Thermodynamics of Dirty Superconductors

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We use a method due to Tsekhmistrenko to eliminate from the Fröhlich Hamiltonian the electron-phonon interaction term. We then evaluate the thermodynamic properties of a superconductor described by this Hamiltonian, using a formalism developed by Zubarev and Tserkovnikov which is based on a paper by Bloch and De Dominicis. We introduce an extra term in the Hamiltonian to take the impurity scattering into account and study the effect of this extra term on the transition temperature. For the product of the mean free path and the relative change in the transition temperature we find values of 7×10^{-6}, 9×10^{-6}, and 8×10^{-6} cm for Sn, In, and Al.

1. INTRODUCTION

RECENTLY Lynton and co-workers[1,2] have shown that the effect of impurities on the transition temperature of superconductors is to a first approximation to lower it by an amount which is inversely proportional to the mean free path. This lowering can be readily understood qualitatively as it has been shown by Pippard[3] that the electron-phonon interaction—which is responsible for the superconductivity transition—is reduced if the electrons are scattered by impurities. This effect has been studied by Nakamura[4] using the Bardeen-Cooper-Schrieffer theory[5] of the thermodynamic properties of a superconductor, and he found a rough agreement between his calculated value and the experimental value for tin. One can raise several objections to the way the thermodynamic properties of a pure superconductor are derived in BCS, and we have therefore applied a more rigorous method to derive the thermodynamic properties of a superconductor. The method is due to Bloch and De Dominicis[6] and was applied by Zubarev and Tserkovnikov[7] to the Fröhlich Hamiltonian, that is, the Hamiltonian which contains an electron-phonon interaction term. For many calculations it is more convenient to work with a BCS-type Hamiltonian where the electron-phonon interaction term is replaced by an effective electron-electron interaction term. Tsekhmistrenko[8] has recently shown how one can use Feynman-diagram techniques to change from the Fröhlich Hamiltonian to the BCS Hamiltonian. Unfortunately there seem to be a few small errors in his paper and we have therefore repeated his calculations to arrive at essentially the same result. As our derivation goes a little farther than Tsekhmistrenko's, we give the main arguments in the next section. Having thus obtained a BCS-type Hamiltonian, we apply in Sec. 3 the Bloch-De Dominicis-Zubarev-Tserkovnikov method for obtaining the thermodynamic properties of a pure superconductor, after having made the essential BCS assumption about the electron-electron interaction matrix elements. In Sec. 4 we evaluate the influence of impurities on the transition temperature applying the method developed in Sec. 3 and using Nakamura's expression for the electron-impurity interaction term.

2. ELIMINATION OF THE ELECTRON-PHONON INTERACTION TERM

In this section we use Tsekhmistrenko's method[8] to eliminate from the total Hamiltonian H,

$$H=H_{\mathrm{el}}+H_{\mathrm{ph}}+V_{\mathrm{int}}, \tag{1}$$

$$H_{\mathrm{el}}=\sum\nolimits_{\mathbf{k},\sigma}E_{\mathbf{k}}a_{\mathbf{k},\sigma}{}^{\dagger}a_{\mathbf{k},\sigma}, \tag{2}$$

$$H_{\mathrm{ph}}=\sum\nolimits_{\mathbf{q}}\hbar\omega(\mathbf{q})b_{\mathbf{q}}{}^{\dagger}b_{\mathbf{q}}, \tag{3}$$

$$V_{\mathrm{int}}=\sum_{\mathbf{k},\mathbf{q},\sigma}g(\mathbf{q})[\hbar\omega(\mathbf{q})/2\Omega]^{\frac{1}{2}}\times[a_{\mathbf{k},\sigma}{}^{\dagger}a_{\mathbf{k}+\mathbf{q},\sigma}b_{\mathbf{q}}{}^{\dagger}+a_{\mathbf{k}+\mathbf{q},\sigma}{}^{\dagger}a_{\mathbf{k},\sigma}b_{\mathbf{q}}], \tag{4}$$

the term V_{int}. In Eq. (1) we have neglected the Coulomb interaction term; this is justified as long as the average phonon energy is small compared with the average energy of an electron transition, as we shall assume to be the case. In Eqs. (2), (3), and (4), $a_{\mathbf{k},\sigma}{}^{\dagger}$ and $a_{\mathbf{k},\sigma}$ are the creation and annihilation operators for electrons with momentum $\mathbf{k}$ and spin σ, $b_{\mathbf{q}}{}^{\dagger}$ and $b_{\mathbf{q}}$ are the creation and annihilation operators for phonons of momentum $\mathbf{q}$, $E_{\mathbf{k}}$ is the kinetic energy of an electron of momentum $\mathbf{k}$, taken relative to the Fermi surface energy, $\hbar\omega(\mathbf{q})$ is the energy of a phonon of momentum $\mathbf{q}$, $g(\mathbf{q})$ is the electron-phonon coupling constant, and Ω is the volume of the system. The Hamiltonian of Eq. (1) was introduced by Fröhlich[9] in 1952.

We eliminate V_{int} by considering $H_{\mathrm{el}}+H_{\mathrm{ph}}\equiv H_0$ to be the unperturbed Hamiltonian and by changing over

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to the interaction representation, retaining only those terms which are of the lowest order in ω (as was done by Tsekhmistrenko). The new interaction term H_{int} is given by the symbolical equation

$$H_{\text{int}}=T\left[V_{\text{int}}(0)\exp(-i/\hbar)\int_{-\infty}^{0}V_{\text{int}}(t'')dt''\right],\quad(5)$$

where T indicates time-ordering and where

$$V_{\text{int}}(t)=\exp(iH_0t/\hbar)V_{\text{int}}\exp(-iH_0t/\hbar).\quad(6)$$

It is convenient to introduce a canonical transformation from the electron $a^\dagger$ and a to those for electrons and holes. This means that the vacuum state will correspond to a Fermi sphere which is just filled and that H_0 is given by the equation

$$H_0=\sum_{\mathbf{q}}\hbar\omega(\mathbf{q})b_{\mathbf{q}}^\dagger b_{\mathbf{q}}+\sum_{\mathbf{k},\sigma}\epsilon(\mathbf{k})a_{\mathbf{k},\sigma}^\dagger a_{\mathbf{k},\sigma},\quad(7)$$

where

$$\epsilon(\mathbf{k})=E_{\mathbf{k}},\ \text{if } |\mathbf{k}|>\mathbf{k}_F;\quad \epsilon(\mathbf{k})=-E_{\mathbf{k}},\ \text{if } |\mathbf{k}|<k_F,\quad(8)$$

with k_F the radius of the Fermi sphere, and where the $a^\dagger$ (a) create (annihilate) an electron, if $|\mathbf{k}|>k_F$ and a hole, if $|\mathbf{k}|<k_F$.

