

pretation of the resonance as a metastable exciton implausible.

What, then, is the nature of the proposed new collective state? Having ruled out as implausible the foregoing possibilities, we believe the most likely explanation for this "Mayer-El Naby" resonance is that the Landau framework itself fails for K, i. e., that K can no longer be regarded as a normal metal. Preliminary data kindly provided us by Professor Mayer show evidence for similar phenomena in Cs. Should Na also prove to be abnormal, the argument<sup>10</sup> between Cohen and Matthias concerning its electronic ordering at  $T=0$  would be resolved in favor of both, i. e., Na, like K, may be neither normal nor superconducting.

Because the collective resonance occurs at  $\hbar\omega \sim \frac{1}{4}E_F$ , a detailed explanation requires studying Landau quasiparticle interactions "off the energy shell." The theoretical questions raised by the resonance are thus complex. With regard to experiment, however, one can say that tunneling,<sup>11,12</sup> optical and magneto-optical studies, and soft x-ray emission and absorption experiments all may exhibit these collective effects. To characterize collective resonances as such, sufficient resolution is required to display the antiresonance at low temperatures. Having established the presence of both resonance and antiresonance in the solid, the persistence of the collective

state into the liquid is then definitive. The latter also suggests studies of liquid metal alloys in order to vary  $r_S$  in hopes of finding a transition back to the normal state as  $r_S$  decreases.

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<sup>5</sup>Recent measurements by J. N. Hodgson [Phys. Letters **7**, 300 (1963)] on potassium films that were probably less pure than the specimens used by Mayer and El Naby did not show the low-energy peak.

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## COHERENT PAIRING OF THE SECOND KIND FOR STRONGLY INTERACTING FERMIONS\*

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Mayer and El Naby<sup>1</sup> have recently observed a remarkable resonance in the optical absorption of metallic potassium at 0.6 eV. Phillips and the present author<sup>2</sup> have inferred from the resonance that K is not a normal metal. Is there then another metallic state distinct from either the normal or the superconducting state?

Coherent, singlet pairs of conduction electrons occur in the superconducting state.<sup>3</sup> We propose to look for new coherently paired states before broadening the search to include states of more complex collective character.

Generalization of the *s*-wave pairing in superconductors to *p*-wave pairing, *d*-wave pairing, etc. has been proposed.<sup>4</sup> Such *l*-dependent pairing can exist at equilibrium only in a macroscop-

ically anisotropic system and is therefore relevant only to the excited states of isotropic systems. We propose instead possible radial dependences of the *s*-wave singlet pairing alternative to those in superconductors.

The BCS integral equation for the energy-gap parameter of isotropic systems is

$$\Delta(\epsilon) + \int d\epsilon' n(\epsilon) K(\epsilon, \epsilon') \tanh \frac{1}{2} \beta E(\epsilon') / E(\epsilon') \Delta(\epsilon') = 0, \quad (1)$$

with  $\epsilon$  the single-particle energy relative to the Fermi energy,  $n(\epsilon)$  the density of single-particle states,  $\beta = 1/k_B T$  and  $E$  the Bogoliubov quasiparticle energy<sup>3,5</sup>

$$E = [\epsilon^2 + \Delta^2(\epsilon)]^{1/2}. \quad (2)$$

The symmetric kernel  $K(\epsilon, \epsilon')$  is the sum of all

matrix elements of the dynamic Landau-quasi-particle interaction<sup>6,7</sup> which scatter a Cooper pair<sup>8</sup> from the energy surface  $\epsilon'$  to the energy surface  $\epsilon$ ; that is,

$$K(\epsilon, \epsilon') = \frac{1}{2kk'} \int_{|k-k'|}^{k+k'} q v_q(\epsilon, \epsilon') dq. \quad (3)$$

Here the wave vector  $k$  lies on the energy surface  $\epsilon$ ,  $k'$  lies on  $\epsilon'$ ,  $\vec{q} = \vec{k} - \vec{k}'$  is the scattering vector, and we have allowed for some momentum dependence of the retarded interaction  $v_q(\epsilon, \epsilon')$ . An alternative radial dependence of the  $s$ -wave pairing implies a new solution of (1) with an energy dependence  $\Delta(\epsilon)$  distinct from that of the BCS type of solution.

