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Dependence of the Superconducting Energy Gap on the Phonon Spectrum and Order-Disorder Effects[1])

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(14. IX. 67)

Abstract. The superconducting gap equation is solved for a general phonon spectrum in the weak coupling limit and at $T = 0$. The result is expressed by a limiting phonon momentum q_M which reduces the energy gap if $q_M < 2\, k_F$. An application to ordered and disordered alloys is discussed.

I. Introduction

In this note [1] we discuss the influence of the phonon spectrum on the energy gap of a superconductor. The basic physical remark is that in the absence of Umklapp processes [2], the existence of a limiting phonon momentum q_M may lead to a reduction of the phase space available for the scattering of the Cooper pairs and, as a consequence reduce the energy gap. To obtain a quantitative result we solve the gap equation proposed by BOGOLIUBOV et al. [3] at $T = 0$ in the weak coupling limit and for a spherical Fermi surface. The solution, which is given in Section II and in an appendix generalizes somewhat the result of BOGOLIUBOV et al. [3] and exhibits the reduction of the phase space in the simple form of a cut-off factor. In Section III we discuss the consequence of this effect for ordered and disordered alloys where one expects a variation of the transition temperature with concentration.

II. The Super Conducting Gap Equation

We start from the gap equation proposed by BOGOLIUBOV et al. [3],

$$C(\boldsymbol{k}) = \frac{\lambda}{2(2\pi)^3} \int d^3k' \, \frac{\omega\,(\boldsymbol{k}-\boldsymbol{k}')\, g^2\,(\boldsymbol{k}-\boldsymbol{k}')}{\omega\,(\boldsymbol{k}-\boldsymbol{k}') + |\,\xi(\boldsymbol{k})\,| + |\,\xi(\boldsymbol{k}')\,|} \, \frac{C(\boldsymbol{k}')}{(C^2(\boldsymbol{k}') + \xi^2(\boldsymbol{k}'))^{1/2}} \tag{1}$$

where $C(\boldsymbol{k})$ is the energy gap, $\lambda\, g^2(\boldsymbol{q})$ is the coupling constant, $\omega(\boldsymbol{q})$ the phonon frequency and $\xi(\boldsymbol{k})$ the excitation energy measured from the Fermi surface. The kernel of (1) is only important in the neighbourhood of the Fermi surface which we take to be spherical. Then one can set $|\boldsymbol{k}| = |\boldsymbol{k}'| = k_F$ in the phonon frequency and in the coupling constant. Defining $t \equiv \boldsymbol{k}\,\boldsymbol{k}'/k_F^2$ (1) can be written as

$$C(\xi;\lambda) = \lambda \int_0^\infty d\xi' \, A(\xi;\xi')\, C(\xi';\lambda)\, [C^2(\xi';\lambda) + \xi'^2]^{-1/2} \tag{2}$$

with

$$A(\xi;\xi') = \frac{1}{2} \int_{-t_M}^{1} dt \, \frac{\omega\,(k_F\,[2\,(1-t)]^{1/2})\; g\,(k_F\,[2\,(1-t)]^{1/2})\; N(\xi')}{\omega\,(k_F\,[2\,(1-t)]^{1/2}) + |\,\xi\,| + |\,\xi'\,|}\,. \tag{3}$$

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Here

$$t_M = \begin{cases} \frac{1}{2}\,[(q_M/k_F)^2 - 2] & \text{for} \quad q_M \leqslant 2\,k_F \\ 1 & \text{for} \quad q_M > 2\,k_F \end{cases} \tag{3a}$$

and $N(\xi)$ is the density of states. To solve (2) we notice that $C(\xi;\lambda)$ is non-analytic in λ as $\lambda \to 0$ so that an Ansatz which factorizes this singularity is appropriate:

$$C(\xi;\lambda) = \overline{\omega}(\xi;\lambda)\,\sigma(\lambda)\,. \tag{4}$$

The analytic $\overline{\omega}(\xi;\lambda)$ can be chose such that $\overline{\omega}(\xi;\lambda=0) \neq 0$ while on physical grounds $\sigma(\lambda=0)=0$. Deferring the details of the derivation to an appendix the solution in this weak coupling limit is given by

$$C(\xi;\lambda) = \exp(-1/\lambda\,A(0;0))\,\frac{A(\xi;0)}{A(0;0)}\,\overline{\omega}(0;0) \tag{5}$$

where

$$\ln\overline{\omega}(0;0) = A^{-2}(0;0)\int_0^\infty d\xi'\,\ln\left(\frac{\sqrt{e}}{2\,\xi'}\right)\frac{\partial}{\partial\xi'}\,A(\xi';0)\,A(0;\xi')\,. \tag{6}$$

