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On Dirty Superconductors*)

Toshihiko TSUNETO

Research Institute for Fundamental Physics
Kyoto University, Kyoto

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The purpose of this work is to study the mean free path effect of non-magnetic impurities on superconductors. It is shown by including the impurities in the electron-phonon system that, contrary to the results of the earlier theories, there is no change in the transition temperature which is of the order of $1/\omega_c\tau$, where ω_c is the cutoff frequency of the BCS theory and τ the relaxation time in the normal state due to the scattering. The same effect on the superconductor with the anisotropic energy gap is studied explicitly. The scattering in this case leads to the reduction of the transition temperature which is initially linear in $1/\tau$ but becomes logarithmic when $\tau T_c < 1$. The gap in the excitation spectrum is shown to become isotropic when the mean free path is smaller than the coherence length. Thus, Anderson's theory of dirty superconductors is formulated and justified.

§ 1. Introduction

Many interesting facts have been known about the effects of non-magnetic impurities on superconductors. Although several theoretical papers have been devoted to this subject, it seems that even the most salient features of the experimental results are not yet fully elucidated. The experimental studies of the transition temperature T_c of dilute alloys carried out by Lynton, Serin and Zucker,[1] Chanin, Lynton and Serin,[2] and by Quinn and Budnick[3] have established that, as the impurities are added, In, Sn, Zn, Al and Ta with a single exception of Tl show an initial decrease of T_c which is linear in the impurity concentration. As the concentration is further increased, this initial sharp drop turns over to a more gradual decrease followed by a behavior depending on the specific nature of the solute. This apparent saturation seems to occur at the concentration at which the electronic mean free path in the normal state becomes comparable to the coherence length ξ_0. The recent experiment by Lynton and McLachlan[4] concerning the boundary scattering effect on the transition temperature of indium seems to give a strong support to the conclusion that this initial decrease is indeed due to the mean free path effect and does not depend on what mechanism determines the path. In the case of thallium T_c increases although the initial increase is again linear in the concentration.

There exist two different theoretical explanations of this initial linear decrease

*) Main part of this work were carried out at the Institute for Solid State Physics, Tokyo University, Tokyo.

of T_c, the one due to Suhl and Matthias,[5] Nakamura,[6] and Kenworthy and ter Haar,[7] and the other based on Anderson's theory of dirty superconductors.[8] Although the methods used by the former group of people are somewhat different from one another, they all start with the original BCS model and treat the scattering as a perturbation, and their results agree in that the reduction of T_c depends on the parameter $1/\omega_c\tau$ where ω_c is the cutoff frequency in the BCS theory and τ the relaxation time due to the impurity scattering in the normal state. On the other hand, according to Anderson's theory of dirty superconductors, the basic idea of which is to pair the one electron state $\psi_{n\uparrow}$ in the presence of the impurities with its time reversal state $\psi^*_{n\downarrow}$, there is no change in the properties of a superconductor unless the density of states $N(0)$ or the electron-electron interaction characterized by V and ω_c are changed. Therefore, one may well question whether the effect involving $1/\omega_c\tau$ obtained by Suhl-Matthias and others has any real physical significance or not.

On the basis of the same idea Anderson has suggested that the anisotropy of the energy gap, if present in the pure superconductor, may be washed out by the impurity scattering and this could be the cause of the initial decrease of T_c, since the scattered waves can not make as good use of the attractive interaction as the unscattered waves. When the mean free path becomes smaller than the coherence length, the anisotropy is completely washed out and there will be no further decrease of T_c. This is in conformity with the qualitative picture of the experimental results mentioned above. Anderson's idea has also been supported by the recent experiment by Richards[9] on infra-red absorption in pure and impure single crystals of tin. His results show that as the impurities are added the gap edge becomes sharper and the anisotropy disappears. The measurement of nuclear spin-lattice relaxation in superconducting aluminium alloys carried out by Masuda[10] gives further evidence in favor of the theory. However, Anderson's theory has not been given any explicit formulation so that, for instance, one does not know just how the decrease of T_c is related to the anisotropy of the energy gap.

The purpose of the present paper is the following. Firstly, it is shown that the reduction of T_c depending on the parameter, $1/\omega_c\tau$, is simply a consequence of introducing the artificial cutoff and one does not get such an effect when one includes the impurity scattering in the electron-phonon system right from the beginning. When there is no anisotropy, the effect of the scattering on T_c or on the energy gap arises only through terms of the order of $1/\bar{q}l$ where $\bar{q}$ is the average phonon momentum. In the next section we shall show this with the help of the theory of electron-phonon interaction in superconductors developed by Eliashburg.[11] Secondly, the effects of the scattering on a superconductor with the anisotropic energy gap is studied explicitly and in detail. The theory we need in order to discuss this problem has already been developed by Abrikosov and Gor'kov[12] in connection with superconducting alloys with

paramagnetic impurities. In fact, it turns out that the present problem is quite similar mathematically to that of paramagnetic impurities. For the detail of the calculation involved their paper should be referred to. To treat dirty superconductors Anderson has suggested a procedure of first recalculating the effective interaction $V_{nn'}$ between the scattered waves. Actually, as long as one is concerned with the mean free path effect, one realizes it is sufficient to use a theory such as ours which makes use of nothing more than the standard treatment of the impurity scattering in metals.[13] In § 3 we shall present a simple model of an anisotropic superconductor, which will be used in the succeeding sections to study the mean free path effect on the excitation spectrum and the transition temperature.