Suppose, in particular, that  $\Delta(\epsilon)$  vanishes at the Fermi surface,  $\Delta(0) = 0$ , and varies linearly with  $\epsilon$  away from the Fermi surface up to energy separations of order the Fermi energy  $E_F$  itself, as illustrated in Fig. 1(a). A metal having such pairing would not be a superconductor. There would be no energy gap at the Fermi surface because  $\Delta(0) = 0$ . The momentum distribution would resemble that of a normal metal, as in Fig. 1(b). There would be neither a Meissner effect nor persistent currents because supercurrents would be destroyed even by elastic scat-

tering. Indeed, all properties involving low-energy excitations would resemble those of a normal metal.

Coherent pairing requires real excitation of pairs of particles out of the normal Fermi sea, leaving pairs of holes behind. The pairing energy is comprised of (1) the single-particle excitation energy, (2) the particle-particle interaction, (3) the hole-hole interaction, and (4) the particle-hole interaction. The Landau quasi-particles in a metal interact primarily via the dynamically screened Coulomb interaction.<sup>7,9</sup> Terms (1)-(3) are thus positive, whereas (4) is negative. However, because the screening decreases as the energy change  $|\epsilon - \epsilon'|$  on scattering increases, the effective Coulomb interaction can be larger in magnitude for (4) than for (2) and (3). Further, the attractive phonon-induced interaction<sup>9,10</sup> reduces (2) and (3) while leaving (4) essentially unaffected. It is thus plausible that a new coherently paired state can have lower energy than the normal state when the net interaction becomes comparable to single-particle energies, i.e., in simple metals of relatively low electron densities or in transition metals with narrow  $d$  bands. The stabilization of the paired state would arise from excitation energies of order the Fermi energy so that the transition temperature would be unobservably high.

A simple example introduced by Falicov<sup>11</sup> illustrates clearly some properties of the proposed state. Suppose  $K(\epsilon, \epsilon')$  to have the simple form

$$K(\epsilon, \epsilon') = K_0(\epsilon, \epsilon') + K_1(\epsilon, \epsilon'); \quad (4a)$$

$$K_0(\epsilon, \epsilon') = V_0, \quad K_1(\epsilon, \epsilon') = V_1 \epsilon \epsilon', \quad \text{both } |\epsilon|, |\epsilon'| < \xi;$$

$$K_0(\epsilon, \epsilon') = K_1(\epsilon, \epsilon') = 0, \quad |\epsilon| \text{ and/or } |\epsilon'| > \xi; \quad (4b)$$

$$V_0 > 0, \quad |V_1| \xi^2 < V_0 \text{ so that } K(\epsilon, \epsilon') \geq 0. \quad (4c)$$

$K_0(\epsilon, \epsilon')$  is the usual square-well approximation to the Coulomb interaction; the cutoff  $\xi$  is of order the Fermi or plasma energy.  $K_1(\epsilon, \epsilon')$  corrects  $K_0(\epsilon, \epsilon')$  somewhat for the energy dependence of the screening; a negative  $V_1$  corresponds to less screening for larger  $|\epsilon - \epsilon'|$ . We suppose  $n(\epsilon)$  to equal  $n(0)$ . There is no BCS or superconducting solution of (1) for the kernel (4). However, a solution of the type proposed here,

$$\begin{aligned} \Delta(\epsilon) &= b\epsilon, \quad |\epsilon| < \xi, \\ &= 0, \quad |\epsilon| > \xi, \end{aligned} \quad (5)$$

with  $b$  given by

$$(1 + b^2)^{1/2} = -2n(0) V_1 \int_0^\xi \epsilon \tanh\left[\frac{1}{2}\beta(1 + b^2)^{1/2}\epsilon\right] d\epsilon, \quad (6)$$

