cell volume expansion of about one part in 10^3. Both of these determinations are in agreement with a macroscopic measurement of the volume. Using a strain gauge technique, the volume of a pressed pellet of polycrystalline $NiCr_2O_4$ was observed to increase about 0.8 parts in 10^3 on passing through the transformation temperature.[33]

[33] P. J. Wojtowicz and L. A. Zanoni (unpublished results, 1958).

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Isotope Effect in the Bardeen-Cooper-Schrieffer and Bogoliubov Theories of Superconductivity

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It is shown that the Bardeen-Cooper-Schrieffer and Bogoliubov theories of superconductivity predict an isotope effect which is the same for all superconductors, so long as the Coulomb interaction is neglected. This is demonstrated by writing the system of integral equations in a mass-invariant form, and it does not involve finding actual solutions. The theories predict that H_0, T_c, and the energy gap at $T=0$ are proportional to $M^{-\frac{1}{2}}$. The inclusion of the Coulomb interaction destroys the invariance of the equations and introduces deviations from the $-\frac{1}{2}$ in the exponent. The magnitude of the deviation depends on the particular superconductor considered.

I. INTRODUCTION

THE experimentally determined fact that the critical temperature T_c of a superconductor is proportional to $M^{-\frac{1}{2}}$ where M is the atomic mass, the so-called isotope effect, is one of the phenomena that must be explained by any successful theory of superconductivity.[1] This effect now seems to hold without exception for the superconductors tested, Sn, Hg, Tl, and Pb. For the recent theory of Bardeen, Cooper, and Schrieffer,[2] the proof of the isotope effect as given by these authors is based on an approximate solution. First the electron-electron interaction is set equal to zero if either electron in either the initial or final state is outside a certain region R about the Fermi surface. It is then found that T_c is proportional to the width of R in terms of the energy. This width is taken to be $\langle\hbar\omega\rangle_{\text{Av}}$, an average phonon energy, which[3] is proportional to $M^{-\frac{1}{2}}$. Hence the isotope effect follows. The proof is thus directly dependent on the choice for the width of the interaction range R. This particular value for the width is taken since the phonon part of the electron-electron interaction changes from a negative to a positive quantity if the energy change of one of the electrons becomes larger than the phonon energy corresponding to the momentum transferred. However, it does not seem justifiable to discard the interaction where it is repulsive. Besides, for the Bardeen-Pines interaction[3] the phonon part becomes repulsive when the energy *difference* becomes larger than $\hbar\omega$, whereas BCS cuts off the interaction if either electron energy falls outside R.[4]

We give here a proof of the isotope effect for the BCS and Bogoliubov[5] theories which is based on the invariance properties of the Bogoliubov[5]-Valatin[6] integral equations under changing mass and does not involve finding explicit solutions. Neglecting the Coulomb interaction, the isotope effect can be demonstrated by this method even when band structures, anisotropies, and the functional dependence of $\mu(\nu)$ [$2\mu(0)$ is the energy gap] are considered as well as the exchange energy by a Hartree-Fock approximation. It is found that T_c, H_0, and the energy gap at $T=0$ are all proportional to $M^{-\frac{1}{2}}$.

[1] For a discussion of the experimental results and references to the literature, see B. Serin, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 15, p. 237. The most recent work on Pb is by Hake, Mapother, and Decker, Phys. Rev. **112**, 1522 (1958).

[2] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957); referred to as BCS.

[3] J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955); referred to as BP.

[4] It has been pointed out by J. Bardeen (private communication) that the scale of energies is determined by $\hbar\omega$ since it is the only energy which enters the problem. Thus even if there is a distribution of frequencies, the energy scale is proportional to $M^{-\frac{1}{2}}$. Despite these general arguments, it seems desirable to the author to see the proof carried through explicitly. The author wishes to thank Professor Bardeen for communicating this argument.

[5] N. N. Bogoliubov, Nuovo cimento **7**, 794 (1958); Bogoliubov, Tolmachev, and Shirkov, *A New Method in the Theory of Superconductivity* (Consultants Bureau, Inc., New York, 1959).

[6] J. G. Valatin, Nuovo cimento **7**, 843 (1958).

We also find a general condition that must be satisfied by any other phonon interaction that might be used in the BCS theory if it is to give the isotope effect.

The integral equations are not completely invariant with respect to the mass, but the errors involved are very small as long as the solution $\mu(\nu)$ of the integral equation goes to zero in an order of magnitude of $k\theta_D$ away from the Fermi surface. This criterion is satisfied for the case that the Coulomb interactions are neglected. It has been shown by means of an approximate solution[5] that when the Coulomb interaction is included $\mu(\nu)$ does not vanish a distance of the order of magnitude of the Fermi energy away from the Fermi surface. The integral equations can no longer be written in an invariant form. However, the contribution from the phonon part dominates that from the Coulomb part (the criterion for superconductivity) and the former part can still be expressed in a mass invariant way. The exponent is now $-\frac{1}{2}$ only to a first approximation with the deviation from this value depending on the particular superconductor considered.

II. THE GENERAL FORMULATION OF THE BCS THEORY

We use the formulation and notation of Valatin[6] which is more general than that in the BCS paper. The Hamiltonian for the n-electron system is

$$H=\sum_{\mathbf{k}\sigma}\epsilon_{\mathbf{k}}a_{\mathbf{k}\sigma}{}^{*}a_{\mathbf{k}\sigma}+\tfrac{1}{2}\sum_{\mathbf{k}\mathbf{k}'\mathbf{q}\sigma\sigma'}V_{\mathbf{k}\mathbf{k}'}a_{\mathbf{k}'\sigma}{}^{*}a_{\mathbf{q}-\mathbf{k}'\sigma'}{}^{*}a_{\mathbf{q}-\mathbf{k}\sigma'}a_{\mathbf{k}\sigma}, \quad (1)$$

where $a_{\mathbf{k}\sigma}$ annihilates an "electron" in Bloch state $\mathbf{k}$ with spin σ, and $\epsilon_{\mathbf{k}}$ is the energy of this single-electron state. These are not ordinary electrons in a periodic potential, but they carry an associated virtual plasmon and phonon cloud.[3] Here $\mathbf{k}$ is used to denote the band as well as the wave vector, so that k vectors in different zones refer to different bands.

The BCS trial wave function for the ground state is a linear combination of Slater determinants in which the one-electron states are occupied in pairs, the pairs taken from states of opposite wave vector and opposite spin in the same band.

$$\Psi_0=\prod_{\mathbf{k}}\frac{(1+g_{\mathbf{k}}a_{\mathbf{k}\uparrow}{}^{*}a_{-\mathbf{k}\downarrow}{}^{*})}{(1+|g_{\mathbf{k}}|^2)^{\frac{1}{2}}}\Phi_0, \quad (2)$$

where Φ_0 is the vacuum. For certain rather anomalous potentials, one may obtain a lower energy if pairs of opposite k but parallel spins are correlated. This depends on the exact form of the potential[7] $V_{\mathbf{k}\mathbf{k}'}$. In either case the isotope effect is derived in the same way.

