This procedure is very useful for metals with low transition temperatures, for which it is necessary to extrapolate over a substantial range in t^2 to estimate H_0. The old method of stating the critical field as a power series in T^2 cannot be used in this way; and assuming purely parabolic behavior at low temperatures is equivalent to ignoring the curvature of the deviation plots.

It is tempting to seek an analytic connection between the gap behavior (1) and the critical field (3) or (4). This is excluded by the nonlinear way in which the gap-function enters the critical-field expression [(3.38) of BCS].

The maximum deviation D_0 is related to the interaction strength by its relation to the critical-field derivative at $T=T_c$: from (3)

$$(dh/dt)_{t=1}=-2/(1+D_0\pi) \tag{5}$$

and $(dh/dt)_1$ in turn is related to the interaction strength.[12,9] This point will be discussed in the following paper.

[12] T. P. Sheahen, following paper, Phys. Rev. **149**, 370 (1966).

PHYSICAL REVIEW VOLUME 149, NUMBER 1 9 SEPTEMBER 1966

Effective Interaction Strength in Superconductors*

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(Received 21 February 1966)

A semiempirical extension of the BCS model to intermediate- and strong-coupling superconductors is used to derive a set of simple rules by which the following thermodynamic quantities can be related to one another: the absolute-zero energy gap $2\Delta_0$; the critical field H_0; the critical temperature T_c; the jump ΔC in specific heat at T_c; and the slope at T_c of the critical-field curve, $(dh/dt)_1$. The procedure determines an "effective interaction strength" N_0V^* (larger than the value of N_0V obtained from T_c/Θ_D) for each superconductor. A "temperature-variation" of this N_0V^* is the major departure from the original BCS model. N_0V^* is obtained for 9 superconductors from their specific-heat jumps, and used to predict values of the ratios $(dh/dt)_1$, Δ_0/kT_c, and $\gamma T_c^2/V_mH_0^2$ which agree well with experiment. The resulting values for the "effective cutoff" Θ_c lie close to $\Theta_D/9$.

I. INTRODUCTION

SINCE the appearance of the BCS[1] theory of superconductivity, attention has gradually focused more and more on the problem of determining the behavior of the energy-gap function $\Delta(\epsilon,T)$. It is well established that the simple square-well BCS interaction, and the original BCS gap function (independent of energy up to a cutoff) are not adequate for an understanding of the strong-coupling superconductors. Such basic BCS concepts as quasiparticles, density of states, and the sum over states have been called into question[2] in attempting to understand data on lead and mercury.

Nevertheless, the thermodynamic properties of superconductors can be treated using a very simple BCS model, with certain semiempirical corrections. These corrections do not give a fundamental understanding of the superconducting mechanism, but do serve to tie together a set of reduced quantities for which BCS give "laws of corresponding states." The various laws of corresponding states which relate this set of quantities in BCS can be extended to account for experimental values which deviate from the BCS values. This extension can be justified by discarding the assumptions that: (1) the interaction is independent of temperature, and (2) the cutoff energy is near the Debye temperature.

In this paper, the ratios[3] $\Delta C/\gamma T_c$, Δ_0/kT_c, $(dh/dt)_1$, and $\gamma T_c^2/V_mH_0^2$ will be related to one another within the BCS framework by simply choosing unusually large values of the interaction parameter N_0V. Experimental data for $\Delta C/\gamma T_c$ can be used to find the values of an "effective-interaction strength" N_0V^* which can then be used to predict values of Δ_0/kT_c and the free energy [and therefore $(dh/dt)_1$ and $\gamma T_c^2/V_mH_0^2$] which agree well with experiment. Each N_0V^* value is also used to find an "effective cutoff temperature" Θ_c; these cutoffs turn out to be close to $\Theta_D/9$ for most superconductors.

The values of N_0V^* obtained in this way are not the depths of attractive square-well interactions. Rather, N_0V^* becomes a convenient parameter with which to characterize a superconductor within the BCS frame-

* This research was supported in part by the Advanced Research Projects Agency under Contract No. SD-90.
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[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[2] G. J. Culler, B. D. Fried, R. W. Huff, and J. R. Schrieffer, Phys. Rev. Letters **8**, 399 (1962).

[3] T_c=transition temperature; $(dh/dt)_1$=slope of reduced critical field $h\equiv H_c(T)/H_0$ at $T=T_c$; the electronic-specific-heat coefficient is $\gamma=\frac{2}{3}\pi^2N_0k^2$; H_0=critical field at 0°K; V_m=molar volume; ΔC=jump in specific heat at $T=T_c$; the energy gap at 0°K is $2\Delta_0$, but frequently in this paper we refer to Δ_0 as the "energy gap."

work; it summarizes all the various contributions to the interaction which are ordinarily handled by machine computations. In essence, the values of N_0V^* arise from integrating over the structure of the gap function, taking proper account of lifetime effects, anisotropy, etc. The thermodynamic functions are given by their BCS values corrected for all these, and the correction factor is expressed as a stronger "effective interaction."

In Sec. II the BCS solution is reviewed and extended to the case of a stronger interaction. The values of N_0V^* are determined in Sec. III and used to predict other thermodynamic ratios, and the cutoff temperatures Θ_c. Section IV presents an argument and some calculations to support the key assumption of Sec. III. Section V is a summary.

II. THE BCS SOLUTION FOR STRONG INTERACTIONS

The original "BCS equation" [Eq. (3.27) of Ref. 1] is

$$\frac{1}{N_0V}=\int_0^{\hbar\omega}\frac{\exp(\beta E)-1}{\exp(\beta E)+1}\frac{d\epsilon}{E}, \tag{1}$$

where $E^2=\epsilon^2+\Delta(T)^2$ and $\beta=1/kT$. At 0°K, this yields

$$\frac{\Delta_0}{\hbar\omega_0}=\frac{1}{\sinh(1/N_0V_0)}, \tag{2}$$

where ω_0 and V_0 are the phonon-frequency cutoff and the interaction strength at zero temperature, and N_0 is the density of states at the Fermi surface.

