increases by about 5% for each percent Zr. It is argued that such mass increases may indicate crossing of a small and a large mass band as Zr is added. The model used predicts superconductivity at very low carrier concentrations in 3% Zr-doped specimens.

ACKNOWLEDGMENTS

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Grüneisen Functions for Some Type-I Superconductors

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The thermal expansion of some type-I superconductors (indium, lead, tantalum, and tin) is discussed thermodynamically in terms of Grüneisen functions, which describe the volume dependence of the entropy. The Grüneisen functions for the normal and superconducting states can be taken to differ only in their electronic components, γ^{en} and γ^{es}. Values of γ^{en} obtained from thermal-expansion measurements in the normal state are shown to be more reliable than values obtained from critical-field measurements on superconductors, because the magnetic data are not accurate enough in the limiting low-temperature region determining γ^{en}. The values of γ^{es} for the four metals all appear to be negative, unlike γ^{en}. Theoretical values of γ^{es} calculated using the BCS theory for weak coupling and the similarity principle are consistent with experiment for all the metals except lead. The disagreement for lead is probably due to its particularly strong electron-phonon coupling. According to the theory, the values of γ^{es} depend through $d\ln T_c/d\ln V$ on the volume dependence of the electron-phonon interaction, as well as on properties of the normal state. The experimental evidence for significant changes in lattice properties is discussed; such a change appears to be established for indium but not for lead.

1. INTRODUCTION

SINCE superconductivity occurs only at very low temperatures, the thermal expansion of superconductors is very small. However, experimental techniques developed in the last ten years are sufficiently sensitive to measure such small thermal expansions, and data are now available down to about 2°K for a variety of metals in both the normal and superconducting states. In this paper, we analyze and discuss measurements for some type-I superconductors.

As is usual, we discuss thermal expansion in terms of the thermodynamic *Grüneisen functions* (defined in Sec. 2). These are dimensionless parameters of the order of unity, which are often slowly varying functions of temperature, unlike the thermal expansion itself. A further advantage is that they are related to the strain dependence of the entropy, which is simpler to discuss theoretically than the thermal expansion. The strain dependence of the entropy is in turn a quantity fundamental to the discussion of the strain (and stress) dependence of thermal properties.

Since the normal-to-superconducting transition is fundamentally an electronic effect, we shall be concerned principally with Grüneisen functions for the electronic contribution to the entropy in each state. For the normal state, the electronic Grüneisen function has been measured by two methods, magnetic and thermal expansion, but these have often given conflicting results. The origin of such discrepancies is discussed in Sec. 3. Numerical values of Grüneisen functions for the superconducting state of indium, lead, tantalum and tin are presented in Sec. 4, and the theoretical interpretation of these results is considered in Sec. 5.

2. GRÜNEISEN FUNCTIONS AND THERMAL EXPANSION

Definition of Grüneisen Functions

The volume coefficient of thermal expansion β can be expressed, using thermodynamic formulas, as[1]

$$\beta=\gamma C_\eta \chi_T/V. \qquad (1)$$

Here C_η is the heat capacity at constant strain, χ_T is the isothermal compressibility, and γ is the Grüneisen function defined by

$$\gamma=(1/C_\eta)(\partial S/\partial \ln V)_T. \qquad (2)$$

Equation (2) is valid for noncubic as well as cubic solids, provided that the change of volume takes place under isotropic stress.[1] In superconductors and other systems where magnetic effects are important, the quantities in Eqs. (1) and (2) depend on the magnetic conditions

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[1] T. H. K. Barron and R. W. Munn, Phil. Mag. 15, 101 (1967).

under which they are evaluated. Here, we shall always use quantities evaluated at constant magnetic field and so do not need to indicate this explicitly.

Superconductivity occurs only at low temperatures where the difference between heat capacities or compressibilities under different restraints is negligible. We therefore use C or χ without subscripts to denote the common values of the heat capacities or compressibilities. Similarly, we use V or χ to denote the volume or compressibility of both the normal and the superconducting states (the *differences* between these quantities in the two states may of course be significant in other contexts). We use superscripts n and s to denote normal and superconducting state properties.

