Effects of Gap Anisotropy in Superconductors Containing Paramagnetic Impurities*

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(Received 27 January 1965)

The effect of the gap anisotropy on the transition temperature of a superconductor containing paramagnetic impurities is calculated by an extension of the theory of Markowitz and Kadanoff. Deviations from the linear decrease of transition temperature with impurity concentration as predicted by Abrikosov and Gorkov will depend on the relative magnitudes of the spin-flip and the no-spin-flip parts of the impurity scattering potential. It is shown that such a deviation should be observable and provide a test of the Abrikosov-Gorkov theory.

RECENT experiments[1] have shown that it is becoming possible to investigate the influence of dilute solutions of paramagnetic impurities on otherwise pure superconductors.[2] At low impurity concentration one might expect a mean-free-path effect on the transition temperature due to an anisotropic order parameter in the superconducting sample. In order to provide the theoretical background for expected experimental work we want to extend the work of Markowitz and Kadanoff,[3] which treats those effects in the presence of nonmagnetic impurities, to the paramagnetic-impurity case, using the theory of Abrikosov and Gorkov.[4] As will be shown, such a calculation leads to a simple result for the change of transition temperature T_c. The anisotropy effect (a term introduced in Ref. 3) will be of the same form as for nonmagnetic impurities, while the pair-breaking character of the magnetic impurities gives a linear decrease of T_c with concentration which we can formally add to the valence effect. Since the pair-breaking effect overrides the ordinary valence effect, the slope will always be negative. The purpose of this investigation is to show that for small impurity concentrations the two effects are comparable and that therefore a deviation from the Abrikosov-Gorkov theory should be observable. The result depends essentially on the relative magnitudes of the no-spin-flip and the spin-flip scattering rates of the magnetic impurities. It will be shown that experiments along that line could prove useful to check the applicability of the Abrikosov-Gorkov theory. While one might expect good agreement for rare-earth impurities, it is doubtful that transition-element impurities will be describable in that way

The calculations can be done by using a temperature-dependent Green's-function formalism as developed by Nambu and applying it to the case of magnetic impurities.[5] The anisotropy of the gap is taken into account as in Ref. 3, by assuming the following form for the matrix elements $V_{\mathbf{p}\mathbf{p}'}$ of the electron-electron interaction

$$V_{\mathbf{p}\mathbf{p}'}=V[1+a(\hat{\Omega})][1+a(\hat{\Omega}')]; \tag{1}$$

$\hat{\Omega}$ and $\hat{\Omega}'$ are unit vectors along $\mathbf{p}$ and $\mathbf{p}'$. The average $\langle a\rangle$ of $a(\hat{\Omega})$ over all directions vanishes, so that the characteristic parameter entering will be $\langle a^2\rangle$. In Ref. 4 it is shown that for the calculation of the self-energy $\sum(\mathbf{p},\omega_n)$ due to the impurities only, the diagram shown in Fig. 1 is of importance. The wavy line indicates that scattering takes place at the same impurity atom. Let $\sigma_0\cdots\sigma_3$ denote the unit matrix and the three Pauli matrices. Then in Nambu notation the temperature-dependent Green's function $G_0(\mathbf{p},\omega_n)$ can be written as

$$G_0^{-1}(\mathbf{p},\omega_n)=\epsilon_p\sigma_3-i\omega_n\sigma_0+\Delta\sigma_1, \tag{2}$$

where ϵ_p is the single-particle energy calculated from the Fermi surface and Δ is the order parameter. ω_n is given by $\omega_n=\pi T(2n+1)$, where n runs over all integers. The Dyson equation for the Green's function, taking the self-energy contribution $\sum(\mathbf{p},\omega_n)$ into account, is

$$G(\mathbf{p},\omega_n)^{-1}=G_0(\mathbf{p},\omega_n)^{-1}-\sum(\mathbf{p},\omega_n), \tag{3}$$

where

$$\sum(\mathbf{p},\omega_n)=n_i\int\frac{d^3p'}{(2\pi)^3}v(\mathbf{p}',\mathbf{p})\sigma_3G(\mathbf{p}',\omega_n)\sigma_3v(\mathbf{p},\mathbf{p}'). \tag{4}$$

Here n_i denotes the impurity density and $v(\mathbf{p}',\mathbf{p})$ is the scattering potential of the impurities, which we write as

$$v(\mathbf{p},\mathbf{p}')=v_1(\mathbf{p},\mathbf{p}')+v_2(\mathbf{p},\mathbf{p}')\mathbf{S}\mathbf{s}. \tag{5}$$

