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# Solutions of the BCS Integral Equation and Deviations from the Law of Corresponding States

**Abstract: The BCS integral equation has been studied for nonseparable interactions of the Bardeen-Pines form, $V(|\varepsilon\varepsilon'|)$. Numerical solutions were obtained using an IBM 7090 for a simple interaction of this form which included the effect of the Coulomb repulsion. The results for the ratio of the energy gap to the critical temperature and for the temperature dependence of the energy gap, the electronic specific heat, and the critical field in terms of the proper reduced quantities were rather insensitive to the form or strength of the interaction. This indicates that the BCS theory gives the law of corresponding states. The calculated ratio of energy gap to critical temperature varies with the ratio of critical temperature to the Debye temperature, and this variation is of the correct order of magnitude if the Coulomb interaction is included. The same model is used to study the isotope effect. With the plausible assumption that the Coulomb cutoff is independent of the ionic mass, there are deviations from the $M^{-1/2}$ law that are larger for small $T_c/\theta_D$ superconductors.**

## Introduction

In the original paper of the BCS theory,[1] the superconducting state of a metal is found by minimizing the free energy with respect to trial wave functions made up of paired single-electron states. This leads to a nonlinear integral equation for the energy-gap function with the electron-electron interaction occurring in the kernel. In order to obtain analytic solutions of this integral equation, the interaction was treated as a small separable function which is constant. The argument used was that, in terms of the proper reduced variables, all superconductors behave in essentially the same way; i.e., there is a law of corresponding states, even though different superconductors would be expected to have quite different band structures, phonon spectra, and electron-electron interactions. Therefore, the superconducting properties should be rather insensitive to the precise form of the interaction. The very good agreement between the results of the theory and a "typical" superconductor tended to justify this approximation.

In this work, we have considered a rather different form of the interaction in order to see if the results of the theory really are insensitive to this form. This interaction is taken to be a nonseparable function of a form more closely related to that derived by Fröhlich,[2] and by Bardeen and Pines.[3,4] The effect of a Coulomb interaction is also included, and the attractive part is not limited to a weak interaction. The resulting complication has made it necessary to obtain solutions numerically, and these have been found on an IBM 7090 digital computer. In addition to seeing whether the theory gives the law of corresponding states with changes in the interaction, we were also able to determine whether the observed deviations from the law of corresponding states in superconductors, such as Pb and Hg, could be understood in terms of the form and strength of the interaction.

The effect of the Coulomb interaction on the exponent in the isotope effect is considered and compared with previous calculations[5] based on Tolmachev's handling of the integral equation.[6] The possibility of interpreting the experimental results of Geballe and Matthias[7] is discussed.

## Formulation of the problem

We consider the trial wave function of BCS[1] made up of paired single-electron states in which, at temperature $T$,

$$h_{\mathbf{k}} = \tfrac{1}{2}\left(1 - \frac{\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}}\right) \qquad (1)$$

is the probability of occupancy of the single-electron states $\mathbf{k}\uparrow$, $-\mathbf{k}\downarrow$ for the ground pairs, and

$$f_{\mathbf{k}} = [\varepsilon^{\beta E_{\mathbf{k}}} + 1]^{-1} \qquad (2)$$

is the thermodynamic probability of excitation out of the ground pair state, $\beta = 1/k_B T$, $\varepsilon_{\mathbf{k}}$ is the single-electron energy with respect to the Fermi surface, and $E_{\mathbf{k}}$ is defined by

$$E_{\mathbf{k}} = [\varepsilon_{\mathbf{k}}^2 + \Delta_{\mathbf{k}}^2]^{1/2} \qquad (3)$$

in terms of the parameter $\Delta_{\mathbf{k}}(T)$. Minimization of the free energy leads to a nonlinear integral equation for $\Delta_{\mathbf{k}}$,

$$\Delta_{\mathbf{k}} = -\tfrac{1}{2}\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'}\frac{\Delta_{\mathbf{k}'}}{E_{\mathbf{k}'}}\tanh\tfrac{1}{2}\beta E_{\mathbf{k}'}\,, \qquad (4)$$

in which occurs the electron-electron interaction $V_{\mathbf{k}\mathbf{k}'}$. The interaction consists of the Coulomb interaction plus a part via the phonons. The latter has been described by Fröhlich[2] and by Bardeen and Pines[3] in the form

$$V_{\mathbf{k}\mathbf{k}'}^{\text{phonon}} = -\frac{\hbar\omega_{\mathbf{k}-\mathbf{k}'}|M_{\mathbf{k}-\mathbf{k}'}|^2}{(\hbar\omega_{\mathbf{k}-\mathbf{k}'})^2 - (\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'})^2}\,, \qquad (5)$$

where $\omega_{\mathbf{q}}$ is the phonon frequency of wave number $\mathbf{q}$, and $M_{\mathbf{k}-\mathbf{k}'}$ is the matrix element for the scattering of an electron from $\mathbf{k}$ to $\mathbf{k}'$ with the emission or absorption of a phonon.

The interaction (5) has the property that

$$V_{\mathbf{k}\mathbf{k}'}^{\text{phonon}} < 0 \quad \text{for} \quad |\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}| < \hbar\omega_{\mathbf{k}-\mathbf{k}'}\,,$$
$$> 0 \quad \text{for} \quad |\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}| > \hbar\omega_{\mathbf{k}-\mathbf{k}'}\,.$$

In order to obtain analytic solutions of the integral equation (4), BCS approximated the interaction by

$$V_{\mathbf{k}\mathbf{k}'} = -V \quad \text{for} \quad |\varepsilon_{\mathbf{k}}|, |\varepsilon_{\mathbf{k}'}| \quad \text{both} < \langle\hbar\omega\rangle_{\text{av}}\,, \qquad (6)$$
$$= 0 \text{ otherwise,}$$

where $V > 0$. With this interaction, $\Delta_{\mathbf{k}}$ is a constant at each temperature (denoted as $\varepsilon_0$ by BCS) to a distance $\hbar\omega$ from the Fermi surface and is zero at a greater distance. The integral equation then reduces to an integral and can be solved analytically. In order to include the effect of the Coulomb interaction, Tolmachev[6] used an approximation

$$\begin{aligned} V_{\mathbf{k}\mathbf{k}'} &= -V \quad \text{for} \quad |\varepsilon_{\mathbf{k}}|, |\varepsilon_{\mathbf{k}'}| \quad \text{both} < \hbar\omega\,, \\ &= +V_1 \quad \text{for} \quad |\varepsilon_{\mathbf{k}}|, |\varepsilon_{\mathbf{k}'}| \quad \text{both} < \hbar\omega_1\,, \qquad (7) \\ &\qquad \text{and} \quad |\varepsilon_{\mathbf{k}}| \quad \text{and/or} \quad |\varepsilon_{\mathbf{k}'}| > \hbar\omega \\ &= 0 \text{ otherwise,} \end{aligned}$$

to calculate $\Delta_k$ at zero temperature. The solution is a positive constant for $|\varepsilon| < \hbar\omega$, a negative constant for $\hbar\omega < |\varepsilon| < \hbar\omega_1$, and zero for larger values of $|\varepsilon|$. None of the thermodynamic functions was determined with this solution.