If we evaluate $V_{\text{int}}(t)$ by the usual diagram technique, it turns out that main contribution is given by the ring diagrams of Fig. 1. It was shown by Tsekhmistrenko that other diagrams give contributions of a higher order in ω. The diagram of Fig. 1(i) gives a contribution

$$V_{\text{int}}^{(i)}=-(i/2\Omega)\int_{-\infty}^{0}dt\sum_{\mathbf{k},\mathbf{k}',\mathbf{q},\mathbf{q}',\sigma,\sigma'}g(\mathbf{q})g(\mathbf{q}')\times\hbar[\omega(\mathbf{q})\omega(\mathbf{q}')]^{\frac{1}{2}}a_{\mathbf{k},\sigma}^\dagger(0)a_{\mathbf{k}+\mathbf{q},\sigma}(0)\times\dot{B}_{\mathbf{q}}(0)a_{\mathbf{k}',\sigma'}^\dagger(t)a_{\mathbf{k}'+\mathbf{q}',\sigma'}(t)\dot{B}_{\mathbf{q}'}(t),\quad(9)$$

where

$$B_{\mathbf{q}}(t)=b_{\mathbf{q}}^\dagger(t)+b_{-\mathbf{q}}(t),\quad(10)$$

where the dots indicate as usual the contraction of a pair of operators and where the sum is only over such momenta that $|\mathbf{k}'-\mathbf{q}|<k_F$ and $|\mathbf{k}'|>k_F$. In integrating over t we introduce an adiabatic factor $e^{\lambda t}(\lambda>0)$ into the integral and take the limit $\lambda\to0$. Using the relations $\omega(\mathbf{q})=\omega(-\mathbf{q})$ and $g(\mathbf{q})=g(-\mathbf{q})$ and the relation

$$\dot{B}_{\mathbf{q}}(t)\dot{B}_{\mathbf{q}'}(t')=[\theta(t-t')e^{i\hbar\omega(\mathbf{q})(t'-t)}+\theta(t'-t)e^{i\hbar\omega(\mathbf{q})(t-t')}]\delta_{\mathbf{q}+\mathbf{q}',0},\quad(11)$$

$$\theta(t)=0,\quad \text{if } t<0;\quad \theta(t)=1,\quad \text{if } t>0,$$

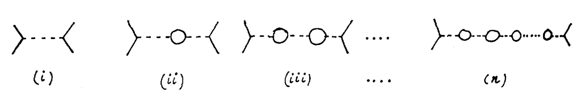

FIG. 1. The ring diagrams which contribute to $V_{\text{int}}(t)$. Solid lines are electron and hole lines and dashed lines are phonon lines.

we get from Eq. (9),

$$V_{\text{int}}^{(i)}=(2\Omega)^{-1}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q},\sigma,\sigma'}\left[\frac{\hbar\omega(\mathbf{q})g^2(\mathbf{q})}{\{z(\mathbf{k}',\mathbf{q})+\hbar\omega(\mathbf{q})\}}\right]\times a_{\mathbf{k},\sigma}^\dagger(0)a_{\mathbf{k}+\mathbf{q},\sigma}(0)a_{\mathbf{k}',\sigma'}^\dagger(0)a_{\mathbf{k}'-\mathbf{q},\sigma'}(0),\quad(12)$$

where

$$z(\mathbf{k}',\mathbf{q})=E_{\mathbf{k}'}-E_{\mathbf{k}'-\mathbf{q}}.\quad(13)$$

Equation (12) differs from the one derived by Tsekhmistrenko by a factor $\hbar\omega/[\hbar\omega-z(\mathbf{k}',\mathbf{q})]$. This is a minor correction which occurs as an additional factor in all terms in $V_{\text{int}}(t)$ and thus also in the final Eq. (23).

To evaluate the higher-order contributions we need the factor $C(t',t)$ given by Tsekhmistrenko's Eq. (11). [Note that Tsekhmistrenko uses units in which $\hbar=1$, so that his ω corresponds to our $\hbar\omega$.] This factor corresponds to the diagram of Fig. 2. It is equal to

$$C(t',t)=2\sum_{\mathbf{q}}\sum_{\mathbf{k}}^{(\mathbf{q})}C_{\mathbf{k},\mathbf{q}}(t',t)B_{-\mathbf{q}}(t),\quad(14)$$

where

$$\begin{aligned}C_{\mathbf{k},\mathbf{q}}(t',t)=&[2\theta(t'-t)/i(Y^2-\hbar^2\omega^2)]\\&\times[Ye^{i\hbar\omega(t-t')}-\hbar\omega e^{iY(t-t')}]\\&-[e^{i\hbar\omega t+iYt}/i(\hbar\omega+Y)]\\&+[2\theta(t-t')/i(Y^2-\hbar^2\omega^2)]\\&\times[Ye^{i\hbar\omega(t'-t)}-\hbar\omega e^{iY(t'-t)}],\end{aligned}\quad(15)$$

$$Y=Y(\mathbf{k},\mathbf{q})=\epsilon(\mathbf{k}+\mathbf{q})+\epsilon(\mathbf{k}),\quad(16)$$

and where $\sum_{\mathbf{k}}^{(\mathbf{q})}$ indicates a summation for which $|\mathbf{k}+\mathbf{q}|>k_F$ and $|\mathbf{k}|<k_F$. As $Y\gg\hbar\omega$, we can in the approximation in which we work put

$$C_{\mathbf{k},\mathbf{q}}(t',t)\approx(-2i/Y)[\theta(t'-t)e^{i\hbar\omega(t-t')}+\theta(t-t')e^{i\hbar\omega(t'-t)}].\quad(17)$$

