magnetic field [i.e., the critical field has the functional dependence $H_c = M^{-\alpha}F(M^{\alpha}T)$ on the isotopic mass M, where α is a constant equal to about 1/2], the difference in the specific heats $(C_n - C_s)$ must have the form $M^{-\alpha}f(M^{\alpha}T)$. The electronic terms have this dependence, but $\alpha_n \propto M^{3/2}$, so that the lattice term in the normal state does not have the required form, from which Chester concludes that $\alpha_n T^3$ must be cancelled by an identical term in C_s.

Though the similarity rule for isotopic mass holds accurately for some elements,[6,7] we are not aware of critical field measurements on the two natural isotopes of indium. However, Muench reported that another similarity rule, namely that the shape of the critical field curve is independent of pressure, does not hold for indium.[7] It would be desirable to have critical field measurements on the In isotopes, as well as extended heat capacity measurements on other soft superconductors having high T_c and relatively large lattice terms.

A detailed discussion of our data up to 4°K will appear in a forthcoming article.

*Supported by a Signal Corps contract.

†National Science Foundation Cooperative Graduate Fellow.

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GIANT SPIN DENSITY WAVES

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(Received April 4, 1960)

The observations made in this paper call into serious question many details of the modern electron theory of metals. It will be shown below that, almost certainly, the Hartree-Fock ground state of a Fermi gas with Coulomb interactions is not the familiar Fermi sphere of occupied momentum states, but rather a state in which there are large static spin density waves, and in which large energy gaps exist in the single-particle excitation spectrum.

In order to emphasize the essential physical simplicity of the new low-energy states, we shall treat first a one-dimensional model. (Only translational freedom will be restricted to one dimension; the ordinary spin degrees of freedom will be retained.) The kinetic energy operator will be the usual one; and we shall assume that the repulsive interactions are delta functions:

$$V_{ij} = \gamma\delta(z_i - z_j). \tag{1}$$

The normal state of such a gas—N electrons in a box of length L—has all (plane wave) states occupied for $|k| \leq k_0 = \pi N/2L$. The total kinetic energy is $\frac{1}{3}NE_F$, where $E_F = \hbar^2 k_0^2/2m$; and the expectation value of the interactions (direct plus exchange) is $\gamma N^2/4L$. It is of interest to compare the energy of the normal state with that of the ferromagnetic state (all spins parallel):

$$W_{\text{ferro}} - W_{\text{normal}} = NE_F(1 - n^{-1}), \tag{2}$$

where

$$n = (N/L)/(2m\gamma/\pi^2\hbar^2), \tag{3}$$

a dimensionless quantity proportional to the electron density, N/L. The critical density, at which a transition between the normal and ferromagnetic states would occur, corresponds to $n = 1$. We shall prove, however, that the normal state is never the Hartree-Fock ground state, and that the ferromagnetic state is stable only for $n \leq \frac{3}{4}$.

We shall "begin" by writing down the self-consistent Hartree-Fock potential for the solutions of interest.

$$U(z) = 2gE_F(\sigma_x \cos qz + \sigma_y \sin qz), \tag{4}$$

where g and q are parameters to be determined later, and σ_x and σ_y are the usual Pauli matrices. The z direction need not be perpendicular to the (spin) x-y plane, but the spiral exchange potential (4) is perhaps easiest to visualize for that special case. This potential has the remarkable property that its only nonzero matrix elements are between the states (k,α) and $(k+q,\beta)$, where α and β are the spin-up and spin-down spin functions. The exact single-particle solutions for this potential are

$$\phi_k^+ = [ge^{ikz}\alpha + (E_k^+ - \omega_k)e^{i(k+q)z}\beta]/L^{1/2}[g^2 + (E_k^+ - \omega_k)^2]^{1/2}, \tag{5a}$$

for spin-up states, and

$$\phi_k^- = [ge^{ikz}\beta + (E_k^- - \omega_k)e^{i(k-q)z}\alpha]/L^{1/2}[g^2 + (E_k^- - \omega_k)^2]^{1/2}, \tag{5b}$$

for spin-down states. The free-particle energies are $2E_F\omega_k$, where

$$\omega_k = \tfrac{1}{2}(k/k_0)^2, \tag{6}$$

and the perturbed single-particle energies, $2E_FE_k$, are given by

$$E_k^+ = \tfrac{1}{2}(\omega_k + \omega_{k+q}) \pm [\tfrac{1}{4}(\omega_k - \omega_{k+q})^2 + g^2]^{1/2}, \tag{7}$$

together with a similar expression for E_k^- having q replaced by $-q$. The single-particle energy spectrum is shown in Fig. 1. Note the unusual feature that the energy gap, $4gE_F$, occurs on only one side of $k=0$ for a given spin. Near the energy gaps the real spin directions spiral in a plane perpendicular to the axis of spin quantization.