If one considers the Bardeen-Pines interaction (5) with the "jellium" model for the electron-phonon interaction, and adds to this the screened Coulomb interaction, one obtains[8]

$$V_{\mathbf{k}\mathbf{k}'} = \frac{4\pi e^2(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'})^2}{k_s^2(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'})^2 + 4k_F^2 \times [(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'})^2 - \hbar^2\Omega_p^2]\sin^2\theta/2}\,, \qquad (8)$$

where $\theta$ is the angle between $\mathbf{k}$ and $\mathbf{k}'$, $k_F$ is the Fermi momentum, $k_s$ is the inverse Fermi-Thomas screening length, and $\Omega_p$ is the plasma frequency for the positive ions:

$$\Omega_p^2 = 4\pi N(Ze)^2/M, \qquad (9)$$

with $N$ the number of ions of charge $Ze$ and mass $M$ per unit volume. In Eq. (8) the assumption is made that the distances of $\mathbf{k}$ and $\mathbf{k}'$ from the Fermi surface are small compared to $k_F$. Also, simplifying assumptions have been made regarding *umklapp* processes.

For the spherically symmetric solution, i.e., for no anisotropy in the energy-gap function $\Delta_k$, the integrals over angles in Eq. (4) can be performed if one takes principal parts in the integrand. On transforming from $|\mathbf{k}|$ to $x = \varepsilon/\hbar\Omega_p$ as the independent variable, we find for the integral equation

$$y(x) = -\tfrac{1}{2}\int dx' V(|x - x'|)\frac{y(x')}{w'}\tanh\tfrac{1}{2}\eta w'\,, \qquad (10)$$

where

$$\begin{aligned} y(x) &\equiv \Delta(x)/\hbar\Omega_p\,, \\ w' &\equiv w(x') = [\varepsilon'^2 + \Delta(x')^2]^{1/2}/\hbar\Omega_p\,, \\ \eta &\equiv \beta\hbar\Omega_p\,, \end{aligned} \qquad (11)$$

and

$$V(x) = \frac{1}{2}\frac{a^2x^2}{(x^2 - 1)}\ln\left|1 + \frac{x^2 - 1}{a^2x^2}\right| \qquad (12)$$

is the interaction in terms of $a^2 = k_s^2/4k_F^2$ which in turn is proportional to the interelectron spacing. The interaction (12) is dimensionless and includes the density of states of the free-electron gas; it thus corresponds to $N(0)V$ of BCS. A plot of this function is given by the dashed line in Fig. 1. Equation (10) has the trivial solution $y(x) \equiv 0$. If $y(x)$ is a nontrivial solution, so is $-y(x)$; we shall consider the solution that is positive at the Fermi surface. Both solutions lead to the same physical results. Finally the solutions of (10) are symmetrical about the Fermi surface; $y(x) = y(-x)$.

Since the Bardeen-Pines interaction (12) has a logarithmic singularity at $x^2 = 1/(1 + a^2)$, and since this singularity is probably cut off by lifetime effects, we have carried out the initial calculations using a square well in $|\varepsilon - \varepsilon'|$ of the form plotted by the solid line. The Bardeen-Pines interaction changes sign at $|\varepsilon - \varepsilon'| = \hbar\Omega_p/(1 + 2a^2)^{1/2}$. A typical value of $a^2$ for a superconductor is 0.4 for which $k_s^2 = 1.6\ k_F^2$. If the maximum phonon wave vector in the metal is $2k_F$, then from

$$\omega_k = \Omega_p k/(k^2 + k_s^2)^{1/2}$$

for the phonon frequency,[8] one finds that the interaction changes sign at an energy difference equal to $k_B\theta_D$, the Debye energy. This is the point at which we take the change in sign in the simplified interaction.

In order to obtain finite solutions, the constant repulsive interaction must be cut off. The Coulomb interaction drops off as $1/k^2$ to a small value at a distance of about $k_F$ from the Fermi surface. Lifetime effects also tend to cut off the Coulomb interaction,[9] but for electron-hole damping the cutoff is still at about a distance of $k_F$.* In order to simplify the calculation, we have arbitrarily taken a much smaller cutoff ($\hbar\omega_1$) of from two to four times the Debye energy. The value of the repulsive part of the interaction was taken as the screened Coulomb interaction averaged over the Fermi surface.[10] The strength of the attractive interaction is the last remaining parameter, and this is chosen to give the desired ratio of $T_c/\theta_D$.

## Solutions of the integral equation

Two methods of solution of the integral equation (10) were employed. The first was a straight iterative procedure in which a guess was made as to the form of the function $y(x)$; this was substituted in the right side of the equation, and a new $y(x)$, presumably better, was calculated. This procedure was found to converge only if the trial function were good enough, and then the convergence was slow.

A second method which proved to be more powerful was based on an idea of Tolmachev.[6] This consists of a "quasi-linearization" of the equation by noting that

$$w = [x^2 + y(x)^2]^{1/2} \approx [x^2 + y(0)^2]^{1/2} ,$$

since it is only for $x \approx 0$ (near the Fermi surface) that $y$ makes an important contribution to $w$. To allow for a more general type of solution, we have expanded $y(x)$ at the Fermi surface in a Taylor expansion

$$y(x) = y(0)[1 - Ax^2] + 0(x^4) \tag{13}$$

so that a more accurate expression for $w$ is

$$w \approx [x^2 + y(0)^2(1 - Ax^2)^2]^{1/2} . \tag{14}$$

There are no odd terms in $x$ in the expansion (13) since Eq. (10) is the same for $y(-x)$ as for $y(x)$. The additional term in (14) allows for the possibility of a solution in which the minimum value of $w$ is at $x_1 \neq 0$. This would mean that the energy gap would not be $2\Delta(\varepsilon = 0)$ but $2E_{\min} = 2[\varepsilon_1{}^2 + \Delta(\varepsilon_1)^2]^{1/2}$, where $\varepsilon_1 = \hbar\Omega_p x_1$. For all of the solutions we found, $A$ was positive but it was not large enough to move the minimum value of $w$ away from $x = 0$.