By minimizing the energy with respect to the $g_{\mathbf{k}}$, the latter are determined to be

$$g_{\mathbf{k}}=(\mu_{\mathbf{k}}{}^{*})^{-1}(E_{\mathbf{k}}-\nu_{\mathbf{k}}), \quad (3)$$

with

$$E_{\mathbf{k}}\equiv+(\nu_{\mathbf{k}}{}^2+|\mu_{\mathbf{k}}|^2)^{\frac{1}{2}}, \quad (4)$$

where the functions $\mu_{\mathbf{k}}$ and $\nu_{\mathbf{k}}$ together with the constant λ satisfy

$$\nu_{\mathbf{k}}=\xi_{\mathbf{k}}-\lambda+\tfrac{1}{2}\sum_{|\mathbf{k}'|<k_F}V_1(\mathbf{k},\mathbf{k}')[1+\nu_{\mathbf{k}'}/E_{\mathbf{k}'}]-\tfrac{1}{2}\sum_{|\mathbf{k}'|>k_F}V_1(\mathbf{k},\mathbf{k}')[1-\nu_{\mathbf{k}'}/E_{\mathbf{k}'}], \quad (5a)$$

$$\mu_{\mathbf{k}}=-\tfrac{1}{2}\textstyle\sum_{\mathbf{k}'}V_2(\mathbf{k},\mathbf{k}')\mu_{\mathbf{k}'}/E_{\mathbf{k}'}, \quad (5b)$$

$$n=\textstyle\sum_{\mathbf{k}}(1-\nu_{\mathbf{k}}/E_{\mathbf{k}}), \quad (5c)$$

in which

$$\xi_{\mathbf{k}}\equiv\epsilon_{\mathbf{k}}-\sum_{|\mathbf{k}'|<k_F}V_1(\mathbf{k},\mathbf{k}'), \quad (6a)$$

$$V_1(\mathbf{k},\mathbf{k}')\equiv\tfrac{1}{4}(V_{\mathbf{k}\mathbf{k}'}+V_{-\mathbf{k}-\mathbf{k}'}+V_{\mathbf{k}'\mathbf{k}}+V_{-\mathbf{k}'-\mathbf{k}})-\tfrac{1}{2}(V_{\mathbf{k}\mathbf{k}}+V_{\mathbf{k}'\mathbf{k}'}+V_{-\mathbf{k}-\mathbf{k}}+V_{-\mathbf{k}'-\mathbf{k}'}), \quad (6b)$$

$$V_2(\mathbf{k},\mathbf{k}')\equiv\tfrac{1}{2}(V_{\mathbf{k}'\mathbf{k}}+V_{-\mathbf{k}'-\mathbf{k}}), \quad (6c)$$

are known functions. The constant λ is introduced as a Lagrangian multiplier to insure that the total number of electrons is n, that is that (5c) is satisfied. Here k_F is the k value at the Fermi surface and is a function of the direction and band.[8]

The energy $\xi_{\mathbf{k}}$ has a significance for the normal state as we shall now see. We mean by the normal state at 0°K, χ_0, that state of lowest energy which diagonalizes the electron number operators.

$$\chi_0=\prod_{|\mathbf{k}|<k_F\sigma}a_{\mathbf{k}\sigma}{}^{*}\Phi_0. \quad (7)$$

Of course it is only a conjecture that this corresponds to the normal state of a superconductor at 0°K in a critical magnetic field. However, this assumption appears reasonable since the superconductor in a magnetic field larger than critical behaves like a normal conductor, which in turn can be adequately described in its ground state by the wave function (7). The energy of this state, including the exchange energy but not the correlation effects beyond those included in the plasmon variables, is

$$W_n=(\chi_0,H\chi_0)=\sum_{|\mathbf{k}|<k_F}2\epsilon_{\mathbf{k}}-\sum_{|\mathbf{k}|,|\mathbf{k}'|<k_F}V_1(\mathbf{k},\mathbf{k}'),$$

or

$$W_n=\sum_{|\mathbf{k}|<k_F}(\epsilon_{\mathbf{k}}+\xi_{\mathbf{k}})=\sum_{|\mathbf{k}|<k_F}2\tilde{\epsilon}_{\mathbf{k}}, \quad (8)$$

[7] This fact has also been noted by L. N. Cooper in a remark at the International Conference on the Electronic Properties of Metals at Low Temperatures, Geneva, New York, 1958 (unpublished). See also J. C. Fisher (to be published).

[8] The sign of $g_{\mathbf{k}}$ is not determined from the variation of the energy with respect to $g_{\mathbf{k}}$. If $g_{\mathbf{k}}$ were restricted to $g_{\mathbf{k}}\geq 0$, then for those $\mathbf{k}$ for which $\mu_{\mathbf{k}}<0$, the energy is not minimized by the expression obtained for $g_{\mathbf{k}}$ from the variation of the energy, but rather the energy is lowered by[9] $g_{\mathbf{k}}(1+|g_{\mathbf{k}}|^2)^{-1}=0$. However this is too restrictive to assume $g_{\mathbf{k}}>0$, and in fact for $\mu_{\mathbf{k}}<0$, the minimum of the energy is obtained[6] for $g_{\mathbf{k}}<0$. The author is grateful to Dr. Valatin for pointing out this fact and for an informative discussion of his paper.

[9] J. C. Swihart, Proceedings of the Kamerlingh Onnes Conference on Low-Temperature Physics, Leiden, 1958 [Physica 24, S147 (1958)].

where $\tilde{\epsilon}_k$ is given in Appendix A, Eq. (A9). The exchange energy should be included for the normal state as it has been in (8) if it is considered in the superconducting state as was done by Valatin.[6] This has been done for the Bogoliubov theory by Rickayzen[10] and by Bogoliubov.[5]

Although the energy of an electron in state $\mathbf{k}$ can be considered to be $\frac{1}{2}(\epsilon_k+\xi_k)$, the total contribution to W_n from an electron in state $\mathbf{k}$ is

$$\epsilon_k-\tfrac{1}{2}\sum_{|k'|<k_F}[V_1(\mathbf{k},\mathbf{k}')+V_1(\mathbf{k}',\mathbf{k})]=\xi_k.$$

Thus the Fermi surface is a sphere in ξ space, since if an electron occupies a state of ξ_1 say while a state of ξ_2 is empty with $\xi_2<\xi_1$, then the total energy would be lowered by an amount $\xi_1-\xi_2$ by filling the state ξ_2 and emptying the state ξ_1. This could be done successively until all states with ξ below a certain value ξ_0 are filled and those above are empty.