BCS also give an expression for the free-energy difference, which leads to a value of the critical field at 0°K given by

$$V_mH_0^2=4\pi N_0\Delta_0^2(1-\exp[-2/N_0V_0]). \tag{3}$$

Since this is derived at absolute zero, it is an exact result of BCS, regardless of how small the cutoff may be, or how strong the interaction is. The factor $(1-\exp[-2/N_0V_0])$ will carry through the subsequent manipulations and recur in each of the formulas for the dimensionless thermodynamic ratios, but it arises originally from Eq. (3). As long as the BCS model is used, (3) will hold. By using measured values of V_m, H_0, Δ_0, and N_0, one can employ (3) to estimate values of the interaction parameter N_0V_0, since the cutoff $\hbar\omega_0$ has cancelled out. When this is done, the resulting values of N_0V_0 are much larger[4] than those obtained conventionally from the experimental ratios T_c/Θ_D. For example, lead requires $N_0V_0=1.14$ to fit the data to Eq. (3). But because of the very large experimental uncertainties in Δ_0 measurements, (3) is not the best means of obtaining N_0V_0. By further manipulations, it is possible to cancel out Δ_0 and show that the specific heat jump is the most sensitive thermodynamic probe of this "effective interaction strength."

From (3) it follows trivially that

$$\frac{V_mH_0^2}{\gamma T_c^2}=\frac{6}{\pi}(\Delta_0/kT_c)^2(1-\exp[-2/N_0V_0]). \tag{4}$$

Also, by thermodynamics, the jump in specific heat is

$$\frac{\Delta C}{\gamma T_c}=\frac{V_mH_0^2}{4\pi\gamma T_c^2}\left(\frac{dh}{dt}\right)_1^2. \tag{5}$$

Combining (4) with (5) yields

$$\frac{\Delta C}{\gamma T_c}=\frac{3}{2\pi^2}\left(\frac{\Delta_0}{kT_c}\right)^2\left(\frac{dh}{dt}\right)_1^2(1-\exp[-2/N_0V_0]). \tag{6}$$

It is known that in general, for a second-order transition involving an energy gap[5] (as in superconductivity), the free-energy difference must vary as $\Delta F\propto\Delta^4$. Making use of this fact, it has been shown that for weak-coupling superconductors[6] the reduced critical field is given by

$$\lim_{t\to1}h=C_0(\Delta_0/kT_c)(\delta^2/t),$$

where the constant C_0 has a value very close to $1/\pi$. Since the reduced energy gap $\delta\equiv\Delta(T)/\Delta(0)$ follows very closely a universal function of temperature,[7] we can differentiate with respect to temperature to obtain

$$\left(\frac{dh}{dt}\right)_1=C_0\frac{\Delta_0}{kT_c}\left(\frac{d(\delta^2/t)}{dt}\right)_1=1.004\frac{\Delta_0}{kT_c} \tag{7}$$

in the weak-coupling limit. Finnemore and Mapother[8] have evaluated the BCS free-energy integral using values of Δ_0/kT_c which exceed 1.76, corresponding to intermediate and strong-coupling superconductors. In each case the slope of the resulting critical field curve equals the chosen value of Δ_0/kT_c (to within the accuracy of their graphs). This technique of "scaling"

[4] In particular, the values of N_0V_0 obtained from (3) exceed the limiting value of 0.5, above which point the lattice is expected to become unstable. This problem will be discussed further in Sec. III.

[5] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, (Pergamon Press Ltd, London, 1958), pp. 434–436.

[6] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Mechanics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963), pp. 304–307. They give an expression for the free-energy difference

$$\lim_{T\to T_c}\Delta F=N_0\frac{7\zeta(3)}{16\pi^2}\frac{\Delta^4}{T^2} \tag{36.9}$$

into which they proceed to insert a linear dependence of the energy gap on temperature. Moreover, their entire treatment is carried through without retaining terms in $\exp[-2/N_0V]$; combining their Eq. (36.9) with Eq. (3) of the present paper would give an erroneous result for h.

[7] T. P. Sheahen, preceding article, Phys. Rev. **148**, 368 (1966). In this paper it is stated that experimental points for the energy gap as a function of temperature lie closer to the curve $\delta^2=\cos[\pi t^2/2]$ than to the BCS expression. Taking the derivative at $t=1$ leads to $(dh/dt)_1=(\pi)^{1/2}\equiv1.7725$ instead of 1.7367 as in the strict BCS case. This also accounts for the numerical factor (1.48) which will appear in the formula for the specific-heat jump.

[8] D. K. Finnemore and D. E. Mapother, Phys. Rev. **140**, A507 (1965).

Δ_0/kT_c does not strictly follow from the BCS treatment: in particular, they did not use a smaller cutoff $\hbar\omega_0$ in conjunction with their larger energy-gap ratios. Nevertheless, their model is so closely akin to BCS that the result (7) can be said to arise from the simple BCS model, with a very minor modification (large cutoff), even in the strong-coupling case. Moreover, Toxen[9] has observed empirically that (7) holds over the entire range of interaction strengths. Therefore we insert (7) into (6) to obtain

$$\frac{\Delta C}{\gamma T_c}=\frac{3}{2\pi^2}\left(\frac{\Delta_0}{kT_c}\right)^4(1-\exp[-2/N_0V_0]). \tag{8}$$

Fundamentally, Eq. (8) is valid only to the extent that (7) holds; the scatter in experimental values of Δ_0 is sufficiently great that we can only say that (7) is not violated (within experimental error) by the majority of superconducting elements. One calculation[10] (based on an extremely crude model, involving an energy gap independent of temperature) suggested that (7) is merely a numerical coincidence; however, the calculations of Finnemore and Mapother indicate that (7) is a result of a simple BCS model with increased values of Δ_0/kT_c. Accordingly, it is legitimate within the present context of staying close to the BCS square-well model to use $(dh/dt)_1$ and Δ_0/kT_c interchangeably.