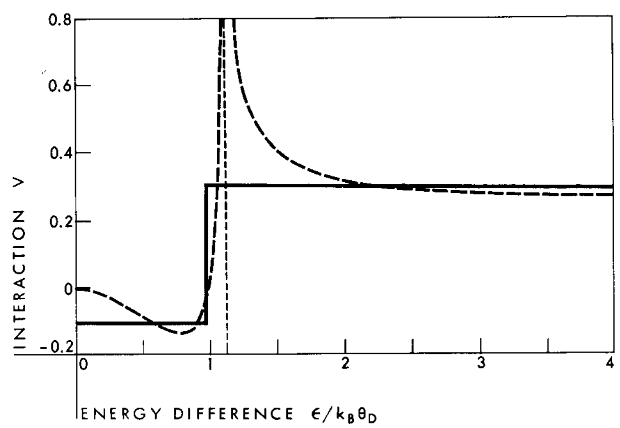
The integral in (10) can now be divided into two regions, $R_1$ near the Fermi surface, where $x'$ is small enough that $y(x')$ can be approximated by the first two terms of (13) in the numerator of the integrand, as well as in $w'$, and $R_2$ where $y(x')$ is retained as an unknown in the numerator. The equation then is in the form of an inhomogeneous linear integral equation for $y(x)$ in $R_2$ in terms of the two parameters $y(0)$ and $A$.

$$y(x) = f(x) + \int_{R_2} R(x, x')y(x')\,dx' ;\ x \subset R_2 , \tag{15}$$

where

$$f(x) = -\frac{1}{2}\int_{R_1} dx' V(|x - x'|) \times \frac{y(0)(1 - Ax'^2)}{w'} \tanh \tfrac{1}{2}\eta w' \tag{16}$$

*Figure 1* **Plot of the interaction as a function of the energy difference.** *The angular dependence has been integrated out. The dimensionless interaction contains the density of states and corresponds to $N(0)V$ of BCS, except that the latter is a separable interaction and is not a function of the energy difference. The dashed curve is a plot of Eq. (12), the Bardeen-Pines interaction, for $a^2 = 0.4$. This interaction is zero at an energy difference of zero, it changes sign at $\varepsilon = \hbar\Omega_p/(1 + 2a^2)^{1/2}$, it has a logarithmic singularity at $\varepsilon = \hbar\Omega_p/(1 + a^2)^{1/2}$, and it has the value 0.5 (regardless of the value of $a^2$) at $\varepsilon = \hbar\Omega_p$. The solid curve is the simplified square-well type of interaction used in this calculation.*




* On the other hand, it is thought that for the strong-coupling superconductors for which the electron-phonon interaction is large, the cutoff may be only the order of the energy gap from the Fermi surface, a distance smaller even than the Debye energy (see the article by J. Bardeen in this issue, p. 3). The results we have found are so close to those of BCS, in which they assumed weak coupling and no Coulomb interaction, that it is doubtful that a value of the cutoff different from what we have taken would modify these results significantly. This does not apply to the isotope effect, however, as we shall see.

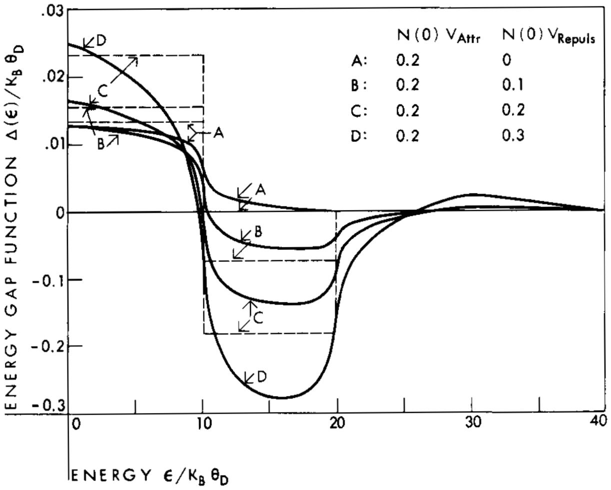



*Figure 2* **The energy-gap function at zero temperature as a function of energy for the square-well interaction.** *$N(0)V_{Attr}$ is the value of the attractive part of the interaction, and $N(0)V_{Repuls}$ is the value of the repulsive part. The repulsive part was cut off at an energy difference of $2k_B\theta_D$. The dashed curves are the corresponding BCS and Tolmachev solutions.*

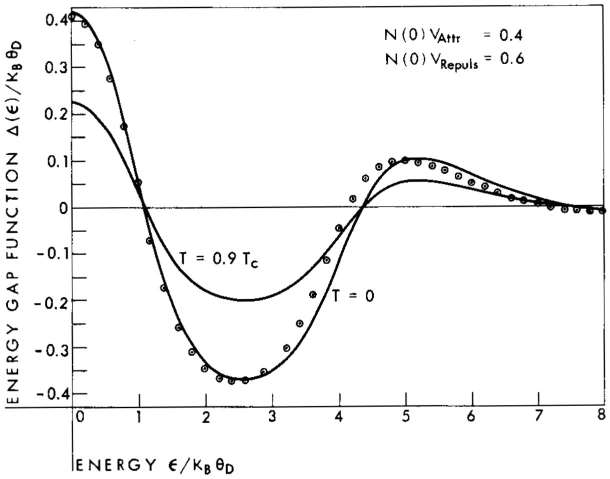



*Figure 3* **The energy-gap function for two different temperatures as a function of energy.** *The solid curves are for the cutoff of the Coulomb interaction at an energy difference of $4k_B\theta_D$. The circles are the solution at zero temperature for a cutoff of $3.6k_B\theta_D$.*

and

$$R(x, x') = -\frac{1}{2}\frac{\tanh \frac{1}{2}\eta w'}{w'} \times [V(x + x') + V(|x - x'|)]\,. \quad (17)$$

We have made use of the fact that $y(x) = y(-x)$; the region $R_2$ in (15) is then only over positive $x$ with the definition (17). In (17), $w$ was approximated by (14) only to the point that (13) became negative. For larger $x$, $w$ is very nearly equal to $x$ and was so taken.

