theory of superconductivity. He showed that the criterion for the occurrence of such a state could possibly be satisfied for certain organic polymers. This conclusion was based on the BCS Hamiltonian and did not take into account the effect of compressional modes of collective excitations. Ferrell,[2] in a recent Letter, pointed out that the compressional modes played an important role in one-dimensional systems and, in fact, prevented the establishment of long-range order which is required for superconductivity.

Ferrell arrived at this conclusion by writing the Gor'kov[3] function [see Eqs. (5), (6), and (11) of reference 2]

$$F(x)=\Delta\langle e^{i\varphi(x)}\rangle=\Delta e^{-M}, \qquad (1)$$

where

$$M=\frac{G^2}{2mnL\hbar}\sum_k\frac{1}{\omega_k}(\langle N_k\rangle+\tfrac{1}{2})=\frac{G^2}{4\pi mnv\hbar}\int\frac{dk}{k},\ \text{for } T=0.$$

In order to have superconductivity it is necessary that $F(x)$ be nonzero. Ferrell noted that e^{-M} has the same functional dependence on frequency as the Debye-Waller factor and concluded that since the Debye-Waller factor vanishes for one-dimensional systems, so does $F(x)$. This result is correct in the limit of very large systems (as the number of electrons becomes arbitrarily large). On the other hand, a simple calculation shows that a "macromolecule" with perhaps 10^5 electrons does not constitute a "large" system. The purpose of this note is to show that e^{-M} is nonzero for finite systems and to examine the dependence of M on the size of the system.

In Eq. (1), we note that the sum over k should exclude $k=0$ since this mode corresponds to a translation of the entire electron gas. One is concerned with the value of M in a frame of reference in which the molecule is stationary (i.e., the center-of-mass system). If one uses cyclic boundary conditions, then the smallest allowed value of k is $2\pi/L$. Thus one needs to evaluate the integral

$$M=\left(\frac{G^2}{4\pi mnv\hbar}\right)\int_{2\pi/L}^{k_{\max}}\frac{dk}{k}\coth\frac{\hbar vk}{2k_{\text{B}}T}, \qquad (2)$$

where $\omega=vk_{\max}=\Delta/\hbar v$, $\hbar$ is Planck's constant divided by 2π, k_{B} is the Boltzmann constant, T the temperature in °K, and L the total length of the system Noting that $G^2/4\pi mnv\hbar=\frac{1}{2}$, with $n=2k_f/\pi$, where $\hbar k_f=mv$, one obtains at $T=0$

$$M=\tfrac{1}{2}\ln(k_{\max}L/2\pi)=\tfrac{1}{2}\ln(L\Delta/hv). \qquad (3)$$

The value of M may be calculated from the values of Δ and v suggested by Little.[1] If one takes $\Delta=0.1$ eV, $v=3\times10^8$ cm/sec, then $\Delta/hv\sim10^{-3}$ Å^{-1}. For $L=10^5$ Å one obtains $M=2.3$ at $T=0$. It should be pointed out that M increases rapidly with temperature. To see this let us rewrite Eq. (2) in the form

$$M=\tfrac{1}{2}\int_1^{L\Delta/hv}\frac{dk}{k}\coth\left(\frac{T_L}{2T}k\right). \qquad (4)$$

If $T\ll\frac{1}{2}T_L$, where $T_L=hv/k_{\text{B}}L$, then

$$M\cong\tfrac{1}{2}\ln\left(\frac{L\Delta}{hv}\right)+\int_1^{L\Delta/hv}\frac{dk}{k}\exp\left(\frac{-T_L}{T}k\right), \qquad (5)$$

or

$$M\cong\tfrac{1}{2}\ln\left(\frac{L\Delta}{hv}\right)+\frac{T}{T_L}\left\{\exp\left(\frac{-T_L}{T}\right)-\left(\frac{hv}{L\Delta}\right)\right.$$
$$\left.\times\exp\left[-\left(\frac{L\Delta}{hv}\right)\frac{T_L}{T}\right]\right\}+O\left(\frac{T}{T_L}\right)^2+\cdots. \qquad (6)$$

The high-temperature behavior is obtained when $T>\Delta/2\pi k_{\text{B}}$, and gives $M=T/T_L$.