It is necessary at this point to develop a relation between Δ_0/kT_c and the interaction parameter N_0V. In the limit of zero energy gap, the metal becomes normal, so (1) reduces to

$$\frac{1}{N_0V_c}=\int_0^{\hbar\omega_c}\frac{\exp(\epsilon/kT_c)-1}{\exp(\epsilon/kT_c)+1}\frac{d\epsilon}{\epsilon}. \tag{9}$$

This integral is evaluated numerically, being customarily approximated by the limiting case of a very large cutoff (or equivalently the case of $N_0V_c<0.5$):

$$kT_c/\hbar\omega_c=1.14\exp(-1/N_0V_c), \tag{10}$$

where now ω_c and V_c are the cutoff and interaction strength at the transition temperature.

In BCS, it was assumed that $V_c=V_0$ and $\omega_c=\omega_0$. In this case, combining (2) with the integral equation (9) gives

$$\frac{1}{N_0V_0}=\int_0^{(\Delta_0/kT_c)\sinh(1/N_0V_0)}\frac{\exp(x)-1}{\exp(x)+1}\frac{dx}{x}. \tag{11}$$

This uniquely determines a relation between Δ_0/kT_c and N_0V_0; this relation is given by the dashed curve in Fig. 1. In the weak-coupling limit, (2) and (10) combine to give

$$\Delta_0/kT_c=1.764/(1-\exp[-2/N_0V_0]). \tag{12}$$

This appears as the solid curve in Fig. 1, where it is seen to be an excellent approximation to the strict BCS result (11) for $N_0V_0<0.5$. Also shown in Fig. 1 (dotted curve) is the expression given by Mühlschlegel[11] for finite cutoffs. At no value of N_0V_0 does Mühlschlegel's approximation lie as close to the BCS curve as the simple choice $\Delta_0/kT_c=1.764$.

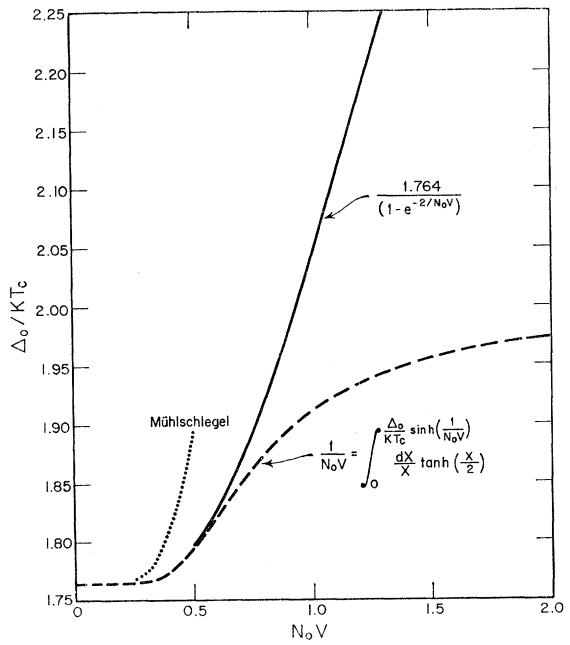

FIG. 1. The relative energy-gap ratio (Δ_0/kT_c) as a function of the interaction strength N_0V. Dashed curve: the solution of (11) in the strict BCS case. Solid curve: Eq. (12) extended to large values of N_0V. Dotted curve: Mühlschlegel's approximation to the strict BCS case.

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III. EFFECTIVE INTERACTION STRENGTH

At this point we introduce the principal assumption of this paper: we assume that the energy gap varies as

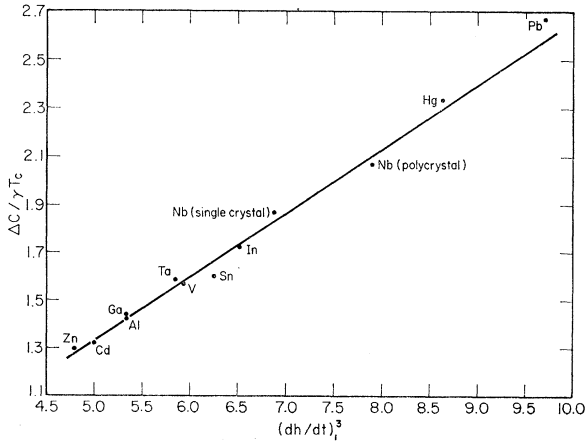

FIG. 2. The empirical relation between the specific-heat jump and the reduced critical-field derivative at $t=1$. The solid line is Eq. (14). The points are experimental.

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TABLE I. Thermodynamic parameters of superconductors.