$\mathbf{S}_i$ is the spin of the ith impurity and $\mathbf{s}$ is the electron spin. The order parameter Δ is given by the σ_1 component of the self-energy $(\mathrm{SE})_{\mathrm{ph}}$ due to the electron-phonon interaction

$$(\mathrm{SE})_{\mathrm{ph}}=-\sum_{\omega_n}\int\frac{d^3p'}{(2\pi)^3}V_{\mathbf{p}\mathbf{p}'}\sigma_3G(\mathbf{p}',\omega_n)\sigma_3. \tag{6}$$

It is convenient to split $\sum(\mathbf{p},\omega_n)$ into σ_0 and σ_1 dependent parts $\sum_0$ and $\sum_1$ and to introduce two new quantities $\tilde{\omega}_n$ and $\tilde{\Delta}_n$ defined by

$$\begin{aligned}\tilde{\omega}_n(\hat{\Omega},\omega_n)&=\omega_n+\sum_0(\hat{\Omega},\omega_n),\\ \tilde{\Delta}_n(\hat{\Omega},\omega_n)&=\Delta(\hat{\Omega})-\sum_1(\hat{\Omega},\omega_n).\end{aligned} \tag{7}$$

* Work supported by the U. S. Office of Naval Research and the National Science Foundation.

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[2] H. Bömmel has been able to dissolve Eu in Pb (private communication).

[3] D. Markowitz and L. P. Kadanoff, Phys. Rev. **131**, 563 (1963).

[4] A. A. Abrikosov and L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **39**, 1781 (1960) [English transl.: Soviet Phys.—JETP **12**, 1243 (1961)].

[5] V. Ambegaokar and A. Griffin, Phys. Rev. **137**, A1151 (1965).

The angular dependence of the quantities has been indicated explicitly. If we then set $\tilde{\omega}_n/\tilde{\Delta}_n=u_n(\hat{\Omega})$, we obtain from Eqs. (7)

$$\tilde{\omega}_n=\omega_n+n_i\pi N(0)\int\frac{d\hat{\Omega}'}{4\pi}|v_1(\hat{\Omega}')|^2\frac{u_n}{(1+u_n^2)^{1/2}}$$
$$+\frac{n_i}{4}S(S+1)\pi N(0)\int\frac{d\hat{\Omega}'}{4\pi}|v_2(\hat{\Omega}')|^2\frac{u_n}{(1+u_n^2)^{1/2}} \quad (8)$$
$$\tilde{\Delta}_n=\Delta+n_i\pi N(0)\int\frac{d\hat{\Omega}'}{4\pi}\frac{|v_1(\hat{\Omega})|^2}{(1+u_n^2)^{1/2}}$$
$$-\frac{n_i}{4}S(S+1)\pi(0)\int\frac{d\hat{\Omega}'}{4\pi}\frac{|v_2(\hat{\Omega})|^2}{(1+u_n^2)^{1/2}}.$$

In the following we will assume isotropic scattering potentials v_1 and v_2. Introducing two scattering rates $1/\tau_1$ and $1/\tau_2$ by

$$1/2\tau_1=n_i\pi N(0)\{v_1^2+\tfrac{1}{4}S(S+1)v_2^2\}$$
$$1/2\tau_2=n_i\pi N(0)\{v_1^2-\tfrac{1}{4}S(S+1)v_2^2\}, \quad (9)$$

the above equations simplify to

$$\tilde{\omega}_n(\hat{\Omega})=\omega_n+\frac{1}{2\tau_1}\int\frac{d\hat{\Omega}'}{4\pi}\frac{u_n(\hat{\Omega}')}{(1+u_n(\hat{\Omega}')^2)^{1/2}}$$
$$\tilde{\Delta}_n(\hat{\Omega})=\Delta(\hat{\Omega})+\frac{1}{2\tau_2}\int\frac{d\hat{\Omega}'}{4\pi}\frac{1}{(1+u_n(\hat{\Omega}')^2)^{1/2}}. \quad (10)$$

They determine the connection between $\tilde{\omega},\tilde{\Delta}$ and ω,Δ and will be used in calculating the transition temperature. In order to obtain the latter, we have to write down the equation for the order parameter $\Delta(\hat{\Omega})$ [see Eq. (6)]

$$\Delta(\hat{\Omega})=N(0)T\int\frac{d\hat{\Omega}'}{2\pi}d\epsilon_{p'}\sum_{\omega_n}\frac{\hat{\Delta}_n(\hat{\Omega}')V_{pp'}(\hat{\Omega},\hat{\Omega}')}{\tilde{\omega}_n^2(\hat{\Omega}')^2+\epsilon_{p'}^2+\tilde{\Delta}_n^2(\hat{\Omega}')}. \quad (11)$$