The N-electron wave function will be a single Slater determinant of wave functions (5). For any given q, the lowest energy is achieved if the occupied states satisfy $-\frac{1}{2}q \le k \le 2k_0 - \frac{1}{2}q$ for spin up, and $-2k_0 + \frac{1}{2}q \le k < \frac{1}{2}q$ for spin down. The amplitude g must then be determined so that the Hartree-Fock equations are satisfied. Such a procedure yields the required value of g immediately. An alternative way is to calculate the expectation value of the total energy, and subsequently to minimize that energy with respect to g. A somewhat long, but straightforward, calculation gives the following result for the kinetic energy of the N-electron wave function, relative to that for the normal state:

$$\Delta T = NE_F(1-b)^2 + NE_F[2b - (4b^2+g^2)^{1/2} + (g^2/2b)\ln S], \tag{8}$$

where

$$S = [2b + (4b^2+g^2)^{1/2}]/g, \tag{9}$$

and $b = q/2k_0$. Since the total electron density of the new state is spatially uniform (as it is for the normal state), the only new contribution to the potential energy is an (algebraic) decrease of the total exchange energy, J. After another lengthy calculation, one finds

$$\Delta J = -(NE_F/4n)[(g/b)\ln S]^2. \tag{10}$$

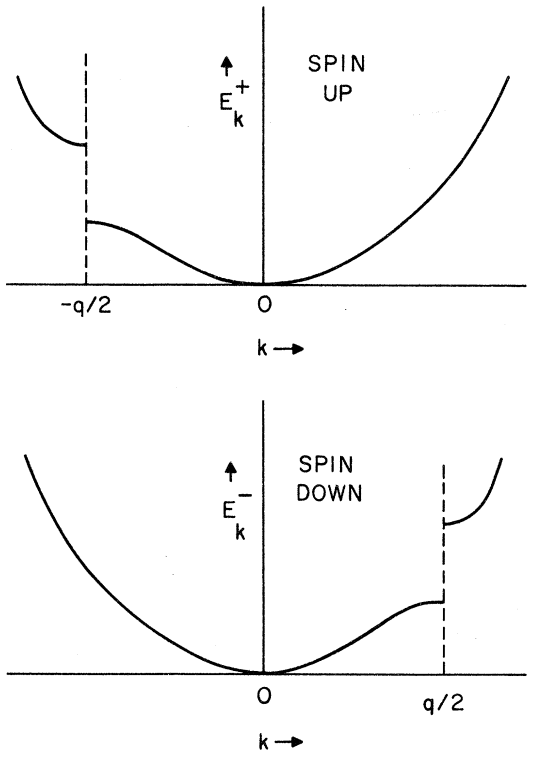

FIG. 1. Single-particle energy level spectrum for an electron gas with a giant spiral spin density wave.

An appreciable number of additional algebraic steps allows one to conclude that the sum of (8) and (10) is a minimum when

$$g = 2b/\sinh(2nb). \tag{11}$$

If this value is inserted into (8) and (10), the total energy of the new N-electron wave function relative to the normal state becomes

$$W = NE_F[1 + b^2 - 2b\coth(2nb)]. \tag{12}$$

This result is negative definite for $b = 1$, the value which corresponds to the same k-state occupation as the normal state. Consequently, the normal state is always a highly excited state. In fact, within the field of variation employed here, for $b = 1$, the normal state is an energy maximum.

The value (11) may be inserted into the wave functions (5), and the exchange potential operator computed according to its basic definition. One obtains a constant plus (4), the coefficient of the latter being in agreement with (11). Therefore, an N-electron state employing the functions (5) provides an exact solution of the Hartree-Fock equations for arbitrary b. One can show easily that the value of b which, in turn, minimizes (12) is less than unity. In fact, as n decreases (decreasing density or increasing interaction strength), $b \to 0$, at which value (12) and (2) become equal. This occurs at $n = \frac{3}{4}$. It should not be necessary to emphasize that the new lowest energy state has not been proved to be the Hartree-Fock ground state. However, we shall refer to it as the lowest (known) state. This lowest state has a spiral antiferromagnetic structure. The wavelength of the spiral is small, $\sim \pi/k_0$, for high density and gradually becomes larger, approaching ∞, as the density is reduced. Consequently the transition from spiral antiferromagnetism to ferromagnetism is a gradual one.