Element	T_c(°K)[a]	Θ_D	γ(mJ/mole °K²)	V_m(cc/mole)	N_0[b]	ΔC(mJ/mole °K)	$H_0(G)$	$-D_0$	$(dh/dt)_1$	Δ_0/kT_c	$\gamma T_c^2/V_m H_0^2$
Cd	0.52	209[o]	0.688[o]	13.0	0.425	0.83[o]	29.6[o]	−0.046[o]	1.71[o]		0.177
Zn	0.85	309[d]	0.64[d]	9.03	0.566	0.61[d]	53.4[d]	−0.042[d]	1.70[d]		0.177
Ga	1.083[e]	325[e]	0.596[e]	11.65	0.408	0.892[f]	59.2[e]	−0.035[e]	1.72[e]		0.173
Al	1.17	427[g]	1.35[g]	9.87	1.09	2.06[g]	103.0[g]	−0.040[g]	1.75[g]	1.68–1.75[h]	0.171
Tl	2.38[i]	78.5[i]	1.47[i]	16.9	0.690	5.26[i]	175[j]	−0.030[i]	1.79[j]	1.85[k]	0.161
In	3.405[l]	109[m]	1.69[l]	15.37	0.863	10.0[l]	282.7[o]	−0.021[o]	1.87[o]	1.82[n]	0.157
Sn	3.722[o]	201[m]	1.78[l]	16.06	0.885	10.55[p]	305.5[o]	−0.026[o]	1.84[o]	1.73[n], 1.80	0.166
Hg	4.154[o]	72.0[n,q]	1.86[q]	13.85	1.073	18.3[r]	411.0[o]	+0.017[o]	2.05[o]	2.0, 2.3[s]	0.139
Ta	4.482[t]	255[u]	5.7[u]	10.9	4.18	40.5[p]	780[u]	−0.032[t]	1.80[t]	1.80[v]	0.161
V	5.03	338[w]	9.26[w]	8.5	8.75	72.9[w]	1310[w]	−0.030[w]	1.79[w]	1.75[x]	0.161
Pb	7.193	105[q]	3.00[q]	17.85	1.34	57.5[y]	802.5[z]	+0.023[z]	2.13[z]	2.16[n]	0.136
Nb(s)[ff]	9.20[aa]	275[bb]	7.79[bb]	10.8	5.80	134[aa]	1994[aa]	−0.012[aa]	1.90[aa]	1.87[cc]	0.154
Nb(p)[ff]	9.46[dd]	238[ee]	7.53[ee]	10.8	5.61	147[ee]	1920[dd]		1.99[dd]	1.92[v]	0.170

[a] Except where otherwise noted, these values were taken from B. T. Matthias, T. H. Geballe, and V. B. Compton, Rev. Mod. Phys. **35**, 1 (1963).
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[ff] The designation Nb(s) refers to single-crystal niobium; Nb(p) refers to polycrystal niobium.

TABLE II. Calculation of N_0V^* and Θ_c.

Element	$\Delta C/\gamma T_c$	$1-\exp(-2/N_0V^*)$	N_0V^*	Θ_c (°K)	Θ_c/Θ_d	Predicted $2\Delta_0/kT_c$	Predicted $(dh/dt)_1$	Predicted $\gamma T_c^2/V_m H_0^2$
BCS[a]	1.43	1.0	0		1.0	3.53	1.74	0.168
This work[b]	1.48	(1.0)	(0)			3.53	1.77	0.168
Cd	1.32	1.038				3.40	1.71	0.175
Zn	1.30	1.044				3.36	1.70	0.176
Ga	1.40	1.018				3.48	1.75	0.173
Al	1.43	1.012				3.48	1.76	0.173
Tl[c]	(1.69)	0.957	0.65	9.6	0.122	3.68	1.85	0.161
In	1.73	0.949	0.67	13.3	0.122	3.72	1.87	0.159
Sn	1.60	0.974	0.55	20.4	0.101	3.62	1.82	0.163
Hg	2.37	0.855	1.04	9.5	0.132	4.12	2.07	0.143
Ta	1.59	0.976	0.54	25.2	0.101	3.62	1.81	0.164
V	1.57	0.981	0.50	32.7	0.103	3.60	1.80	0.165
Pb	2.67	0.822	1.16	14.9	0.142	4.32	2.15	0.136
Nb(s)	1.87	0.925	0.77	29.5	0.108	3.82	1.92	0.155
Nb(p)	2.07	0.895	0.89	25.5	0.107	3.96	1.98	0.150

[a] See Refs. 1 and 11.
[b] Values listed are for the special case $N_0V^*=0$.
[c] N_0V^* for thallium was obtained from Eq. (4), not (13). The value listed for $\Delta C/\gamma T_c$ is a prediction.

(12) for all values of the interaction parameter N_0V_0. This is equivalent to assuming that (10) holds instead of (9) even when $N_0V_0>0.5$. Thus, in Fig. 1 we follow the solid curve (12) rather than the dashed curve (11). To denote that this is an extension of the weak-coupling formula to a region beyond its proper bounds, we substitute an "effective interaction strength" N_0V^* in place of N_0V_0.

Inserting (12) into (8) gives at once

$$\Delta C/\gamma T_c=1.48/(1-\exp[-2/N_0V^*])^3. \quad (13)$$

On the other hand, using (12) to eliminate $(1-\exp[-2/$

$N_0V^*]$) gives

$$\Delta C/\gamma T_c = 0.27(\Delta_0/kT_c)^3 = 0.27(dh/dt)_1^3, \quad (14)$$

where (7) has been used in the last step.

The validity of the prediction (14) is demonstrated by Fig. 2, which displays reduced specific-heat jumps versus reduced critical-field derivatives [Eq. (14) is the solid line and the points are experimental]. This prediction (14) occurs only if (12) is chosen to represent the behavior of the energy gap with increasing strength; any other functional form would leave an extra factor involving N_0V^* in (14). Of course it is always possible to reverse the above procedure: If we had chosen to regard Fig. 2 as an empirical observation, then the condition (8) requires the choice of (12) to represent Δ_0/kT_c for all N_0V^*.