Separate Contributions to γ

We make the common approximation that the entropy of the metals considered here is the sum of separable lattice and electronic contributions. We denote such separate lattice and electronic quantities by superscripts l and e, so that $S=S^e+S^l$. It then follows by differentiation that the heat capacity can be written as $C=C^e+C^l$, and that the volume derivative of the entropy also consists of two contributions. We can then define separate Grüneisen functions from Eq. (2) by

$$\gamma^e=\frac{1}{C^e}\left(\frac{\partial S^e}{\partial \ln V}\right)_T;\quad \gamma^l=\frac{1}{C^l}\left(\frac{\partial S^l}{\partial \ln V}\right)_T. \tag{3}$$

The total Grüneisen function is not the sum of these two components, but a weighted average:

$$\gamma=(\gamma^eC^e+\gamma^lC^l)/(C^e+C^l). \tag{4}$$

From Eq. (1), β is given by

$$\beta=(\chi/V)(\gamma^eC^e+\gamma^lC^l). \tag{5}$$

In general, χ also contains lattice and electronic contributions, but at low temperature these are negligible compared with the contribution arising from the static lattice energy. It is then convenient to define separate contributions to β such that $\beta=\beta^e+\beta^l$, where

$$\beta^e=\gamma^eC^e\chi/V;\quad \beta^l=\gamma^lC^l\chi/V. \tag{6}$$

We also assume that the lattice contributions are the same in both states and do not need to be distinguished by superscripts n or s. This assumption cannot be strictly valid because of the coupling between nuclear and electronic motion, but it is usually found experimentally that the lattice contributions to the heat capacity and thermal expansion do not change measurably on transition (one or two apparent exceptions are discussed in Appendix A). Furthermore, the changes in elastic constants on transition have been measured for some metals and found to be only a few parts per million.[2]

On these assumptions the only change in γ on transition arises from the change in the electronic component. For the normal state the electronic heat capacity and entropy are given by

$$C^{en}=S^{en}=\Gamma T, \tag{7}$$

so that from Eq. (3)

$$\gamma^{en}=d\ln\Gamma/d\ln V. \tag{8}$$

The calculation of γ^{en} from experimental data is considered in detail in Sec. 3.

The superconducting-state electronic Grüneisen function γ^{es} is given by $\beta^{es}V/\chi C^{es}$, from Eq. (6). Another expression for γ^{es} can be obtained by manipulating the two forms of Eq. (4) for the normal and superconducting states:

$$\gamma^{es}=(1/C^{es})[C^{en}\gamma^{en}-(C^n\gamma^n-C^s\gamma^s)]. \tag{9}$$

Substituting from Eq. (1), we obtain the equation

$$\gamma^{es}=C^{en}\gamma^{en}/C^{es}-(V/\chi C^{es})(\beta^n-\beta^s), \tag{10}$$

which proves to be convenient for calculating γ^{es} as $\beta^n-\beta^s$ is directly measurable.

There is a more accurate method of obtaining γ^{es}, applicable only at the critical temperature. At these low temperatures, heat capacities can be measured more accurately than thermal expansions, and at T_c, $\beta^n-\beta^s$ can be replaced in Eq. (10) using the Ehrenfest relationship[3]

$$\beta^n-\beta^s=\frac{1}{V}(C^n-C^s)(d\ln T_c/dp) \tag{11}$$

to give

$$\gamma^{es}(T_c)=C^{en}\gamma^{en}/C^{es}+[(C^n-C^s)/C^{es}]\times(d\ln T_c/d\ln V). \tag{12}$$

We shall see later that γ^{es} is often negative. Now in Eq. (12) the heat capacities must be positive, with $C^n<C^s$ at T_c, and γ^{en} has usually been found to be positive.[4] The negative values of $\gamma^{es}(T_c)$, therefore, arise from sufficiently large positive values of $d\ln T_c/d\ln V$.

Andres[5] has obtained a general thermodynamic expression for γ^{es} in terms of temperature and strain derivatives of the reduced critical field function H_c/H_0, where H_c is the critical magnetic field required to suppress superconductivity at a given temperature and H_0 its value at 0°K.

3. EXPERIMENTAL VALUES OF γ^{en}

Experimental Methods

Two principal methods have been used to determine γ^{en}. One is a thermal expansion method which involves

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[2] G. A. Alers and D. L. Waldorf, Phys. Rev. Letters **6**, 677 (1961).