It must be emphasized here that throughout the following discussions we assume that the density of electrons is not changed by the addition of the impurities. In other words we are concerned strictly with the mean free path effect on the properties of superconductors.

§ 2. Electron-phonon system with impurities

The Hamiltonian of the system that we shall consider in this section consists of the Fröhlich Hamiltonian and of the impurity potential,

$$H=H_e+H_{ph}+H_{e-ph}+H_{imp}, \tag{1}$$

where

$$H_{e-ph}=\sum_{p,q}\alpha_q^2\,(a_{p+q}^+\,a_p\,b_q+a_p^+\,a_{p+q}\,b_q^+) \tag{2}$$

and

$$H_{imp}=\sum_{p,p',i}u(\boldsymbol{p}-\boldsymbol{p}')\,a_{p'}^+\,a_p\exp\,[i(\boldsymbol{p}'-\boldsymbol{p})\boldsymbol{R}_i]. \tag{3}$$

Here, among rather obvious notations, $\boldsymbol{R}_i$ denotes positions of the impurities randomly distributed in space and $\alpha_q^2=\lambda_0\pi^2qc/p_0$, where c is the velocity of sound, p_0 the Fermi momentum and λ_0 a dimensionless constant, $\lambda_0\lesssim 1$. In the absence of the scattering Eliashburg[11] has shown that the superconducting state of the system can be described by the two Green's functions of electrons,

$$\hat{\delta}_{\alpha\beta}\,G(x,\,x')=-i\langle T\psi_\alpha(x)\,\psi_\beta^+(x)\rangle, \tag{4}$$

$$\hat{I}_{\alpha\beta}\,F^+(x,\,x')=\langle T\psi_\alpha^+(x)\,\psi_\beta^+(x')\rangle,\quad \hat{I}^2=-1, \tag{5}$$

and the Green's function of phonons,

$$D(x,\,x')=-i\langle T\varphi(x)\,\varphi(x')\rangle, \tag{6}$$

for which we can use the expression for the normal state obtained by Migdal,[14]

$$D(\boldsymbol{q},\,\omega)=\alpha_q^2\frac{\omega_q^{(0)}}{\omega_q}\left(\frac{1}{\omega-\omega_q+i\delta_1}-\frac{1}{\omega+\omega_q-i\delta_1}\right) \tag{7}$$

(For convenience the strength of the coupling is included in it). Then, keeping only the simplest type of the self-energy parts, one gets

$$G(\boldsymbol{p}, \omega) = [\omega + \xi + \Sigma_1(\boldsymbol{p}, -\omega)] \times \{[\omega - \xi - \Sigma_1(\boldsymbol{p}, \omega)][\omega + \xi + \Sigma_1(\boldsymbol{p}, -\omega)] - [\Sigma_2(\boldsymbol{p}, \omega)]^2\}^{-1}, \tag{8}$$

$$F(\boldsymbol{p}, \omega) = i\Sigma_2(\boldsymbol{p}, \omega) G(\boldsymbol{p}, \omega) / [\omega + \xi + \Sigma_1(\boldsymbol{p}, -\omega)], \tag{9}$$

where

$$\Sigma_1(\boldsymbol{p}, \omega) = \frac{i}{(2\pi)^4} \int d\boldsymbol{p}' d\omega' G(\boldsymbol{p}', \omega') D(\boldsymbol{p} - \boldsymbol{p}', \omega - \omega'), \tag{10}$$

$$\Sigma_2(\boldsymbol{p}, \omega) = \frac{i}{(2\pi)^4} \int d\boldsymbol{p}' d\omega' F(\boldsymbol{p}', \omega') D(\boldsymbol{p} - \boldsymbol{p}', \omega - \omega') \tag{11}$$

and

$$\xi = (p^2 - p_0^2)/2m.$$

In the presence of the scattering, according to the well-known theory of the impurity scattering in metals, the Green's function of electrons in the normal state is given by

$$G(\boldsymbol{p}, \omega) = (\omega - \xi + i \operatorname{sign} \omega / 2\tau)^{-1}. \tag{12}$$