The function $A(\xi;\xi')$ is defined by (3), (3a); for $t_M = 1$ one has $A(0;0)=1$. In this case we recover essentially the solution given by BOGOLIUBOV et al. [3].

By introducing a mean coupling constant η in the interval $1 > t > -t_M$ the energy gap at the Fermi surface is given by:

$$C(0) = \exp\,(-1/\eta\,N(0)\,P)\,\overline{\omega}(0;0) \tag{7}$$

where P is the cut-off factor,

$$P = \begin{cases} 1;\; q_M > 2\,k_F \\ (q_M/2\,k_F)^2;\; q_M \leqslant 2\,k_F. \end{cases} \tag{8}$$

For $q_M < 2\,k_F$ the reduction of the energy gap due to P and, as a consequence, the reduction of the transition temperature T_c can be very important.

III. Order-Disorder Effect on the Transition Temperature

For a superconducting alloy A–B, which can be prepared in an ordered and a disordered phase [5], the cut-off factor P gives rise to a concentration dependence of the ratio of T_c in the two phases.

Consider first the delute case. In the disordered phase the periodic A-lattice (lattice constant a) is only slightly perturbed by the B-atoms (mean separation b), which scatter the phonons defined in the A-lattice. Thus the self-energy of these phonons due the B-atoms is small, implying a small change of the Debye frequency ω_D and sound velocity c. Thus the limiting phonon momentum in the disordered phase $q_M^d \cong \omega_M^d/c$ is expected to be of the same order of magnitude as q_M defined in the absence of the B-atoms, $q_M^d \cong q_M$. In the ordered phase on the other hand the lattice constant is given bv the distance b ($\gg a$) between the B-atoms, which now

form a superlattice. One expects then[2]) $q_M^0 \cong q_M\, a/b$, or combined with the relation for the disordered case,

$$q_M^d/q_M^0 \cong b/a \gg 1 \tag{9}$$

and thus by (7) and (8)

$$T_c^d/T_c^0 > 1\,. \tag{10}$$

Next consider an alloy composition such that $a \leqslant b$. In the disordered phase, the eigenmodes of the system are not true phonons any more; we shall call these 'pseudophonons' and label them by an index α (frequency ω_α). It is easy to see that these pseudophonons interact with electrons in the same way as ordinary phonons.

Writing the Fourier component of the pseudophonon field as[3])

$$\varphi_{\boldsymbol{q}} = \sum_\alpha \psi_\alpha(\boldsymbol{q})\, a_\alpha + \psi_\alpha^*(\boldsymbol{q})\, a_\alpha^* \tag{11}$$

this interaction has the same form as for true phonons (see e.g. SCHRIEFFER, Ref. [7]). Eliminating the pseudophonons by a canonical transformation in the usual way one obtains an effective reduced interaction between electrons

$$H_{int} = \sum_{\boldsymbol{k},\boldsymbol{q},s} |g(\boldsymbol{k}, \boldsymbol{k}+\boldsymbol{q})|^2\, \vartheta(\boldsymbol{k}, \boldsymbol{q})\, c_{\boldsymbol{k}+\boldsymbol{q},s}^*\, c_{\boldsymbol{k},s}\, c_{-\boldsymbol{k}-\boldsymbol{q},-s}^*\, c_{-\boldsymbol{k},-s} \tag{12}$$

with

$$\vartheta(\boldsymbol{k}, \boldsymbol{q}) = \int d\omega\, \frac{\sigma(\boldsymbol{q}, \omega)}{(\xi_{\boldsymbol{k}} - \xi_{\boldsymbol{k}-\boldsymbol{q}})^2 - \omega^2} \tag{13}$$

where

$$\sigma(\boldsymbol{q}, \omega) = \sum_\alpha |\psi_\alpha(\boldsymbol{q})|^2\, \delta(\omega - \omega_\alpha) \tag{14}$$

is a spectral function.