We first consider the Bardeen-Pines interaction, Eq. (A13), for $V_{kk'}$ and neglect the Coulomb interaction. The $E_{k'}^{-1}$ factor in the sum of (5b) weighs the contributions most heavily for $\mathbf{k}'$ near the Fermi surface while the $V_{kk'}$ ensures that only the contributions for $|\tilde{\epsilon}_k-\tilde{\epsilon}_{k'}|$ of the same order of magnitude or smaller than $\hbar\omega_{k-k'}$ will be important. The combined effect is that $|\mu_k|$ goes rapidly to zero at a distance of the order of magnitude of $\hbar\omega_{max}=k\theta_D$ on each side of the Fermi surface, where θ_D is the Debye temperature. Hence the sum in (5b) is effectively limited by the region of approximately $2k\theta_D$ in width at the Fermi surface. We shall denote this region by R_1. The precise width of R_1 is determined from the integral equations (5). We shall only make use of the fact that it is much smaller than the Fermi energy.

It is convenient to use ν, $\mathbf{j}\equiv\mathbf{k}/|\mathbf{k}|$ as the independent variables in Eqs. (5) and (6) rather than $\mathbf{k}$. The sums over $\mathbf{k}$ are replaced by integrations over angles and ν with the function $N(\nu,\mathbf{j})$, the density of states, entering.

The functions N, $\bar{\omega}_q$, and $\bar{P}_q$ depend roughly on ν and ν' in terms of powers of $k^2=(2m^*\nu/\hbar^2)+k_F^2$, but not in terms of differences of ν and ν' as in the denominator of V^{ph} [see Eq. (A15)]. The relative change in k^2 in the region R_1 about the Fermi surface is of the order of magnitude of 10^{-3}. Hence it seems quite justifiable to drop the ν, ν' dependence of N, $\bar{\omega}_q$, and $\bar{P}_q$ in $V_{kk'}$ in Eq. (5b), retaining only the angular dependencies of these quantities. This approximation is examined in more detail in Appendix B.

To the extent that the sum in Eq. (A16) is negligible, we have for the Bardeen-Pines interaction

$$V(\nu,\mathbf{j};\nu',\mathbf{j}')=V(-\nu,\mathbf{j};-\nu',\mathbf{j}') \text{ in } R_1, \qquad (9)$$

and consequently, the solution $\mu(\nu,\mathbf{j})$ of (5b) is an even function of ν. From Eq. (5c), it is seen that the surface $\nu=0$, if not identical with the Fermi surface $\xi=\xi_0$ a constant, must at least intertwine with it so that

$$\int d\Omega\int_0^{\nu_0}N(0,\mathbf{j})d\nu=0,$$

where $\nu_0=\nu(\xi_0,\mathbf{j})$. Of course in the case of spherical symmetry, $\nu=0$ is identical to the Fermi surface. Equation (5a) shows that to first approximation $\nu=\xi-\lambda$ and thus the two surfaces are identical to this approximation. Using this result, one can now calculate the effect of the last two terms in (5a) for $\nu=0$:

$$\frac{1}{2}\int d\Omega'\,N(0,\mathbf{j}')\left\{\int_{-a}^{0}d\nu'\,V_1(0,\mathbf{j};\nu',\mathbf{j}')(1+\nu'/E')-\int_0^a d\nu'\,V_1(0,\mathbf{j};\nu',\mathbf{j}')(1-\nu'/E')\right\}=0$$

by Eq. (9). Here $a(\mathbf{j})$ is the boundary of R_1.

Thus the surface $\nu=0$ and the Fermi surface are identical and the constant λ equals ξ_0 to second approximation. This would be true to all orders of approximation if Eq. (9) were rigorously true, regardless of the potential used.

III. THE ISOTOPE EFFECT

The Bardeen-Pines interaction $V(\nu,\mathbf{j};\nu',\mathbf{j}')$, Eq. (A13), depends on the ionic mass M through $\bar{P}_q$ and $\bar{\omega}_q$ with[3]

$$\bar{\omega}_q\propto M^{-\frac{1}{2}},\quad \bar{P}_q\propto M^{-\frac{1}{4}}. \qquad (10)$$

If the numerator and denominator of V^{ph}, Eqs. (A13) and (A15), are multiplied by M, then $V_{kk'}$ is seen to be a function of M only in terms of (see Eq. (A16))

$$M^{\frac{1}{2}}\left\{\nu-\nu'-\frac{1}{4}\int d\Omega''\,N(0,\mathbf{j}'')\int d\nu''[V_1(\nu',\mathbf{j}';\nu'',\mathbf{j}'')-V_1(\nu,\mathbf{j};\nu'',\mathbf{j}'')](1-\nu''/E'')\right\}.$$

We now make the transformation to the set of variables

$$x\equiv M^{\frac{1}{2}}\nu,\quad y\equiv M^{\frac{1}{2}}\mu,\quad z\equiv M^{\frac{1}{2}}(\xi-\lambda), \qquad (11)$$

so that in terms of x, $V(x,\mathbf{j};x',\mathbf{j}')$ is independent of M if $y(x,\mathbf{j})$ is.

The system of Eqs. (5) becomes in terms of the variables (11)

$$z(x,\mathbf{j})=x-\frac{1}{2}\int d\Omega'\,N(0,\mathbf{j}')\times\int^{x_0}dx'\,V_1(x,\mathbf{j};x',\mathbf{j}')(1+x'/w')+\frac{1}{2}\int d\Omega'\,N(0,\mathbf{j}')\int_{x_0}dx'\times V_1(x,\mathbf{j};x',\mathbf{j}')(1-x'/w'), \qquad (12a)$$

[10] G. Rickayzen, Phys. Rev. 111, 817 (1958).

$$y(x,\mathbf{j})=-\frac{1}{2}\int d\Omega' N(0,\mathbf{j}')\int dx' \times V_2(x,\mathbf{j};x',\mathbf{j}')y(x',\mathbf{j}')/w', \quad (12b)$$

$$\int d\Omega N(0,\mathbf{j})\left\{\int^{x_0} dx(1+x/w)-\int_{x_0} dx(1-x/w)\right\}=0, \quad (12c)$$

where

$$w(x,\mathbf{j})\equiv+[x^2+|y(x,\mathbf{j})|^2]^{\frac{1}{2}}. \quad (13)$$

Instead of the constant λ, we now have the function $x_0(\mathbf{j})$, the value of x at the Fermi surface, which must satisfy Eq. (12c) and also the condition that $z_0\equiv z(x_0,\mathbf{j})$ be independent of $\mathbf{j}$ since the Fermi surface is a sphere in ξ space. As we discussed in the last section, $x_0\approx 0$, but we do not restrict ourselves to this. Once $x_0(\mathbf{j})$ and $z(x,\mathbf{j})$ are determined from Eqs. (12), λ can be found by

$$\lambda=\xi_0-M^{-\frac{1}{2}}z_0,$$

since ξ_0, the energy of the Fermi surface, is known from the supposed solution of the normal state problem. Thus Eqs. (12) are equivalent to Eqs. (5).