The nth order diagram of Fig. 1(n) gives a contribution which after contraction and after using Eq. (17) is equal to

$$V_{\text{int}}^{(n)}=-\sum_{\mathbf{k},\mathbf{k}',\mathbf{q},\sigma,\sigma'}[g^2(\mathbf{q})\hbar\omega(\mathbf{q})/2\Omega]^n\times[\textstyle\sum_{\mathbf{k}}^{(\mathbf{q})}(4/Y)]^{n-1}I_n(z,\omega)a_{\mathbf{k},\sigma}^\dagger(0)\times a_{\mathbf{k}+\mathbf{q},\sigma}(0)a_{\mathbf{k}',\sigma'}^\dagger(0)a_{\mathbf{k}'-\mathbf{q},\sigma'}(0),\quad(18)$$

where

$$I_n(z,\omega)=i^n\int_{-\infty}^{0}\cdots\int dt_1\cdots dt_n\exp(izt_n)\times\exp(i\hbar\omega t_1)\exp[-i\hbar\omega|t_n-t_{n-1}|]\cdots\times\exp[-i\hbar\omega|t_2-t_1|].\quad(19)$$

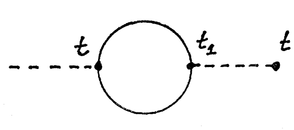

FIG. 2. The diagram corresponding to $C(t',t)$.

This multiple integral is evaluated in the Appendix and the result is

$$I_n(z,\omega)=\sum_{\lambda=0}^{n-1} K_n{}^{\lambda} J(n-\lambda,\lambda), \tag{20}$$

where

$$K_n{}^{\lambda}=\binom{n+\lambda-2}{\lambda}-\binom{n+\lambda-2}{n},$$

$$J(\beta,\gamma)=(z+\hbar\omega)^{-\beta}(2\hbar\omega)^{-\gamma}. \tag{21}$$

In our present approximation we retain only the term with the largest value of ω^{-1} and we have thus

$$\begin{aligned} I_n(z,\omega) &\approx K_n{}^{n-1} J(1,n-1) \\ &=\{2(2n-3)!/[n!(n-2)!]\} \\ &\qquad\times(z+\hbar\omega)^{-1}(2\hbar\omega)^{-n+1}, \end{aligned} \tag{22}$$

so that we get for H_{int}

$$\begin{aligned} H_{\text{int}}=-(2\Omega)^{-1} &\sum_{\mathbf{k},\mathbf{k}',\mathbf{q},\sigma,\sigma'} [g^2(\mathbf{q})\hbar\omega(\mathbf{q})/\{z(\mathbf{k}',\mathbf{q})+\hbar\omega(\mathbf{q})\}] \\ &\times\Xi(A)a_{\mathbf{k},\sigma}{}^{\dagger}(0)a_{\mathbf{k}+\mathbf{q},\sigma}(0)a_{\mathbf{k}',\sigma'}{}^{\dagger}(0)a_{\mathbf{k}'-\mathbf{q},\sigma'}(0), \end{aligned} \tag{23}$$

with

$$\begin{aligned} \Xi(A)&=1+\sum_{n=1}^{\infty}[2(2n-1)!(n-1)!(n+1)!]A^n \\ &=[1-(1-4A)^{\frac{1}{2}}]/2A, \end{aligned} \tag{24}$$

$$A=[g^2(\mathbf{q})/\Omega]\sum_{\mathbf{k}}{}^{(\mathbf{q})}[\epsilon(\mathbf{k})+\epsilon(\mathbf{k}-\mathbf{q})]^{-1}. \tag{25}$$

Apart from the factor $\hbar\omega/[\hbar\omega-z]$ mentioned before, Eq. (23) differs from the one derived by Tsekhmistrenko in the expression for $\Xi(A)$ for which he finds $(1-A)/(1-2A)$. This means that we do not agree with a result of Wentzel,[10] who estimated a radius of convergence of $A=\frac{1}{2}$—as was found by Tsekhmistrenko. Our series has a radius of convergence equal to $\frac{1}{4}$.

By the Tsekhmistrenko method we have succeeded in replacing V_{int} by H_{int} which is of the form

$$H_{\text{int}}=\sum_{\mathbf{k},\mathbf{k}',\mathbf{q},\sigma,\sigma'} I(\mathbf{k},\mathbf{k}',\mathbf{q})a_{\mathbf{k},\sigma}{}^{\dagger}a_{\mathbf{k}+\mathbf{q},\sigma}a_{\mathbf{k}',\sigma'}{}^{\dagger}a_{\mathbf{k}'-\mathbf{q},\sigma'}, \tag{26}$$

which is a BCS type electron-electron interaction term. In the following we shall use the actual BCS Hamiltonian, where $I(\mathbf{k},\mathbf{k}',\mathbf{q})$ is zero, except when $\mathbf{k}'=-\mathbf{k}$, $\sigma=-\sigma'$, which reduces Eq. (26) to

$$H_{\text{int}}=\sum_{\mathbf{k},\mathbf{k}'} J(\mathbf{k},\mathbf{k}')a_{-\mathbf{k},-}{}^{\dagger}a_{+\mathbf{k},+}{}^{\dagger}a_{+\mathbf{k}',+}a_{-\mathbf{k}',-}, \tag{27}$$

and where, moreover, $J(\mathbf{k},\mathbf{k}')$ is assumed to be a constant, negative, isotropic interaction if both $E_{\mathbf{k}}$ and $E_{\mathbf{k}'}$ are within an interval to width $2\hbar\omega$ centered around the Fermi energy, and is assumed to vanish otherwise.

[10] G. Wentzel, Phys. Rev. **83**, 168 (1951).

3. THERMODYNAMIC PROPERTIES OF A PURE SUPERCONDUCTOR

It is well known[11] that the thermodynamic properties of a quantum-mechanical system can be obtained from the grand canonical density matrix or, alternatively, from the grand partition function

$$Z(\beta)=\mathrm{Tr}e^{-\beta H}, \tag{28}$$

where H is the Hamiltonian

$$H=H_{\text{el}}+H_{\text{int}}; \tag{29}$$

we can from now on neglect the phonon part of the Hamiltonian, as it is independent of the electron part. In Eq. (28), $\beta=1/k_BT$ (k_B is Boltzmann's constant; T is the absolute temperature).