[3] D. Schoenberg, *Superconductivity* (Cambridge University Press, London, 1960), p. 74; A. B. Pippard, *Classical Thermodynamics* (Cambridge University Press, London, 1966), p. 135.

[4] The exceptions are certain transition and rare-earth metals, e.g., lanthanum [K. Andres, Phys. Rev. **168**, 708 (1968)].

[5] K. Andres, Phys. Kondensierten Materie **2**, 294 (1964).

obtaining the limiting slope as $T^2 \rightarrow 0$ of the fractional volume change for the normal state as a function of T^2.[6] The other is a magnetic method applicable only to superconductors, which involves obtaining the limiting slope of $(\partial H_c^2/\partial p)_T$ as a function of T^2.[7] There is also another method,[8] which we shall not discuss as it uses normal-to-superconducting volume changes to obtain $(\partial H_c^2/\partial p)_T$ and thence γ^{en}.

The values of γ^{en} obtained by the magnetic method have often been considerably larger than those obtained for the same metals by the thermal-expansion method. For example, in Table I the results obtained by the two methods are compared for three of the metals discussed below. In this section we show that the magnetic method is likely to be less reliable than the thermal expansion method.

Thermal-Expansion Measurement of γ^{en}

Experimental volume changes are obtained from measurements of length changes in the principal crystallographic directions. For normal metals at the lowest temperatures the thermal expansion is of the form[6]

$$\beta^n \approx aT + bT^3(+cT^5+\cdots) \tag{13}$$

and, therefore,

$$(V-V_0)/V_0 \approx \tfrac{1}{2}aT^2 + \tfrac{1}{4}bT^4(+\tfrac{1}{6}cT^6+\cdots), \tag{14}$$

where V and V_0 are the volumes at T and 0°K. The linear term in Eq. (13) is identified with β^{en}, and γ^{en} is calculated from Eq. (6):

$$\gamma^{en} = \beta^{en}V/\chi C^{en} = aV/\chi\Gamma. \tag{15}$$

Probably the most reliable method of obtaining the coefficient a is[6] to extrapolate $V(T)$ to zero and then to plot values of $(V-V_0)/T^2$ against T^2, when the intercept is $\tfrac{1}{2}aV_0$.

The accuracy of this method depends on knowing the importance of the higher terms in β^n, bracketed in Eq. (13), at the lowest temperatures of measurement. These terms cause the plot of $(V-V_0)/T^2$ against T^2 to be curved rather than linear, and so complicate the extrapolation to 0°K on which the value of a depends. Sufficiently accurate low-temperature thermal expansion data can themselves define the curvature quite closely, while less accurate data can be extrapolated linearly, given some external indication of the temperature below which the curvature is negligible. For most solids, terms in T^5 and higher are negligible at temperatures of 1 or 2% of the heat capacity Debye temperature; but for any particular solid, the importance of these terms can be estimated from that of the corresponding terms in the low-temperature series expansion for the heat capacity, which is generally known accurately. Usually, measurements of thermal expansion below 4°K determine γ^{en} with an uncertainty of the order of 10%. The uncertainty may be somewhat larger if the electronic term is particularly small compared with the lattice terms, as in indium.

TABLE I. Comparison of magnetic and thermal values of γ^{en} for three metals.

Metal	Magnetic γ^{en}	Thermal γ^{en}
Lead	$6\ \pm 1$[a]	1.7 ± 0.5[b] 0.7 ± 1.5[c]
Tantalum	3.9 ± 0.7[d]	1.3 ± 0.1[e] 1.3 ± 0.2[c]
Tin	1.2 ± 0.4[f]	1.0 ± 0.2[g]

[a] See Ref. 25.
[b] See Ref. 14.
[c] See Ref. 15.
[d] See Ref. 7.
[e] See Ref. 16.
[f] See Ref. 18.
[g] See Ref. 17.

Magnetic Measurement of γ^{en}

The determination of γ^{en} from $(\partial H_c^2/\partial p)_T$ as a function of T^2 is analogous to the determination of Γ from H_c^2 as a function of T^2. Since magnetic methods of measuring Γ have been thoroughly discussed, we shall merely summarize the essentials of the most reliable method to provide a basis for our discussion of the measurement of γ^{en}.