For ordered alloys the pseudophonons coincide with the true longitudinal phonons, $\sum_\alpha \psi_\alpha(\boldsymbol{q})\, \delta(\omega_\alpha - \omega_{\boldsymbol{q}})\, a_\alpha = a_{\boldsymbol{q}}$ and

$$\sigma^0(\boldsymbol{q}, \omega) = \delta(\omega - \omega_{\boldsymbol{q}})\,. \tag{15}$$

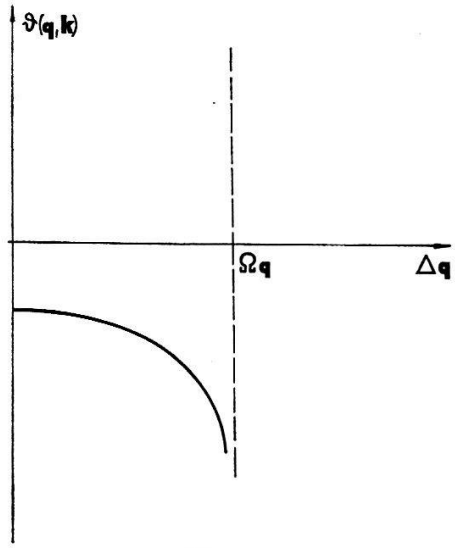
Equation (15) is not valid for a disordered alloy, but we expect that for sufficient small q the average of $\sigma(\boldsymbol{q}, \omega)$ (on an ensemble of homogenous distribution [9] to be defined below) will have a threshold frequency $\Omega_{\boldsymbol{q}} > 0$ such that $\sigma(\boldsymbol{q}, \omega) = 0$ for $\omega < \Omega_{\boldsymbol{q}}$. Then (12) still gives rise to an attractive electron-electron interaction as is seen from Figure 1, where $\vartheta(\boldsymbol{k}, \boldsymbol{q})$ is plotted as a function of $\Delta_{\boldsymbol{q}} \equiv |\xi_{\boldsymbol{k}} - \xi_{\boldsymbol{k}-\boldsymbol{q}}|$. The function $\vartheta(\boldsymbol{k}, \boldsymbol{q})$ has a cut along the $\Delta_{\boldsymbol{q}}$-axis for $\Delta_{\boldsymbol{q}} > \Omega_{\boldsymbol{q}}$.

Let us now discuss the ensemble of homogenous distribution. In any solid (ordered or disordered) the translational symmetry is broken by the self consistent (Hartree) potentials [8] $\varphi_i\,(\boldsymbol{r}_i - \boldsymbol{R}_i)$ which bind the atoms i to their equilibrium position $\boldsymbol{R}_i$. Clearly the range r_0 of the φ_i is of the order of the mean separation between nearest

[2]) The degrees of freedom of both phases being the same, optical branches must appear in the ordered phase. If the mass ratio $M_A/M_B \gg 1$ or $\ll 1$ and b/a is not too big one expects a large separation between optical and acoustical modes, and the optical modes can be disregarded in the superconducting mechanism.

[3]) Unfortunately, the literature concerned with disordered lattices does not give any information about the wavefunction $\psi_\alpha(\mathbf{q})$ but only about the density of states (see e.g. Ref. [6]). See, however the second paper by PAYTON and VISSCHER which contains computer calculations of normal modes of disordered lattices.

neighbours $d = n^{-1/3}$ where $n = a^{-3} + b^{-3}$ is the mean particle density (as before a and b are the mean separation between nearest A–A pairs and B–B pairs respectively).