Here the relaxation time τ is defined by

$$\frac{1}{\tau} = \frac{n_i p_0 m}{(2\pi)^2} \int d\Omega |u(\boldsymbol{p} \cdot \boldsymbol{p}' / p p')|^2, \tag{13}$$

where n_i is the number density of the impurities. Contributions from the processes neglected in getting the expression (12) are estimated to be at most of the order of $1/p_0 l$ where $l = v_0 \tau$. Let us then consider how the Green's function of phonons is modified by the scattering. If we neglect the direct effect of the impurity atoms on the spectrum of the lattice vibration, which is expected to be small in the important region of short wavelength, the change in $D(\boldsymbol{q}, \omega)$ occurs only through its self-energy part. Now it can readily be seen and is already known from the study of ultrasonic attenuation in metals[15] that the correction due to the electronic mean free path is only of the order of $1/ql$ rather than $1/\omega\tau$. Similarly, the correction to the vertex part of the electron-phonon interaction is of the same order of magnitude. Therefore, as long as the impurity concentration is such that $1/p_0 l \sim 1/\bar{q} l \ll 1$ where $\bar{q}$ is the average phonon momentum, a condition amply met in most experiments, we may use the D-function for the pure metal also in the presence of the impurities. In doing so, we are not throwing away terms of the order of $1/\omega_c \tau$ which is larger by a factor of v_0/c. This conclusion naturally remains valid for the superconducting state.

Consequently, the sole modification due to the scattering appears in the

self-energy part of G and F. Clearly it is just to add

$$\bar{G}(\omega)=\frac{1}{(2\pi)^3}\int d\boldsymbol{p}'|u(\boldsymbol{p}-\boldsymbol{p}')|^2G(\boldsymbol{p}',\omega) \tag{14}$$

and

$$i\bar{F}(\omega)=\frac{i}{(2\pi)^3}\int d\boldsymbol{p}'|u(\boldsymbol{p}-\boldsymbol{p}')|^2F(\boldsymbol{p}',\omega) \tag{15}$$

to Σ_1 and to Σ_2, respectively. We may suppose that $\Sigma_1(p,\omega)+\bar{G}(\omega)$ is an odd function of ω with the understanding that the chemical potential is adequately renormalized. Furthermore, Migdal and Eliashburg have shown that for $\omega\ll E_F$ and $p\sim p_0$ the functions Σ_1 and Σ_2 do not depend on p. This is evidently true in our case also. Therefore, we get, assuming the isotropic scattering,

$$\bar{G}(\omega)=[\omega-\Sigma_1(\omega)-\bar{G}(\omega)]\frac{1}{(2\pi)^3}\int d\boldsymbol{p}'|u|^2/\{[\omega-\Sigma_1(\omega)-\bar{G}(\omega)]^2-\xi^2-[\Sigma_2(\omega)+i\bar{F}(\omega)]^2\}, \tag{16}$$

$$\bar{F}(\omega)=[\Sigma_2(\omega)+i\bar{F}(\omega)]\frac{1}{(2\pi)^3}\int d\boldsymbol{p}'|u|^2/\{[\omega-\Sigma_1(\omega)-\bar{G}(\omega)]^2-\xi^2-[\Sigma_2(\omega)+i\bar{F}(\omega)]^2\}, \tag{17}$$

from which follows a simple relation,

$$\bar{F}(\omega)=i\Sigma_2(\omega)\bar{G}(\omega)/[\omega-\Sigma_1(\omega)]. \tag{18}$$

Substituting (18) in (14) and (15), we obtain

$$\bar{G}(\omega)=-\frac{i}{2\tau}\frac{\omega-\Sigma_1}{\sqrt{(\omega-\Sigma_1)^2-\Sigma_2^2}}\quad\text{and}\quad\bar{F}(\omega)=\frac{1}{2\tau}\frac{\Sigma_2}{\sqrt{(\omega-\Sigma_1)^2-\Sigma_2^2}}. \tag{19}$$

Hence, the effect of the scattering amounts to replacing $\omega-\Sigma_1$ and Σ_2 by $\eta(\omega-\Sigma_1)$ and $\eta\Sigma_2$, respectively, where

$$\eta=1+\frac{i}{2\tau\sqrt{(\omega-\Sigma_1)^2-\Sigma_2^2}}, \tag{20}$$

just as Abrikosov and Gor'kov have shown on a simpler model. Since the analytical property of the Green's functions remains unchanged, we can transform the equation for Σ_2 into the form similar to that obtained by Eliashburg,

$$\Sigma_2(\omega)=\frac{i}{(2\pi)^3p_0}\int dq\int d\xi\int d\omega' qD(q,\omega-\omega')\times\eta(\omega')\Sigma_2(\omega')/\{\xi^2-\eta^2(\omega')([\omega'-\Sigma_1(\omega')]^2-[\Sigma_2(\omega')]^2)\}. \tag{21}$$

Since we can first carry out the integration over ξ and there is no need for the cutoff, the factor η disappears from the expression after the integration. Consequently, we may conclude that there is no reduction of the transition

temperature as long as $1/\bar{q}l$ can be neglected. The presence of the screened Coulomb interaction does not affect our conclusion.

