# Superconductivity in many-valley semiconductors

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Many-valley superconductors are endowed with a number of special properties not shared by ordinary superconductors. In general, superconductivity is possible for either sign of the initial interaction constant; in addition, it is possible to have phase oscillations between various components of the order parameter (i.e., corresponding to the different valleys), similar to phase oscillation of the order parameters in Josephson junctions. Such systems can have one of several types of ground state: 1) a singlet BCS state; 2) a singlet state in which Cooper pairs belonging to different valleys have different phases, and 3) a triplet state. Corresponding to these three states, there are three types of phase oscillation, which are present over a wide range of interaction constants. Fermi-liquid effects are substantial in these oscillations even in the weak-coupling limit, and are found to change the results in both qualitative and quantitative ways.

# **1. INTRODUCTION**

It is well known that a transition to the superconducting state can be observed in many-valley semiconductor alloys in the presence of a sufficiently high density of free carriers. The many-valley nature of the semiconductor is important, if only because it makes the corresponding density of states at the Fermi surface larger than that of a singlevalley semiconductor with the same density; therefore it is natural to expect that the effective interaction will be enhanced, and with it the transition temperature.

Although the many-valley property plays a decisive role in bringing about the superconducting state, it does not follow by any means that its role ends there. On the contrary, one can expect many-valley semiconductors to have other special properties not shared by ordinary semiconductors. The elucidation of some of these properties is the goal of the present work.

We will make use of the simplest type of Bardeen-Cooper-Schrieffer (BCS) model,<sup>2</sup> in which electron-electron interactions are taken into account only between electrons of equal but antiparallel spins and momenta (more precisely, quasimomenta), located in a narrow layer near the Fermi surface. The model Hamiltonian takes the form

$$H = \sum_{\mathbf{p}\mathbf{v}} \xi_{\mathbf{p}} a_{\mathbf{p}\mathbf{v}}^{\perp} a_{\mathbf{p}\mathbf{v}} + \frac{1}{V} \sum_{|\xi_{\mathbf{p}}|, |\xi_{\mathbf{p}'}| < \infty_{o}} \lambda(\mathbf{p}, \mathbf{p}') a_{\mathbf{p}\uparrow}^{+} a_{-\mathbf{p}\downarrow}^{+} a_{-\mathbf{p}\downarrow}^{-} a_{\mathbf{p}\uparrow}, (1)$$

where  $\xi_{\mathbf{p}}$  is the energy of an electron with momentum p, measured from the Fermi energy,  $a_{\mathbf{p}\nu}(a_{\mathbf{p}\nu}^+)$  is the annihilation (creation) operator for an electron with momentum  $\mathbf{p}$  and spin  $\nu = \uparrow, \downarrow$ , and V is the volume.

To proceed further, we must make some concrete assumptions about the character of the band structure. We will postulate conduction-electrons in a conduction band like that of  $SrTiO_3$ . The conduction band of strontium titanate resembles that of the well-known semiconductor silicon, i.e., it consists of six valleys oriented in pairs along three mutually-orthogonal directions. We then make the following assumptions about the interaction:

$$\lambda(\mathbf{p},\mathbf{p}') = \begin{cases} \lambda_1 \text{ if } \mathbf{p} \text{ and } \mathbf{p}' \text{ belong to the same valley} \\ \lambda_2 \text{ if } \mathbf{p} \text{ and } \mathbf{p}' \text{ belong to opposite valleys} \\ \lambda_3 \text{ in all other cases} \end{cases}$$
(2).

The symmetry of the problem requires that we introduce a minimum of three interaction constants which in general can differ both in magnitude and sign. Our simplification consists of replacing three functions by three constants. It follows from the symmetry of the problem that these constants are real.

Let us turn to the formulation of the fundamental physical ideas in this work. Many-valley superconductors, in contrast to the usual kind, are described by multi-component order parameters. In principle, it should be possible in such systems for the various components of the order parameter, to have phase oscillations reminiscent of those seen in Josephson junctions. In order to make clear what we are saying, we consider the limit  $|\lambda_2|$ ,  $|\lambda_3| \ll |\lambda_1|$ . Then in zeroorder approximation (i.e., neglecting  $\lambda_2$  and  $\lambda_3$ ), the phases of the various components of the order parameter (in different valleys) are arbitrary (just as the pair phases in two identical superconductors not coupled by a tunneling transition). By taking  $\lambda_2$ ,  $\lambda_3$  into account, we fix these phase differences; when they deviate from their equilibrium values, currents will flow from valley to valley (similar to Josephson currents). Corresponding to these currents, we will observe oscillations which change the particle distributions in the valleys. Thus, the analogy with Josephson junctions points to the possibility of special oscillations in many-valley superconductors. Such (homogeneous) oscillations will be the subject of the third section.

In the second section, we will investigate equilibrium properties, or more accurately, the possible types of ordering as functions of the relations between the interaction constants. In section 4 we analyze the role of Fermi-liquid effects in the oscillations. Finally, in the fifth section we discuss the results.