The linear equation (15) can be solved numerically by the usual methods to give $y(x; y(0), A)$. With this solution in $R_2$ and Eq. (13) in $R_1$, the integral in Eq. (10) can be determined for $x \subset R_1$. We then check to see that $y(x)$ determined in this way in $R_1$ fits Eq. (13) with our initial parameters $y(0)$ and $A$. In other words, we vary the two initial parameters until we have a self-consistent solution.

Both of these methods of computation were carried out on IBM 704 and 7090 computers using the FORTRAN method of programming. For the one case where the same problem was done both by iteration and by "quasi-linearization", the solution $y(x)$ agreed to four places. Figure 2 is a plot of $\Delta(\varepsilon)$ for temperature $T = 0$ with different values of the repulsive part of the square-well interaction. The cutoff in the repulsive part was taken at $2k\theta_D$ here. Also plotted (with the dashed lines) are the BCS and Tolmachev solutions with the interactions (6) and (7). Notice that with the same strength of the interaction, the solution at $\varepsilon = 0$ (half the energy gap) with the nonseparable interaction is smaller than with the BCS or Tolmachev interaction. Also the BCS and Tolmachev solutions are identically zero for $\varepsilon$ larger than $k\theta_D$ or $2k\theta_D$ respectively, while with the nonseparable interaction the solution goes to zero asymptotically, oscillating in sign for the cases with a repulsive part of the interaction.

Figure 3 is a plot of $\Delta(\varepsilon)$ for a stronger interaction and at two temperatures. It was found that the solution at $T \neq 0$ was very nearly a simple scaling of the solution at $T = 0$. This is illustrated in Fig. 3 where, for this particular case, $\Delta(\varepsilon, T = 0.9T_c) \approx 0.54\Delta(\varepsilon, T = 0)$ for all $\varepsilon$.

In BCS it was shown that, near $T_c$, the square of the energy gap is a linear function of $T$. The same was found to be true for our solutions with the nonseparable potential, and this was used to determine $T_c$, the highest temperature for which a nontrivial solution exists. Figure 4 is a plot of the square of $\Delta(T)$—the value of $\Delta(\varepsilon, T)$ at the Fermi surface—versus the temperature. Both quantities are in reduced units. A comparison is made of four solutions, the BCS solution in the weak coupling limit as tabulated by Mühlschlegel,[11] the BCS solution in the strong coupling limit as worked out by Thouless,[12] the nonseparable weak interaction, and the nonseparable interaction used for Fig. 3, which we shall denote as the *intermediate coupling case*. The limiting slope of the curves in terms of the reduced variables is very nearly the same for these four solutions. The points

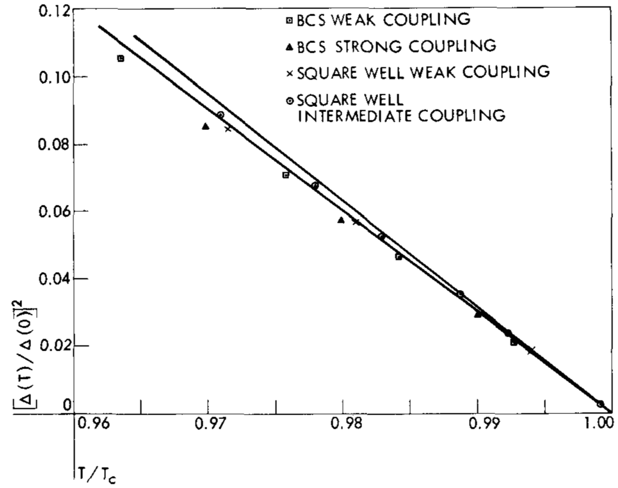



*Figure 4* **The square of the half-energy gap as a function of temperature near $T_c$.** *The points are calculated points. The solid lines are two of the limiting lines at $T_c$, the upper being for square-well intermediate coupling case calculated here and the lower line being for the BCS weak coupling case.*[11]

are calculated points while the straight lines are the limiting lines for the BCS weak coupling case (lower line) and the square-well nonseparable interaction for the intermediate coupling case (upper line). The slopes of the limiting lines are 3.03 for the BCS weak coupling case,[11] 3.00 for the BCS strong coupling case,[12] and 3.18 for the intermediate coupling with the nonseparable potential used in this calculation. One sees that the temperature dependence of the energy gap near $T_c$ is very little affected by the interaction.

Table I gives the results for the ratio of the energy gap at zero temperature ($2\Delta(0)$) to $k_BT_c$ for the various calculations. This ratio is much more sensitive to the form and strength of the interaction than is the temperature dependence of the energy gap. For the BCS approximation and for the nonseparable interaction, both $T_c/\theta_D$ and $2\Delta(0)/k_BT_c$ tend to increase with increasing interaction strength. This correlation between these two quantities is found experimentally, at least for the nontransition elements, as indicated at the bottom of Table I. With the BCS approximation, the largest ratio of energy gap to $T_c$ is apparently 4.0, and this occurs for the nonphysical situation for which $T_c/\theta_D$ is infinite.*

For the two cases with the nonseparable interaction for which the coupling is weak ($T_c/\theta_D < 0.01$) the ratio of energy gap to $k_BT_c$ is 3.5, just as in the BCS approximation. Notice that the one solution is for zero attractive interaction, corresponding the closest to the Bardeen-Pines interaction. For stronger interactions, the energy gap to $k_BT_c$ ratio can be larger than 4.0, as for example the last case, and this occurs for $T_c/\theta_D$ values of the same order of magnitude as those of Pb and Hg. We have also obtained solutions for the actual Bardeen-Pines interaction of Eq. (12) but with an arbitrary cutoff in the singularity. For $a^2 = 0.4$, the result is that $T_c/\theta_D = 0.01$, a weak-coupling case. This gives 3.48 for the ratio $2\Delta(0)/k_BT_c$ in agreement with the other weak-coupling calculations.