§ 3. A model for anisotropic superconductors

It is clear from Eqs. (14) and (15) that if there exists anisotropy in the system so that in particular Σ_2 depends also on the direction of $\boldsymbol{p}$, the simple relation (18) does not hold between $\bar{G}$ and $\bar{F}$. As a result τ enters into the Green's function in a more complicated manner and does not, for instance, drop out of the gap equation. In order to study the anisotropic case explicitly, we first try to construct a simple model which to a certain extent reflects the anisotropy we encounter in real metals.[16]

The energy of an electron with momentum $\boldsymbol{p}$ measured from the Fermi surface is denoted by $\xi(\boldsymbol{p})$, which now depends on the angle (θ, φ) of $\boldsymbol{p}$ with respect to a particular crystalline axis, taken along the z-axis. The velocity of sound and the coupling constant are also anisotropic: $c(\boldsymbol{q})$ and $\alpha(\boldsymbol{p}-\boldsymbol{p}'; \boldsymbol{p})$. We make a change of variables from (p, θ, φ) to (ξ, θ, φ), assuming of course that this is possible. It will be assumed that none of $\partial\xi/\partial p$, $c(\boldsymbol{q})$ and $\alpha(\boldsymbol{p}-\boldsymbol{p}', \boldsymbol{p})$ depend strongly on the energy ξ near the Fermi surface. Then, in the lowest approximation in which we neglect the lifetime and the dependence of Σ_2 on ξ, we obtain the gap equation in the form

$$\Sigma_2(\theta, \varphi, \omega) = \frac{\pi}{(2\pi)^4} \int_0^\infty dz \int d\Omega' \left(\frac{\partial\xi'}{\partial p'}\right)^{-1} \alpha^2(\boldsymbol{p}-\boldsymbol{p}', \boldsymbol{p}) \times \mathrm{Re}\left\{\frac{\Sigma_2(\theta', \varphi', z)}{\sqrt{z^2-\Sigma_2^2(\theta', \varphi', z)}}\right\} \left(\frac{1}{z-\omega+c(\boldsymbol{p}-\boldsymbol{p}')|\boldsymbol{p}-\boldsymbol{p}'|-i\delta} + \frac{1}{z+\omega+c(\boldsymbol{p}-\boldsymbol{p}')|\boldsymbol{p}-\boldsymbol{p}'|-i\delta}\right). \tag{22}$$

One can easily include the screened Coulomb interaction in this equation. It seems that the anisotropy of the Fermi surface is reflected in the gap in a slightly more direct manner through the Coulomb interaction than the one via phonons. The discussions given in the preceding section and the above equation justify the use of the simple model of the BCS type with the anisotropic effective interaction $v(\boldsymbol{p}; \boldsymbol{p}')$ between electrons for the purpose of discussing the mean free path effect on a superconductor with the anisotropic energy gap.

With this interaction it is easy to derive the Gor'kov equations,

$$(\omega-\xi)G(\boldsymbol{p}, \omega) - i\Delta(\boldsymbol{p})F(\boldsymbol{p}, \omega) = 1, \tag{23}$$

$$(\omega+\xi)F(\boldsymbol{p}, \omega) + i\Delta(\boldsymbol{p})G(\boldsymbol{p}, \omega) = 0 \tag{24}$$

for the Green's functions in the absence of the scattering. Here $\Delta(\boldsymbol{p})$ is defined by

$$\Delta(\boldsymbol{p})=\int \frac{d\boldsymbol{p}'d\omega'}{(2\pi)^4}v(\boldsymbol{p},\boldsymbol{p}')F(\boldsymbol{p}',\omega'). \tag{25}$$

We assume that the effective interaction is approximately a function of the directions of $\boldsymbol{p}$ and $\boldsymbol{p}'$, so that the gap $\Delta(\boldsymbol{p})$ depends only on the angles θ and φ of the vector $\boldsymbol{p}$. When we decompose $v(\theta,\varphi;\theta',\varphi')$ in terms of the spherical harmonics,

$$v(\theta,\varphi;\theta',\varphi')=\sum_{\substack{-l<m<l\\-l'<m'<l'}} v_{lm;l'm'}\,Y_{lm}(\theta,\varphi)\,Y_{l'm'}(\theta',\varphi'), \tag{26}$$

the gap equation (25) becomes

$$\Delta(\theta,\varphi)=N(0)\Sigma v_{lm;\,l'm'}\,Y_{lm}(\theta,\varphi)\times\int\frac{d\Omega'}{4\pi}\int d\xi\int\frac{d\omega}{2\pi}\,Y_{l'm'}(\theta',\varphi')\frac{i\Delta(\theta',\varphi')}{\omega^2-\xi^2-|\Delta(\theta',\varphi')|^2}. \tag{27}$$

When there is no off-diagonal element of v, that is, when there is no anisotropy, this equation reduces to the one obtained by Anderson and Morel[17] for the higher l-state pairing (Eq. (4·4)).