#### 2. THE VARIOUS ORDERED PHASES: SUPERCONDUCTIVITY WITH REPULSIVE INTERACTIONS

We will limit ourselves to an investigation of the properties of the order parameter at the transition point. The order parameter  $\Delta(\mathbf{p})$  is introduced in the usual way:

$$\Delta(\mathbf{p}) = \frac{1}{V} \sum_{\mathbf{p}'} \lambda(\mathbf{p}, \mathbf{p}') \langle a_{-\mathbf{p}'\downarrow} a_{\mathbf{p}'\downarrow} \rangle, \qquad (3)$$

where the angle brackets denote thermodynamic averaging. At the transition point  $T_c$  we obtain from (3)

$$\Delta(\mathbf{p}) = -\frac{1}{2V} \sum_{\mathbf{p}'} \lambda(\mathbf{p}, \mathbf{p}') \Delta(\mathbf{p}') \frac{\operatorname{th}(\xi_{\mathbf{p}'}/2T_{\mathrm{c}})}{\xi_{\mathbf{p}'}}.$$
 (4)

For the model we are using here, this expression is in fact a system of six linear algebraic equations for the six components of the order parameter  $\Delta_v$ , v = 1, 2, ..., 6 (i.e., the valley index). We adopt the following notation: pairs of opposite valleys will be denoted by the indices 1, 2 (first pair), 3, 4 (second pair) and 5, 6 (third pair). We have then in place of (4),

$$(1/L+g_{1})\Delta_{1}+g_{2}\Delta_{2}+g_{3}(\Delta_{3}+\Delta_{4}+\Delta_{5}+\Delta_{6})=0,$$
  

$$g_{2}\Delta_{1}+(1/L+g_{1})\Delta_{2}+g_{3}(\Delta_{3}+\Delta_{4}+\Delta_{5}+\Delta_{6})=0$$
(5)

plus four more equations which are obtained from these by interchanging pairs of indices  $(1,2)\leftrightarrow(3,4)$  and  $(1,2)\leftrightarrow(5,6)$ . Here, we use the notation

$$L = \int_{-\omega_0}^{\omega_0} \frac{d\xi}{2\xi} \operatorname{th} \frac{\xi}{2T_c}, \quad g_i = \gamma \lambda_i \quad (i = 1, 2, 3),$$

where  $\gamma$  is the density of states at the Fermi surface per valley, and the  $g_i$  are dimensionless coupling constants.

The transition temperature  $T_C$  is expressed in terms of an effective interaction constant g, which must be negative, in the usual way:

 $T_c = 1,14\omega_0 \exp[-1/|g|].$ 

It is not hard to see that the symmetry of the system of equations (5) leads to three types of solution:

1) All  $\Delta_{v}$  equal:

$$\Delta_1 = \Delta_2 = \ldots = \Delta_6, \quad g = g_1 + g_2 + 4g_3. \tag{6}$$

This is a BCS type of ground state, i.e., the Cooper pairs are singlet, and a common phase for all pairs.

2) There is also another type of ground state with singlet pairs, in which the  $\Delta_{\nu}$  have equal values for opposite valleys; these values are connected by an additional relation:

$$\Delta_1 = \Delta_2, \quad \Delta_3 = \Delta_4, \quad \Delta_5 = \Delta_6, \quad \Delta_1 + \Delta_3 + \Delta_5 = 0. \tag{7}$$

That is to say, the phases of Cooper pairs belonging to different pairs of opposing valleys are different. Relation (7) fixes the relative phases of the three different Cooper pairs. Here, the role of g is played by the quantity  $g_s = g_1 + g_2 - 2g_3$ .

3) Finally, the last possibility is a triplet state  $(\Delta_{\mathbf{p}} = -\Delta_{-\mathbf{p}})$ . The quantities  $\Delta_{\nu}$  differ in sign for opposite valleys, but are otherwise arbitrary:

$$\Delta_1 = -\Delta_2, \quad \Delta_3 = -\Delta_4, \quad \Delta_5 = -\Delta_6. \tag{8}$$

The effective interaction constant is

# $g_1 = g_1 - g_2$ .

The solutions listed above exhaust all the possibilities, as follows if only from a comparison of the number of "degrees of freedom" of the system (six complex order parameters) and the number of solutions (also six). The latter follows from the fact that solution 2 is doubly degenerate (two arbitrary parameters) and solution 3 is triply degenerate (three arbitrary parameters).

Usually it is assumed that all the  $g_i$  are negative (attractive); then, naturally, the state realized is 1, which is the analog of the usual superconducting BCS state. For other choices of sign of the constants  $g_i$ , there will be a competition between state 1 and the states 2 and 3. Furthermore, even if all the  $g_i$  are positive (i.e., the initial interaction is repulsive) so that the BCS state is impossible in principle, it is nonetheless possible for superconductivity to appear, provided only that some one of the two effective constants  $g_s$  or  $g_i$  is negative, i.e., that there is an effective attraction in the states with symmetries 2 or 3. This is analogous to pairing with nonzero momenta in the isotropic case. Another point of view is set forth in the Conclusions.