Hinrichs and Swenson[7] introduced the quantity

$$Q = [1 - H_c^2/H_0^2]/t^2,$$

where H_0 is the critical field at 0°K and t is the reduced temperature T/T_c (T_c is the critical temperature above which superconductivity cannot exist at zero pressure). At sufficiently low temperatures Q flattens off to the value $(4\pi T_c^2/H_0^2V)\Gamma$. For a solid obeying the simple weak-coupling BCS theory[9] this limiting behavior is approached only below $t^2=0.05$. At low temperatures, Q is very sensitive to uncertainties in the experimental data: at $t^2=0.05$ an uncertainty of 0.05% in H_0 gives an uncertainty of 1% in Q. By comparing the dependence of Q on t^2 for various metals with that predicted by the BCS theory, values of Γ in good agreement with calorimetric measurements were obtained.[7,10] The method was further exploited by Finnemore and Mapother.[11] Both sets of authors emphasized that although the temperature dependence of H_c can be used to determine Γ, the temperature dependence of H_c^2 is preferable for this purpose because it approaches its limiting behavior at higher temperatures.

Now the quantity

$$R = [1 - (\partial H_c^2/\partial p)_T/(dH_0^2/dp)]/t^2$$

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[6] J. G. Collins and G. K. White, *Progress in Low Temperature Physics, IV* (North-Holland Publishing Co., Amsterdam, 1964), p. 450.

[7] C. H. Hinrichs and C. A. Swenson, Phys. Rev. **123**, 1106 (1961).

[8] J. L. Olsen and H. Rohrer, Helv. Phys. Acta **33**, 872 (1960).

[9] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[10] J. E. Schirber and C. A. Swenson, Phys. Rev. **123**, 1115 (1961).

[11] D. K. Finnemore and D. E. Mapother, Phys. Rev. **140**, A510 (1965).

could be used in obtaining γ^{en} just as Q has been used in obtaining Γ. At sufficiently low temperatures, R flattens off to the value $[4\pi\Gamma\chi/V(dH_0^2/dp)](\gamma^{en}-1)$. By analogy with Q we might expect R to approach its limiting behavior around $t^2=0.05$. This is confirmed on the BCS theory by calculations using the method to be described in Sec. 5; some details of the calculations are given in Appendix B. Like Q, R is very sensitive to uncertainties in the experimental data, especially at low temperatures. The important *difference* between Q and R is that H_c can be measured to within 0.1 Oe, or a few hundredths of a per cent, whereas because of uncertainties in the pressure $(\partial H_c^2/\partial p)_T$ can only be measured to within a few per cent—some hundred times less accurately. Consequently, while the uncertainty in Q at $t^2=0.05$ may be typically 1%, that in R may be 100%. This suggests at once that magnetic values of γ^{en} may be subject to large errors.

In practice, no two authors have used exactly the same method to obtain γ^{en}, and none has used R itself. Most methods actually used have involved fitting a graph or power series to the experimental values of $(\partial H_c^2/\partial p)_T$ as a function of t^2; graphical or analytical methods have then been used to obtain the limiting slope at $t^2=0$ from which γ^{en} can be calculated. It has been realized that the limiting slope is very sensitive to uncertainties in the lowest-temperature data, and the estimates have accordingly been more heavily weighted by the data at higher temperatures. We shall see that it is this plausible procedure which gives rise to the frequent overestimates of γ^{en} characteristic of the magnetic method.

The theoretical calculations mentioned above indicate that the slope of $(\partial H_c^2/\partial p)_T$ as a function of t^2 increases rapidly outside its region of limiting behavior (it may double between $t^2=0.05$ and $t^2=0.1$), owing to an exponential contribution like that in C^{es}. We expect the behavior of $(\partial H_c^2/\partial p)_T$ for real metals to be qualitatively the same as this, just as the behavior of H_c^2 for real metals is qualitatively the same as predicted by the BCS theory. Any estimate of the limiting slope biased by the higher-temperature data will therefore be too large, leading to an overestimate of γ^{en}. The low-temperature behavior of $(\partial H_c^2/\partial p)_T$ is illustrated in Fig. 1; typical accuracy is insufficient to detect the changing curvature and hence to obtain the limiting slope which determines γ^{en}.