Another comparison that can be made is to look at different cases in which $T_c/\theta_D$ is the same. For example, $T_c/\theta_D = 0.22$. For the BCS approximation the ratio of energy gap to $k_BT_c$ is 3.65. This is increased to 3.68 on going to the nonseparable interaction with no repulsive part. Finally the ratio is larger than 4.0 when a repulsive part of the interaction is included.

*Table 1* **The ratio of the energy gap to the critical temperature for various calculations compared to actual superconductors.** *The larger ratios of $T_c/\theta_D$ correspond to stronger interactions. ($\hbar\omega_1/k_B\theta_D$) is the value of the cutoff of the repulsive interaction.*

*BCS Approximation*

| $N(0)V$ | $\frac{T_c}{\theta_D}$ | $\frac{2\Delta(0)}{k_BT_c}$ |
|---|---|---|
| 0.15 | 0.001 | 3.526 |
| 0.30 | 0.040 | 3.532 |
| 0.45 | 0.12 | 3.569 |
| 0.625 | 0.22 | 3.65 |
| ∞ | ∞ | 4.000 |

*Square well in $|\varepsilon - \varepsilon'|$ (nonseparable interaction)*

| $N(0)V_{\text{attractive}}$ | $N(0)V_{\text{repulsive}}$ | $\frac{\hbar\omega_1}{k_B\theta_D}$ | $\frac{T_c}{\theta_D}$ | $\frac{2\Delta(0)}{k_BT_c}$ |
|---|---|---|---|---|
| 0 | 0.50 | 2 | 0.0008 | 3.53 |
| 0.20 | 0.10 | 2 | 0.007 | 3.52 |
| 0.20 | 0.50 | 2 | 0.023 | 3.63 |
| 0.68 | 0 | – | 0.22 | 3.68 |
| 1.00 | 0 | – | 0.38 | 4.16 |
| 0.40 | 0.60 | 4 | 0.21 | 4.01 |
| 0.60 | 0.60 | 4 | 0.29 | 4.2 |

*Experimental results*

| | $\frac{T_c}{\theta_D}$ | $\frac{2\Delta(0)}{k_BT_c}$ |
|---|---|---|
| Aluminum[13] | 0.0027 | 3.37 |
| Tin[14] | 0.019 | 3.1–3.5 |
| Indium[14] | 0.031 | 3.6 |
| Mercury[15] | 0.059 | 4.6 |
| Lead[14] | 0.075 | 4.0–4.3 |

* *Note added in proof:* P. M. Marcus (private communication) has shown that the maximum ratio does occur at the strong-coupling limit for the BCS approximation.

The second from the last calculation simulates the stronger coupling superconductors Pb and Hg in several ways. The repulsive part of the interaction ($N(0)V_{\mathrm{repulsive}} = 0.6$) is equal to the value of the screened Coulomb interaction averaged over the Fermi surface of Hg.[10] Also the ratios $T_c/\theta_D = 0.21$ and $2\Delta(0)/k_BT_c = 4.0$ are reasonable approximations to the corresponding quantities for Pb and Hg. We have denoted this calculation as the intermediate coupling case in Figs. 3 and 4, and we have calculated the specific heat and critical field for this case to see if these functions approximate Pb or Hg.

Figure 5 gives the reduced energy gap as a function of reduced temperature over the complete temperature range. The solid line is for the BCS approximation for both the weak-coupling[11] and strong-coupling[12] limits. These two cases give the same function to the accuracy of this graph. Incidentally, the functional form for the strong coupling case as found by Thouless can be expressed in the simple form

$$\frac{\Delta(T)}{\Delta(0)} = \tanh\left[\frac{T_c}{T}\frac{\Delta(T)}{\Delta(0)}\right],$$

and this also gives the weak-coupling case within 0.1 percent error over most of the temperature range. The fact that the temperature dependence of the energy gap for the intermediate-coupling case, given by the circles in Fig. 5, is nearly the same as the BCS weak-coupling case even though $2\Delta(0)/k_BT_c$ is appreciably larger than 3.5, is in agreement with the experimental data on Pb.[14]

### The specific heat and critical field

With the solutions $\Delta(\varepsilon, T)$ discussed in the previous section, it is possible to calculate the specific heat, critical field, and other thermodynamic functions. These calculations follow as in the BCS paper[1] with slight modifications to allow for the energy dependence of $\Delta$. The electronic specific heat in the superconducting state is determined from the temperature dependence of the entropy

$$\frac{C_{es}}{\gamma T_c} = \frac{T}{\gamma T_c}\frac{dS_{es}}{dT} = \frac{C_{es}{}^{(1)}}{\gamma T_c} + \frac{C_{es}{}^{(2)}}{\gamma T_c}, \tag{18}$$

where for convenience we have split $C_{es}$, into two parts: $C_{es}{}^{(1)}$, which depends on the temperature dependence of the distribution of quasiparticles with constant energy gap, and $C_{es}{}^{(2)}$, which depends on the temperature dependence of $\Delta(\varepsilon, T)$.

$$\frac{C_{es}{}^{(1)}}{\gamma T_c} = \frac{6}{\pi^2}\left(\frac{T}{T_c}\right)\eta^3\int_0^\infty dx\,\frac{w(x)^2e^{\eta w}}{[1+e^{\eta w}]^2}, \tag{19}$$

where $(1/\eta)$ is the temperature and $w$ and $x$ are the energies with respect to $\hbar\Omega_p$ as in Eq. (11). Notice that the energy-gap function $\Delta(\varepsilon, T)$ determines $w$.