## 3. NATURAL OSCILLATIONS

Let us turn to an investigation of the natural oscillations. We will assume that the Cooper pairs are singlet (states 1 or 2), and limit ourselves to homogeneous oscillations at zero temperature. In this case it is perhaps simplest to make use of the Anderson pseudospin approach, in which each pair of electron states  $(p\uparrow, -p\downarrow)$  there is associated with a spin-1/2 operator in the following way:

$$\begin{aligned}
1 - a_{p_{\uparrow}} + a_{p_{\uparrow}} - a_{-p_{\downarrow}} + a_{-p_{\downarrow}} = 2S_{p_{z}}, \\
a_{p_{\uparrow}} + a_{-p_{\downarrow}} + = S_{p} - S_{p_{x}} - iS_{p_{y}}, \\
a_{-p_{\downarrow}} a_{p_{\uparrow}} = S_{p} + S_{p_{x}} + iS_{p_{y}}.
\end{aligned}$$
(9)

With the help of these operators, we rewrite the Hamiltonian operator (1) in the form

$$H = -\sum_{\mathbf{p}} 2\xi_{\mathbf{p}} S_{\mathbf{p}\mathbf{z}} + \frac{1}{V} \sum_{\mathbf{p}\mathbf{p}'} \lambda(\mathbf{p}, \mathbf{p}') S_{\mathbf{p}}^{-} S_{\mathbf{p}'}^{+}, \qquad (10)$$

where we discard an inessential constant. The equations of motion

$$id\mathbf{S}/dt = [\mathbf{S}, H]$$

take the form

$$i \frac{dS_{\mathbf{p}^{+}}}{dt} = 2\xi_{\mathbf{p}}S_{\mathbf{p}^{+}} + \frac{2}{V}\sum_{\mathbf{p}'}\lambda(\mathbf{p},\mathbf{p}')S_{\mathbf{p}z}S_{\mathbf{p}'}^{+},$$

$$i \frac{dS_{\mathbf{p}z}}{dt} = \frac{1}{V}\sum_{\mathbf{p}'}\lambda(\mathbf{p},\mathbf{p}')(S_{\mathbf{p}'}-S_{\mathbf{p}}^{+}-S_{\mathbf{p}}^{-}S_{\mathbf{p}'}^{+}).$$
(11)

Equation (3) for the order parameter now appears as follows

$$\Delta(\mathbf{p}) = \frac{1}{V} \sum_{\mathbf{p}'} \lambda(\mathbf{p}, \mathbf{p}') \langle S_{\mathbf{p}'}^{+} \rangle.$$
(12)

In Eqs. (11), the operators can be regarded as simple numbers; this is equivalent to the self-consistent-field approximation, which, has been used successfully in the theory of superconductivity. As for the oscillations, we will consider classical oscillations of the spin system, instead of trying to find the corresponding magnon spectrum.

In order to determine the equilibrium parameters, we equate the time derivative in (11) to zero, from which we obtain

$$S_{\mathbf{p}}^{+} = -\frac{\Delta_{0}(\mathbf{p})}{2E_{\mathbf{p}}}, \quad S_{\mathbf{p}z} = \frac{\xi_{\mathbf{p}}}{2E_{\mathbf{p}}}, \quad E_{\mathbf{p}} = (\xi_{\mathbf{p}}^{2} + |\Delta_{0}(\mathbf{p})|^{2})^{\frac{1}{2}}, (13)$$

where  $\Delta_0(\mathbf{p})$  is the equilibrium order parameter, which is determined with the help of (12) and (13). Here it is assumed that the modulus of the order parameter  $|\Delta_0|$  is the same for all the valleys; this is certainly true for state 1, for which all components of the order parameter are the same (see (6)). The equation for  $|\Delta_0|$  takes the form

$$1 = -g \int_{0}^{1} d\xi \, (\xi^{2} + |\Delta_{0}|^{2})^{-\gamma_{2}}. \tag{14}$$

There is also a solution for constant values of  $|\Delta_0|$  for state 2, as is clear from (7). In this case,  $\Delta_0$  (**p**) can be chosen, e.g., in the following form

$$\Delta_{1} = |\Delta_{0}|, \quad \Delta_{3} = |\Delta_{0}|e^{i(2\pi/3)}, \quad \Delta_{5} = |\Delta_{0}|e^{-i(2\pi/3)}, \quad (15)$$

where for  $|\Delta_0|$  we have equations of the type (14) with the replacement  $g \rightarrow g_s$ . No other possibilities were investigated. As for state 3 with triplet pairing, we will not investigate it either since it is not amenable to the pseudospin approach.

Let us investigate small departures from the equilibrium position. The corresponding increments to the equilibrium values we denote as follows:

$$\Delta^{(i)}(p) - \text{increment to } \Delta_0(\mathbf{p}), \ S_{\mathbf{p}} - \text{to } S_{\mathbf{p}^+}, \ \sigma_{\mathbf{p}} - \text{to } S_{pz}.$$
(16)