§ 4. The gap in the excitation spectrum

Starting with the Gor'kov equations (23) and (24), it is easy to obtain the Green's functions in the presence of the impurities. The result is, if we again assume the isotropic scattering for simplicity:

$$G(\boldsymbol{p},\omega)=-\frac{i[\omega-\bar{G}(\omega)]+\xi}{[\omega-\bar{G}(\omega)]^2+\xi^2+[\Delta(\theta,\varphi)-\bar{F}(\omega)]^2}, \tag{28}$$

$$F(\boldsymbol{p},\omega)=\frac{\Delta(\theta,\varphi)-\bar{F}(\omega)}{i[\omega-\bar{G}(\omega)]+\xi}\,G(\boldsymbol{p},\omega), \tag{29}$$

where

$$\bar{G}(\omega)=-\frac{1}{2\tau}[\omega-\bar{G}(\omega)]\int\frac{d\Omega}{4\pi}\frac{1}{\{[\omega-\bar{G}(\omega)]^2+[\Delta(\theta,\varphi)-\bar{F}(\omega)]^2\}^{1/2}} \tag{30}$$

and

$$\bar{F}(\omega)=-\frac{1}{2\tau}\int\frac{d\Omega}{4\pi}\frac{\Delta(\theta,\varphi)-\bar{F}(\omega)}{\{[\omega-\bar{G}(\omega)]^2+[\Delta(\theta,\varphi)-\bar{F}(\omega)]^2\}^{1/2}}. \tag{31}$$

Here we have made a change of variable, $\omega\to i\omega$, for the sake of convenience. In order to solve the above equations, let us introduce

$$\tilde{\omega}\equiv\omega-\bar{G}(\omega),\quad \tilde{\Delta}_0\equiv\Delta_0-\bar{F}(\omega) \tag{32}$$

and

$$I_0\equiv\int\frac{d\Omega}{4\pi}\frac{1}{\sqrt{\tilde{\omega}^2+[\tilde{\Delta}_0+\Delta_1(\theta,\varphi)]^2}},\quad I_1\equiv\frac{1}{\tilde{\Delta}_0}\int\frac{d\Omega}{4\pi}\frac{\tilde{\Delta}_0+\Delta_1(\theta,\varphi)}{\sqrt{\tilde{\omega}^2+[\tilde{\Delta}_0+\Delta_1(\theta,\varphi)]^2}}, \tag{33}$$

where

$$\Delta_0 \equiv \int \frac{d\Omega}{4\pi} \Delta(\theta, \varphi), \quad \Delta_1 \equiv \Delta(\theta, \varphi) - \Delta_0. \tag{34}$$

We have

$$\tilde{\omega} = \omega/(1 - I_0/2\tau) \text{ and } \tilde{\Delta}_0 = \Delta_0/(1 - I_1/2\tau). \tag{35}$$

Since we are interested in the case where $\Delta_1 \ll \Delta_0$, we can expand these quantities in the powers of Δ_1. To the second order in Δ_1 we obtain

$$\begin{aligned} I_0 &= 1/\eta\Omega_0 - (\overline{\Delta_1^2}/2\eta^3\Omega_0^3)(1 - 3\Delta_0^2/\Omega_0^2), \\ I_1 &= 1/\eta\Omega_0 - 3\overline{\Delta_1^2}\omega^2/2\eta^3\Omega_0^5, \end{aligned} \tag{36}$$

where

$$\Omega_0 = \sqrt{\omega^2 + \Delta_0^2}, \quad \eta = 1 + 1/2\tau\Omega_0 \text{ and } \overline{\Delta_1^2} = \int \frac{d\Omega}{4\pi} \Delta_1^2(\theta, \varphi). \tag{37}$$

One can determine $\Delta(\theta, \varphi)$ by substituting (35) and (36) into the gap equation. Let us just suppose that $\Delta(\theta, \varphi)$ in the presence of the scattering is determined in this way. Clearly it still depends on the angles. However, while in the pure superconductor the quantity $\Delta(\theta, \varphi)$ is itself equal to the gap in the excitation spectrum, they are not necessarily the same in the presence of the scattering, just as in the case of superconducting alloys with paramagnetic impurities. Let us, therefore, examine the threshold of the excitation spectrum. The denominator of the Green's function is equal to $\mathcal{D} \equiv \tilde{\omega}^2 - [\tilde{\Delta}_0 + \Delta_1(\theta, \varphi)]^2$ for $\xi = 0$, where we have returned to the real ω. The threshold $\omega_0(\theta, \varphi)$ of the excitation with momentum in a given direction (θ, φ) on the Fermi surface is equal either to Δ_0 at which η becomes complex or to the root of $\mathcal{D} = 0$, according to which of the two is smaller. For $\Delta_1(\theta, \varphi) > 0$ the threshold is obviously Δ_0. When $\Delta_1(\theta, \varphi) < 0$, η is real for ω such that $\Delta_0 + \Delta_1(\theta, \varphi) \leq \omega \leq \omega_0$. In the limit $\tau\Delta_0 \gg 1$, we get from $\mathcal{D} = 0$, with the help of (36),

$$\omega_0(\theta, \varphi) = \Delta_0 - |\Delta_1(\theta, \varphi)| + \frac{1}{2\tau}\sqrt{\frac{|\Delta_1(\theta, \varphi)|}{2\Delta_0}}\left(1 - \frac{\overline{\Delta_1^2}}{8\Delta_1^2(\theta, \varphi)}\right). \tag{38}$$