Figure

Now consider the ensemble in which the equilibrium positions are uniformly distributed over a volume $v(\boldsymbol{R}_i^0) < V$ centered at the most probable values $\boldsymbol{R}_i^0$ of $\boldsymbol{R}_i$. Since $r_0 \cong d < a < b$ the ensemble average of the φ_i has the property [9]

$$\langle \varphi_i(\boldsymbol{r}_i) \rangle = \frac{1}{v(\boldsymbol{R}_i^0)} \int\limits_{v(\boldsymbol{R}_i^0)} d^3R_i \, \varphi_i \, (\boldsymbol{r}_i - \boldsymbol{R}_i) = \text{const.} \tag{16}$$

if $v(\boldsymbol{R}_i^0) > b^3$.

Thus in this ensemble translational invariance is restored, so that its low lying excitations are again plane waves which we call 'hydrodynamical phonons'.

From the condition $v(\boldsymbol{R}_i^0) > b^3$ in Equation (16) it follows that these hydrodynamical phonons exist up to a limiting wave number[4)5)]

$$q_M^d < \frac{\pi}{b} < \frac{\pi}{a}. \tag{17}$$

To complete the discussion we also give an explicite expression for the average of the spectral function $\sigma(\boldsymbol{q}, \omega)$. Since the pseudophonons depend parametrically on the equilibrium positions $\boldsymbol{R}_i$, $\omega_\alpha = \omega_\alpha(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots \boldsymbol{R}_N)$, $\psi_\alpha(\boldsymbol{q}) = \psi_\alpha(\boldsymbol{q}; \boldsymbol{R}_1, \boldsymbol{R}_2, \ldots \boldsymbol{R}_N)$ we obtain the spectral function for the ensemble by taking the average (16) of Equation (14),

$$\sigma^d(\boldsymbol{q}, \omega) = \langle \sum_\alpha |\psi_\alpha(\boldsymbol{q})|^2 \, \delta \, (\omega - \omega_\alpha) \rangle . \tag{18}$$

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4) For $q \ll q_M^d$ the hydrodynamical phonons obey the wave equation of elasticity theory with velocity $c = (\mu/\varrho)^{1/2}$, where μ is the average bulk modulus and ϱ the average mass density; their frequency is given by $\Omega_{\boldsymbol{q}} = c\, q$.

5) The ensemble as described by Equation (16) is a continum, thus only the low frequency modes of the individual (descrete) disordered system can be obtained by the average procedure. At wave numbers $q > q_M^d$ for which the description by hydrodynamical phonons is no longer valid, wave modes may still be eigenmodes of the individual disordered system, but the latter being not periodical in space the wave number of this modes is still smaller than π/b.

Since hydrodynamical phonons exist in any normal system we expect indeed that this $\sigma^d(\boldsymbol{q}, \omega)$ has a finite threshold value $\Omega_{\boldsymbol{q}}$ for $q < q_M^d$ and hence according to Figure, that an attractive electro-electron interaction exists for $q < q_M^d$.

Combining (17) with the condition of the ordered phase, $q_M^d = \pi/b$, obtained by an analogous consideration as in the dilute case we find

$$q_M^d/q_M^0 < 1\,. \tag{19}$$

From (7) and (8) we then expect[6])

$$T_c^d < T_c^0\,. \tag{20}$$

The main conclusion expressed by (10) and (20) is that T_c^d/T_c^0 decreases from values > 1 to values < 1 is the alloy concentration increases from 0 to $^1/_2$ (a/b increases from 0 to 1).

SADAGOPAN et al. [5] have measured such order-disordered effect on superconducting Mo-Ir (with 1:1 atom composition). They found $T_c^0 = 8.8\,°\mathrm{K}$ and $T_c^d = 1.85\,°\mathrm{K}$ in qualitative accord with our relation (20). Unfortunately no measurement of the electronic specific heat and no concentration dependence are reported in this reference.