After linearization, Eqs. (11) and (12) take the form

$$i\frac{dS_{\mathbf{p}}}{dt} = 2\xi_{\mathbf{p}}S_{\mathbf{p}} + \frac{\Delta_{0}(\mathbf{p})}{\xi_{\mathbf{p}}} [\Delta_{0}^{*}(\mathbf{p})S_{\mathbf{p}} + \Delta_{0}(\mathbf{p})S_{\mathbf{p}}^{*}] + \frac{\xi_{\mathbf{p}}}{E_{\mathbf{p}}}\Delta^{(1)}(\mathbf{p}),$$

$$\sigma_{\mathbf{p}} = \frac{1}{2\xi_{\mathbf{p}}} [\Delta_{0}^{*}(\mathbf{p})S_{\mathbf{p}} + \Delta_{0}(\mathbf{p})S_{\mathbf{p}}^{*}],$$

$$\Delta^{(1)}(\mathbf{p}) = \frac{1}{V} \sum_{\mathbf{p}'} \lambda(\mathbf{p}, \mathbf{p}')S_{\mathbf{p}'}.$$
(17)

The second of these equations is a consequence of the constancy of the length of the spin vector. We seek solutions in the form

$$\Delta^{(1)}(\mathbf{p}) = e^{i\varphi_{\mathbf{p}}} \left( \Delta_{\omega} e^{-i\omega t} + \Delta_{-\omega} e^{i\omega t} \right),$$
  

$$S_{\mathbf{p}} = e^{i\varphi_{\mathbf{p}}} \left( S_{\omega} e^{-i\omega t} + S_{-\omega} e^{i\omega t} \right).$$
(18)

From the first equation of (17) we obtain

$$S_{\omega} = \frac{-(2E^2 - |\Delta_0|^2 + \omega\xi)\Delta_{\omega} + |\Delta_0|^2\Delta_{-\omega}}{E(4E^2 - \omega^2)}.$$
 (19)

Substituting (18) and (19) into the third equation of (17), we obtain

$$\Delta_{\omega}(\mathbf{p}) = \frac{1}{V} \sum_{\mathbf{p}'} \tilde{\lambda}(\mathbf{p}, \mathbf{p}') \\ \times \left\{ \frac{-(2E^2 - |\Delta_0|^2 + \omega\xi) \Delta_{\omega} + |\Delta_0|^2 \Delta_{-\omega}}{E(4E^2 - \omega^2)} \right\}_{\mathbf{p}'},$$

$$\tilde{\lambda}(\mathbf{p}, \mathbf{p}') = e^{-i\varphi_{\mathbf{p}}} \lambda(\mathbf{p}, \mathbf{p}') e^{i\varphi_{\mathbf{p}'}}.$$
(20)

It is not difficult to analyze this equation by following the procedures used to analyze (4). We hardly lose anything of importance if we first simplify (20) by discarding from under the summation sign the terms which contain  $\xi$  to first order, and which upon summing give only a small contribution (zero for a constant density of states). Having done this, we obtain in place of (20)

$$\Delta_{\omega} \approx \frac{1}{V} \sum_{\mathbf{p}'} \tilde{\lambda}(\mathbf{p}, \mathbf{p}') \left\{ \frac{-(2E^2 - |\Delta_0|^2) \Delta_{\omega} + |\Delta_0|^2 \Delta_{-\omega}}{E(4E^2 - \omega^2)} \right\}_{\mathbf{p}'}.$$
(21)

Let us investigate the simplest case—state 1, for which  $\varphi_{\mathbf{p}}$  is a constant and  $\tilde{\lambda} = \lambda$ . In this case, the solutions can be of two types:

a) 
$$\Delta_{\omega} = \Delta_{-\omega}^*$$
, b)  $\Delta_{\omega} = -\Delta_{-\omega}^*$ .

In case (a) we have oscillations of the modulus and in case (b) oscillations of the phase of the order parameter; in the lowest-order approximation these oscillations turn out thus to be independent. Let us first investigate the phase oscillations  $\Delta_{\omega} = -\Delta_{-\omega}^{*}$  (we will study the modulus oscillations later). The system of equations for these oscillations coincides precisely with (5) if in place of L we substitute the quantity  $L_{\varphi}$ , which is defined in the following way:

$$L_{\varphi} = \int_{-\omega_{0}}^{\omega_{0}} d\xi \frac{2E}{4E^{2} - \omega^{2}}.$$
 (22)

Again there are three sets of solutions:

A)  $\Delta_{\omega}$  is independent of the valley number (a condition similar to (6)). The equation for the frequency takes the form

$$1 = -gL_{\varphi}.$$
 (23)

A comparison with (14) shows that there is a unique solution to this equation:  $\omega = 0$ ; This solution is connected as usual, with the degeneracy of the state with respect to the phase of the order parameter, and does not correspond to any oscillations.

B) The quantities  $\Delta_{\omega}$  are related by conditions of type (7). The equation for the natural frequency

$$1 = -g_s L_{\varphi} \tag{24}$$

has a solution for coupling constants in the interval  $g < g_s < 0$ ; for  $g_s \rightarrow 0$  we obtain  $\omega \rightarrow 2|\Delta|$ , while for  $g_s \rightarrow g$  we obtain  $\omega \rightarrow 0$  (the stability boundary for the initial state). In these limiting cases the frequency of the oscillations is easily calculated from (24). Thus, for  $g_s \rightarrow g$  ( $\omega \ll 2|\Delta|$ ) it equals

$$\omega^2 = 4|\Delta|^2 (g_s - g)/gg_{\varepsilon}.$$
(25)

For  $g_s \rightarrow 0$   $(2|\Delta| - \omega \leq |\Delta|)$  we obtain the following expression:

$$\omega^{2} = 4 |\Delta|^{2} \left[ 1 - \frac{\pi^{2}}{4} \left( \frac{gg_{\bullet}}{g_{\bullet} - g} \right)^{2} \right].$$

$$(26)$$

C) The quantities  $\Delta_{\omega}$  are subject to a condition of type (8). The equation for the frequency takes the form

$$1 = -g_t L_{\varphi}. \tag{27}$$

Here, we can repeat everything that was said concerning the previous case (substituting  $g_t$  for  $g_s$ ).