The system (12) is completely independent of ionic mass if $V(x,\mathbf{j};x',\mathbf{j}')$ is.[11] The latter is true for the Bardeen-Pines interaction as shown below Eq. (11). Hence the solutions $y(x,\mathbf{j})$, $z(x,\mathbf{j})$, and z_0 are then also independent of M, and according to Eq. (11)

$$\mu(x,\mathbf{j})\propto M^{-\frac{1}{2}}, \quad (14)$$

for fixed x.

The excitations induced in the superconductor by absorption of infrared radiation or high-frequency phonons are produced by an interaction

$$H_I=\sum_{\mathbf{k}\mathbf{k}'\sigma} B_{\mathbf{k}\mathbf{k}'}a_{\mathbf{k}'\sigma}{}^*a_{\mathbf{k}\sigma}, \quad (15)$$

which has matrix elements that connect the ground state, Eq. (2), only with excited states with *two* excited electrons. Thus the energy gap, observed by means of these experiments, is the minimum difference in energy between the ground state and the collection of excited states with *two* excited electrons. The reason the single-electron excitations are not considered is due to the nature of the interaction (15) rather than to the requirement that the number of electrons be conserved as suggested by Yosida.[12] In fact, it is possible to excite a *single* electron [but not by (15)] and conserve the total number by having that electron be on the Fermi surface.

If the two excited electrons are in Bloch states $\mathbf{k}\sigma$ and $\mathbf{k}'\sigma'$, the energy difference is[13]

$$E_{\mathbf{k}_1}+E_{\mathbf{k}_2}=(\nu_{\mathbf{k}_1}{}^2+|\mu_{\mathbf{k}_1}|^2)^{\frac{1}{2}}+(\nu_{\mathbf{k}_2}{}^2+|\mu_{\mathbf{k}_2}|^2)^{\frac{1}{2}}; \quad (16)$$

so the energy gap in any direction $\mathbf{j}$ is $2|\mu(\nu=0,\mathbf{j})|$. It follows from Eq. (14) that the isotope effect holds for the energy gap:

$$2|\mu(0,\mathbf{j})|\propto M^{-\frac{1}{2}}. \quad (17)$$

The critical field at $T=0$, H_0, is determined by the energy difference between the ground state W_s and the normal state W_n, where[6]

$$W_s=\sum_{\mathbf{k}}\tfrac{1}{2}(1-\nu_{\mathbf{k}}/E_{\mathbf{k}})[\epsilon_{\mathbf{k}}+(\nu_{\mathbf{k}}+\lambda)]-\sum_{\mathbf{k}}\tfrac{1}{2}|\mu_{\mathbf{k}}|^2/E_{\mathbf{k}}. \quad (18)$$

From the difference of Eqs. (8) and (18), with the use of Eqs. (5a) and (6a),

$$H_0{}^2/(8\pi)=\frac{1}{2}\int d\Omega N(0,\mathbf{j})\left\{\int^{\nu_0} d\nu(1+\nu/E)[\nu+(\xi-\lambda)]-\int_{\nu_0} d\nu(1-\nu/E)[\nu+(\xi-\lambda)]+\int d\nu|\mu|^2/E\right\}. \quad (19)$$

It is permissible to use $N(0,\mathbf{j})$ since the integrals give contributions only in R_1. Equation (19) can be expressed entirely in terms of the quantities x, y, z, and w of Eqs. (11) and (13) to give

$$MH_0{}^2/(8\pi)=\frac{1}{2}\int d\Omega N(0,\mathbf{j})\left\{\int^{x_0} dx(1+x/w)(x+z)-\int_{x_0} dx(1-x/w)(x+z)+\int dx|y|^2/w\right\}. \quad (20)$$

The right side of (20) is independent of ionic mass; so

$$H_0\propto M^{-\frac{1}{2}}, \quad (21)$$

which is the isotope effect for the critical field at 0°K.

The considerations up to now have been only for $T=0$. For $T\neq 0$, it is the free energy that must be minimized. One is led[6] to a series of equations similar to (5):

$$\nu_{\mathbf{k}}=\epsilon_{\mathbf{k}}-\lambda-\sum_{\mathbf{k}'} V_1(\mathbf{k},\mathbf{k}')\times[(1-h_{\mathbf{k}'})f_{\mathbf{k}'}+h_{\mathbf{k}'}(1-f_{\mathbf{k}'})], \quad (22a)$$

$$\mu_{\mathbf{k}}=-\tfrac{1}{2}\sum_{\mathbf{k}'} V_2(\mathbf{k},\mathbf{k}')(\mu_{\mathbf{k}'}/E_{\mathbf{k}'})(1-2f_{\mathbf{k}'}), \quad (22b)$$

$$n=2\sum_{\mathbf{k}}[(1-h_{\mathbf{k}})f_{\mathbf{k}}+h_{\mathbf{k}}(1-f_{\mathbf{k}})], \quad (22c)$$

[11] The equation of Valatin[6] corresponding to (5a) has part of the sum incorporated in $\xi_{\mathbf{k}}$, so that the latter is defined differently than in (6a). However we have split up the two parts as in (5a) not only because $\xi_{\mathbf{k}}$ of Eq. (6a) then has a physical significance for the normal state, as we have discussed, but also because the sums in (5a) then contribute only in R_1. It is necessary to make use of the latter property in using $N(0,\mathbf{j}')$ in (12a).

[12] K. Yosida, Phys. Rev. **111**, 1255 (1958).

[13] It has been shown[6] that the excitation energy for a single excited electron in state $\mathbf{k}_1\sigma_1$ is $E_{\mathbf{k}_1}$. For the double excitation $\mathbf{k}_1\sigma_1$ and $\mathbf{k}_2\sigma_2$, in addition to $E_{\mathbf{k}_1}+E_{\mathbf{k}_2}$, there are contributions from the third term of Valatin's Eq. (8c) for the energy.[6] However these contributions are minimized by $\nu_{\mathbf{k}_1}=\nu_{\mathbf{k}_2}=0$ and are zero there except for one contribution for $\sigma_1=\sigma_2$ of $W=\frac{1}{2}V_{-\mathbf{k}_1\mathbf{k}_2}\times[(1+\nu_{\mathbf{k}_1}/E_{\mathbf{k}_1})(1-\nu_{\mathbf{k}_2}/E_{\mathbf{k}_2})+\mu_{\mathbf{k}_2}{}^*\mu_{\mathbf{k}_1}/(E_{\mathbf{k}_1}E_{\mathbf{k}_2})]$ plus another term with $\mathbf{k}_1$ and $\mathbf{k}_2$ interchanged. For $\nu_{\mathbf{k}_1}=\nu_{\mathbf{k}_2}=0$, the value of this term is about $V_{-\mathbf{k}_1\mathbf{k}_2}\sim N(0)V/N(0)\sim 10^{-34}$ erg while $|\mu_{\mathbf{k}F}|\sim kT_c\sim 10^{-16}$ erg. Thus this term is truly negligible.

where

$$\begin{aligned} f_{\mathbf{k}}&=[1+\exp(\beta E_{\mathbf{k}})]^{-1},\\ h_{\mathbf{k}}&=\tfrac{1}{2}(1-\nu_{\mathbf{k}}/E_{\mathbf{k}}),\\ E_{\mathbf{k}}&\equiv+(\nu_{\mathbf{k}}^2+|\mu_{\mathbf{k}}|^2)^{\frac{1}{2}},\\ \beta&\equiv(kT)^{-1}. \end{aligned} \tag{23}$$

Of course, $\mu_{\mathbf{k}}$ and $\nu_{\mathbf{k}}$ are now functions of the parameter T as well as of $\mathbf{k}$.