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Appendix

Solution of the gap equation. Inserting the Ansatz (4) in the gap Equation (2) we have after division by $\lambda\,\sigma(\lambda)$

$$\frac{\overline{\omega}(\xi, \lambda)}{\lambda} = \int_0^\infty d\xi' \, \frac{A(\xi, \xi')\,\overline{\omega}(\xi', \lambda)}{[\sigma^2(\lambda)\,\overline{\omega}^2(\xi', \lambda) + \xi'^2]^{1/2}}\,. \tag{A1}$$

It is now convenient to introduce the following functions:

$$F(\xi, \lambda, \tau, \delta) \equiv \int_0^\infty (\tau^2\,\overline{\omega}^2(\xi', \lambda) + \xi'^2)^{1/2} \, \frac{A(\xi, \xi')}{\overline{\omega}(\xi', \lambda)} \, d\xi' \tag{A2}$$

and

$$G(\xi, \lambda, \delta) \equiv \int_\sigma^\infty A(\xi, \xi')\,\overline{\omega}(\xi', \lambda)\,[\sigma^2(\lambda)\,\overline{\omega}^2(\xi', \lambda) + \xi'^2]^{1/2}\, d\xi'\,. \tag{A3}$$

The gap Equation (A1) then reads

$$\frac{\overline{\omega}(\xi, \lambda)}{\lambda} = \frac{1}{\sigma(\lambda)} \left(\frac{\partial}{\partial \tau} F(\xi, \lambda, \tau, \delta)\right)_{\tau = \sigma(\lambda)} + G(\xi, \lambda, \delta)\,. \tag{A4}$$

Choosing δ such that

a) $\left|\dfrac{\overline{\omega}(\xi_1, \lambda) - \overline{\omega}(\xi_2, \lambda)}{\omega(\xi_1, \lambda)}\right| \ll 1$ for $0 \leqslant (\xi_1 \text{ and } \xi_2) \leqslant \delta$

b) $\left|\dfrac{A(\xi, \xi_1) - A(\xi, \xi_2)}{A(\xi, \xi_1)}\right| \ll 1$ for all ξ and $0 \leqslant (\xi_1 \text{ and } \xi_2) \leqslant \delta$

c) $\dfrac{\sigma(\lambda)}{\delta} \ll 1$

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[6]) More precisely one should compare $\eta\, N(0)\, P$ in both phases since the electronic density of states may depend on the ordering.

and making use of the analiticity of $\overline{\omega}(\xi, \lambda)$ in the limit $\lambda \to 0$ we find

$$F(\xi, \lambda, \tau, \delta) \cong \frac{\overline{\omega}(0; \lambda)\, \tau\, A(\xi, 0)}{\overline{\omega}(0, \lambda)} \int_0^\delta \left[1 + \frac{\xi'^2}{\tau^2\, \overline{\omega}(0; \lambda)}\right]^{1/2} d\xi'$$

$$\cong \frac{1}{2} \left(\frac{\delta}{\overline{\omega}(0, \lambda)\, \tau}\right)^2 A(\xi, 0)\, \tau^2\, \overline{\omega}(0; \lambda)$$

$$+ \frac{1}{2} \ln \left(\frac{2\,\delta}{\overline{\omega}(0, \lambda)\, \tau}\right) A(\xi, 0)\, \tau^2\, \overline{\omega}(0; \lambda)\,. \tag{A5}$$

The function $G(\xi, \lambda, \delta)$ is regular for $\lambda \to 0$ and we shall consider it only in this limit.

Inserting (A5) in (A4) one has:

$$\overline{\omega}(\xi, \lambda) = -A(\xi, 0)\, \overline{\omega}(0, \lambda)\, \lambda \ln \sigma(\lambda)$$

$$+ \lambda\, A(\xi, 0)\, \overline{\omega}(0, \lambda) \left[\ln 2\,\delta - \frac{1}{2} + \ln \overline{\omega}(0, \lambda)\right]$$

$$+ \lambda \int_0^\infty \frac{d\xi'}{\xi'}\, A(\xi, \xi')\, \overline{\omega}(\xi', \lambda) \tag{A6}$$

or after one iteration

$$\frac{\overline{\omega}(\xi, \lambda)}{\overline{\omega}(0, \lambda)} = -A(\xi, 0)\, \lambda \ln \sigma(\lambda) - \lambda\, A(\xi, 0) \ln \overline{\omega}(0, \lambda)$$