In order to be able to interchange the order of summation and integration we add and subtract a term containing the quantities without tilde. In this way we obtain

$$\Delta(\hat{\Omega})=N(0)VT\pi[1+a(\hat{\Omega})]\sum_{\omega_n}\int\frac{d\hat{\Omega}'}{4\pi}[1+a(\hat{\Omega}')]$$
$$\times[1/(1+u_n^2)^{1/2}-\Delta/(\Delta^2+\omega_n^2)^{1/2}]$$
$$+N(0)VT[1+a(\hat{\Omega})]\sum_{\omega_n}\int\frac{d\hat{\Omega}'}{4\pi}d\epsilon_{p'}$$
$$\times[1+a(\hat{\Omega}')]\Delta(\hat{\Omega}')/(\omega_n^2+\epsilon_{p'}^2+\Delta^2). \quad (12)$$

This shows that $\Delta(\hat{\Omega})$ is of the form

$$\Delta(\hat{\Omega})=\epsilon_0[1+a(\hat{\Omega})].$$

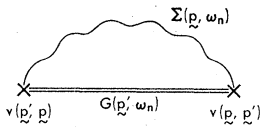

FIG. 1. Important self-energy diagram due to the presence of impurities. The wavy line indicates that scattering takes place at the same impurity atom.

We are interested in the transition temperature T_c in the presence of paramagnetic impurities as compared with T_{c0} for the pure case. From Eqs. (10) it is apparent that in that case ($u_n\gg1$) we can set

$$1/u_n(\hat{\Omega})=A_n+B_na(\hat{\Omega}). \quad (13)$$

The quantities A and B are calculated from Eqs. (10) to be

$$A_n=\frac{\epsilon_0}{\omega_n(1+1/\tau_s|\omega_n|)}\quad B_n=\frac{\epsilon_0}{\omega_n(1+1/2\tau_1|\omega_n|)},$$

where $\tau_s^{-1}=(2\tau_1)^{-1}-(2\tau_2)^{-1}$. In this way we obtain from Eq. (12)

$$1=-N(0)VT_c\pi\Big[\sum_{\omega_n}\frac{1}{\tau_s|\omega_n|(|\omega_n|+1/\tau_s)}$$
$$+\langle a^2\rangle\sum_{\omega_n}\frac{1}{2\tau_1|\omega_n|(|\omega_n|+1/2\tau_1)}\Big]$$
$$+NV[1+\langle a^2\rangle]\ln(2\omega_D\gamma/\pi T_c); \quad (14)$$

ω_D is the Debye frequency and γ is Euler's constant. It should be mentioned that the sum over ω_n should extend only over $|\omega_n|<\omega_D$ owing to the Debye cutoff in the electron-phonon interaction. But for our purposes it is completely justified to extend the summation to all ω_n (see Ref. 3).

This allows us to express T_c in a convenient way in terms of the digamma function $\psi(x)$:

$$\ln(T_{c0}/T_c)=\psi(\tfrac{1}{2}+\rho_s/2)-\psi(\tfrac{1}{2})$$
$$+\langle a^2\rangle[\psi(\tfrac{1}{2}+\rho/2)-\psi(\tfrac{1}{2})]. \quad (15)$$

Here we have set $\rho_s=1/\tau_s\pi T_c$ and $\rho=\frac{1}{2}\tau_1\pi T_c$. Use has been made of the fact that $\langle a^2\rangle$ is small compared to unity. For $\langle a^2\rangle=0$ we recover Abrikosov and Gorkov's result for the change in transition temperature with paramagnetic-impurity concentration. If $1/\tau_s=0$ (nonmagnetic impurities) we find the result of Markowitz and Kadanoff for the anisotropy effect, written in a more compact way than in Ref. 3. It is interesting to note that the smoothing out of the anisotropy in the energy gap by nonmagnetic impurities has the same effect on the transition temperature as does the pair-breaking effect of paramagnetic impurities in an isotropic superconductor if we replace T by T to the $\langle a^2\rangle^{-1}$ power in the former case.