Again it is convenient to consider $\nu, \mathbf{j}\equiv\mathbf{k}/|\mathbf{k}|$ as the independent variables. To the extent that Eq. (A16) holds, $V_{\mathbf{k}\mathbf{k}'}$ is once again independent of M when expressed in terms of the variables

$$x=M^{\frac{1}{2}}\nu, \quad y=M^{\frac{1}{2}}\mu, \quad \eta=M^{-\frac{1}{2}}\beta, \tag{24}$$

and Eq. (22b) is also. The critical temperature corresponds to the lowest value of the parameter η, η_c say, for which a solution $y(x,\mathbf{j})$ exists for (22b). This η_c is independent of M, and hence by (24)

$$T_c\propto M^{-\frac{1}{2}}, \tag{25}$$

which is the isotope effect for the critical temperature.

The isotope effect for T_c, H_0, and the energy gap at $T=0$ has been proved for the Bardeen-Pines interaction in the BCS theory, neglecting the Coulomb interaction. One sees that it is the form of the interaction for nonzero values of $\tilde{\epsilon}_{\mathbf{k}}-\tilde{\epsilon}_{\mathbf{k}'}$ that is important, both for the proof given here and that in the BCS paper. Since the series of which the Bardeen-Pines interaction is the first term[3] does not converge for $(\hbar\bar{\omega}\mathbf{q})^2-(\tilde{\epsilon}_{\mathbf{k}}-\tilde{\epsilon}_{\mathbf{k}'})^2$ too small, there may be some doubt about the validity of using this interaction. Pines[14] has derived the same interaction by means of the dielectric formulation of the electron-ion problem. His results show that the denominator has additional small terms so that the former does not vanish. He also finds that the energy difference in the denominator is $(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})$ rather than $(\tilde{\epsilon}_{\mathbf{k}}-\tilde{\epsilon}_{\mathbf{k}'})$. The isotope effect holds for this case if we again make an approximation as in Eq. (A16).

The quantitative results of the BCS paper, except for the isotope effect, do not depend on the form of the interaction $V_{\mathbf{k}\mathbf{k}'}$ since everything is worked out in terms of an average V. Hence it is possible that the theory is essentially correct but that the potential is something other than the Bardeen-Pines interaction. In order for another potential to be able to give the isotope effect, it is necessary that when it is expressed in terms of x, $\mathbf{j}$ and x', $\mathbf{j}'$ it be independent of M so that the Eqs. (12) will be independent of M. This puts a restriction on the possible forms $V_{\mathbf{k}\mathbf{k}'}$ can have in the BCS theory.

Although the Bogoliubov theory[5] starts from a different H than (1), mathematically the results are very similar to the Valatin formulation[6] of the BCS theory. In fact if we define

$$V_{\mathbf{k}\mathbf{k}'}\equiv-\frac{2|P_{\mathbf{q}}(\mathbf{k}'-\mathbf{k})|^2}{[\hbar\omega_{\mathbf{q}}+E_{\mathbf{k}}+E_{\mathbf{k}'}]}, \tag{26}$$

and

$$\xi_{\mathbf{k}}\equiv\epsilon_{\mathbf{k}}-\tfrac{1}{2}\sum_{|\mathbf{k}'|<k_F}V_{\mathbf{k}\mathbf{k}'}+\tfrac{1}{2}\sum_{|\mathbf{k}'|>k_F}V_{\mathbf{k}\mathbf{k}'}, \tag{27}$$

then the Bogoliubov integral equations[5] are precisely those of Valatin,[6] Eqs. (5). Since the interaction (26) is independent of M when expressed in terms of the variables (11) and when the approximation in the paragraph preceding Eq. (9) is applied, the solution $\mu(0,\mathbf{j})$ is proportional to $M^{-\frac{1}{2}}$. The energy gap is again[5] $2\mu(0,\mathbf{j})$; so the isotope effect holds for this quantity.

The energy of the superconducting and normal states at $T=0$ is different in terms of $\xi_{\mathbf{k}}$, $\nu_{\mathbf{k}}$, and $V_{\mathbf{k}\mathbf{k}'}$ for the Bogoliubov case from Eqs. (8) and (18). Rather it is[5]

$$W_n=\sum_{|\mathbf{k}|<k_F}2\epsilon_{\mathbf{k}}+\sum_{|\mathbf{k}|<k_F}\sum_{|\mathbf{k}'|>k_F}V_{\mathbf{k}\mathbf{k}'}, \tag{28}$$

$$\begin{aligned} W_s=&\textstyle\sum_{\mathbf{k}}\epsilon_{\mathbf{k}}(1-\nu_{\mathbf{k}}/E_{\mathbf{k}})\\ &+\tfrac{1}{4}\textstyle\sum_{\mathbf{k}\mathbf{k}'}V_{\mathbf{k}\mathbf{k}'}(1+\nu_{\mathbf{k}}/E_{\mathbf{k}})(1-\nu_{\mathbf{k}'}/E_{\mathbf{k}'})\\ &-\tfrac{1}{4}\textstyle\sum_{\mathbf{k}\mathbf{k}'}V_{\mathbf{k}\mathbf{k}'}(\mu_{\mathbf{k}}/E_{\mathbf{k}})(\mu_{\mathbf{k}'}/E_{\mathbf{k}'}). \end{aligned} \tag{29}$$

Since for the normal case $E_{\mathbf{k}}$ is different from in the superconducting case (in the former $\mu_{\mathbf{k}}\equiv0$), $V_{\mathbf{k}\mathbf{k}'}$ of (26) is slightly different in W_n and W_s; however we shall ignore this difference. We then find after a short calculation by using $V_{\mathbf{k}\mathbf{k}'}=V_{\mathbf{k}'\mathbf{k}}$ and Eqs. (5a) and (27) that the energy difference is precisely the same expression as (19). The isotope effect for H_0 then follows in the same way by Eqs. (20) and (21).

Rickayzen[10] has shown how to handle nonzero temperatures by the Bogoliubov method of compensating dangerous graphs. He finds an integral equation that can be treated in precisely the same way as (22b) to find that the mass dependence of T_c is (25).