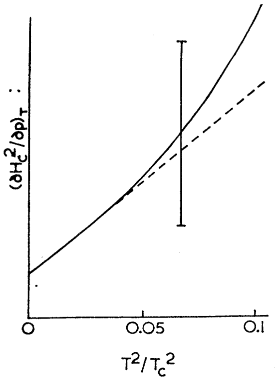

FIG. 1. Schematic behavior of $(\partial H_c^2/\partial p)_T$ at low temperatures. The broken line is the limiting tangent at 0°K, and the error bar corresponds to an uncertainty of ±1%. Note that $(\partial H_c^2/\partial p)_T$ is negative.

We noted above that the magnetic method can give values of Γ (at zero pressure) in agreement with calorimetric measurements. If, in the same way, values of Γ are derived for a range of pressures, γ^{en} can be determined directly from the pressure derivative of Γ. Since the extrapolations to 0°K are then performed *before* introducing the uncertainties of the pressure derivatives, there is no longer a systematic tendency to produce overestimates. However, uncertainties of the order of 100% remain, because the change in Γ between 0 and 10 kbar may be only as large as its experimental uncertainty, while at higher pressures Γ may no longer be linearly dependent on pressure. A recent example of this version of the magnetic method[12] gave $\gamma^{en}=1.5\pm0.3$ for indium and 2.0 ± 0.3 for tin (cf. Table I) using temperatures down to 0.1°K and pressures up to 30 kbar. This is in principle the best version of the magnetic method, but it is still much less reliable than the thermal-expansion method.

Selection of Experimental Values

In this subsection, we select thermal expansion values of γ^{en} for the four metals to be discussed in Secs. 4 and 5: indium, lead, tantalum, and tin.

Indium. Recent thermal expansion measurements[13] give $\gamma^{en}=2.9\pm0.8$.

Lead. The thermal expansion values of White[14] and of Andres[15] agree within experimental error (see Table I). We adopt White's value as it is estimated to have the smaller uncertainty.

Tantalum. The thermal expansion values of White[16] and of Andres[15] coincide (see Table I), and we adopt this common value.

Tin. We adopt the single thermal expansion value,[17] which agrees within experimental error with the magnetic value[18] (see Table I).

4. EXPERIMENTAL VALUES OF γ^{es}

Choice of Metals

We present values of γ^{es} for the type-I superconductors indium, lead, tantalum, and tin. These metals have sufficiently high critical temperatures for their thermal expansion to be measured in the superconducting state, and for each of them thermal expansion values of γ^{en} are available.

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[12] I. V. Berman, N. B. Brandt, and N. I. Ginzburg, Zh. Eksperim. i Teor. Fiz. **53**, 124 (1967) [English transl.: Soviet Phys.—JETP **26**, 86 (1968)].

[13] J. G. Collins, J. A. Cowan, and G. K. White, Cryogenics **7**, 219 (1967).

[14] G. K. White, Phil. Mag. **7**, 271 (1962).

[15] K. Andres, Cryogenics **2**, 93 (1961).

[16] G. K. White, Cryogenics **2**, 292 (1962).

[17] G. K. White, Phys. Letters **8**, 294 (1964).

[18] J. E. Schirber and C. A. Swenson, Phys. Rev. **127**, 72 (1962).

Indium

We take values of the thermal expansion in both states from Collins *et al.*[13]; heat capacity from O'Neal and Phillips[19]; and compressibility from Chandrasekhar and Rayne.[20] The resulting values of γ^{es} are shown in Fig. 2; they are all negative.

Lead

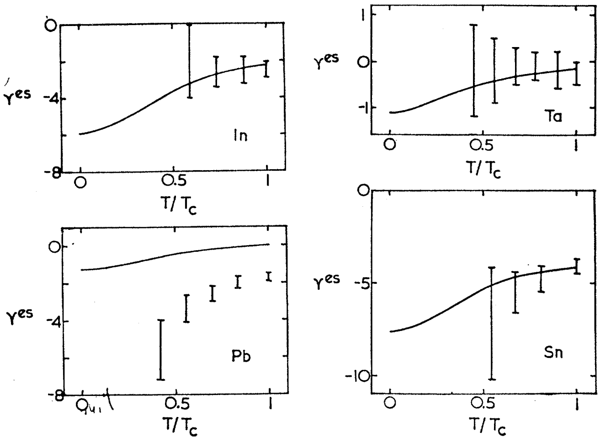
Heat capacities are taken from Keesom and van der Hoeven,[21] and the compressibility from Alers and Waldorf.[22] The experimental values of $\beta^n-\beta^s$ due to White[14] and to Andres[15] do not agree well, and those of White show considerable irregularity. Further values of $\beta^n-\beta^s$ have therefore been calculated from the thermodynamic equation[23]