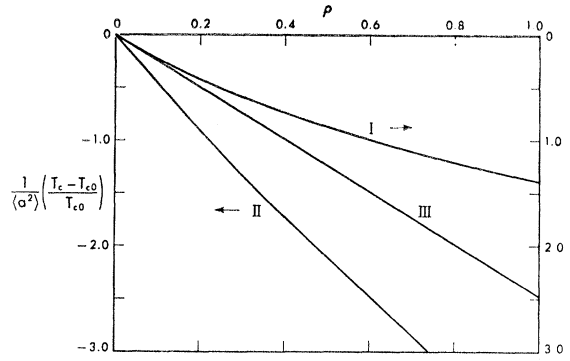

FIG. 2. Curve I shows the function $\psi(\frac{1}{2}+\rho)-\psi(\frac{1}{2})$ plotted versus ρ. Curve II shows as an example how $(T_c-T_{c0})/\langle a^2\rangle T_{c0}$ changes with ρ if $2\tau_s^*=\tau_1\langle a^2\rangle$. Curve III indicates the slope which II will have at higher impurity concentrations.

In order to discuss Eq. (15) let us first consider the case of extremely dilute impurity. In that case we can expand the ψ functions and obtain

$$T_c=T_{c0}-\pi/4\tau_s-\pi\langle a^2\rangle/8\tau_1. \tag{16}$$

The interesting point to notice is that $\langle a^2\rangle$ is of order 10^{-2} for metals like Pb, In, Sn, while τ_s is roughly two orders of magnitude larger than τ_1.[4] Therefore, the second and third terms of Eq. (16) should be of the same order of magnitude, and one should obtain an appreciable effect due to gap anisotropy. It is now apparent that for concentrations of interest τ_s will be such that we can always expand the first term in Eq. (15). Hence we can write

$$\delta T_c=-\pi/4\tau_s-\langle a^2\rangle[\psi(\tfrac{1}{2}+\rho/2)-\psi(\tfrac{1}{2})]T_{c0}. \tag{17}$$

A plot of the term proportional to $\langle a^2\rangle$ as a function of ρ_2 is shown in Fig. 2.

Up to now we have not yet talked about changes in the values of ω_D, $N(0)$, and V, etc. caused by the presence of impurities. These effects belong to the so-called valence effects and give a linear change of T_c with impurity concentration. From Eq. (17) it is clear that these effects can be incorporated into our calculations by formally replacing $-\pi/4\tau_s$, which is also proportional to the impurity concentration, by $-\pi/4\tau_s^*$. Concentrations which are so high that the term proportional to $\langle a^2\rangle$ in Eq. (17) varies very slowly compared to the $-\pi/4\tau_s^*$ term will allow the measurement of τ_s^*. Curve I in Fig. 2 shows, as an example, how $(T_c-T_{c0})/T_{c0}\langle a^2\rangle$ varies with ρ if $\tau_s^*=\tau_1\langle a^2\rangle/2$. The slope in the low-concentration region is appreciably different from that of higher concentration as can be seen by comparing it with the slope of curve III.

Equations (15) and (17) show that with respect to the change of the transition temperature the pair-breaking effect of the magnetic impurities adds to that of the smoothing out of the gap anisotropy. No cross term appears. This is a consequence of the Abrikosov-Gorkov theory, which assumes that for the self-energy all diagrams other than that shown in Fig. 1 can be neglected. Among those are all diagrams with intersecting wavy lines.

It appears that experiments with dilute solutions of magnetic impurities in superconductors would provide a check on that assumption, which has been used in many theoretical investigations. Inspection of Eq. (17) shows that the relative magnitude of the spin-flip and no-spin-flip scattering times would have to be known in order to have no adjustable parameters left. Therefore, one would either have to measure this relative magnitude separately or add nonmagnetic impurities in addition to the magnetic impurities to the superconductor. The latter method was applied in Ref. 1. It allows an independent variation of τ_1 and τ_s. It is easy to show that, in the presence of paramagnetic impurities of concentration n_a and nonmagnetic impurities of concentration n_b with an isotropic scattering potential u, the change in transition temperature is given by

$$\delta T_c=K_b n_b-(\pi/4\tau_s^*)+\langle a^2\rangle[\psi(\tfrac{1}{2}+\rho/2)-\psi(\tfrac{1}{2})],$$

where $\rho=1/2\tau\pi T_c$ and $1/2\tau=N(0)\pi(n_a v_1^2+n_b u^2)$. In defining τ we have assumed $\tau\ll\tau_s$. The quantity K_b is the valence effect due to the nonmagnetic impurities and is known for many impurities in Pb, Sn, In, and Al (Ref. 3).

Note added in proof. In a recent publication D. M. Brink and M. J. Zuckermann, Proc. Phys. Soc. (London) **85**, 329 (1965) independently obtained results similar to those derived in this paper.

ACKNOWLEDGMENT

I would like to thank Dr. A. Fetter for several interesting discussions.