So far we have neglected the effect of the Coulomb interaction. When this is included, the integrand of (5b) no longer goes to zero fast enough to ensure that there are contributions only near the Fermi surface. This can be seen most easily by considering the integral equation with ν and ν' as the independent variables. For ν and ν' small compared to the Fermi energy, the Coulomb interaction is independent of ν and ν', being a function only of the angles. Taking into account the E'^{-1} factor in the integrand, one would find a logarithmic contribution to (5b) which would be important for large ν' unless $\mu(\nu')$ would go to zero. Consider ν large enough that the phonon part of V does not give a contribution to (5b), but ν small compared to the Fermi energy. This is possible since the phonon part of (5b) goes to zero as $1/\nu$ for large ν even if $\mu(\nu')$ would be a constant. Thus if $\mu(\nu)$ would go to zero for ν small compared to the Fermi energy, the Coulomb contribution to (5b) would necessarily vanish for all ν near the Fermi surface since it is independent of ν. This would not only be fortuitous, but it could not be true in every case; otherwise all metals would be superconductors if the Coulomb interaction is the agent that prevents superconductivity.

[14] D. Pines (to be published).

These observations are borne out by an approximate solution found by Bogoliubov[5] in which the effect of the Coulomb interaction is to introduce contributions to (5b) a distance of a Fermi energy away from the Fermi surface. This prevents us from carrying out the transformation (11) to obtain a completely mass invariant system of equations.

However if we do carry out the transformation (11) and separate the phonon and Coulomb parts, we can apply the approximation above Eq. (9) to the former since we still have contributions from it only in R_1 even though $\mu(\nu')$ does not go to zero in R_1. The Coulomb part will have mass contributions in $N(x'M^{-\frac{1}{2}},\mathbf{j}')$ and similarly in the Coulomb interaction itself. The criterion for the existence of superconductivity, whether the strong criterion of Pines[15] or the weaker one of Bogoliubov,[5] ensures that for ν near the Fermi surface the phonon part of the integral equation will dominate the Coulomb part. This is caused in part by the fact that $\mu(\nu')$ changes sign at a distance of approximately $k\theta_D$ from the Fermi surface, and thus the contribution from the Coulomb part for small ν' tends to cancel that for large ν'. To the extent that the phonon part is dominant, $y(x)$ is the same for different masses for x near zero, and the isotope effect for the energy gap follows. However this is true only to a first approximation. There will be deviations from the $-\frac{1}{2}$ exponent due to the Coulomb term and these deviations will depend on the relative size of the Coulomb interaction and the functional form of N. That is, the magnitude will be different for different elements.

We can best estimate the size of the deviations from the approximate solution of Bogoliubov.[5] There it is found that $\mu(0)\equiv\mu_0$ must satisfy

$$\ln\frac{k\theta_D}{\mu_0}\left\{\rho\left(1+\rho_c\ln\frac{2E_F}{k\theta_D}\right)-\rho_c\right\}=1+\rho_c\ln\frac{2E_F}{k\theta_D}, \quad (30)$$

where E_F is the Fermi energy, $\rho\equiv-4\pi NV^{\text{phon}}>0$ in the notation of Appendix B, and $\rho_c\equiv4\pi NV^{\text{Coul}}>0$. We find from Eq. (30)

$$\frac{\delta\mu_0}{\mu_0}=\left\{1-\frac{\rho_c^2}{[\rho(1+\rho_c\ln 2E_F/k\theta_D)-\rho_c]^2}\right\}\frac{\delta\theta_D}{\theta_D}. \quad (31)$$

The first term on the right side gives the ordinary $-\frac{1}{2}$ for the exponent. Due to the second term the exponent will be $-\frac{1}{2}(1-\zeta)$ with $\zeta>0$ and given by the second term in the brackets.

Using the experimental values of θ_D, μ_0, and E_F; a calculated estimate[15] of ρ_c; and then Eq. (30) to determine ρ, we find $\zeta=+0.05$ for Pb and $+0.30$ for Ti as two examples with widely different T_c's and θ_D's. These values are just at the edge of experimental accuracy.[1]

[15] D. Pines, Phys. Rev. **109**, 280 (1958); P. Morel, J. Phys. Chem. Solids (to be published).

Note added in proof.—The value of $\zeta=+0.10$ for Sn from Eq. (31) agrees in sign and roughly in magnitude with the value $\zeta=+0.08$ found experimentally.

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APPENDIX A. THE BARDEEN-PINES INTERACTION

We derive here the Bardeen-Pines interaction[3] between electrons taking into consideration the renormalized energies from the beginning. We start from the electron-phonon system of BP after separation of the plasmon variables. Our Hamiltonian is

$$H=H_0+H_1+H_2+H_3+H_{\text{sc}}, \quad (A1)$$

$$H_0=\sum_{\mathbf{k}\sigma}\bar{\epsilon}_{\mathbf{k}}a_{\mathbf{k}\sigma}{}^*a_{\mathbf{k}\sigma}+\sum_{\mathbf{q}}\hbar\bar{\omega}_{\mathbf{q}}b_{\mathbf{q}}{}^*b_{\mathbf{q}}, \quad (A2)$$

$$H_1=\sum_{\mathbf{k}\mathbf{k}'\sigma}\bar{P}_{\mathbf{q}}(\mathbf{k}'-\mathbf{k})(b_{\mathbf{q}}+b_{-\mathbf{q}}{}^*)a_{\mathbf{k}'\sigma}{}^*a_{\mathbf{k}\sigma}, \quad (A3)$$

$$H_2=\sum_{\mathbf{k}\sigma}(\epsilon_{\mathbf{k}}-\bar{\epsilon}_{\mathbf{k}})a_{\mathbf{k}\sigma}{}^*a_{\mathbf{k}\sigma}+\sum_{\mathbf{q}}\hbar(\omega_{\mathbf{q}}-\bar{\omega}_{\mathbf{q}})b_{\mathbf{q}}{}^*b_{\mathbf{q}}, \quad (A4)$$

$$H_3=-\sum_{\mathbf{k}'\mathbf{k}\sigma}(\bar{P}_{\mathbf{q}}-P_{\mathbf{q}})(b_{\mathbf{q}}+b_{-\mathbf{q}}{}^*)a_{\mathbf{k}'\sigma}{}^*a_{\mathbf{k}\sigma}, \quad (A5)$$

$$H_{\text{sc}}=\tfrac{1}{2}\sum_{|\mathbf{k}'-\mathbf{k}|>k_c}M(\mathbf{k}'-\mathbf{k})^2a_{\mathbf{k}'\sigma}{}^*a_{\mathbf{k}_1-\mathbf{k}'\sigma'}{}^*a_{\mathbf{k}_1-\mathbf{k}\sigma'}a_{\mathbf{k}\sigma}, \quad (A6)$$