Thus, one can see that the gap edge tends to be isotropic by the scattering.

In the opposite limit of the short mean free path one cannot use the expansion in powers of Δ_1. Although one can show, using (36), that

$$\omega_0 - \Delta_0 \propto -(1/\Delta_0)(2\tau\Delta_0^2\overline{\Delta_1^2})^{2/3} \tag{39}$$

when $\Delta_0\tau \ll 1$, the higher order terms in Δ_1 give contribution to ω_0 of the same order of magnitude as the ones kept in (36). In the case of a simple model whose energy gap is equal to $\Delta_0' + \Delta_1'$ in a region A of area $4\pi a$ and to Δ_0' outside A, it can be shown after rather lengthy calculation that

$$\omega_0=\Delta_0\left\{1-\frac{3}{2}\left(\frac{|\Delta_1|}{\Delta_0}\right)[4a^2(1-a)^2\tau^2\Delta_0|\Delta_1|]^{1/3}\right.$$
$$\left.+O(\tau^2\Delta_0|\Delta_1|)^{2/3}\right\} \tag{40}$$

in the region where $\Delta_1<0$. Thus, one can conclude that in this simple case the gap edge becomes isotropic when $(\tau^2\Delta\Delta_1)^{1/3}\ll 1$. We believe that this conclusion would remain valid in a more general case.

§ 5. Change in the transition temperature

In order to determine the transition temperature T_c of the anisotropic superconductor in the presence of the impurities, it is more convenient to use the linearized integral equation for Δ,

$$\langle\Delta(\boldsymbol{x})\rangle_{av}=T_c\sum_{\omega_n}\int d\boldsymbol{x}'v(\boldsymbol{x},\boldsymbol{x}')\langle\Delta(\boldsymbol{x}')G^0{}_{\omega_n}(\boldsymbol{x},\boldsymbol{x}')G^0{}_{-\omega_n}(\boldsymbol{x}',\boldsymbol{x})\rangle_{av}, \tag{41}$$

where $G^0{}_{\omega_n}(\boldsymbol{x},\boldsymbol{x}')$ is now the thermal Green's function for the normal state with $\omega_n=(2n+1)\pi T_c$ and $\langle\ \rangle_{av}$ means the average over the positions of impurities. After averaging we have

$$G^0{}_{\omega_n}(p)=1/(i\omega_n\eta_0-\xi), \tag{42}$$
$$\eta_0=1+1/2\tau|\omega_n|. \tag{43}$$

In obtaining $\langle\Delta G^0G^0\rangle_{av}$ one has to take into account the correlation between the two propagators, i.e. to include the ladder type diagrams. The integral equation for the Fourier transform of $\langle\Delta G^0G^0\rangle_{av}$ can easily be written down:

$$K_{\omega_n}(\boldsymbol{p})=G^0{}_{\omega_n}(\boldsymbol{p})G^0_{-\omega_n}(\boldsymbol{p})$$
$$\times\left[\Delta(\theta,\varphi)+\frac{n_i}{(2\pi)^3}\int d\boldsymbol{p}'|u|^2K_{\omega_n}(\boldsymbol{p}')\right]. \tag{44}$$

Solving this for the isotropic scattering we get

$$K_{\omega_n}(\boldsymbol{p})=G^0{}_{\omega_n}(\boldsymbol{p})G^0_{-\omega_n}(\boldsymbol{p})$$
$$\times\left[\Delta(\theta,\varphi)+\frac{1}{2\tau|\omega_n|}\int\frac{d\Omega'}{4\pi}\Delta(\theta',\varphi')\right]. \tag{45}$$

Therefore, the equation determining T_c is

$$\Delta(\theta,\varphi)=N(0)T_c\sum_{\omega_n}\int d\xi\int\frac{d\Omega}{4\pi}\frac{1}{\eta_0^2\omega_n^2+\xi^2}$$
$$\times[v(\theta,\varphi;\theta',\varphi')+\frac{1}{2\tau|\omega_n|}v_1(\theta,\varphi)]\Delta(\theta',\varphi') \tag{46}$$

where

$$v_1(\theta, \varphi) \equiv \int \frac{d\Omega}{4\pi} v(\theta, \varphi ; \theta', \varphi'). \tag{47}$$