It is convenient to introduce new fermion operators, which conserve both momentum and spin, but not the number of electrons or holes, by the canonical transformation

$$\begin{aligned} \xi_{+\mathbf{k},+}&=\cos\alpha_{\mathbf{k}}a_{+\mathbf{k},+}{}^{\dagger}-\sin\alpha_{\mathbf{k}}a_{-\mathbf{k},-}, \\ \xi_{-\mathbf{k},-}&=\cos\alpha_{\mathbf{k}}a_{-\mathbf{k},-}{}^{\dagger}+\sin\alpha_{\mathbf{k}}a_{+\mathbf{k},+}, \end{aligned} \tag{30}$$

where the $\alpha_{\mathbf{k}}(=\alpha_{-\mathbf{k}})$ are arbitrary parameters to be determined presently. The transformation (30) is such that the ξ operators satisfy the same commutation relations as the a operators.

From Eqs. (30) it follows that

$$\begin{aligned} a_{+\mathbf{k},+}&=\cos\alpha_{\mathbf{k}}\xi_{+\mathbf{k},+}{}^{\dagger}+\sin\alpha_{\mathbf{k}}\xi_{-\mathbf{k},-}, \\ a_{-\mathbf{k},-}&=\cos\alpha_{\mathbf{k}}\xi_{-\mathbf{k},-}{}^{\dagger}-\sin\alpha_{\mathbf{k}}\xi_{+\mathbf{k},+}, \end{aligned} \tag{31}$$

and in terms of the ξ operators the Hamiltonian is equal to

$$H=H_0+H',\quad H'=H_1+H_2+H_3+H_4+H_5, \tag{32}$$

where

$$H_0=\sum_{\mathbf{k}}\epsilon_{\mathbf{k}}[\xi_+\xi_+{}^{\dagger}+\xi_-\xi_-{}^{\dagger}]+2\sum_{\mathbf{k}}E_{\mathbf{k}}\sin^2\alpha_{\mathbf{k}}, \tag{33}$$

$$H_1=\sum_{\mathbf{k}}(E_{\mathbf{k}}\cos2\alpha_{\mathbf{k}}-\epsilon_{\mathbf{k}})(\xi_+\xi_+{}^{\dagger}+\xi_-\xi_-{}^{\dagger}), \tag{34}$$

$$\begin{aligned} H_2=\tfrac{1}{4}\sum_{\mathbf{k},\mathbf{k}'} J(\mathbf{k},\mathbf{k}')\sin2\alpha_{\mathbf{k}}\sin2\alpha_{\mathbf{k}'}&(1-\xi_+\xi_+{}^{\dagger}-\xi_-\xi_-{}^{\dagger}) \\ &\times(1-\xi_+'\xi_+'^{\dagger}-\xi_-'\xi_-'^{+}), \end{aligned} \tag{35}$$

$$\begin{aligned} H_3&=\sum_{\mathbf{k},\mathbf{k}'} J(\mathbf{k},\mathbf{k}')[\cos^2\alpha_{\mathbf{k}}\xi_+\xi_--\sin^2\alpha_{\mathbf{k}}\xi_-{}^{\dagger}\xi_+{}^{\dagger}] \\ &\quad\times[\cos^2\alpha_{\mathbf{k}'}\xi_-'^{\dagger}\xi_+'^{\dagger}-\sin^2\alpha_{\mathbf{k}'}\xi_+'\xi_-'] \\ &=\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{k}'} J(\mathbf{k},\mathbf{k}')[(\sin^2\alpha_{\mathbf{k}}\sin^2\alpha_{\mathbf{k}'}+\cos^2\alpha_{\mathbf{k}}\cos^2\alpha_{\mathbf{k}'}) \\ &\quad\times(\xi_+\xi_-\xi_-'^{\dagger}\xi_+'^{\dagger}+\xi_+'\xi_-'\xi_-{}^{\dagger}\xi_+{}^{\dagger}) \\ &\quad-(\sin^2\alpha_{\mathbf{k}}\cos^2\alpha_{\mathbf{k}'}+\sin^2\alpha_{\mathbf{k}'}\cos^2\alpha_{\mathbf{k}}) \\ &\qquad\times(\xi_+\xi_-\xi_+'\xi_-'+\xi_-{}^{\dagger}\xi_+{}^{\dagger}\xi_-'^{\dagger}\xi_+'^{\dagger})], \end{aligned} \tag{36}$$

$$H_4=\sum_{\mathbf{k}}E_{\mathbf{k}}\sin2\alpha_{\mathbf{k}}(\xi_-{}^{\dagger}\xi_+{}^{\dagger}+\xi_+\xi_-), \tag{37}$$

[11] For instance, D. ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, New York, 1954), Chap. VII.

$$H_5=\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{k}'} J(\mathbf{k},\mathbf{k}')[\sin 2\alpha_{\mathbf{k}}(1-\xi_-\xi_-^\dagger-\xi_+\xi_+^\dagger)$$
$$\times(\cos^2\alpha_{\mathbf{k}'}\xi_-'^\dagger\xi_+'^\dagger-\sin^2\alpha_{\mathbf{k}'}\xi_+'\xi_-')$$
$$+\sin 2\alpha_{\mathbf{k}'}(1-\xi_-'\xi_-'^\dagger-\xi_+'\xi_+'^\dagger)$$
$$\times(\cos^2\alpha_{\mathbf{k}}\xi_+\xi_--\sin^2\alpha_{\mathbf{k}}\xi_-^\dagger\xi_+^\dagger)$$
$$=\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{k}'} J(\mathbf{k},\mathbf{k}')\cos 2\alpha_{\mathbf{k}}\sin 2\alpha_{\mathbf{k}'}(\xi_+\xi_-+\xi_-^\dagger\xi_+^\dagger)$$
$$\times(1-\xi_-'\xi_-'^\dagger-\xi_+'\xi_+'^\dagger), \quad (38)$$

where we have used the fact that $J(\mathbf{k},\mathbf{k}')=J(\mathbf{k}',\mathbf{k})$ and where

$$\xi_+=\xi_{+\mathbf{k},+},\quad \xi_-=\xi_{-\mathbf{k},-},\quad \xi_+'=\xi_{+\mathbf{k}',+},\quad \xi_-'=\xi_{-\mathbf{k}',-}. \quad (39)$$

Let $|0\rangle$ denote the state in which no electrons are present, and Φ_0 the vacuum state for the ξ operators. Writing for Φ_0 the product expression

$$\Phi_0=\prod_{\mathbf{k}}\phi_{0\mathbf{k}},\quad \phi_{0\mathbf{k}}=(\cos\alpha_{\mathbf{k}}+\sin\alpha_{\mathbf{k}}a_{+\mathbf{k},+}^\dagger a_{-\mathbf{k},-}^\dagger)|0\rangle \quad (40)$$

we see that

$$\xi_+^\dagger\phi_{0\mathbf{k}}=0,\quad \xi_-^\dagger\phi_{0\mathbf{k}}=0, \quad (41)$$

so that Φ_0 is a reasonable assumption for the vacuum state.