which is the BP Eq. (4.5) with the neglect of the plasmon variables. Here $\epsilon_{\mathbf{k}}$ and $\omega_{\mathbf{q}}$ are the unrenormalized Bloch energy of the electron and frequency of the phonon respectively, while $\bar{\epsilon}_{\mathbf{k}}$ and $\bar{\omega}_{\mathbf{q}}$ are the corresponding renormalized quantities; our $\omega_{\mathbf{q}}{}^2$ corresponds to BP's $\Omega_{\mathbf{q}}{}^2$ for $q>k_c$ and to $\Omega_{\mathbf{q}}{}^2-u_{\mathbf{q}}{}^2$ for $q<k_c$. The unrenormalized electron-phonon interaction $P_{\mathbf{q}}(\mathbf{k}'-\mathbf{k})=P_{-\mathbf{q}}(\mathbf{k}-\mathbf{k}')^*$ corresponds to $v_{\mathbf{q}}(\hbar/2\bar{\omega}_{\mathbf{q}})$ of BP, while $\bar{P}_{\mathbf{q}}$ is the renormalized function. Here $\mathbf{q}=\mathbf{k}'-\mathbf{k}+\mathbf{K}$ where $\mathbf{K}$ is a reciprocal lattice vector such that $\mathbf{q}$ is in the first zone. The last term in H is the screened Coulomb interaction.

We carry out the canonical transformation

$$H'=e^{-iS}He^{iS}=H+i[H;S]-\tfrac{1}{2}[[H;S];S]+\cdots, \quad (A7)$$

where

$$S=\sum_{\mathbf{k}\mathbf{k}'\sigma}[h(\mathbf{k}',\mathbf{k})b_{\mathbf{q}}+h(\mathbf{k},\mathbf{k}')^*b_{-\mathbf{q}}{}^*]a_{\mathbf{k}'\sigma}{}^*a_{\mathbf{k}\sigma},$$

and $h(\mathbf{k}',\mathbf{k})$ is chosen so that the electron-phonon interaction is eliminated to first order:

$$i[H_0;S]+H_1=0.$$

Similarly to BP, this gives

$$h(\mathbf{k}',\mathbf{k})=\frac{-iP_{\mathbf{q}}(\mathbf{k}'-\mathbf{k})}{\hbar\bar{\omega}_{\mathbf{q}}-(\bar{\epsilon}_{\mathbf{k}'}-\bar{\epsilon}_{\mathbf{k}})}. \quad (A8)$$

Then from

$$-\tfrac{1}{2}[[H_0;S];S]+i[H_1;S]=\tfrac{1}{2}i[H_1;S],$$

one finds (a) terms diagonal in the electron and phonon number representation which vanish for the phonon vacuum, (b) diagonal terms which do not vanish for the phonon vacuum, (c) an electron-electron interaction, (d) nondiagonal terms involving phonon variables, and (e) terms without phonon variables giving interband transitions (for one electron). The expressions electron and phonon now mean the particles after the unitary transformation, so that the electron has a virtual phonon cloud associated with it and the phonon has a screening electron cloud. Terms (a) are combined with the phonon part of H_2 with the requirement that the result vanish. This determines the renormalized phonon frequency $\bar{\omega}_q$ and was carried out in BP. Terms (d) are neglected in the random-phase approximation, while terms (e) give no contribution to the expectation value of H for any of the states we consider. We are interested in terms (b) and (c).

Combining terms (b) with the electron part of H_2 and the diagonal part of H_{sc} (the exchange interaction) and requiring that this vanish, determines the renormalized energy $\bar{\epsilon}_k$:

$$\bar{\epsilon}_k=\epsilon_k'-\tfrac{1}{2}\textstyle\sum_{k'} V_1(\mathbf{k},\mathbf{k}')n_{k'}, \tag{A9}$$

where

$$\epsilon_k'\equiv\epsilon_k-\sum_{k'}\frac{|\bar{P}_q(\mathbf{k}'-\mathbf{k})|^2}{\hbar\bar{\omega}_q+(\bar{\epsilon}_{k'}-\bar{\epsilon}_k)}, \tag{A10}$$

$$n_k=\langle c_{k\uparrow}{}^*c_{k\uparrow}\rangle=\langle c_{k\downarrow}{}^*c_{k\downarrow}\rangle, \tag{A11}$$

and $V_1(\mathbf{k},\mathbf{k}')$ is defined in terms of $V_{kk'}$ by Eq. (6b), while

$$\begin{aligned} V_{kk'}&\equiv V_{kk'}{}^{ph}+M(\mathbf{k}'-\mathbf{k})^2 \quad \text{for} \quad |\mathbf{k}-\mathbf{k}'|>k_c,\\ V_{kk'}&\equiv V_{kk'}{}^{ph} \qquad\qquad\quad \text{for} \quad |\mathbf{k}-\mathbf{k}'|<k_c, \end{aligned} \tag{A12}$$

with

$$V_{kk'}{}^{ph}=-\frac{2\hbar\bar{\omega}_q|\bar{P}_q(\mathbf{k}'-\mathbf{k})|^2}{(\hbar\bar{\omega}_q)^2-(\bar{\epsilon}_{k'}-\bar{\epsilon}_k)^2}, \tag{A13}$$

where

$$\mathbf{q}=\mathbf{k}'-\mathbf{k}+\mathbf{K}.$$

The terms of type (c) and the nondiagonal part of H_{sc} that together give the electron-electron interaction are then

$$H_{el\text{-}el}=\tfrac{1}{2}\sum_{k\sigma k'\sigma' k''K}{}' V_{kk'K'}a_{k'\sigma}{}^*\times a_{k''-k'+K'\sigma'}{}^*a_{k''-k\sigma'}a_{k\sigma} \tag{A14}$$

with

$$\begin{aligned} V_{kk'K'}&=-\frac{2\hbar\bar{\omega}_q\bar{P}_q(\mathbf{k}'-\mathbf{k}-\mathbf{K}')^*\bar{P}_q(\mathbf{k}'-\mathbf{k})}{(\hbar\bar{\omega}_q)^2-(\bar{\epsilon}_{k'}-\bar{\epsilon}_k)^2} \quad \text{for} \quad \mathbf{K}'\neq 0\\ &=V_{kk'} \quad \text{for} \quad \mathbf{K}'=0, \end{aligned}$$

and where the prime on the sum means the diagonal terms ($\mathbf{k}'=\mathbf{k}$, and $\mathbf{k}'=\mathbf{k}''-\mathbf{k}$ for $\sigma=\sigma'$, both for $\mathbf{K}'=0$) are omitted. The terms with $\mathbf{K}'\neq 0$, where $\mathbf{K}'$ is a reciprocal lattice vector, corresponds to transitions in which the one electron changes a different number of bands than the other. These terms give no contribution to the expectation value of H for any of the states we consider and are dropped as were the terms (e) below Eq. (A8).

The renormalized interaction $\bar{P}_q$ is determined by requiring that the coefficients in the sum of H_3 and the commutator of H_{sc} with S vanish, and has been worked out by BP. One should also include the appropriate terms from $(\frac{1}{3}!)[[[H_0;S];S];S]$ and $-\frac{1}{2}[[H_1;S];S]$. This procedure, as pointed out by BP, does not include the effect of exchange terms on the renormalized interaction.

