

## Rules for the Energy Gap and Critical Field of Superconductors\*

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Two simple empirical rules are given by which to characterize the energy gap and critical field of most superconductors: for the reduced energy gap  $\delta$ ,

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

where  $t = T/T_c$ ; and for the reduced critical field  $h$ ,

$$h + D_0 \sin \pi h = 1 - t^2,$$

where  $D_0$  is the maximum deviation from a parabola. An improved method of extrapolating critical-field data to 0°K is described.

THE BCS<sup>1</sup> model of a superconductor predicts a law of corresponding states which results in certain curves for the various thermodynamic functions, but real superconductors show deviations from these curves.

We observe here that the energy gap of typical superconductors depends on temperature approximately as

$$[\Delta(T)/\Delta(0)]^2 \equiv \delta^2 = \cos(\pi t^2/2) \equiv \sin[(\pi/2)(1-t^2)], \quad (1)$$

where  $t \equiv T/T_c$  is the reduced temperature. This curve lies just above the numbers tabulated<sup>2</sup> for the BCS model (see Fig. 1). The BCS curve is often represented by the implicit relation<sup>3</sup>

$$\delta(t) = \tanh(\delta(t)/t) \quad (2)$$

or by a power series in  $(1-t)^{1/2}$ ; neither of these laborious procedures fits experimental data<sup>4-6</sup> as well as (1), which is available on a slide rule. Experimental data are scattered about (1), in some cases (tin, aluminum) lying above it, in other cases (lead, tantalum) lying closer<sup>6</sup> to the BCS curve. Measurements of the energy-gap versus temperature have not generally been accurate enough to warrant plotting deviations from any particular curve, but the simple form of (1) naturally suggests it as a basis for such a plot.

It has been customary to represent critical-field curves either as polynomials in  $(T/T_c)^2 \equiv t^2$ , with unrelated coefficients, or graphically as deviations from a parabola. We observe here that for most real superconductors, only three constants ( $H_0$ ,  $D_0$ , and  $T_c$ ) suffice to give the critical field when they are used in

the form

$$h + D_0 \sin \pi h = (1 - t^2), \quad (3)$$

where  $h = H_c(T)/H_0$ ,  $H_0$  is the critical field at  $T = 0^\circ\text{K}$ , and  $D_0$  decreases with increasing interaction strength. When  $H_0$  is unknown, (3) is no longer useful; since  $D_0$  is always small, an alternative expression is nearly as good:

$$h = (1 - t^2) - D_0 \sin(\pi t^2). \quad (4)$$

Figure 2 compares the weak-coupling BCS limit of the critical field as computed by Swihart<sup>7</sup> with (4); clearly, (4) represents the BCS critical field  $h$  to well within

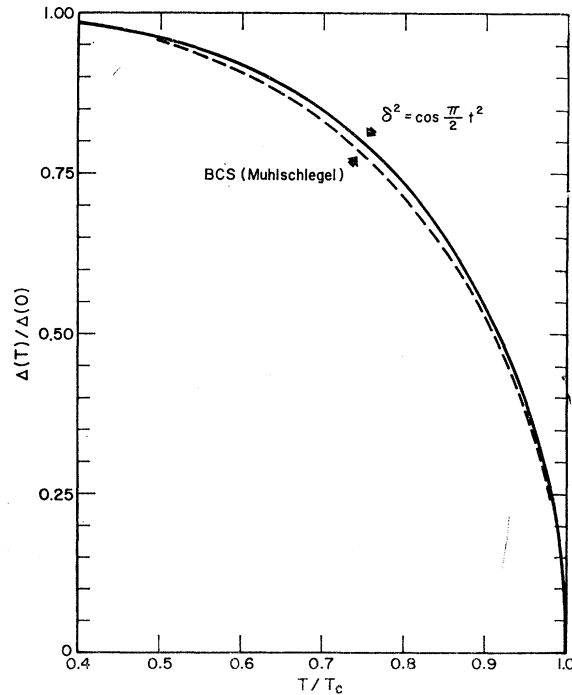


FIG. 1. The temperature dependence of the reduced energy gap of a superconductor. Dashed curve: solution of the weak-coupling BCS model as given by Muhlschlegel. Solid curve: Eq. (1), which represents experimental data more accurately.

<sup>7</sup> J. C. Swihart, IBM J. Res. Develop. 6, 14 (1962).

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<sup>1</sup> J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

<sup>2</sup> B. Muhlschlegel, Z. Physik 155, 313 (1959).

<sup>3</sup> D. J. Thouless, Phys. Rev. 117, 1256 (1960).

<sup>4</sup> I. Giaever and K. Megerle, Phys. Rev. 122, 1101 (1961).

<sup>5</sup> P. Townsend and J. Sutton, Phys. Rev. 128, 591 (1962); also M. A. Biondi, M. P. Garfunkel, and W. A. Thompson, Phys. Rev. 136, A1471 (1964).

<sup>6</sup> R. F. Gaspovic, B. N. Taylor, and R. E. Eck, Solid State Commun. 4, 59 (1966).