The second part of the reduced specific heat is

$$\frac{C_{es}{}^{(2)}}{\gamma T_c} = \frac{3}{\pi^2}\left[\frac{\Delta(0,0)}{k_BT_c}\right]^2\left[-\frac{d(\Delta(0,T)/\Delta(0,0))^2}{d(T/T_c)}\right] \times \frac{\eta}{y(0)^2}\int_0^\infty dx\,\frac{y(x)^2e^{\eta w}}{[1+e^{\eta w}]^2}. \tag{20}$$

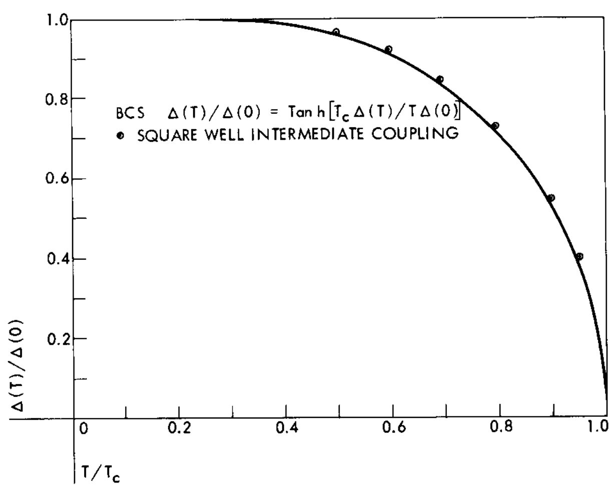
Here we have made the approximation that $y(x) \equiv \Delta(\varepsilon, T)/\hbar\Omega_p$ for any particular temperature is just $y(x)$ for $T = 0$ times a factor independent of $x$. We have already illustrated this for an actual solution in Fig. 3. With this approximation,

$$\frac{dy(x)}{dT} = \frac{y(x)}{y(0)}\frac{dy(0)}{dT}, \tag{21}$$

and we need the derivative of the energy-gap function with respect to temperature only at the Fermi surface. The temperature derivative as expressed in the bracket in (20) in reduced form is just the negative of the slope of the plot in Fig. 4 and this approaches a constant near $T_c$ where $C_{es}{}^{(2)}$ is an important part of $C_{es}$. At $T = T_c$, the energy gap function goes to zero and $C_{es}{}^{(1)} = \gamma T_c$. Thus $C_{es}{}^{(2)}$, which has a finite value here, is the jump in the specific heat at $T_c$. On the other hand, at $T = 0$ the temperature derivative goes to zero and the only contribution to $C_{es}$ is from $C_{es}{}^{(1)}$.

We have carried out numerical integrations of Eqs. (19) and (20) for the solution in the intermediate coupling case (Fig. 3). Figure 6 gives the results near $T_c$. The electronic specific heat is larger for the intermediate coupling case than for the BCS weak coupling

*Figure 5* **Temperature dependence of the energy gap in terms of reduced quantities.** *The solid line is for the strong coupling limit[12] and is given by the simple functional relation. The weak coupling limit is identical to the accuracy of this graph. The intermediate coupling case with the nonseparable potential is given by the circles and lies only slightly higher than the BCS approximation.*



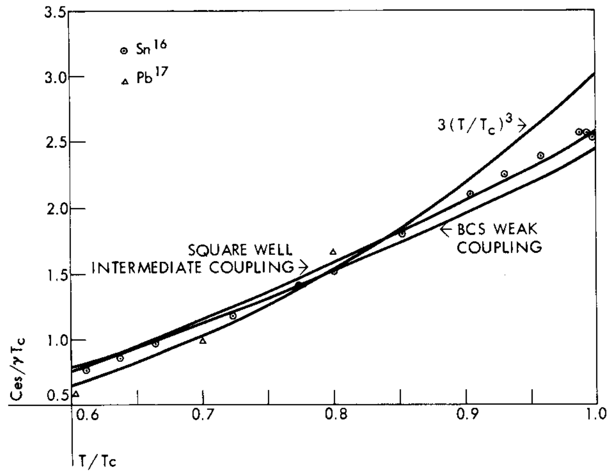



*Figure 6* **Temperature dependence of the superconducting electronic specific heat near the critical temperature $T_c$.** *The solid lines are calculated theoretical curves. The points are calculated from the experimental data.*[16,17] *The jump in the reduced specific heat at $T_c$ is the value of the reduced specific heat minus one.*

case, but the increase is not nearly large enough to explain the results for lead. Figure 7 is a plot of the specific heat at low temperatures. On this plot an exponential specific heat is a straight line. The intermediate-coupling case lies lower than the BCS weak-coupling case, merely reflecting the larger ratio of energy gap to $k_BT_c$ in the former. The lead data begin lower but bend above both calculated curves at the lower temperatures. This may reflect an anisotropic energy gap as suggested by Boorse,[19] and which has not been considered in the present calculation.

The jump in the specific heat at $T_c$ given by $C_{es}^{(2)}$ has a particularly simple form:

$$\frac{\Delta C_e}{\gamma T_c}=\frac{C_{es}^{(2)}(T_c)}{\gamma T_c}$$

$$=\frac{3}{\pi^2}\left[\frac{\Delta(0,0)}{k_BT_c}\right]^2\left[-\frac{d(\Delta(0,T)/\Delta(0,0))^2}{d(T/T_c)}\right]$$

$$\times\int_0^\infty\frac{d\bar{x}[y(x)/y(0)]^2e^{\bar{x}}}{[1+e^{\bar{x}}]^2}\,. \quad (22)$$

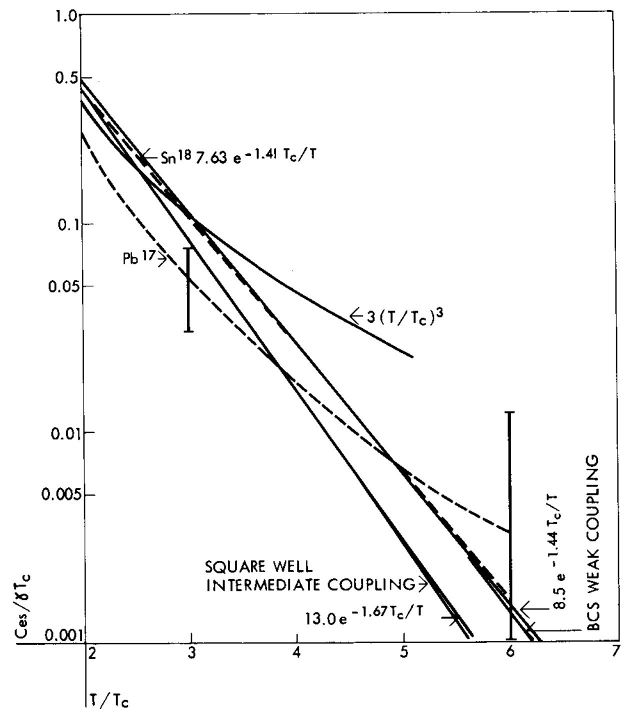
We have made use of the fact that $y(x)$ is zero at $T_c$, and have transformed to $\bar{x}=x\eta$. The ratio $[y(x)/y(0)]$ is finite, and, as we have already discussed, is nearly temperature independent. For the BCS approximation in which $\Delta(\varepsilon,T)$ is independent of $\varepsilon$, $y(x)/y(0)=1$, and the integral is simply[1]

$$\int_0^\infty d\bar{x}\frac{e^{\bar{x}}}{[1+e^{\bar{x}}]^2}=1/2\,. \quad (23)$$

For the solutions we have found, $[y(x)/y(0)]^2\leqq 1$ near the Fermi surface. Thus the integral is less than 1/2. For the solution in the intermediate-coupling case, the integral had the value of 0.405.