We note that in case (B) there is a double degeneracy and in case (C) a triple degeneracy.

The equations for oscillations of the modulus of the order parameter are obtained by substituting  $L_{\mu}$  for  $L_{\varphi}$ , where

$$L_{\mu} = \int_{-\infty}^{\infty} d\xi \frac{2\xi^{2}}{E(4E^{2} - \omega^{2})}.$$

It is not difficult to show that these equations have no solutions.

What is happening in the presence of such oscillations? It is not hard to show that oscillations of type (B) are accompanied by oscillations of the number of particles in each valley (synchronous for opposing valleys); of course, the total number of particles remains constant. For type (C) oscillations, there occurs a redistribution of spins in pairs of opposing valleys: the spin of each valley (zero in the ground state) varies out of phase with the spin of its opposite valley.

#### 4. ROLE OF FERMI LIQUID EFFECTS

Up to now, interactions have been taken into account only to the extent that they lead to the creation of Cooper pairs. It would seem that strictly Fermi-liquid effects, which are also present in the normal state, would in the case of weak interactions lead only to small corrections to our results. It turns out, however, that for oscillations whose frequency is close to  $2|\Delta_0|$ , these corrections become substantial; they will be the topic of discussion in this section.

In order to take into account the Fermi-liquid corrections, it is necessary to generalize the model as follows: in the original equation (11) we must assume that the energy of a normal electron  $\xi_p$  depends on the distribution function, as is usual in the Landau theory of Fermi liquids.<sup>3</sup> We limit ourselves to the case of weak interactions; in lowest-order perturbation theory, the lowest perturbation-theory contributions to the electron self-energy part give the desired correction  $\xi_p^{(1)}$  to the single particle energy  $\xi_p$  in the normal state:

$$\zeta_{\mathbf{p}}^{(\prime)} = \xrightarrow{} + \xrightarrow{} . \quad (28)$$

Here, as usual,<sup>4</sup> the solid line corresponds to the electron Green's function and the dashed line to the interaction. For our purposes it is sufficient to include in (28) the zero-order (non-interacting) Green's function of the electron. Even in the simplest graphs (28), there will in general appear a different set of interaction constants than in the Cooper channel.

Because we want to analyze this question in principle, we limit ourselves to the simplest variant. Namely, we will assume that we can use the same set of constants given in (2), i.e.,  $\lambda_1$  corresponds to interactions between particles without changes in the valley number,  $\lambda_2$  to interactions for transitions between opposing valleys, and  $\lambda_3$  to interactions involving transitions to the other valleys. In this case, the first graph in (28) makes only a constant (i.e., independent of oscillations) contribution, because its magnitude is determined by the total density. The contribution of the second graph can be written in the form

$$\xi_{\mathbf{p}\sigma}^{(1)} = -\frac{1}{V} \sum_{\mathbf{p}'} \lambda(\mathbf{p}, \mathbf{p}') n_{\mathbf{p}'\sigma}, \qquad (29)$$

where  $n_{\mathbf{p}'\sigma}$  is the distribution function for electrons with given spin and quasimomentum.

We are interested in the change produced in  $\xi_p$  in the course of the oscillations (we will call this deviation  $\tilde{\xi}_p$ ). It turns out that we can connect  $\tilde{\xi}_p$  with the variable  $\sigma_p$  introduced earlier [Eq. (16)]; actually,  $\sigma_p$  is related to the change in the sum  $(n_{p1} + n_{-p1})$ , and the problem is symmetric in the states  $(\mathbf{p}\uparrow)$  and  $(-\mathbf{p}\downarrow)$ . We can therefore, write

$$\tilde{\xi}_{\mathbf{p}} = \frac{1}{V} \sum_{\mathbf{p}'} \lambda(\mathbf{p}, \mathbf{p}') \sigma_{\mathbf{p}'}.$$
(30)

Let us linearize equation (11) including the increment  $\xi_{\mathbf{p}}$  (30). The first of these equations then takes the form

$$i\frac{dS_{\mathbf{p}}}{dt} = 2\xi_{\mathbf{p}}S_{\mathbf{p}} + \frac{\Delta_{\mathbf{0}}}{\xi_{\mathbf{p}}}(\Delta_{\mathbf{0}}^{*}S_{\mathbf{p}} + \Delta_{\mathbf{0}}S_{\mathbf{p}}^{*}) + \frac{\xi_{\mathbf{p}}}{E_{\mathbf{p}}}\Delta_{\mathbf{p}}^{(i)} - \frac{\Delta_{\mathbf{0}}}{E_{\mathbf{p}}}\tilde{\xi}_{\mathbf{p}}.$$
 (31)