The resulting Hamiltonian has the form of Eq. (1) if one uses ϵ_k' of Eq. (A10) instead of ϵ_k for the electron energy and if one combines the remaining terms of Eq. (A9) with (A14) so that the sum in the interaction is no longer restricted.

In the superconducting state, at $T=0$, $n_k=\frac{1}{2}\times(1-\nu_k/E_k)$, and, by Eq. (5a),

$$\bar{\epsilon}_{k'}-\bar{\epsilon}_k=\nu_{k'}-\nu_k+\tfrac{1}{2}\textstyle\sum_{k''}[V_1(\mathbf{k}',\mathbf{k}'')-V_1(\mathbf{k},\mathbf{k}'')]n_{k''}. \tag{A15}$$

For $\mathbf{k}''$ below the region R_1 (the region near the Fermi surface), $n_{k''}=1$, while $n_{k''}=0$ for $\mathbf{k}''$ above. For $\mathbf{k}$ and $\mathbf{k}'$ in R_1, most of the contribution to the sum in (A15) is from $\mathbf{k}''$ in R_1. In fact, neglecting anisotropies, the contribution from $\mathbf{k}''$ below R_1 is very nearly zero. Thus

$$(\hbar\bar{\omega}_q)^2-(\bar{\epsilon}_{k'}-\bar{\epsilon}_k)^2\approx(\hbar\bar{\omega}_q)^2-\{\nu_{k'}-\nu_k+\tfrac{1}{2}\sum_{k''\subset R_1}[V_1(\mathbf{k}',\mathbf{k}'')-V_1(\mathbf{k},\mathbf{k}'')]n_{k''}\}^2, \tag{A16}$$

for $\mathbf{k}$, $\mathbf{k}'\subset R_1$.

In the superconducting state for $T\neq 0$,

$$\langle n_k\rangle_{Av}=[(1-h_k)f_k+h_k(1-f_k)],$$

where h_k and f_k are given by Eq. (23). Then by Eq. (22a), we again find Eq. (A16) but with $n_{k''}$ replaced by $\langle n_{k''}\rangle_{Av}$ and with ν_k now being a function of the temperature by Eqs. (22).

APPENDIX B. THE EFFECT OF THE DENSITY OF STATES ON THE ISOTOPE SHIFT

We shall examine more critically the effect of the energy dependence of N, $\bar{\omega}_q$, and $\bar{P}_q$ on the proof of the isotope effect when the Coulomb interaction is neglected. If we retain this dependence, then Eqs. (12) would not be independent of mass, since M now enters in the arguments of N, $\bar{\omega}_q$, and $\bar{P}_q$ in the form of $M^{-\frac{1}{2}}x$. On the other hand, by taking the proper average of N, $\bar{\omega}_q$, and $\bar{P}_q$, over the energy region of the integration of Eqs. (12), the energy dependence of these quantities is eliminated without any approximation. However, this region in energy is also proportional to

$M^{-\frac{1}{2}}$ as is evidenced by the transformation (11) to give Eqs. (12). Hence N, $\bar{\omega}_q$, and $\bar{P}_q$ are averaged over a different energy region for a different mass. This change in the average values of N, $\bar{\omega}_q$, and $\bar{P}_q$ with mass will produce a variation in H_0, T_c, and the energy gap in addition to that of Eqs. (17), (21), and (25).

We now give an estimate of this correction due only to the change in the density of states $N(\nu,\mathbf{j})$. For this we assume that N is the function for a free electron gas, independent of direction $\mathbf{j}$;

$$N(\nu)=C(\nu+\epsilon_F)^{\frac{1}{2}}, \tag{B1}$$

where C is a constant independent of ν and $\mathbf{j}$.

We also assume that the average value of N that is used in Eqs. (12) is the arithmetic average over the region R_1 rather than $N(0,\mathbf{j})$:

$$N\equiv\langle N(\nu)\rangle_{Av}=\tfrac{1}{2}[N(a)+N(-a)], \tag{B2}$$

where $|\nu|=a$ is the boundary of R_1. With the transformation (11), we have found that the boundary a is proportional to $M^{-\frac{1}{2}}$. Thus if it is $|\nu|=a$ for mass M_1, the boundary becomes $a(M_1/M_2)^{\frac{1}{2}}$ for mass M_2. The corresponding change in N is

$$\delta N=-\frac{d^2N(\nu)}{d\nu^2}\bigg|_{\nu=0}\left[1-\left(\frac{M_1}{M_2}\right)^{\frac{1}{2}}\right]a^2. \tag{B3}$$

An approximate solution to (12b) has been given by BCS:

$$y=2a\exp[-(4\pi NV)^{-1}] \tag{B4}$$

where $V\equiv-\langle V_{\mathbf{k}\mathbf{k}'}\rangle_{Av}$. Thus the change in the energy gap due to δN is

$$\frac{\delta(2\mu)}{(2\mu)}=\frac{\delta y}{y}=\frac{1}{(4\pi NV)}\frac{\delta N}{N},$$

or with (B3) and (B1)

$$\delta(2\mu)/(2\mu)=\tfrac{1}{4}(4\pi NV)^{-1}(a/\epsilon_F)^2[1-(M_1/M_2)^{\frac{1}{2}}]. \tag{B5}$$

When this variation due to the change of N is combined with that found in Eq. (17), the result is

$$\delta(2\mu)/(2\mu)=-(1-\zeta)[1-(M_1/M_2)^{\frac{1}{2}}],$$

or

$$2\mu\propto M^{-\frac{1}{2}(1-\zeta)}, \tag{B6}$$

where

$$\zeta=\tfrac{1}{4}(4\pi NV)^{-1}(a/\epsilon_F)^2. \tag{B7}$$

If the same correction is carried out for H_0 and T_c, one easily finds that Eqs. (21) and (25) are replaced by equations analogous to (B6). Thus the effect of the energy dependence of the density of states is merely to change the exponent slightly from $\frac{1}{2}$. Using

$$(4\pi NV)^{-1}\sim 10, \quad (a/\epsilon_F)\sim(k\theta_D/\epsilon_F)\sim 2\times 10^{-3},$$

we find

$$\zeta\sim 10^{-5}. \tag{B8}$$

This is completely negligible. However these considerations are not altogether trivial since the difference between using $N(0)$ and $N(k\theta_D)$ for the average of N in (12) leads to a change in μ of the same order of magnitude as the isotope shift. Also the calculation leading to (B7) assumed that N is for a free-electron gas and thus the second derivative in (B3) is quite small. This is probably not the case for the transition elements such as vanadium and tantalum. In fact, Olsen and Rohrer's results[16] on the change of the electronic specific heat with volume indicate that for tantalum the density of states changes drastically at the Fermi surface, giving the possibility of a large second derivative.

[16] J. L. Olsen and H. Rohrer, Helv. Phys. Acta **30**, 49 (1957).