As

$$\begin{gathered}\xi_+\phi_{0\mathbf{k}}=a_{+\mathbf{k},+}^\dagger|0\rangle,\quad \xi_-\phi_{0\mathbf{k}}=a_{-\mathbf{k},-}^\dagger|0\rangle,\\ \xi_+\xi_-\phi_{0\mathbf{k}}=(\cos\alpha_{\mathbf{k}}a_{+\mathbf{k},+}^\dagger a_{-\mathbf{k},-}^\dagger-\sin\alpha_{\mathbf{k}})|0\rangle,\end{gathered} \quad (42)$$

we can construct any wave function Ψ which is a combination of $|0\rangle$, $a_{+\mathbf{k},+}^\dagger|0\rangle$, $a_{-\mathbf{k},-}^\dagger|0\rangle$, and $a_{+\mathbf{k},+}^\dagger a_{-\mathbf{k},-}^\dagger|0\rangle$ as a combination of $\phi_{0\mathbf{k}}$, $\xi_+\phi_{0\mathbf{k}}$, $\xi_-\phi_{0\mathbf{k}}$, and $\xi_+\xi_-\phi_{0\mathbf{k}}$, or

$$\Psi=\prod_{\mathbf{k}}[p_{\mathbf{k}}^{\frac{1}{2}}\xi_+\xi_-+s_{\mathbf{k}}^{\frac{1}{2}}(\xi_++\xi_-)+(1-2s_{\mathbf{k}}-p_{\mathbf{k}})^{\frac{1}{2}}]\Phi_0. \quad (43)$$

The expectation value E of the energy corresponding to the state Ψ follows from Eqs. (32) to (38) and (43) and turns out to be equal to

$$E=\sum_{\mathbf{k}} 2E_{\mathbf{k}}\{\cos 2\alpha_{\mathbf{k}}(s_{\mathbf{k}}+p_{\mathbf{k}})+\sin^2\alpha_{\mathbf{k}}$$
$$+\sin 2\alpha_{\mathbf{k}}[p_{\mathbf{k}}(1-2s_{\mathbf{k}}-p_{\mathbf{k}})]^{\frac{1}{2}}\}+\sum_{\mathbf{k},\mathbf{k}'} J(\mathbf{k},\mathbf{k}')$$
$$\times\{\cos 2\alpha_{\mathbf{k}}[p_{\mathbf{k}}(1-2s_{\mathbf{k}}-p_{\mathbf{k}})]^{\frac{1}{2}}$$
$$+\tfrac{1}{2}\sin 2\alpha_{\mathbf{k}}(1-2s_{\mathbf{k}}-2p_{\mathbf{k}})\}$$
$$\times\{\cos 2\alpha_{\mathbf{k}'}[p_{\mathbf{k}'}(1-2s_{\mathbf{k}'}-p_{\mathbf{k}'})]^{\frac{1}{2}}$$
$$+\tfrac{1}{2}\sin 2\alpha_{\mathbf{k}'}(1-2s_{\mathbf{k}'}-2p_{\mathbf{k}'})\}. \quad (44)$$

To find the ground state of the system, we minimize E with respect to the $\alpha_{\mathbf{k}}$, $s_{\mathbf{k}}$, and $p_{\mathbf{k}}$, and find the following equations (for the sake of simplicity we have everywhere dropped the indices $\mathbf{k}$):

$$\partial E/\partial\alpha=2E\{\sin 2\alpha(1-2p-2s)$$
$$+2\cos 2\alpha[p(1-2s-p)]^{\frac{1}{2}}\}$$
$$-2J\{\cos 2\alpha(1-2p-2s)$$
$$-2\sin 2\alpha[p(1-2s-p)]^{\frac{1}{2}}\}, \quad (45)$$

$$\partial E/\partial s=2E\{\cos 2\alpha-\sin 2\alpha[p/(1-2s-p)]^{\frac{1}{2}}\}$$
$$+2J\{\sin 2\alpha+\cos 2\alpha[p/(1-2s-p)]^{\frac{1}{2}}\}, \quad (46)$$

$$\partial E/\partial p=E\{2\cos 2\alpha+\sin 2\alpha[(1-2s-2p)^2/$$
$$p(1-2s-p)]^{\frac{1}{2}}\}+J\{2\sin 2\alpha-\cos 2\alpha$$
$$\times[(1-2s-2p)^2/p(1-2s-p)]^{\frac{1}{2}}\}, \quad (47)$$

where

$$J\equiv J_{\mathbf{k}}=\sum_{\mathbf{k}'} J(\mathbf{k},\mathbf{k}')\{\cos 2\alpha_{\mathbf{k}'}[p_{\mathbf{k}'}(1-2s_{\mathbf{k}'}-p_{\mathbf{k}'})]^{\frac{1}{2}}$$
$$+\tfrac{1}{2}\sin 2\alpha_{\mathbf{k}}(1-2s_{\mathbf{k}'}-2p_{\mathbf{k}'})\}. \quad (48)$$

Equations (45) to (47) can be simplified by introducing quantities λ and γ as follows:

$$\lambda\cos 2\gamma=1-2s-2p,\quad \lambda\sin 2\gamma=2[p(1-2s-p)]^{\frac{1}{2}}, \quad (49)$$

or,

$$\lambda=1-2s,\quad \tan^2\gamma=(1-2s-p)/p. \quad (50)$$

We then get, instead of Eqs. (45)–(47),

$$E\sin 2(\alpha+\gamma)=J\cos 2(2\alpha+\gamma), \quad (51)$$

$$2\sec\gamma[E\cos(2\alpha+\gamma)+J\sin(2\alpha+\gamma)]=0, \quad (52)$$

$$(2/\lambda)[E\sin 2(\alpha+\gamma)-J\cos 2(\alpha+\gamma)]\csc\gamma=0. \quad (53)$$