The remaining equations coincide with the second and third equations in (17); naturally, we must also solve equation (30) along with them. We note that the quantity  $\xi_{p}$  which appears in these equations includes the equilibrium Fermiliquid correction (28), which in the model under investigation here is not significant because it reduces simply to a renormalization of the chemical potential. As before, we look for a solution in the form (18), and write for  $\xi_{p}$ 

$$\xi_{\mathfrak{p}} = (\xi_{\omega} e^{-i\omega t} + \xi_{-\omega} e^{i\omega t}) \tag{32}$$

 $(\xi_{\omega} = \xi^*_{-\omega})$  because of the reality condition). We then proceed as before: from (31) we obtain

$$S_{\omega} = [-(2E^{2} - |\Delta|^{2} + \omega\xi)\Delta_{\omega} + |\Delta|^{2}\Delta_{-\omega} + |\Delta|(\omega + 2\xi)\xi_{\omega}]/E(4E^{2} - \omega^{2}).$$
(33)

Taking this relation into account in the other equations, we obtain

$$\Delta_{\omega}(\mathbf{p}) = \frac{1}{V} \sum_{\mathbf{p}'} \tilde{\lambda}(\mathbf{p}, \mathbf{p}') \\ \times \left[ \frac{-(2E^2 - |\Delta|^2 + \omega\xi) \Delta_{\omega} + |\Delta|^2 \Delta_{-\omega} + |\Delta| (\omega + 2\xi) \xi_{\omega}}{E (4E^2 - \omega^2)} \right]_{\mathbf{p}'}$$
(34)

$$\begin{split} \boldsymbol{\xi}_{\boldsymbol{\omega}}(\mathbf{p}) &= \frac{1}{V} \sum_{\mathbf{p}'} \lambda(\mathbf{p}, \mathbf{p}') \\ &\times \left\{ \frac{4 |\Delta|^2 \boldsymbol{\xi}_{\boldsymbol{\omega}} - |\Delta| \left[ (2\boldsymbol{\xi} + \boldsymbol{\omega}) \Delta_{\boldsymbol{\omega}} + (2\boldsymbol{\xi} - \boldsymbol{\omega}) \Delta_{-\boldsymbol{\omega}}^* \right]}{2E \left( 4E^2 - \boldsymbol{\omega}^2 \right)} \right\}_{\mathbf{p}'} \end{split}$$

As we did earlier in (21), we discard in (34) terms linear in  $\xi_p$ ; in addition, we limit ourselves to oscillations in state 1; in this case, we can use the equations

$$\begin{aligned} (\Delta_{\omega} + \Delta_{-\omega} \cdot)_{\mathbf{p}} \\ \approx -\frac{1}{V} \sum_{\mathbf{p}'} \lambda(\mathbf{p}, \mathbf{p}') \left[ \frac{2\xi^{2}}{E(4E^{2} - \omega^{2})} (\Delta_{\omega} + \Delta_{-\omega} \cdot) \right]_{\mathbf{p}'}, \\ (\Delta_{\omega} - \Delta_{-\omega} \cdot)_{\mathbf{p}} \\ \approx \frac{1}{V} \sum_{\mathbf{p}'} \lambda(\mathbf{p}, \mathbf{p}') \left[ \frac{-2E^{2}(\Delta_{\omega} - \Delta_{-\omega} \cdot) + 2\omega |\Delta| \xi_{\omega}}{E(4E^{2} - \omega^{2})} \right]_{\mathbf{p}'}, \end{aligned}$$
(35)  
$$\xi_{\omega}(\mathbf{p}) \approx \frac{1}{V} \sum_{\mathbf{p}'} \left[ \lambda(\mathbf{p}, \mathbf{p}') - 2\lambda(\mathbf{p}, \mathbf{p}) \right] \\ \times \left[ \frac{4|\Delta|^{2} \xi_{\omega} - \omega |\Delta| (\Delta_{\omega} - \Delta_{-\omega} \cdot)}{2E(4E^{2} - \omega^{2})} \right]_{\mathbf{p}'}. \end{aligned}$$

The first equation in (35) is the equation for oscillations of the order-parameter modulus. It coincides with the analogous equation derived in the previous section, and has likewise no solution.

The last two equations are connected with oscillations of the phase of the order parameter and of the Fermi liquid increment to the single-particle energy  $\xi_p$ . These equations are analyzed in analogy with the previous section. Again we have the same set of solutions, with the same symmetry of  $\xi_{\omega}$ and  $\Delta_{\omega} - \Delta_{-\omega}^*$ . Let us investigate these solutions.

A) The quantities  $\Delta_{\omega}$  and  $\xi_{\omega}$  do not depend on the valley index. In this case we obtain Eq. (23) again, since the Fermi-liquid correction does not enter here.