0.0015 over the entire range, and to within 0.0010 above  $t=0.3$  ( $t^2 > 0.1$ ). Using (3), the critical fields of cadmium, zinc, aluminum, gallium, vanadium, tantalum, tin, and thallium can be stated with accuracy of 0.001  $H_0$  using the values of  $H_0$ ,  $D_0$ , and  $T_c$  listed in Table I. A typical case is shown in Fig. 3, which compares the simple expression,  $-0.0354 \sin \pi h$ , with Phillips<sup>8</sup> experimental deviation curve for gallium (obtained by twice integrating specific-heat data). The agreement is as good as the data themselves. Also shown is a much worse case: the magnetic data of Finnemore and Mapother<sup>9</sup> for indium, together with the function  $-0.0205 \sin \pi t^2$ . This function fits within 0.002 everywhere, and within 0.001 above  $t=0.5$  ( $t^2 > 0.25$ ). Lead and niobium fit (4) within 0.003, but mercury does not fit at all.

Determining  $H_0$  requires extrapolating over some temperature range, and extrapolations from above  $t \approx 0.3$  ( $t^2 \approx 0.1$ ) have not been very reliable. It is interesting to note that by using (3) and (4), it is possible to estimate  $H_0$  from data which extend to just below  $t \approx 0.7$  (which is all that is needed to fix the value of  $D_0$ ). To illustrate this point, several sets of data were least-squares fitted to (4) with  $H_0$  and  $D_0$  as fitting parameters:

(a) The data of Maxwell and Lutes<sup>10</sup> on thallium were fitted with  $H_0=175.0$  G and  $D_0=0.030$ . They estimated  $H_0=172.8$  G on the basis of assuming a pure

TABLE I. Critical-field parameters for superconductors.

Element	$H_0$	$D_0$	$T_c^a$
cadmium	29.6 <sup>b</sup>	0.046 <sup>b</sup>	0.52
zinc	53.4 <sup>c</sup>	0.042 <sup>c</sup>	0.85
gallium	59.2 <sup>b</sup>	0.035 <sup>b</sup>	1.083 <sup>d</sup>
aluminum	103.0 <sup>e</sup>	0.040 <sup>e</sup>	1.17
thallium	175 <sup>f</sup>	0.030	2.38 <sup>e</sup>
indium	282.7 <sup>h</sup>	0.021 <sup>h</sup>	3.407 <sup>h</sup>
tin	305.5 <sup>h</sup>	0.026 <sup>h</sup>	3.722 <sup>h</sup>
mercury <sup>i</sup>	411 <sup>h</sup>	-0.017 <sup>h</sup>	4.154 <sup>h</sup>
tantalum	780 <sup>j</sup>	0.032	4.482
vanadium	1310 <sup>k</sup>	0.030	5.03
lead	802.5 <sup>l</sup>	-0.023	7.193
niobium	1994 <sup>m</sup>	0.011 <sup>m</sup>	9.20
ruthenium	70.0 <sup>n</sup>	0.04 <sup>n</sup>	0.509 <sup>n</sup>
molybdenum	86 <sup>o</sup>	0.0 <sup>o</sup>	0.916 <sup>o</sup>

<sup>a</sup> 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).

<sup>b</sup> See Ref. 8.  
<sup>c</sup> G. Seidel and P. H. Keesom, *Phys. Rev.* **112**, 1083 (1958).  
<sup>d</sup> W. D. Gregory, T. P. Sheahan, and J. F. Cochran (to be published).  
<sup>e</sup> N. E. Phillips, *Phys. Rev.* **114**, 676 (1959).  
<sup>f</sup> Computed from the data of E. Maxwell and O. S. Lutes, *Phys. Rev.* **95**, 333 (1954).

<sup>g</sup> B. J. C. van der Hoeven, Jr. and P. H. Keesom, *Phys. Rev.* **135**, A631 (1964).

<sup>h</sup> See Ref. 9.  
<sup>i</sup> Neither (3) nor (4) fits the mercury data.

<sup>j</sup> D. White, C. Chou, and H. L. Johnston, *Phys. Rev.* **109**, 797 (1959).

<sup>k</sup> W. S. Corak, B. B. Goodman, C. B. Satterthwaite, and A. Wexler, *Phys. Rev.* **102**, 656 (1956).

<sup>l</sup> D. L. Decker, D. E. Mapother, and R. W. Shaw, *Phys. Rev.* **112**, 1888 (1958).

<sup>m</sup> H. A. Leupold and H. A. Boorse, *Phys. Rev.* **134**, A1322 (1964).

<sup>n</sup> J. W. Gibson and R. A. Hein, *Phys. Rev.* **141**, 407 (1966).

<sup>o</sup> I. G. D'yakov and A. D. Snvets, *Zh. Eksperim. i Teor. Fiz.* **49**, 1091 (1965) [English transl.: *Soviet Phys.—JETP* **22**, 759 (1966)].

<sup>8</sup> N. E. Phillips, *Phys. Rev.* **134**, A385 (1964).

<sup>9</sup> D. K. Finnemore and D. E. Mapother, *Phys. Rev.* **140**, A507 (1965).

<sup>10</sup> E. Maxwell and O. S. Lutes, *Phys. Rev.* **95**, 333 (1954).