If we use the BCS potential,

$$J(\mathbf{k},\mathbf{k}')=-V,\quad \text{if } |E_{\mathbf{k}}-E_F|<\hbar\omega \text{ and } |E_{\mathbf{k}'}-E_F|<\hbar\omega;$$
$$=0,\quad \text{otherwise}, \quad (54)$$

we find that

$$J_{\mathbf{k}}=0,\quad \text{if } |E_{\mathbf{k}}-E_F|>\hbar\omega, \quad (55)$$

and

$$J_{\mathbf{k}}=\tfrac{1}{2}\sum_{\mathbf{k}'} J(\mathbf{k},\mathbf{k}')\lambda_{\mathbf{k}'}\sin 2(\alpha_{\mathbf{k}'}+\gamma_{\mathbf{k}'})=\text{constant}$$
$$=\epsilon_0,\quad \text{otherwise}. \quad (56)$$

Equations (51) and (53) are satisfied if

$$E_{\mathbf{k}}\tan 2(\alpha_{\mathbf{k}}+\gamma_{\mathbf{k}})=\epsilon_0, \quad (57)$$

and one finds that Eq. (52) can only be satisfied, if

$$\cos\gamma_{\mathbf{k}}=0. \quad (58)$$

In deriving Eq. (58) one uses Eq. (57).

Using Eq. (58), we get for E the expression

$$E=\sum_{\mathbf{k}} E_{\mathbf{k}}[\cos 2\alpha_{\mathbf{k}}(1-\lambda_{\mathbf{k}}\cos 2\gamma_{\mathbf{k}})+2\sin^2\alpha_{\mathbf{k}}]$$
$$-\epsilon_0^2/V. \quad (59)$$

We see that we can now determine $\lambda_{\mathbf{k}}$ by requiring that $\lambda_{\mathbf{k}}\cos 2\gamma_{\mathbf{k}}$ be a maximum, or, that $1-2s_{\mathbf{k}}-2p_{\mathbf{k}}$ be a maximum, which means that Φ_0 corresponds, indeed, to the ground state, provided the $\alpha_{\mathbf{k}}$ satisfy Eq. (57).

We shall now evaluate the grand partition function and hence the Gibbs free energy G which is related to $Z(\beta)$ by the equation

$$\beta G=-\ln Z. \quad (60)$$

We evaluate Z by considering H' of Eq. (32) to be a perturbation to the H_0 which corresponds to noninteracting excitations. The terms H_1 to H_5 have the following physical meaning: H_1 is the self-energy of the single "particles," H_2 is the self-energy of the particles in pairs, due to the interaction between them, and H_3, H_4, and H_5 correspond to the simultaneous creation or annihilation of one or two pairs of particles. Feynman-diagram perturbation theory is used. In our diagrams a solid line going up marked by $\mathbf{k}$ represents the presence

of a pair of quasi-particles $+\mathbf{k},+$ and $-\mathbf{k},-$; if a solid line goes down it represents a pair of holes; a dashed line, which only occurs through H_1 vertices, represents a single quasi-particle.

For the Gibbs free energy we find

$$G=G_0+G', \tag{61}$$

where G_0 is the Gibbs free energy corresponding to the noninteracting quasiparticles,

$$G_0=-2k_BT\sum_{\mathbf{k}} E_{\mathbf{k}}\sin^2\alpha_{\mathbf{k}} -2k_BT\sum_{\mathbf{k}}\ln[1+\exp(-\beta\epsilon_{\mathbf{k}})], \tag{62}$$

where $\epsilon_{\mathbf{k}}$ is the (as yet unknown) energy of the quasi-particles which will be determined from the requirement that the system is in equilibrium; G' is given by the sum over connected diagrams (indicated by the subscript c)

$$G'=-k_BT\sum_{p=0}^{\infty}[(-1)^p/(p!)]\int_0^\beta\cdots\int_0^\beta dt_1\cdots dt_p \times T[H'(t_1)\cdots H'(t_p)]_c, \tag{63}$$

with

$$H'(t)=\exp(H_0t)H'\exp(-H_0t). \tag{64}$$

In Fig. 3 we have given a number of diagrams corresponding to vertices at which a pair of quasi-particles with momentum $\mathbf{k}$ is created; the vertices (a) arise through H_4, and the vertices (b) and (c) through H_5. These vertices will give large contributions to G' and we shall choose the $\alpha_{\mathbf{k}}$ such that the total contribution from all vertices of this kind will vanish. This means that the $\alpha_{\mathbf{k}}$ must satisfy the relations

$$E_{\mathbf{k}}\sin2\alpha_{\mathbf{k}}+\tfrac{1}{2}\cos2\alpha_{\mathbf{k}}\sum_{\mathbf{k}'}J(\mathbf{k},\mathbf{k}') \times\sin2\alpha_{\mathbf{k}'}(1-2n_{\mathbf{k}'})=0, \tag{65}$$

where

$$n_{\mathbf{k}}=\xi_{\mathbf{k}}\xi_{\mathbf{k}}^{\dagger}. \tag{66}$$

If we use for $J(\mathbf{k},\mathbf{k}')$ Eq. (54), we get

$$E_{\mathbf{k}}\tan2\alpha_{\mathbf{k}}=\tfrac{1}{2}\sum_{\mathbf{k}'}V\sin2\alpha_{\mathbf{k}'}(1-2n_{\mathbf{k}'})=\epsilon_0. \tag{67}$$

where ϵ_0 is defined by Eq. (67).