B) The quantities  $\Delta_{\omega}$  and  $\xi_{\omega}$  are coupled by conditions of the type (7). The equation for the natural frequency takes the form

$$1 + g_s L_{\varphi} - g_s (1 - g_s/g) L_{\Delta} = 0, \tag{36}$$

$$\dot{L}_{\Delta} = \int_{0}^{\infty} d\xi \frac{4|\Delta|^{2}}{E(4E^{2} - \omega^{2})}.$$
 (37)

The last term in (36) is the sought-after contribution due to Fermi-liquid effects. It is not hard to see that the Fermi-liquid increment is significant for frequencies close to  $2|\Delta|$  (because of the weakness of the interaction). In order to convince oneself of this, it is sufficient to write the expressions for the natural frequency in limiting cases. In the low-frequency limit we obtain the expression

$$\omega^2 = 4|\Delta|^2 (1-g_s) (g_s-g)/gg_s.$$
(38)

For  $\omega \rightarrow 2|\Delta|$  we have

$$\omega^{2} = 4 |\Delta|^{2} \left[ 1 - \frac{\pi^{2}}{4} \left( \frac{g_{s}^{2}}{g_{s} - g} \right)^{2} \right].$$
(39)

C) The quantity  $\Delta_{\omega}$  (along with  $\xi_{\omega}$ ) is subject to a condition of the type (8) (oscillations of the triplet increment to the order parameter). We obtain the equation along with all the conclusions of example (B) if we make everywhere the substitution  $g_s \rightarrow g_t$ .

In cases (B) and (C) we have twofold and threefold degeneracy, as before.

Let us compare expressions (38), (39) with (25), (26). The limit  $\omega \ll 2|\Delta|$  occurs when  $(g_s - g) \ll g^2$ ; the limit  $\omega = 2|\Delta|$  is reached when  $g_s - g \gg g^2$ . Both limiting expressions for the natural frequencies contain only small contributions from Fermi-liquid effects so long as  $g_s - g \not\leq |g|$ . For  $g_s - g \gtrsim |g|$ , the correction is appreciable, as is clear from a comparison of (26) and (39).

At first glance, it may seem strange that in the weakinteraction situation Fermi-liquid effects turn out to be not small. They are important in this case in a narrow frequency range (but over a wide range of coupling constants  $g_s$ ); it is this which manifests the weakness of the interaction. As is well-known in the theory of Fermi liquids, even a weak interaction leads to qualitatively new effects (the appearance of zero sound for repulsive interactions). In our case, what is qualitatively new in the solution (39) compared to (26) is that the solution exists for either sign of the coupling constant  $g_s$ , in contrast to the solution (26).

The question of the physical meaning of such oscillations is discussed in Refs. 5 and 6; however, apparently there is as yet no clear answer to this question. By allowing in the calculation for the influence of Fermi-liquid effects, we hope to shed some light on this situation. In the case  $g_s < 0$ , natural oscillations are possible, as we have seen, even when Fermi-liquid effects are not taken into account; the latter turn out to be important only in a narrow frequency interval. Apparently, these oscillations can be interpreted as excitonlike excitations in a Cooper pair system; such excitations are more reminiscent of Wannier-Mott excitons than of Frenkel excitons. This interpretation is close to the point of view of Bardasis and Schrieffer;<sup>5</sup> they, however, proposed it for the case  $g_s > 0$ . It seems to use that the case  $g_s > 0$  must be interpreted in a different way: the appearance of a solution for  $g_s > 0$  is essentially bound up with Fermi-liquid effects, in the absence of which no such solution exists. For this reason, one can suppose that this is an analog of zero sound in a Fermi liquid; one might expect that in such a system, the zero-sound type of oscillations can exist for  $\omega \ge 2|\Delta|$  (with wavelength smaller than the dimensions of a Cooper pair), and that this mode goes over into the oscillations obtained here in the infinite-wavelength limit.

To conclude this section, we note the following facts. Our equations (35) were written down in a form which nowhere contains formally the specific many-valley characteristics. Therefore they can also be used for the isotropic case, thereby taking into account interactions with nonzero angular momentum. For this reason, our results for many-valley superconductors coincide with those of Refs. 5 and 6 for isotropic superconductors; in our case, however, we must speak of excitations whose symmetry differs from that of the Cooper pairs in the ground state, rather than interactions with nonzero angular momentum.

We emphasize that Eq. (35) was obtained by taking explicit account of Fermi-liquid effects; only after doing this do we obtain agreement with the results derived, e.g., in Ref. 6 by a diagrammatic method.<sup>6</sup> It would, however, be difficult to reveal the role of these effects by diagrammatic methods.

## 5. CONCLUSION

The meaning of the various kinds of orderings obtained in this work can be clarified by viewing them in another way: through the Anderson pseudospin formalism. Let us begin with the BCS results. In this theory, the ground state is made up of singlet Cooper pairs with a common phase. This corresponds to all the pseudospins pointing in the same direction (in a plane perpendicular to the z-axis), i.e., independent of the valley index. This "ferromagnetic" state is energetically advantageous if  $\lambda < 0$  (electrons attracting one another). If, however,  $\lambda > 0$  (repulsive interaction of electrons), the "ferromagnetic" ordering (the BCS state) cannot occur; however, it is still possible to have an "antiferromagnetic" type of ordering. This actually takes place in states 2 and 3. Actually, in state 2 all the spins in a given valley, along with those in its opposing valley, are parallel (in the xy-plane), while for different pairs of valleys they are directed at an angle of 120° and sum up to zero; in pseudospin language this is an "antiferromagnetic" type of state. In state 3, the projections of the pseudospins in opposing valleys are antiparallel.