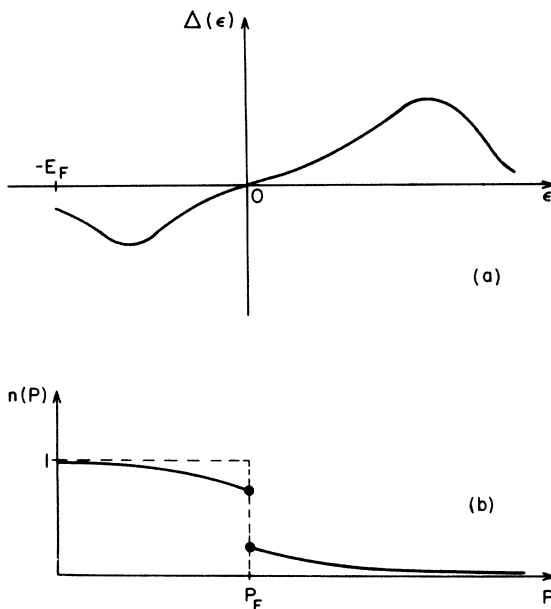


FIG. 1. (a) The dependence of the energy-gap parameter  $\Delta(\epsilon)$  on the single-particle energy  $\epsilon$  measured relative to the Fermi energy  $E_F$  for a hypothetical case of coherent pairing of the second kind, CPII. (b) The corresponding momentum distribution  $n(p)$ .

does exist for  $V_1$  sufficiently negative. Well below the transition temperature,  $b(T) \cong b(0)$ , we have

$$b(0) = [n(0) |V_1| \xi^2 - 1]^{1/2}, \quad V_1 < -[n(0) \xi^2]^{-1}, \\ = 0, \quad V_1 > -[n(0) \xi^2]^{-1}. \quad (7)$$

For small  $b(0)$ , i. e., weak pairing, the transition temperature is proportional to  $b(0)\xi$ :

$$kT_c = (6^{1/2}/2\pi)b(0)\xi. \quad (8a)$$

$T_c$  increases monotonically with  $b(0)$  until for large  $b(0)$ , i. e., strong pairing, it once again is proportional to  $b(0)\xi$ :

$$kT_c = \frac{1}{3}b(0)\xi. \quad (8b)$$

Even for weak pairing, i. e.,  $b \sim 0.1$ ,  $T_c$  would probably be beyond the boiling point of most metals. Moreover, the properties of the new phase exhibit a branch point in the strength of the interaction, in contrast to the essential singularity characteristic of superconductivity.

We have buttressed the above conjectures and plausibility arguments by a rigorous solution of the BCS integral equation (1) for a general interaction and in the weak-pairing and  $T \rightarrow 0$  limits. We have found a denumerably infinite set of potential solutions of (1). Of these, one and one only corresponds to the BCS superconducting state; the remaining states are all of the type conjectured to exist above [Fig. 1(a)]. We may call the BCS superconducting state a state with coherent pairing of the first kind (CPI); the new states may then be called states with coherent pairing of the second kind (CPII). A mixed superconducting state with both CPI and CPII can also occur; above the superconducting transition temperature only the CPII would remain. The explicit mathematical conditions for the stability of CPII reduce to the physical arguments given above.<sup>12</sup> The stability conditions for CPI are essentially unchanged by the presence of CPII.

We have also shown that excited states characterized by the propagation of a real  $p$ -wave singlet pair<sup>13</sup> can occur in both normal metals and metals having CPII. An electromagnetic field can couple to the  $p$ -wave pair, however, only if CPII occurs stably in the ground state. We interpret the Mayer and El Naby resonance in K as optical excitation of a  $p$ -wave pair and hence as evidence for the occurrence of CPII in potassium. Similar observations<sup>14</sup> for Cs suggest that CPII exists in that metal as well. Hodgson has carried out optical measurements on Na films

at room temperature.<sup>15</sup> Structure was seen which may ultimately prove similar to that seen clearly in K and Cs by Mayer and El Naby. Corresponding optical studies have not yet been carried out for Li. For liquid Hg, on the other hand, there is definite evidence that the  $p$ -wave resonance does not occur.<sup>16</sup> All this suggests that the critical value of  $r_s$  above which CPII is stable lies above 2.7 (Hg) and possibly below 4.0 (Na).

The above considerations apply, in principle, to liquid <sup>3</sup>He and to nuclear matter as well as to metals.

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