If we consider the general expansion (63) and bear in mind that V is a small parameter (this can be verified to be the case for actual superconductors; see Table I for values of $N(0)V$, where $N(0)$ is the number of states per unit energy at the Fermi surface which is a large number) we see that the only terms which are left over, if we choose the $\alpha_{\mathbf{k}}$ according to Eqs. (65) or (67), and which are not of a higher order in V, are the ones coming from H_1 and H_2 which give for G'

$$G'=-k_BT[\sum_{\mathbf{k}} n_{\mathbf{k}}(E_{\mathbf{k}}\cos2\alpha_{\mathbf{k}}-\epsilon_{\mathbf{k}}) -\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{k}'}V\sin2\alpha_{\mathbf{k}}\sin2\alpha_{\mathbf{k}'}(1-2n_{\mathbf{k}})(1-2n_{\mathbf{k}'})]. \tag{68}$$

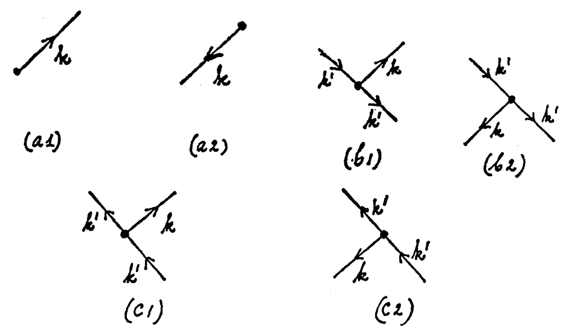

FIG. 3. Vertices at which a pair of quasi-particles is created.

The equilibrium condition is $\partial G'/\partial n_{\mathbf{k}}=0$, and we get from this condition and Eqs. (68) and (67)

$$[E_{\mathbf{k}}\cos2\alpha_{\mathbf{k}}-\epsilon_{\mathbf{k}}]+\sin2\alpha_{\mathbf{k}}E_{\mathbf{k}}\tan2\alpha_{\mathbf{k}}=0,$$

or,

$$E_{\mathbf{k}}=\epsilon_{\mathbf{k}}\cos2\alpha_{\mathbf{k}}; \tag{69}$$

and from Eqs. (67) and (69) we get finally for the energy of the quasi-particles the equation

$$\epsilon_{\mathbf{k}}^2=\epsilon_0^2+E_{\mathbf{k}}^2. \tag{70}$$

Equations (67) and (70) are the BCS equations which we now have derived by the Zubarev-Tserkovnikov method.

Thouless[12] has drawn attention to a possible divergence arising from the contributions to $\partial G'/\partial n_{\mathbf{k}}$ of the "ladder-diagrams" that are made up entirely of vertices in which a pair of quasi-particles is annihilated and another pair of different energy is created to take its place. It is possible to show[12a] that, if we renormalize the energies using H_1 and H_2, this contribution is smaller by at least one order in V than the terms considered and thus can safely be neglected.

4. THERMODYNAMIC PROPERTIES OF IMPURE SUPERCONDUCTORS

In considering impure superconductors, we shall follow Nakamura[4] and add an extra perturbing term H_6 to the Hamiltonian of Eq. (32) which describes the scattering without spin-flip of the electrons by an impurity. We write

$$H_6=\sum_{\mathbf{k},\mathbf{k}',\sigma}v_{\mathbf{k},\mathbf{k}'}a_{\mathbf{k},\sigma}^{\dagger}a_{\mathbf{k}',\sigma}, \tag{71}$$

and assume

$$v_{\mathbf{k},\mathbf{k}'}=v_{-\mathbf{k}',-\mathbf{k}}. \tag{72}$$

In fact, we shall replace $v_{\mathbf{k},\mathbf{k}'}$ by an average value v_F which is an average taken over the Fermi surface (see Nakamura[4]).

Using Eq. (72) and Eqs. (31), we can write H_6 in the

[12] D. J. Thouless, Ann. Phys. (N.Y.) **10**, 553 (1960).
[12a] This proof will be published elsewhere.

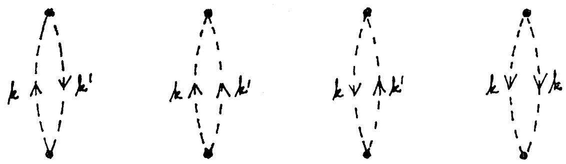

FIG. 4. Second-order diagrams contributing to G' in impure superconductors.

form

$$H_6=\sum_{\mathbf{k},\mathbf{k}'} v_F[2\sin^2\alpha_{\mathbf{k}}\delta_{\mathbf{k},\mathbf{k}'}+\cos(\alpha_{\mathbf{k}}+\alpha_{\mathbf{k}'})\times(\xi_+\xi_+'^{\dagger}+\xi_-'\xi_-^{\dagger})+\sin(\alpha_{\mathbf{k}}+\alpha_{\mathbf{k}'})\times(\xi_-^{\dagger}\xi_+'^{\dagger}+\xi_+\xi_-')]. \quad (73)$$

As we are considering scattering processes the term involving $\delta_{\mathbf{k},\mathbf{k}'}$ may be dropped.

In lowest order the only terms contributing to G' will be those corresponding to the second-order diagrams of Fig. 4. These diagrams give a term B in $-\beta\mathbf{G}'$ which is equal to

$$B=\sum_{\mathbf{k},\mathbf{k}'}|v_F|^2\{\cos^2(\alpha_{\mathbf{k}}+\alpha_{\mathbf{k}'})[n(1-n')-n'(1-n)]\times(\epsilon'-\epsilon)^{-1}+\sin^2(\alpha_{\mathbf{k}}+\alpha_{\mathbf{k}'})\times[(1-n)(1-n')-nn'](\epsilon'+\epsilon)^{-1}\}, \quad (74)$$

where

$$\epsilon=\epsilon_{\mathbf{k}}, \quad \epsilon'=\epsilon_{\mathbf{k}'}. \quad (75)$$

From Eq. (69) it follows that

$$\begin{aligned}\sin^2(\alpha_{\mathbf{k}}+\alpha_{\mathbf{k}'})&=\tfrac{1}{2}+(\epsilon_0^2-EE')/2\epsilon\epsilon',\\ \cos^2(\alpha_{\mathbf{k}}+\alpha_{\mathbf{k}'})&=\tfrac{1}{2}-(\epsilon_0^2-EE')/2\epsilon\epsilon'.\end{aligned} \quad (76)$$