Table I is a collection of relevant data on superconductors. In order to determine the "effective interaction strength" N_0V^*, we may use any one of (3), (4), (12), or (13). Obviously (13) is the most sensitive. In Table II the values of $\Delta C/\gamma T_c$ are listed, and have been used to find N_0V^*, and to predict values of $(dh/dt)_1$, Δ_0/kT_c, and $\gamma T_c^2/V_mH_0^2$. The agreement with existing data is expected, because of the relations (5), (7), and (14). That is, we have only one free parameter (N_0V^*) which gives two numbers ($\Delta C/\gamma T_c$ and Δ_0/kT_c); then $(dh/dt)_1$ is fixed by the BCS free-energy condition (7) and $\gamma T_c^2/V_mH_0^2$ follows by thermodynamics (5).

Table II also lists the values of the "effective cutoff temperature" Θ_c obtained by summarily plugging these N_0V^* values into (10), with $\hbar\omega_c = k\Theta_c$. These cutoffs are consistently in the range $\Theta_c \approx \Theta_D/9$, which implies in many cases that the cutoffs are within the width of the energy gap at 0°K. Further comment on this situation is deferred to Sec. IV.

In weak-coupling superconductors, the effects of anisotropy cause the values of the thermodynamic ratios to drop below their BCS values, which cannot occur for real values of N_0V^*. Clem[12] has calculated correction factors for anisotropic superconductors: denoting the mean-square-anisotropy by $\langle a^2\rangle$, he finds

$$(\Delta_0/kT_c) \propto 1-\tfrac{3}{2}\langle a^2\rangle, \quad (15a)$$

$$(dh/dt)_1 \propto 1-\langle a^2\rangle, \quad (15b)$$

$$(V_mH_0^2/\gamma T_c^2) \propto (1+2\langle a^2\rangle)^{-1}, \quad (15c)$$

$$(\Delta C/\gamma T_c) \propto 1-4\langle a^2\rangle. \quad (15d)$$

TABLE III. Estimation of N_0V^* and $\langle a^2\rangle$ in weak-coupling superconductors.

Element	$\Theta_D/9$ (°K)	Predicted N_0V^*	Observed $\Delta C/\gamma T_c$	$\langle a^2\rangle$
Cd	23	0.25	1.32	0.027
Zn	34	0.26	1.30	0.031
Ga	36.5	0.274	1.40	0.014
Al	48	0.26	1.43	0.0085

[12] J. R. Clem, University of Illinois thesis; Phys. Rev. **148**, 392 (1966).

Since $\langle a^2\rangle$ is always small (<0.05), this set of relations maintains the conditions (7) and (14) to within experimental accuracy. The complete set of thermodynamic relations is therefore

$$\frac{\Delta C}{\gamma T_c} = \frac{1.48(1-4\langle a^2\rangle)}{(1-\exp[-2/N_0V^*])^3}, \quad (16)$$

$$\frac{\Delta_0}{kT_c} = \frac{1.764(1-\frac{3}{2}\langle a^2\rangle)}{(1-\exp[-2/N_0V^*])}, \quad (17)$$

$$\frac{\gamma T_c^2}{V_mH_0^2} = \frac{0.1683(1+2\langle a^2\rangle)}{(1-\exp[-2/N_0V^*])}, \quad (18)$$

$$\left(\frac{dh}{dt}\right)_1 = \frac{-1.7725(1-\langle a^2\rangle)}{(1-\exp[-2/N_0V^*])}. \quad (19)$$

First consider the weak-coupling superconductors: when $N_0V^*<0.3$, the denominators in (16)–(19) are indistinguishable from one; so we use (16) to determine the anisotropy $\langle a^2\rangle$ and then employ this $\langle a^2\rangle$ value to predict (17)–(19). In view of the striking consistency of the cutoff values (all near $\Theta_c \approx \Theta_D/9$), we can make a crude estimate of N_0V^* by *assuming* $\Theta_c = \Theta_D/9$, and then using Eq. (10), which is certainly valid for $N_0V^* < 0.3$. These values of N_0V^* are listed in Table III, together with the estimated anisotropy values for these superconductors.

The element thallium was handled in a different way from the others: Thallium has a large lattice specific heat (Θ_D small) at T_c, which makes the specific-heat jump very difficult to measure accurately. Accordingly, Eq. (4) [instead of (13)] was used to obtain N_0V^* for thallium. The value of $\Delta C/\gamma T_c = 1.69$ in Table II is a prediction based on that value of N_0V^*, assuming $\langle a^2\rangle = 0$. The current best experimental value[13] is $\Delta C/\gamma T_c = 1.50$.

As soon as the relations (16)–(19) exceed their BCS weak-coupling values, we cannot distinguish the effect of anisotropy from a slightly smaller value of N_0V^* for the superconductor. In view of the fact that very few anisotropies are well known, we have set $\langle a^2\rangle = 0$ in (16)–(19) for all the stronger superconductors, thereby absorbing the anisotropy correction into the factor $(1-\exp[-2/N_0V^*])$, where it acts to decrease N_0V^*. Clearly, the importance of anisotropy diminishes as coupling strength increases.