One can perform the ξ-integral and the summation over ω_n by subtracting from the integrand $[v(\theta, \varphi ; \theta', \varphi') + (1/2\tau|\omega_n|)v_1(\theta, \varphi)]/(\omega_n^2+\xi^2)$. The result is

$$\Delta(\theta, \varphi) = N(0)\int \frac{d\Omega'}{4\pi} \{Lv(\theta, \varphi ; \theta', \varphi') - K(\rho)[v(\theta, \varphi ; \theta', \varphi') - v_1(\theta, \varphi)]\}\Delta(\theta', \varphi'), \tag{48}$$

where

$$L = \ln(2\omega_c\gamma/\pi T_c) \tag{49}$$

and

$$K(\rho) = \psi\left(\frac{1+\rho}{2}\right) - \psi\left(\frac{1}{2}\right). \tag{50}$$

Here ψ is the di-Γ function, $\rho = 1/2\pi\tau T_c$ and γ is Euler's constant.

i) *Separable potential.* Let us first study this equation with a separable potential,

$$v(\theta, \varphi ; \theta', \varphi') = \lambda(\theta, \varphi)\lambda(\theta', \varphi'). \tag{51}$$

Then (48) reduces to

$$[N(0)\bar{\lambda}^2]^{-1} = L - K(\rho)\chi \tag{52}$$

where $\chi = (\overline{\lambda^2} - \bar{\lambda}^2)/\bar{\lambda}^2$. When $\tau T_c \gg 1$, we get

$$T_c = T_{c0} - \pi\chi/4\tau \tag{53}$$

with $T_{c0} = (2\omega_c\gamma/\pi)\exp[1/N(0)\bar{\lambda}^2]$. When $\tau T_{c0} \ll 1$, because $K(\rho) \to \ln 2\rho + \gamma$, we have

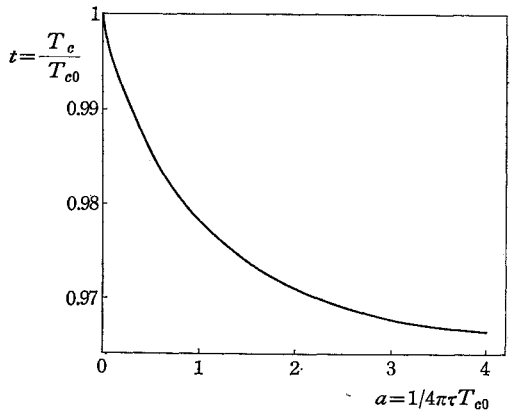

Fig. 1. The reduced transition temperature $t = T_c/T_{c0}$ is plotted against $a = 1/4\pi\tau T_{c0}$ for $\chi = 1/100$.

$$T_c^{1-\chi} = T_{c0}\exp[\chi(\ln\pi\tau - \gamma)]. \tag{54}$$

If $\chi \ll 1$, we obtain

$$T_c \sim T_{c0}[1 - \chi\ln(\gamma/\pi\tau T_{c0})]. \tag{55}$$

Thus the dependence on the mean free path becomes logarithmic when $\tau T_{c0} \ll 1$. In Fig. 1, the reduction of T_c is plotted against $1/4\pi\tau T_{c0}$ for $\chi = 1/100$. One can see how the depression of T_c is saturated once the concentration is such that $\tau T_{c0} \ll 1$.

ii) *Non-separable potential; weak coupling limit.* When $N(0)v$ and $1/\tau T_c$ are both small, one can solve (48) by

Fredholm's expansion theorem. The eigenvalue equation that determines T_c is, to the second order in v,

$$1/N(0)=[L-K(\rho)]\bar{v}+K(\rho)\bar{v}_1+[N(0)/2]\{[L-K(\rho)]^2(\overline{vv}-\bar{v}^2) +2[L-K(\rho)]K(\rho)(\overline{vv}_1-\bar{v}\bar{v}_1)\}, \tag{56}$$

where

$$\bar{v}=\int\frac{d\Omega}{4\pi}v(\theta,\varphi;\theta,\varphi)=\sum v_{l;l},$$

$$\bar{v}_1=\int\frac{d\Omega}{4\pi}v_1(\theta,\varphi)=v_{0;0},$$

$$\overline{vv}=\int\frac{d\Omega d\Omega'}{(4\pi)^2}v(\theta,\varphi;\theta',\varphi')v(\theta',\varphi';\theta,\varphi)=\sum v_{l;l'}\,v_{l';l},$$

$$\overline{vv}_1=\int\frac{d\Omega d\Omega'}{(4\pi)^2}v(\theta,\varphi;\theta',\varphi')v_1(\theta',\varphi')=\sum v_{0;l}\,v_{l;0}. \tag{57}$$