The sums in Eq. (74) are taken on both sides of the Fermi surface and as E is an odd function and ϵ an even function with respect to that surface, we can drop the terms involving EE'. We thus get for B the equation

$$B=\sum_{\mathbf{k},\mathbf{k}'}|v_F|^2\{[(n'-n)/(\epsilon-\epsilon')]+[(1-n-n')/(\epsilon+\epsilon')]-(\epsilon_0^2/\epsilon\epsilon')\times[(n'-n)/(\epsilon-\epsilon')]+(\epsilon_0^2/\epsilon\epsilon')\times[(1-n-n')/(\epsilon+\epsilon')], \quad (77)$$

and we get a contribution C to $-\beta\partial G'/\partial n_{\mathbf{k}}$ from this term which is equal to

$$C=\sum_{\mathbf{k}'}|v_F|^2[2\epsilon-2(\epsilon_0^2/\epsilon)](\epsilon'^2-\epsilon^2)^{-1}. \quad (78)$$

All sums are over the region $-\hbar\omega\leqslant\epsilon,\ \epsilon'\leqslant\hbar\omega$. As we are considering low-impurity concentrations, we can put $\epsilon^2-\epsilon'^2$ in zeroth approximation equal to $E^2-E'^2$. Changing from a sum to an integral, we get

$$C=2N(0)|v_F|^2\int_0^{\hbar\omega}2E^2dE'/[\epsilon(E'^2-E')] \quad (79)$$

$$\approx-2\nu E^2/\epsilon\approx-2\nu\epsilon, \quad (80)$$

where

$$\nu=2N(0)|v_F|^2/\hbar\omega. \quad (81)$$

In deriving Eq. (80) from Eq. (79) we have used the fact that over the range of values in which we are interested, the logarithm resulting from the integration can be expanded in a power series, and only the first term retained (compare Nakamura[4]).

We can now again use Eq. (67) and the condition $\partial G'/\partial n_{\mathbf{k}}=0$ to determine the thermodynamic properties of the superconductor. The equilibrium condition which led in the previous section to Eq. (69) now includes the term $C/(-\beta)$, and instead of Eq. (70) we get, using Eq. (67),

$$(1+\nu)\epsilon_{\mathbf{k}}=(\epsilon_0^2+E_{\mathbf{k}}^2)^{\frac{1}{2}}. \quad (82)$$

To the approximation in which we are working the influence of the impurities is thus a change in the $\epsilon_{\mathbf{k}}$ scale, and thus a change in the temperature scale, as the energy spectrum directly determines the thermodynamic behavior in the BCS theory. We get thus, instead of a transition temperature T_{cp} for a pure superconductor, a transition $T_{c\ \mathrm{imp}}$ for the impure superconductor which is related to T_{cp} by the equation

$$(1+\nu)T_{c\ \mathrm{imp}}=T_{cp}. \quad (83)$$

In order to estimate the shift in the transition temperature, we must find ν. Using Nakamura's result[4] for $|v_F|^2$ we get from Eq. (81)

$$\nu=9\hbar^4/[4(r_sa_0)^3m^2k_B\Theta E_Fl_r], \quad (84)$$

where a_0 is the Bohr radius, r_s the mean distance between the electrons in units of a_0, Θ the Debye temperature, E_F the Fermi energy, and l_r the mean free path corresponding to the residual resistance. Values of E_F can be obtained from electronic specific heat data and those for r_s and Θ are given by Pines.[13] In Table I we have collected for Sn, In, and Al the values of r_s, Θ, E_F, and $N(0)V$ (which enters into Nakamura's expression for the change ΔT_c in the critical temperature), as well as the experimental and theoretical values of $l_r\Delta T_c/T_c$. For comparison we have included the values following from Nakamura's Eq. (21).

We see that our results are rather larger than the experimental data, while Nakamura's values are by about the same factor smaller than the experimental ones.[14]

TABLE I. Experimental and theoretical data for the superconductors Sn, In, and Al.

		Sn	In	Al
r_s		2.21	2.40	2.06
Θ (in °K)		195	109	375
E_F (in 10^{-11} erg)		1.131	1.194	0.583
$N(0)V$		0.296	0.345	0.193
$l_r\Delta T_c/T_c$ in 10^{-6} cm	Experimental	2.7±0.3	2.6±0.7	2.7±0.3
	Nakamura	0.73	0.82	1.39
	From Eqs. (83) and (84)	6.9	9.0	8.6

[13] D. Pines, Phys. Rev. **109**, 280 (1958).

[14] Abrikosov and Gor'kov [J. Exptl. Theoret. Phys. (U.S.S.R). **39**, 1781 (1960)] have recently studied the influence of impurities on the superconducting transition temperature. Their conclusion that the term H_6 of Eq. (61) cannot lead to an appreciable lowering of the transition temperature seems not to be corroborated by either Nakamura's or our analysis.

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APPENDIX

In this Appendix we prove Eq. (20) of Sec. 2. We note first of all that

$$\int_{-\infty}^{0} dt'\, e^{izt'} e^{-i\hbar\omega|t-t'|} = -i[e^{izt}/(z+\hbar\omega)+(e^{i\hbar\omega t}-e^{izt})/(z-\hbar\omega)], \quad \text{(A1)}$$

so that it follows from Eq. (19) that

$$I_n(z,\omega)=I_{n-1}(z,\omega)/(z+\hbar\omega) +[I_{n-1}(\omega,\omega)-I_{n-1}(z,\omega)]/(z-\hbar\omega). \quad \text{(A2)}$$

Consider $I_2(z,\omega)$:

$$\begin{aligned} I_2(z,\omega) &= -\int_{-\infty}^{0}\int dt dt'\, e^{izt'} e^{i\hbar\omega t} e^{-i\hbar\omega|t-t'|} \\ &= i\int_{-\infty}^{0} dt\{e^{2i\hbar\omega t}(z-\hbar\omega)^{-1} \\ &\qquad + e^{i(z+\hbar\omega)t}[(z+\hbar\omega)^{-1}-(z-\hbar\omega)^{-1}]\} \\ &= J(2,0)+J(1,1), \end{aligned} \quad \text{(A3)}$$

where $J(\beta,\gamma)$ is given by Eq. (21).

From Eqs. (A1) and (A3), it follows that

$$I_n(z,\omega)=\sum_{\lambda=0}^{n-1} K_n^{\lambda} J(n-\lambda,\lambda), \quad \text{(A4)}$$

and from Eq. (A1) that

$$K_n^{\lambda}=\sum_{\mu=0}^{\lambda} K_{n-1}^{\mu}. \quad \text{(A5)}$$

The K_n^{λ} can be evaluated by induction and Eq. (21) follows.