There is one more number which is predictable from the data of Tables II and III: the maximum deviation D_0 of the critical field curve from a parabola. In the preceding article[7] it has been shown that the critical field curves of most superconductors can be adequately represented empirically by

$$h + D_0 \sin\pi h = 1 - t^2. \quad (20)$$

If we evaluate the derivative of this expression at $t=1$,

[13] B. J. C. van der Hoeven, Jr., and P. H. Keesom, Phys. Rev. **135**, A631 (1964).

we find with the help of (19) the result

$$D_0=0.041-0.36(\exp[-2/N_0V^*]-\langle a^2\rangle). \quad (21)$$

Unfortunately, (21) is not a good means of determining N_0V^*, since a reasonable amount of anisotropy will change D_0 by 25% (as calculated by Clem[12]) if N_0V^* is small. Clearly, if a superconductor fits Eq. (20) well, then the predicted value of D_0 will be as accurate as the predicted value of $(dh/dt)_1$. Without knowledge of the anisotropy, D_0 remains in doubt.[14]

It must be emphasized that the values of N_0V^* obtained in this entire procedure do not represent square-well interaction strengths of ideal BCS superconductors. Therefore, the fact that many of the values of N_0V^* exceed 0.5 (implying lattice instability) is not of concern here. These N_0V^* values inherently include lifetime effects, Coulomb repulsion, etc., all summarized in a single multiplying factor which occurs consistently in those quantities which average over the energy gap. An understanding of the true superconducting mechanism, and the details of the energy-gap function, still require a more precise study than that available with the BCS model.

IV. TEMPERATURE DEPENDENCE OF THE EFFECTIVE INTERACTION

In the preceding section, it was shown that by following through the derivation of the principal BCS thermodynamic formulas with greater care than usual, new results were obtained. By blindly plugging into these improved formulas it was possible to derive a relation which was found to agree with experiment. That is, the BCS model still works (for thermodynamic properties) outside its range of validity. The only departure from the BCS paper was the assumption that for all interaction strengths, the relation (12) holds; i.e., Δ_0/kT_c varies along the solid curve of Fig. 1. The purpose of this section is twofold: to justify this relation within the framework of the BCS theory, and to suggest in a semiquantitative way that the well-known energy dependence of the gap function might be treated as a temperature dependence of the "effective interaction strength" N_0V^*.

The maximum value of the gap ratio in the constant-interaction BCS model (dashed curve of Fig. 1) is 2.0, when $N_0V_0\rightarrow\infty$. However, experimental values of the gap ratio exceed 2.0, so it is necessary to leave the simple constant-interaction BCS model. Ordinarily this step involves going to a precise formalism which includes lifetime effects and an energy-dependent gap function. In this paper we choose instead to assume a slight temperature dependence of the interaction parameter N_0V^*. This turns out to be an adequate means of characterizing the thermodynamic quantities. Since the thermodynamic ratios involve integrals over the energy-dependence, it may be possible to interpret this "temperature dependence" as simply a way of rolling all the complexities of a rigorous Green's-functional calculation into one single number, the effective interaction strength N_0V^*. Such a procedure is reminiscent of the way in which the time constant τ in the Boltzmann transport equation is actually just a shorthand notation for a rather involved scattering integral.

First of all, let us ask how much of a temperature dependence of N_0V^* is necessary to make (12) hold instead of (11) for the gap ratios of all superconductors. The suppressed zero of Fig. 1 conceals the fact that the difference between these functions is small. In lead, the worst case, only a 10% decrease in N_0V^* between $T=0$ and $T=T_c$ suffices to account for the value of the experimental gap ratio, $\Delta_0/kT_c=2.15$.

The temperature dependence of the phonon spectrum is presumably very small, being due to minor changes in the lattice structure accompanying thermal expansion; and the electrons have energies $\approx E_F\gg kT_c$, so their dynamics should not change appreciably with temperature. However, this does not guarantee that there will be no change in the electron-phonon interaction with temperature. It is known[15] that as the coupling strength increases, lifetime effects become more influential; and these effects are much more important near T_c than at 0°K. Accordingly, it does not seem at all unreasonable to expect that in a strong coupling superconductor the effective interaction strength might diminish by as much as 10% between 0°K and T_c. Assuming just this condition is enough to justify Eq. (12), and thence to make predictions which agree with experiment, as already shown.

It is not enough merely to contrive the values of $N_0V^*(0)$ and $N_0V^*(T_c)$ in order to get from the dashed curve to the solid curve of Fig. 1: the behavior at intermediate temperatures must also be reasonable. Now at any temperature, $N_0V^*(T)$ can be found by carrying out a numerical integration of Eq. (1). This integral is usually performed by extending $\hbar\omega_c$ to infinity, and integrating over the reduced variable ϵ/kT; here we use a reduced variable $x=\epsilon/\hbar\omega_c$, in which case we have for (1)

$$\frac{1}{N_0V(t)}=\int_0^1\tanh\left\{\frac{(x^2+\mathfrak{A}^2)^{1/2}}{2(kT_c/\hbar\omega_0)t}\right\}\frac{dx}{(x^2+\mathfrak{A}^2)^{1/2}}, \quad (22)$$

where $\mathfrak{A}$ is half the energy gap in suitable units: $\mathfrak{A}=\Delta(t)/\hbar\omega_c$. The values of the integral obtained in this way are taken to be $1/N_0V(t)$. The temperature dependence arises primarily through the temperature dependence of the energy gap ($\mathfrak{A}$).

If the numbers tabulated by Mühlschlegel[11] for the

[14] D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. 112, 1888 (1958) suggested a linear variation of D_0 with (T_c/Θ_D), whereas (21) indicates a variation as $(T_c/\Theta_D)^2$. However, the same data plotted on log, semilog, or reciprocal paper give vague straight-line relationships; all of which illustrates the profound effect of anisotropy on D_0.

[15] D. J. Scalapino, Y. Wada, and J. C. Swihart, Phys. Rev. Letters 14, 102 (1965).