By using the experimental values for lead for the other quantities in (22), one could hope to determine how much smaller than 1/2 the integral is, and thus how fast $\Delta(\varepsilon,T)$ for lead drops in value on moving from the Fermi surface. However, substituting the experimental values into (22) (even using the larger value of 4.3 for $2\Delta/k_BT_c$), we find that the integral must be 0.58. This can be accomplished only by having $\Delta(\varepsilon,T)$ increase on moving from the Fermi surface. On the basis of the solutions that have been found of the BCS integral equation for various interactions, it seems unlikely that any reasonable interaction can give such a solution. Another explanation lies in an anisotropy of the energy gap. The ratio $\Delta(0,0)/k_BT_c$ in Eq. (22) should involve the gap averaged in some way. However, the actual gap measured by tunneling or by infrared absorption would tend to be determined by the lower edge, and this would favor the smallest of a distribution of gaps. Such an error in our knowledge of the gap would require that the integral be larger than it actually is, in order for (22) to be satisfied.

*Figure 7* **Temperature dependence of the superconducting electronic specific heat at low temperatures.** *The solid lines are calculated theoretical curves. The dashed curves are experimental. The vertical bars are the estimated experimental errors for Pb as given in Ref. 17.*



The critical field $H_c$ is found by calculating the difference in free energy between the normal and superconducting states:

$$\frac{H_c^2}{8\pi\gamma T_c^2} = \left[\frac{W_n - W_s}{\gamma T_c^2}\right] + \frac{T}{T_c}\left[\frac{S_{es} - S_{en}}{\gamma T_c}\right], \tag{24}$$

where $W_n$ and $W_s$ are the energies of the normal and superconducting states while $S_{en}$ and $S_{es}$ are the corresponding electronic entropies.

$$\frac{W_n - W_s}{\gamma T_c^2} = \frac{3}{\pi^2}\left(\frac{T}{T_c}\right)^2 \eta^2 \int_0^\infty dx \left\{\frac{(w-x)^2}{2w} + \frac{2x}{1+e^{\eta x}} - \frac{x^2+w^2}{w(1+e^{\eta w})}\right\}, \tag{25}$$

$$\frac{S_{es} - S_{en}}{\gamma T_c} = \frac{6}{\pi^2}\left(\frac{T}{T_c}\right)\eta \int_0^\infty dx \left\{\frac{\eta w}{1+e^{\eta w}} + \ln(1+e^{-\eta w}) - \frac{\eta x}{1+e^{\eta x}} - \ln(1+e^{-\eta x})\right\}. \tag{26}$$

The contributions from the normal state, the second term of (25) and the third and fourth terms of (26), can be determined analytically. However, since for large $x$ they cancel corresponding contributions from the superconducting state, a greater accuracy is obtained in the numerical calculation by evaluating Eqs. (25) and (26) in the form given.

Figure 8 is a plot of the deviation of the critical field from a parabolic curve. The experimental curves are given by the dashed lines, and they show the upward movement of the maximum deviation on going from low to high values of $T_c/\theta_D$ as pointed out by Mapother. The same trend is shown by the calculated curves. However, the intermediate-coupling case, which simulated lead or mercury in the ratios $T_c/\theta_D$ and $2\Delta/k_BT_c$, has not moved up far enough on the critical field curve to agree with the actual superconductors.

### The isotope effect

The isotope effect in the BCS theory has been considered previously[5] by observing that when the integral equation is expressed in terms of the proper variables, as in Eqs. (10)–(12), the ionic mass does not occur in the interaction. Hence the integral equation itself does not depend on the mass and neither do the solutions $y(x)$ and $\eta_c$ (the inverse critical temperature). Then on transforming to $\Delta$ and $T_c$, we find, since $\Omega_p \propto M^{-1/2}$,

$$\Delta(0) \propto M^{-1/2}, \quad T_c \propto M^{-1/2}. \tag{27}$$

This argument is valid only if there are no mass-dependent cutoffs in Eq. (10). With the inclusion of the Coulomb interaction there must be some cutoff of the interaction as we have already discussed. If the

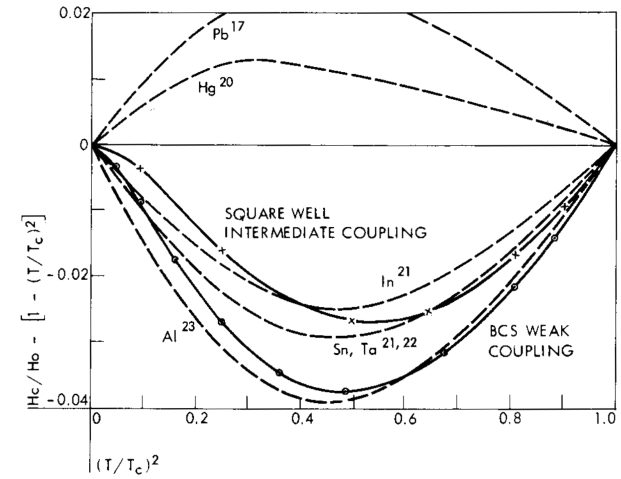



*Figure 8* **Deviation of the critical field from a parabolic curve.** *The points are calculated from theory. The solid lines are drawn to connect the points. The dashed curves are experimental.*

cutoff is just the $1/k^2$ decrease of the Coulomb interaction or if it is due to lifetime effects involving excitation of electron-hole pairs[9], then the cutoff is mass-independent in the original integral equation (4). This cutoff is then mass dependent after the transformation to Eq. (10), and there will be a modification of the relations (27).