$$\beta^n-\beta^s=\frac{1}{8\pi}\left[\frac{\partial^2 H_c^2}{\partial T\partial p}-\chi\frac{\partial H_c^2}{\partial T}\right], \tag{16}$$

using experimental critical-field data.[24,25] The three sets of values of $\beta^n-\beta^s$ are shown in Table II. Except at low temperatures the values calculated from Eq. (16) lie between the values measured directly, and we therefore adopt this set of values as most probable. The values at low temperatures could still be subject to quite large errors for the reasons outlined in discussing the magnetic determination of γ^{en}, but these errors should be less than in γ^{en}, which is related to the limiting *slope* of $\beta^n-\beta^s$ at $T=0$. The resulting values of γ^{es} are shown in Fig. 2. They are all negative, decreasing as the temperature falls, and at the lowest temperatures are of large but uncertain magnitude.

Tantalum

Experimental values of $\beta^n-\beta^s$ are calculated from values of $(\partial H_c/\partial p)_T$ quoted by White[16] as obtained from his thermal-expansion measurements. Heat capacity data are taken from Hultgren *et al.*[26] and compressibility from Featherston and Neighbours.[27] The resulting values of γ^{es} are shown in Fig. 2. Although they all appear to be negative and practically constant, the large uncertainties could allow positive or changing values, except that at T_c, γ^{es} obtained using Eq. (12) is certainly negative.



(a) (b)

FIG. 2. Experimental and theoretical values of γ^{es} for indium, lead, tantalum, and tin. The error bars give the uncertainties on the experimental points, while the curves give the theoretical values with uncertainties less than the smallest error bars. There is an additional point for lead at $T/T_c=0.28$, not shown for lack of space: $\gamma^{es}=-16\pm7$. Note the different scale for tantalum.

Tin

We obtain $\beta^n-\beta^s$ from White's results,[17] as for tantalum; heat capacities from O'Neal and Phillips[19] and Bryant and Keesom[28]; and the compressibility from Rayne and Chandrasekhar.[29] The resulting values of γ^{es} are shown in Fig. 2; they are all negative and appear to decrease as the temperature falls. The negative γ^{es} values give rise to values of the total Grüneisen function γ^s that are so much smaller than γ^n as to be negative themselves.

5. THEORETICAL VALUES OF γ^{es}

Description of Theory

Our calculation of theoretical values of γ^{es} is based on some results of the simple weak-coupling form of

TABLE II. Comparison of experimental values of $\beta^n-\beta^s$ for lead, in units of 10^{-8} °K^{-1}. We take $T_c=7.18$°K.

T(°K)	Calculated from Eq. (16)	Source White[a]	Andres[b]
2	3.6±0.3	2.0±0.5	1±0.5
3	5.9±0.5	5 ±1	2±1.5
4	8.3±0.8	9 ±3	6±2
5	11.0±1	6 ±3	15±3
6	14.1±1	12 ±3	...
T_c	17.9±1	6 ±3	...

[a] See Ref. 14.
[b] See Ref. 15.

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[19] H. R. O'Neal and N. E. Phillips, Phys. Rev. 137, A748 (1965).

[20] B. S. Chandrasekhar and J. A. Rayne, Phys. Rev. 124, 1011 (1961).

[21] P. H. Keesom and B. J. C. van der Hoeven, Phys. Letters 3, 360 (1963); Phys. Rev. 137, A103 (1965).

[22] G. A. Alers and D. L. Waldorf, J. Appl. Phys. 33, 2283 (1962); see, also, Ref. 2.

[23] See Ref. 3. The second term in Eq. (16) arises from the temperature-dependent magnetostriction in the superconducting state, and corrects β^s to its zero-field value.

[24] D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. 112, 1888 (1958).

[25] M. Garfinkel and D. E. Mapother, Phys. Rev. 122, 459 (1961).