Apparently, it was Kondo<sup>8</sup> who first called attention to the possibility of superconductivity for either sign of the interband transition constants J; he investigated a two-band model, in which  $T_C$  was determined by an effective coupling constant depending in the general case on  $J^2$ . In our problem of equivalent valleys, it is possible to clarify somewhat the meaning of this result: superconductivity is possible for both signs of the interaction (the constants  $\lambda_1, \lambda_2, \lambda_3$ ) provided only that there is an effective attraction at some "harmonic". However, for valleys separated in momentum space, the Kondo mechanism<sup>8</sup> for enhanced superconductivity is "switched off" (in a model where only the interactions between electrons with opposite momenta is taken into account)-the Cooper pairs cannot move from one valley to another (because of conservation of momentum). This is how the order parameter was chosen in Refs. 8 and 9.

Consider now the possibility of exciting and detecting these oscillations. It appears that one way to excite oscillations is to apply a sufficiently rapid uniaxial stress. It is well known that if such a stress is applied along the  $\langle 100 \rangle$  axis, the corresponding pair of valleys shifts away from the others in energy. If the time of application of the stress is long compared to a period of a natural oscillation, then to first approximation the system will be in equilibrium at each instant of time (the adiabatic approximation); the next approximation, as usual, gives rise to excitation of natural oscillations.

It is interesting to study oscillations of finite wavelength. Apparently, such oscillations will be accompanied by currents; if this is so, then they can be excited and observed by electromagnetic methods.

Finally, we note that in this work we have not included impurity scattering. Apparently, our results remain valid as long as the condition  $|\Delta|\tau_{iv} \ge 1$  is fulfilled, where  $\tau_{iv}$  is the electron mean free time between intervalley scatterings. When it collides with an impurity, an electron can either scatter within its "own" valley or transfer to another valley; these processes have different scattering times. The most effective scattering is the one with a small momentum transfer  $p_0$  (intravalley scattering). This is to be expected (for scattering by charged impurities) in view of the strong Coulomb interaction at small momenta  $\sim p_0$  (intervalley scattering involves a momentum transfer  $\sim 1/a$ , where a is the lattice

period). This assertion is confirmed in experiments, that is  $\tau_{iv} \! \gg \! \tau$ , where  $\tau$  is the mean free time between intravalley scatterings.<sup>11</sup> It is interesting that  $\tau_{iv}$  depends strongly on what sort of impurity is present in the semiconductor, and can vary by several orders of magnitude. Thus, when As atoms are added to Ge, the time  $\tau_{iv}$  has a value of  $\approx 10\tau$ , or  $\approx 3 \times 10^{-13}$  sec for  $n_{\rm As} \approx 10^{19}$  cm<sup>-3</sup>. If we use Sb as a donor instead,  $\tau_{iv}$  increases sharply to  $\approx 10^3 \tau$ , or  $6 \times 10^{-11}$  sec ( $\hbar/$  $\tau_{iv} \approx 0.1$  K) for  $n_{sb} \approx 10^{18}$  cm<sup>-3</sup> (Ref. 11). It is also necessary to keep in mind that for semiconductors one encounters critical temperatures  $T_c \sim 10$  K (Refs. 12, 13). Thus, the question of whether or not the condition  $|\Delta|\tau_{iv} \ge 1$  is fulfilled in some specific semiconductor (and what impurity to use to achieve it) is apparently one which needs more experimental study. It may turn out to be the case that for well-known semiconductors (e.g., Ge) the time  $\tau_{iv}$  will reach saturation as a function of impurity density, while  $T_c$  and  $|\Delta|$  grow as the density increases.

A few comments on the Coulomb interaction: an investigation of its effects on these oscillations reveals that it can modify only the type (A) oscillations, which will then oscillate at the well-known plasma frequency. The frequencies of oscillation of types (B) and (C) are unaffected, since in these oscillations the charge density does not change; electrons are only redistributed among the valleys.

Before the completion of this work, the authors were apprised of the work of Legett.<sup>9</sup> Legett investigated twoband superconductivity with two order parameters, and showed that in a two-band system oscillations in the relative phases of the two condensates were possible. He also discussed in detail the physical meaning of these oscillations. We point out that the primary difference between our work and his is that Legett's approach cannot be directly applied to the case of valleys separated in momentum space, for the same reason that was discussed earlier in connection with Kondo's work.<sup>8</sup> In our work, we have found types of ground state which are different from Legett's; this clarifies the role of Fermi-liquid interactions, which turn out to be important even in the limit of weak coupling.

The authors are grateful to V. L. Ginzburg, B. I. Ivlev, A. I. Larkin, and M. B. Entin for discussing this work, and also Yu. V. Kopaev and E. G. Maksimova for informing us of Legett's work. One of the authors (V. A. Borisyuk) would like to thank V. I. Ponomarev for continuing and thorough discussions.

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Translated by Frank J. Crowne