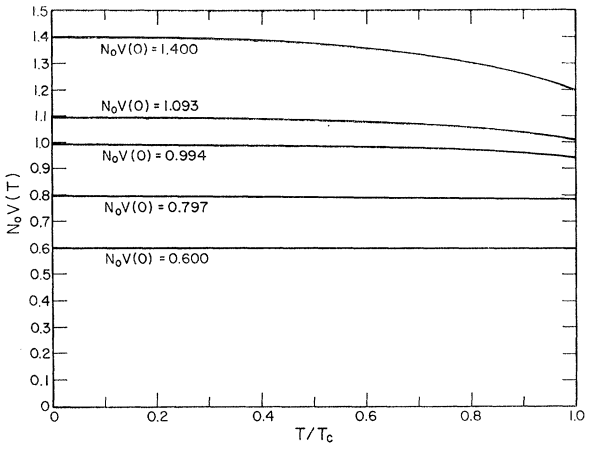

FIG. 3. The variation of the "effective interaction strength" with temperature. The total decrease is negligible for weak- and intermediate-coupling superconductors; but as the effective interaction increases, the temperature dependence also grows.

original temperature-independent BCS model are used for $\Delta(t)$, then (22) will give back again a temperature-independent N_0V. But the experimental[16] values of the reduced energy gap as a function of temperature lie slightly above the original BCS curve, so it would be better to use these actual values. In fact, as has been observed in the preceding article,[7] experimental values lie close to the curve

$$\delta^2 \equiv [\Delta(T)/\Delta(0)]^2 = \cos(\pi t^2/2), \tag{23}$$

and of course $\alpha^2 = \delta^2/(\sinh[1/N_0V_0])^2$ by Eq. (2). This greatly simplifies the numerical integration of (22), and will necessarily result in values of $N_0V(t)$ which vary with temperature. For each value of $N_0V(0)$ we choose $(kT_c/\hbar\omega_0)$ from Eq. (10), and the result is that $N_0V(t)$ decreases monotonically over the entire range $0<t<1$. The results of integrating (22) with the choice (23) for the reduced energy gap are shown in Fig. 3. Clearly, as the interaction strength becomes stronger, the temperature variation also increases.

It is equally possible to choose $(kT_c/\hbar\omega_0)$ from the strict BCS formula (9) for each value of $N_0V(0)$. Doing so gives an $N_0V(t)$ which decreases slowly from $t=0$ to $t\approx 0.95$ and then rises to the starting value $N_0V(0)$ when $t=1$. Such anomalous behavior would seem to indicate that the lifetime effects discussed above had suddenly become rather unimportant in the narrow range near $t\approx 1$.

Thus if we accept the empirical rule (23) as representing the true energy-gap dependence upon temperature, then a temperature-dependent interaction is indicated. Moreover, this dependence is forced into an anomalous form (a shallow minimum near $t\approx 0.95$) by requiring the original BCS condition (9); but the choice (10) for all N_0V^* gives a monotonic behavior of the effective interaction strength. Since (9) gives (11) while (10) gives (12), and (12) permits values of $\Delta_0/kT_c > 2.0$, we see that the choice of an "effective interaction" monotonically decreasing with temperature is an easy way to account for both the observed temperature dependence of the gap function (23) and the fact that Δ_0/kT_c can exceed 2.0.

Finally, note that this temperature dependence does not turn the manipulations of Sec. III into a two-parameter fitting formula: once the choice of $N_0V^*(0)$ is made, the value of $N_0V^*(T_c)$ is determined by the combination of (12), (22) and (23). All the *fitting* in Sec. III was done with only one parameter $[N_0V(0)]$; the temperature-dependence was introduced later in order to *justify* the choice of Eq. (12) for the energy-gap ratio.

This interpretation of a temperature-dependent N_0V^* is by no means unique, nor is it necessarily correct. Two alternatives present themselves at once:

(1) Table II shows that all of the "effective cutoff temperatures" Θ_c are near $\Theta_D/9$. Since $\frac{1}{9}=\exp(-2.2)$, it is a trivial algebraic manipulation to incorporate this cutoff-reducing factor into the interaction strength. Conventionally, N_0V is determined from Eq. (10), i.e.,

$$N_0V_{(\text{conv})} \equiv 1/\ln(1.14\Theta_D/T_c). \tag{24}$$

In Table IV are tabulated the differences between these numbers and the N_0V^* values found earlier. The fact that all these differences lie in the vicinity of 2 is no more surprising that the fact that all the "effective cutoffs" lie near $\Theta_D/9$; the two observations are interchangeable. Still another trivial manipulation permits us to write in place of Eq. (1)

$$\frac{1}{N_0V^*} = \frac{1}{N_0V} - 2 = \int_0^{k\Theta_2} \frac{\exp(\beta E)-1}{\exp(\beta E)+1}\,\frac{d\epsilon}{E}, \tag{25}$$

where now Θ_2 lies reasonably close to Θ_D. (See Table IV.) Of course we are still left with one free parameter by which to fit data: Θ_2. Unfortunately, the BCS paper does not appear to contain any justification for such an additive factor of 2. Rather than speculate on this point, we merely observe here that adding a factor of $+2$ to the right side of (1), thus obtaining (25), would accomplish three things: the N_0V values would be reduced below the instability level $(N_0V=\frac{1}{2})$, the cutoffs Θ_2 would be brought close to Θ_D, and the necessity of a temperature-dependent interaction would be removed. This last point holds for the following reason: when the cutoff is large $\approx\Theta_2$, the integral on the right of (9) is adequately approximated by

$$\int_0^{k\Theta_2} \frac{\exp(\epsilon/kT_c)-1}{\exp(\epsilon/kT_c)+1}\,\frac{d\epsilon}{\epsilon} = \ln\left(\frac{2\gamma_e}{\pi}\right)+\ln\left(\frac{\Theta_2}{T_c}\right), \tag{26}$$

with $\gamma_e=1.781\cdots$, and $2\gamma_e/\pi=1.14$. The important thing to notice here is that the factor 1.14 is preserved by the large cutoff, which means that both (10) and (12) hold when the cutoff is large. By using (25) in place of (1) we only change the factor in the expo-

[16] I. Giaever and K. Megerle, Phys. Rev. 122, 1101 (1961); P. Townsend and J. Sutton, *ibid.* 128, 591 (1962); M. A. Biondi, M. P. Garfunkel, and W. A. Thompson, *ibid.* 136, A1471 (1964).