We have omitted the suffix m for simplicity. If we keep only the first order in K, we get

$$L=[1/N(0)A]\{-[\bar{v}-(A-B)N(0)K(\rho)] \pm[\bar{v}^2+2A+2N(0)(\bar{v}B-\bar{v}_1A)K(\rho)]^{1/2}\}, \tag{58}$$

where

$$A\equiv\overline{vv}-\bar{v}^2=2(\sum{}'v_{0;l}\,v_{l;0}-v_{0;0}\sum{}'v_{l\,l})+A',$$
$$B\equiv\overline{vv}_1-\bar{v}\bar{v}_1=1/2\,(A-A'). \tag{59}$$

Here the important terms are separated from the less important ones; $v_{0;0}$ is of course the largest component and $v_{l;l}$ and $v_{l;0}$ are the ones mainly responsible for the anisotropy. The upper sign in (56) should be taken since the corresponding solution reduces to the BCS solution with $v_{0;0}$ when we switch off the off-diagonal components of the interaction. From the above equations we get

$$\ln(T_{c0}/T_c)=(1/2)K(\rho)\{1+A'/2A-[(v_{0;0}-\sum{}'v_{l;l})+(A'/2A)(v_0+\sum{}'v_{l;l})] \times[(v_{0;0}-\sum{}'v_{l;l})^2+4\sum{}'v_{0;l}\,v_{l;0}+2A']^{-1/2}\}. \tag{60}$$

If A' is negligible and $\sum{}'v_{0;l}v_{l;0}/(v_{0;0}-\sum{}'v_{l;l})^2\ll 1$, we obtain the expression for T_c in the low concentration limit,

$$T_c=T_{c0}-\frac{\pi}{2\tau}\,\frac{\sum{}'v_{0;l}\,v_{l;0}}{(v_{0;0}-\sum{}'v_{l;l})^2}\,. \tag{61}$$

§ 6. Discussion

It has been shown in § 4 that the anisotropy of the gap in the excitation

spectrum, if present in the pure superconductor, is smeared out by the impurity scattering and in the limit of dirty superconductors it tends to be isotropic and equal to the averaged gap parameter Δ_0. This confirms Anderson's idea and is in agreement with the experimental results mentioned in the Introduction. The comparison of the result obtained here concerning the change in T_c with the experimental data is more difficult since we know very little about the actual anisotropy of the gap, not to speak of the anisotropy of the effective interaction. The general behavior of T_c obtained in the last section, consisting of the initial linear decrease and of the much more gradual logarithmic decrease, is indeed what we find in the dilute alloys of Sn, Zn, Al and Ta. Although we have discussed the limit $\tau T_{c0} \ll 1$ only for the separable potential, we believe that the same conclusion would apply to the more general case. According to (44), if we take the limit of $\tau T_{c0} \to 0$, T_c approaches zero. But the decrease is so slow that it looks as if the effect of the scattering saturates after $\tau T_{c0} < 1$, and before having appreciable decrease in this way, other factors not considered here, especially the electronic density, will come to play a role. The slope of the initial decrease depends upon the part of the interaction which is responsible for the anisotropy of the gap. If the relative change of the energy gap over the Fermi surface is of the order of 1/10, as is the case in Sn, we would guess that the factor appearing in the formula (58), $\sum' v_{0;l} v_{l;0} / (v_{0;0} - \sum' v_{l;l})^2$, be of the order of 10^{-2} or perhaps smaller. This leads to the initial slope of the curve of ΔT_c versus $1/l$ of the order of 10^{-5}. According to the result obtained by Chanin, Lynton and Serin, the initial slope is about 2.7×10^{-6} for Al, In and Sn. The discrepancy is not uncomfortably large. A more complete map of the anisotropic gap over the Fermi surface would be desirable in this connection. Since $v_{l;l'}$ is thought to be symmetric and $v_{0;0}$ is the dominant component, the scattering always depresses T_c. It seems that the increase of T_c observed in Tl alloy cannot be explained by the mean free path effect on the anisotropic gap.

In the present theory we have assumed that the impurity potential is δ-function-like and that it does not vary over the Fermi surface. To generalize the theory in this respect does not involve any serious difficulty. The inclusion of the higher l-wave scattering might reduce the slope of the initial decrease of T_c.

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Note added in proof: The statement given in § 4 concerning the threshold of the excitation spectrum must be corrected, since the imaginary parts appearing in I_0 and I_1 are overlooked. The threshold becomes isotropic, strictly speaking, as soon as the scattering is introduced. In the limit $\tau\Delta_0 \gg 1$ its value is given by ω_0 in (38) corresponding to $\min\Delta(\theta, \varphi)$. It tends to Δ_0 in the opposite limit, as one can see from (40) in the simple example. The magnitude of absorptive part is, however, anisotropic and we believe it would become isotropic only in the limit $\tau\Delta_0 \ll 1$. To see this explicitly one must calculate the conductivity. The author is much indebted to Mr. K. Maki for critical and helpful discussions on this problem.

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