$$+ \lambda\, A(\xi, 0) \left[\ln 2\,\delta - \frac{1}{2}\right]$$

$$- \lambda^2 \ln \sigma(\lambda) \int_\delta^\infty \frac{d\xi'}{\xi'}\, A(\xi, \xi')\, A(\xi', 0)$$

$$+ O(\lambda^2) + O(\lambda^3 \ln \sigma(\lambda))\,. \tag{A7}$$

By assumption $\overline{\omega}(\xi, \lambda)$ is analytic and $\overline{\omega}(\xi, 0) \neq 0$ thus

$$\lim_{\lambda \to 0} \lambda \ln \sigma(\lambda) = -A(0, 0)$$

or

$$\ln \sigma(\lambda) = -1/\lambda\, A(0, 0)\,. \tag{A8}$$

Inserting (A8) in (A7) and keeping only the leading terms in λ one has

$$\frac{\overline{\omega}(\xi, 0)}{\overline{\omega}(0, 0)} = \frac{A(\xi, 0)}{A(0, 0)} - \lambda\, A(\xi, 0) \ln \overline{\omega}(0; 0)$$

$$+ \lambda\, A^{-1}(0, 0) \int_0^\infty \ln \frac{\sqrt{e}}{2\,\xi'} \frac{\partial}{\partial \xi'}\, A(\xi, \xi')\, A(\xi', \xi)\, d\xi'\,. \tag{A9}$$

In this last equation we used the fact that the third and fourth term of (A7) can be written as follows:

$$A(\xi;0)\left[\ln 2\,\delta-\frac{1}{2}\right]+A^{-1}(0,0)\int_{\delta}^{\infty}\frac{d\xi'}{\xi'}\,A(\xi,\xi')\,A(\xi',0)=A(\xi,0)\left[\ln 2\,\delta-\frac{1}{2}\right]$$

$$+A^{-1}(0,0)\left[\int_{0}^{\infty}d\xi'-\int_{0}^{\delta}d\xi'\right]\left[\frac{A(\xi,\xi')\,A(\xi',0)}{\xi'}\right]$$

$$\cong A(\xi,0)\left[\ln 2\,\delta-\frac{1}{2}\right]+A^{-1}(0,0)\int_{0}^{\infty}\ln\frac{1}{\xi'}\,\frac{\partial}{\partial\xi}\,[A(\xi,\xi')\,A(\xi',0)]\,d\xi'$$

$$-A(0,0)\,[\ln\xi']_0^{\delta}+A^{-1}(0,0)\,[\ln\xi'\,A(\xi,\xi')\,A(\xi',0)]_0^{\infty}$$

$$=A^{-1}(0,0)\int_{0}^{\infty}\ln\frac{\sqrt{e}}{2\,\xi'}\,\frac{\partial}{\partial\xi'}\,[A(\xi,\xi')\,A(\xi',0)]\,d\xi'.$$

This last expression appears in (A9) and is independent of δ. Setting $\xi=0$ in (A9) we determine the constant $\overline{\omega}(0,0)$:

$$\ln\overline{\omega}(0,0)=A^{-2}(0,0)\int_{0}^{\infty}d\xi'\,\ln\frac{\sqrt{e}}{2\,\xi'}\,\frac{\partial}{\partial\xi'}\,[A(0,\xi')\,A(\xi',0)]\,. \tag{A10}$$

Finally, using (A8) and (A10) the energy gap is found to be

$$C(\xi,\lambda)=\exp(-1/\lambda\,A(0,0))\left\{\frac{A(\xi,0)}{A(0;0)}\,\overline{\omega}(0,0)\right.$$

$$+\lambda\,A(\xi,0)\,\overline{\omega}(0,0)\,\ln\overline{\omega}(0,0)$$

$$\left.+\lambda\,\frac{\overline{\omega}(0,0)}{A(0,0)}\int_{0}^{\infty}\ln\frac{\sqrt{e}}{2\,\xi'}\,\frac{\partial}{\partial\xi'}\,[A(\xi,\xi')\,A(\xi',0)]\,d\xi'\right\}. \tag{A11}$$

Only the leading term in this expression is kept in (5).

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