If we denote the cutoff by $\varepsilon_1 = \hbar\omega_1$ (independent of mass $M$) before the transformation, then after the transformation it becomes $x_1$ with

$$x_1 = \varepsilon_1/\hbar\Omega_p, \tag{28}$$

so that for variations in the mass $M$

$$\frac{\delta x_1}{x_1} = \frac{1}{2}\frac{\delta M}{M}. \tag{29}$$

Now for the energy gap at $T = 0$,

$$\Delta(0,0) = \hbar\Omega_p y(0,0), \tag{30}$$

and thus

$$\frac{\delta\Delta}{\Delta} = \frac{\delta\Omega_p}{\Omega_p} + \frac{\delta y}{y}. \tag{31}$$

Since $\delta\Omega_p/\Omega_p = -\frac{1}{2}\delta M/M$, (29) and (31) give

$$\frac{\delta\Delta}{\Delta} = -\tfrac{1}{2}(1-\zeta)\frac{\delta M}{M}, \tag{32}$$

where $\zeta$ is the coefficient in the change of $y$ with $x_1$,

$$\frac{\delta y(0)}{y(0)} = \zeta\frac{\delta x_1}{x_1}. \tag{33}$$

The exponent in (27) is then changed from $-\frac{1}{2}$ to $-\frac{1}{2}(1-\zeta)$ for the variation of the gap $2\Delta(0,0)$. The same would be true of $T_c$ if the ratio $2\Delta/k_BT_c$ were independent of the cutoff. According to the results in Table 1, this is not exactly true, but the changes are very small compared to the other effects. Thus

$$\Delta(0) \propto M^{-\frac{1}{2}(1-\zeta)}, \quad T_c \propto M^{-\frac{1}{2}(1-\zeta)}. \tag{34}$$

We have determined the coefficient $\zeta$ of Eq. (33) for the intermediate-coupling case. Figure 3 shows the result on the solution of varying the cutoff. The solid line for $T=0$ is the solution for a cutoff $\varepsilon_1 = 4k_B\theta_D$. The circles give the solution at $T=0$ for a cutoff $\varepsilon_1 = 3.6k_B\theta_D$. Notice that the biggest effect of the changed cutoff is at energies larger than $2k_B\theta_D$. The solution at the Fermi surface changes from 0.419 to 0.400 $k_B\theta_D$, giving $\zeta = +0.44$. Carrying out the same calculation for the Tolmachev solution for the corresponding case (see Ref. 5) gives $\zeta = +0.28$. Thus the two different calculations give the same order of magnitude correction $\zeta$ to the isotope effect. Since we are only interested in the order of magnitude of $\zeta$, we shall confine our consideration to cases involving the Tolmachev solution, inasmuch as these can be worked out analytically.

Table 2 gives the calculated correction $\zeta$ to the $-1/2$ exponent in the isotope effect. The results are shown for two different cutoffs $\hbar\omega_1$ of the Coulomb interaction. The value $\hbar\omega_1/k_B\theta_D$ of 1000 corresponds roughly to distances in $k$ space at which the Coulomb interaction dies off without lifetime effects.

*Table 2.* **Calculated correction $\zeta$ to the exponent in the isotope effect**

| *Superconductor* | $\hbar\omega_1/k_B\theta_D = 10$ | 1000 |
|---|---|---|
| Hg, Pb | 0.3 | 0.05 |
| Ru | 1.3 | 0.4 |

The value for $V_1$ in Eq. (7) for the Tolmachev solution was taken to be the value of the screened Coulomb interaction averaged over the Fermi surface. The attractive part $V$ was then chosen to give the proper value of $T_c/\theta_D$. Since $V_1$ is nearly the same for all superconductors, the main effect on $\zeta$ is the relative size of $T_c/\theta_D$. Thus Ru has a larger value of $\zeta$ than Hg or Pb because it has a smaller $T_c$, and this agrees with the experiments.[7] In fact, according to our model, there is no reason why $\zeta$ can not be larger than one, leading to a positive exponent in the isotope effect.

Our model would predict an exponent near zero for Os (as is found[7]), but the exponent for Zn should be intermediate between that of Pb and Hg on the one hand, and Ru and Os on the other. This is so because the value of $T_c/\theta_D$ for Zn is intermediate among values of $T_c/\theta_D$ for these other superconductors. However, the experimental results[7] are that Zn has an exponent of $-0.5$. Thus the model breaks down for this case. In fact, the experimental results indicate, for the seven superconductors tested, that the exponent is either $-1/2$ or 0, while our model predicts a smooth variation from $-1/2$ to 0. An alternative explanation of the lack of an isotope effect in the transition elements Os and Ru has been suggested by Matthias. He has proposed that the transition elements may become superconducting through an interaction other than the electron-phonon interaction, so that there is no effect of the ion mass on the transition. However, in order for the result to be explainable for Zn, the nontransition element superconductors must have a cutoff in the Coulomb interaction that is proportional to $M^{-1/2}$. The explanation of such a cutoff remains an unsolved problem.

## Conclusions

We have seen that with quite different forms and strengths for the interaction $V_{\mathbf{kk}'}$, the results of the BCS theory are nearly invariant. This result is similar to that found earlier by the author[24] for the specific case of the relation between the energy gap and critical field at zero temperatures. These results indicate that the theory is probably insensitive to the effects of bands, and they explain the experimentally found law of corresponding states.

In considering the deviations from the law of corresponding states, the theory worked out here can essentially account for the variations in the ratio of energy gap to critical temperature. It also shows that even when this ratio differs from the value of 3.5, the reduced energy gap as a function of reduced temperature is nearly invariant, as has been found experimentally. In the case of the critical field and the specific heat near $T_c$, the model gives variations in the right direction as a function of $T_c/\theta_D$, but the variations are nearly an order of magnitude too small. It is probably necessary to include anisotropies and lifetimes in order to understand the actual deviations from the law of corresponding states for these thermodynamic functions.

By making the additional plausible assumption that the cutoff in the Coulomb interaction is independent of the ionic mass, this model also gives the deviation of the isotope effect from the $M^{-1/2}$ dependence. The calculations are in qualitative agreement with the results of nearly the $M^{-1/2}$ dependence for Pb, Hg, Tl, and Sn while the lack of an isotope effect in Ru and Os (Ref. 7) is also understood. However, the results with Zn (Ref. 7) can not be explained by this model.

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