As Ferrell pointed out, the strength of the long-range order tends to zero as M becomes large. Since the loss of long-range order results in the loss of superconductivity, it appears that Little's estimate of a transition temperature of 2200°K for macromolecules should be greatly reduced because of the effect of the longitudinal collective excitations.

In conclusion, we emphasize that the above considerations in no way prove that superconductivity will exist in finite one-dimensional systems, but only that it connot be ruled out a priori on the basis of the logarithmic divergence of M. In two dimensions for $T \neq 0$, M similarly has a logarithmic divergence.

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[2] R. A. Ferrell, Phys. Rev. Letters 13, 330 (1964).

[3] L. Gor'kov, Zh. Eksperim. i Teor. Fiz. 34, 735 (1958) [translation: Soviet Phys.–JETP 7, 505 (1958)].

BAND STRUCTURE AND MAGNETISM OF GADOLINIUM METAL

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The type-4f rare-earth metals have been viewed traditionally as consisting of trivalent atomic cores, including the 4f shell, plus three conduction electrons per atom. Previous theoretical work[1] has attempted to explain the available experimental data by assuming that the three conduction electrons occupy essentially free-electron bands perturbed perhaps by a fairly small crystal potential. Much of this theoretical work depends critically on the assumed free-electron nature of the conduction bands. However, it has been difficult to explain by means of the free-electron model the large saturation magnetization[2] of Gd ($7.5\mu_B$/atom) and especially the large electronic specific heat[3] of the rare-earth metals which indicates a density of states at the Fermi surface some eight times that given by the free-electron model.

This Letter reports briefly some results of a nonrelativistic augmented plane wave[4] (APW) calculation of the electronic energy bands in gadolinium metal. The calculated conduction bands differ markedly from those of the free-electron model, and instead closely resemble those of the transition metals. This is due to the fact that bands originating from atomic 5d and 6s states overlap and are strongly mixed. The bands near the Fermi surface are of mixed s-d character and yield a density of states about three times that given in the free-electron model. This accounts for the large observed saturation magnetization of Gd metal and may account for the high electronic specific heats of rare-earth metals.

The one-electron potential, used as input for the APW calculation, was obtained from a superposition of spherically symmetric atomic potentials. Results have been calculated for two different atomic starting potentials: The first was determined from free-atom Hartree-Fock-Slater (HFS) wave functions[5] for the configuration $\mathrm{Gd}^0\ 4f^76s^25d$, while the second was obtained from analytic Hartree-Fock wave functions[6] for the configuration $\mathrm{Gd}^{+1}\ 4f^76s^2$ plus an atomic 5d wave function. The conduction bands obtained using these two potentials were practically identical indicating that they do not depend critically on the potential. We report here the results determined from the HFS potential which was chronologically the first potential used.

Energy eigenvalues were calculated at 45 points in 1/24 of the first Brillouin zone. The calculated $E(k)$ curves for the conduction bands of gadolinium metal along the major symmetry directions are shown in Fig. 1. The strong deviation of these bands from those of a free-electron or nearly free-electron model can be seen in the high density of relatively flat bands, which are largely of d character. The calculation also yields a very narrow 4f band (width ~0.05 eV) about 0.8 Ry below the bottom of the 5d-6s bands. (This separation, however, was found to depend strongly on the potential used and is consequently not very reliable.) The very narrow width of the 4f band indicates that the 4f electrons are, as expected, highly localized.

The density of states of the conduction bands was obtained by dividing the Brillouin zone into 192 identical hexagons, each characterized by the energies calculated at its center. A histogram representing the computed den-