TABLE IV. Calculation of $\left(\frac{1}{N_0V_{\text{conv}}}-\frac{1}{N_0V^*}\right)$.

Element	T_c/Θ_D[a]	N_0V[b] (conventional)	N_0V^*	$\left(\frac{1}{N_0V_{\text{conv}}}-\frac{1}{N_0V^*}\right)$	Θ_2/Θ_D
Tl	0.0304	0.276	0.65	2.09	0.91
In	0.0312	0.278	0.67	2.11	0.90
Sn	0.0185	0.243	0.55	2.30	0.74
Hg	0.0577	0.335	1.04	2.02	0.98
Ta	0.0176	0.239	0.54	2.29	0.75
V	0.0149	0.231	0.50	2.27	0.76
Pb	0.0685	0.355	1.16	1.95	1.05
Nb(s)	0.0335	0.283	0.77	2.23	0.79
Nb(p)	0.0398	0.298	0.89	2.23	0.79

[a] From Table I.
[b] Calculated using Eq. (10) with adjacent T_c/Θ_D values.

nentials of (10) and (12) from N_0V to N_0V^*, while leaving the cutoff large. In this way Eq. (12) could be used without requiring a temperature-dependent interaction for its justification.

In view of these three favorable results, the choice of (25) in place of (1) may seem tempting, but the unexplained factor of $+2$ is a severe obstacle. It is easier to justify a temperature-dependent "effective interaction" as we have done above. It is entirely possible that these consistent differences between $1/N_0V_{\text{conv}}$ and $1/N_0V^*$ are coincidental.

(2) Machine calculations which assume a temperature-independent interaction and an energy-dependent gap function have achieved the same results. For example, Swihart[17] used a "nonseparable" interaction with $N_0V=1.0$ to obtain $\Delta_0/kT_c=2.08$, which lies close to the solid curve of Fig. 1. This is cited not in order to revive the nonseparable interaction, but to indicate that even the simplest improvements to the BCS treatment can be used to justify the choice of (12). It is known that the gap function varies with energy,[18] and the Eliashberg[19] type of interaction has proved very successful in explaining data on strong-coupling superconductors.

The advantage of the present temperature-dependent model is that it returns to the simple BCS treatment, in which all the complicated machine calculations are sidestepped by permitting a small decrease in N_0V^* with temperature. The experimental justification for this arises out of the observed deviations of the experimental $\delta(t)$-versus-t curves from the temperature-independent BCS model, and from the surprisingly accurate correlation rules for Δ_0/kT_c, $(dh/dt)_1$, $\gamma T_c^2/V_mH_0^2$, and $\Delta C/\gamma T_c$ which come out of the simple BCS theory when (12) is used in place of (11).

V. CONCLUSIONS

The thermodynamic quantities in a superconductor can be understood using the simple BCS model with an "effective interaction strength" N_0V^* which represents the average of the true interaction.

It is shown that $\Delta C/\gamma T_c\propto(\Delta_0/kT_c)^3\propto(dh/dt)_1^3$, and this relation is used to predict values of $(dh/dt)_1$ and Δ_0/kT_c from calorimetric data, and to obtain values of N_0V^*. These N_0V^* values are much larger than those conventionally obtained from the ratios T_c/Θ_D. The resulting values of the cutoffs are near $\Theta_D/9$. Making use of this fact, the values of N_0V^* in weak-coupling superconductors can be estimated.

One of the basic BCS weak-coupling equations [Eq. (12)] is extended beyond its limit of validity. To justify this step, the "effective interaction" is assumed to decrease by less than 10% with increasing temperature; this is to be expected for a superconductor in which lifetime effects are important. The temperature dependence of $N_0V(t)$ is calculated assuming an energy gap varying with temperature as $\Delta(T)=\Delta(0)(\cos[\pi t^2/2])^{1/2}$.

In discussing alternatives to a "temperature-dependent interaction" it is shown that the addition of a factor of $+2$ to the BCS gap equation would suffice to (a) restore the old values of N_0V, (b) give cutoffs near the Debye temperature, and (c) eliminate the need for any temperature dependence in the effective interaction. But such a factor of $+2$ has not been justified.

ACKNOWLEDGMENTS

I am indebted to my advisor, Professor J. F. Cochran, for his help and encouragement throughout this work. Dr. C. A. Shiffman provided many helpful discussions, and Professor L. W. Gruenberg aided extensively in clarifying the discussion of the temperature dependence. The National Science Foundation supported me with a graduate fellowship during part of this work. The computations were performed on an IBM 7094 at the MIT Computation Center.

[17] J. C. Swihart, IBM J. Res. Develop. **6**, 14 (1962). The "nonseparable interaction" is an attractive square-well subject to the condition that electrons off the Fermi surface interact with other excited electrons, as long as they lie within $\hbar\omega_D$ of *each other*. This is contrasted with the BCS model, wherein electrons must lie within $\hbar\omega_D$ of the *Fermi level*, and interact only with states on the Fermi surface.
[18] J. C. Swihart, Phys. Rev. **131**, 73 (1963).
[19] G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. **38**, 966 (1960) [English transl.: Soviet Phys.—JETP **11**, 696 (1960)].