States above the energy gap can be occupied (e.g., by thermal excitations), but the spin directions of these states are out of phase with the spin density wave. As a result, the self-consistent amplitude of the spin density wave will be reduced, together with its contribution to the total energy. At a sufficiently high temperature—some fraction of the Fermi temperature—a second order phase transition will occur, and the normal state, with excitations, will (at last) become the state of minimum free energy. One can also construct nonspiral spin density wave states by employing an exchange potential $\propto \sigma_z \cos 2k_0 z$, instead of (4). These states, too, are always much lower than the normal state, but by an amount less than half that of the lowest spiral spin density wave.[1]

The physical reason why the spin density wave states are always lower than the normal state is, of course, the increase in magnitude of the exchange energy resulting from the local augmented parallelism of spins. The opposing term is of course the increase in kinetic energy. But the states most highly perturbed—those near the energy gap—are mixed with states of almost equal kinetic energy. Consequently this increase is sufficiently small to allow the exchange energy to dominate. In fact, in the limit of small g (considered again as a variational parameter), the ratio of exchange energy increase to kinetic energy increase approaches infinity (although only logarithmically). This observation makes it easy to prove that the normal state of a Fermi gas is unstable with respect to spin density wave formation for rather general repulsive interactions. Indeed, if the Fourier transform $V(k)$ of the interaction is large for small k, as it is for Coulomb interactions, the instability is enhanced, since the highly deformed single-particle states are close together in k space. (One must observe here that the fractional transfer of wave function amplitude to states across the Fermi sea is compensated by transfers in the reverse direction.)

The theory for a three-dimensional electron gas is almost identical to that given above for one dimension. It is necessary, however, to divide the electrons into at least three groups, and to allow each group to be deformed by its own spin density wave. For this reason the problem remains essentially one-dimensional. The occupied $\vec{k}$ states of each group will lie within a pyramidal cone (whose central axis is parallel to the wave vector of its spin density wave). For a given spin direction of a given group, the Fermi surface will be a plane on the energy gap side, and (approximately) a spherical polygon on the opposite side, as illustrated by the shaded region in Fig. 2. For strong interactions the complete Fermi surface will consist of a cube, at the surface of which is a large energy gap, and a sphere, at which $E(\vec{k})$ is continuous. Additional kinetic energy is required, of course, to occupy the unperturbed states in this way, but this will be more than compensated by the lower energy resulting from the spin density wave

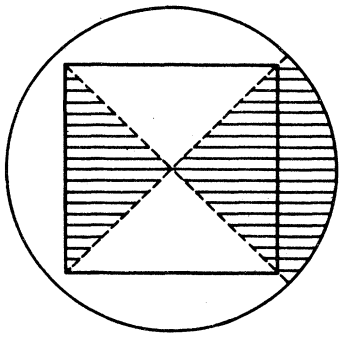

FIG. 2. Fermi surface for an electron gas with large repulsive interactions. The shaded region—a pyramidal cone—indicates the occupied states of a given spin for one (of three) groups of electrons. A large energy gap exists at the surface of the cube.

deformations. For weak interactions the inner Fermi surface will be a many-faced polyhedron, each pair of opposite faces arising from a spin density wave, and its volume will almost equal that of the sphere.

The foregoing description provides a means for "putting together" a three-dimensional electron gas in which the main effects of giant spin density waves are incorporated. The description is accurate only if the (off-diagonal) oscillatory part of the exchange potential between electrons of one group and those of another is neglected. Such effects, if included, will cause additional perturbation of the single-particle wave functions, will lower the total energy even further, and will prevent (fortunately) the boundary planes between different groups from having any sharp physical significance. Also, additional energy gaps in the spectrum of each group will be introduced by these perturbations. Consequently, the spherical part of the Fermi surface will lose some of its continuity. Such refinements need not be elaborated here, however.

A quantitative estimate of the energy gap at the surface of the cube for a typical metal with Coulomb interactions yields ~10 ev. (This estimate involves the formulation and solution of a complex nonlinear integral equation, and will be discussed elsewhere.) There seems to be little doubt that giant spin density waves should have numerous and profound consequences with regard to the properties of metals. Fortunately there remains some semblance of a Fermi sphere, but its states are no longer doubly degenerate. On the other hand, one can think of many experiments which might have revealed the existence of giant spin density waves, but have not: neutrons should suffer coherent magnetic diffraction in any metal, Langevin paramagnetism should not occur in metals or alloys, nuclear resonance lines should not be observed at their expected frequencies, if at all, etc. A possible escape from such enigmas is provided by the existence of collective excited states, of at least three varieties, relative to the spin density waves. Besides providing additional transport mechanisms, the excitation of collective modes (spin waves on the giant spin wave) will cause rapid fluctuations in the local spin density directions. It is by no means obvious that such fluctuations will be sufficiently rapid to avoid the unfortunate consequences just mentioned. Correlation energy differences are probably far too small to invert the new lowest state and the normal state in approximations beyond the Hartree-Fock scheme. Further research is necessary before one can decide whether or not a real paradox exists.

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