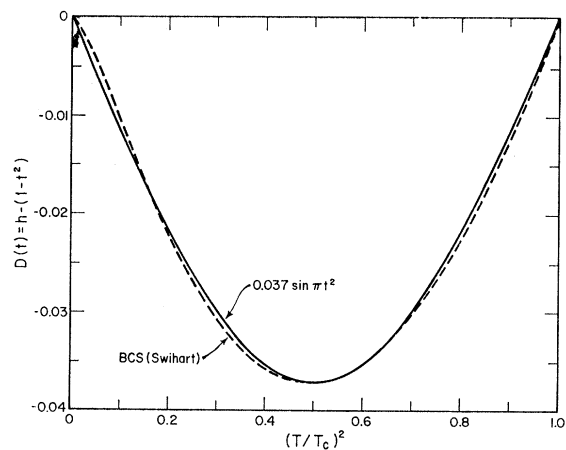


FIG. 2. Comparison of the BCS critical-field curve with a simple sinusoidal form, Eq. (4). Solid curve =  $-0.037 \sin \pi t^2$ ; dashed curve = BCS weak-coupling solution as calculated by Swihart (Ref. 7).

parabola in the low-temperature range, extrapolating from near  $t \approx 0.53$ .

(b) Data for polycrystalline niobium (not listed in Table I) given by White *et al.*<sup>11</sup> were fitted with  $H_0=1947$  G and  $D_0=0.023$ . The best experimental value is  $H_0=1960 \pm 40$  G.

(c) The data of Finnemore and Mapother<sup>9</sup> for indium have been treated as follows: Of their 91 data points, only the 17 points lying above  $t^2=0.5$  were fitted by least-squares to (4), with  $H_0$  now determined as a fitting parameter. The resulting coefficients showed  $D_0=0.02087$  and  $H_0=282.81$  G; their measured value was  $H_0=282.66$  G. (It would be foolhardy to anticipate this sort of agreement for very many superconductors.)

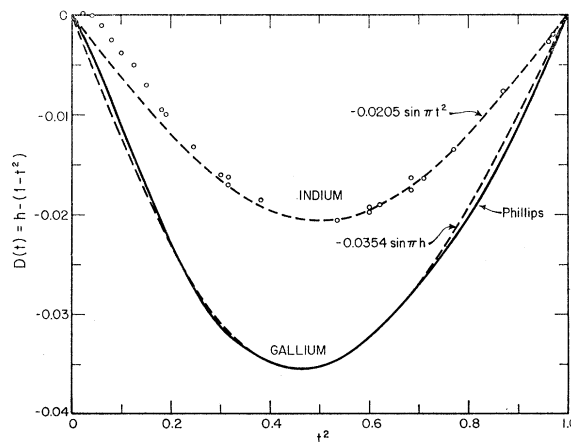


FIG. 3. Comparison of experimental critical fields with the fitting functions (3) and (4). Open circles: data of Finnemore and Mapother (Ref. 9) on indium; upper dashed curve: the function  $-0.0205 \sin \pi t^2$  [data fit Eq. (4) with  $D_0=0.0205$ ]. Solid curve: Critical-field curve for gallium obtained by Phillips (Ref. 8) by doubly integrating specific-heat data; lower dashed curve: the function  $-0.0354 \sin \pi h$  [data fit Eq. (3) with  $D_0=0.0354$ ].

<sup>11</sup> D. White, C. Chou, and H. L. Johnston, *Phys. Rev.* **109**, 797 (1958).

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)

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

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

<sup>12</sup> T. P. Sheahen, following paper, Phys. Rev. 149, 370 (1966).

## Effective Interaction Strength in Superconductors\*

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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  $\Delta C$  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  $T_c/\Theta_D$ ) 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  $(dh/dt)_1$ ,  $\Delta_0/kT_c$ , and  $\gamma T_c^2/V_m H_0^2$  which agree well with experiment. The resulting values for the "effective cutoff"  $\Theta_c$  lie close to  $\Theta_D/9$ .

### I. INTRODUCTION

SINCE the appearance of the BCS<sup>1</sup> 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<sup>2</sup> 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<sup>3</sup>  $\Delta C/\gamma T_c$ ,  $\Delta_0/kT_c$ ,  $(dh/dt)_1$ , and  $\gamma T_c^2/V_m H_0^2$  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  $\Delta_0/kT_c$  and the free energy [and therefore  $(dh/dt)_1$  and  $\gamma T_c^2/V_m H_0^2$ ] which agree well with experiment. Each  $N_0V^*$  value is also used to find an "effective cutoff temperature"  $\Theta_c$ ; 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-

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<sup>1</sup> J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

<sup>2</sup> G. J. Culler, B. D. Fried, R. W. Huff, and J. R. Schrieffer, Phys. Rev. Letters 8, 399 (1962).

<sup>3</sup>  $T_c$ =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  $\gamma = \frac{2}{3}\pi^2 N_0 k^2$ ;  $H_0$ =critical field at 0°K;  $V_m$ =molar volume;  $\Delta C$ =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  $\Delta_0$  as the "energy gap."