[26] R. Hultgren, R. L. Orr, P. D. Anderson, and K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys* (John Wiley & Sons, Inc., New York, 1963).

[27] F. H. Featherston and J. R. Neighbours, Phys. Rev. 130, 1324 (1963).

[28] C. A. Bryant and P. H. Keesom, Phys. Rev. Letters 4, 460 (1960); Phys. Rev. 123, 491 (1961).

[29] J. A. Rayne and B. S. Chandrasekhar, Phys. Rev. 120, 1658 (1960).

the BCS theory[9] which incorporate the assumption that lattice properties do not change on transition. These results can be expressed in the form

$$H_c^2=(8\pi\Gamma T_c^2/V)h(t)\,, \tag{17}$$

$$S^{es}=\Gamma T_c f(t)\,, \tag{18}$$

$$C^{es}=\Gamma T_c g(t)\,, \tag{19}$$

where f, g, and h are universal functions of the reduced temperature $t=T/T_c$. Because of thermodynamic relationships among the left-hand sides of these equations, f, g, and h are related through

$$f=h'+(T/T_c)\,, \tag{20}$$

$$g=(T/T_c)f'=(T/T_c)(h''+1)\,, \tag{21}$$

where the prime denotes differentiation with respect to t. Certain special values of the functions are also fixed by thermodynamic requirements:

$$h(1)=0\,,\quad h'(1)=0\,,\quad f(1)=1\,,$$
$$h'(0)=0\,,\quad f(0)=0\,,\quad g(0)=0\,.$$

If we assume that the BCS theory is applicable for arbitrary strain, the quantities $h(t)$, $f(t)$, and $g(t)$ depend on strain only through the strain dependence of T_c. We can then derive an expression [Eq. (22)] for γ^{es} in terms of the functions f and g and the volume dependence of T_c. In Appendix B we also give the expression for $(\partial H_c^2/\partial p)_T$ which was used in the calculations referred to in Sec. 3. The expression for γ^{es} depends only on the validity of Eqs. (18) and (19) and not on the details of the BCS theory. Consequently, it could be applied to any appropriate theory, or even to experimental data if Eqs. (17)–(19) are taken as defining the functions in terms of the experimental quantities.

The assumption that the function $h(t)$ is independent of strain corresponds to assuming the validity of the similarity principle,[25,30] which has been used quite widely in discussing critical field measurements under pressure. The similarity principle is usually stated in terms of the reduced critical field function H_c/H_0, but the strain independence of this function follows from that of $h(t)$ by Eq. (17).

The expression for γ^{es}, obtained using the definition Eq. (3) and Eqs. (18) and (19), is

$$\gamma^{es}=(f/g)[\gamma^{en}+(1-g/f)(d\ln T_c/d\ln V)]\,. \tag{22}$$

This equation can also be obtained from the general expression for γ^{es} given by Andres.[5] At the critical temperature Eq. (22) reduces correctly to Eq. (12) with C^{es} expressed by Eq. (19). From Eq. (22) we see that, unlike γ^{en}, γ^{es} depends on temperature, through f/g. This is a consequence of the general rule that a constant γ is found only when the entropy is some function of reduced temperature alone.[31]

By writing γ^{es} in the form

$$\gamma^{es}=\frac{f}{g}\frac{d\ln\Gamma T_c}{d\ln V}-\frac{d\ln T_c}{d\ln V}\,, \tag{23}$$

we see that at $T=0$ (where f/g is zero) γ^{es} is negative whenever $d\ln T_c/d\ln V$ is positive. In fact $d\ln T_c/d\ln V$ is positive for almost all nontransition metals as well as for several transition metals,[32] and we saw above that if $d\ln T_c/d\ln V$ is sufficiently large γ^{es} is also negative at T_c. Since f/g is monotonically increasing, γ^{es} will then be negative throughout the superconducting region.

Numerical Results

For numerical calculations, we use the BCS functions as tabulated by Mühlschlegel[33] and quoted by Rickayzen.[34] The required experimental values of $d\ln T_c/d\ln V$ are taken from Jennings and Swenson[35] for indium, from Smith and Chu[36] for lead, from Hinrichs and Swenson[7] for tantalum, and from Schirber and Swenson[18] for tin. The calculated values of γ^{es} are shown in Fig. 2 with the experimental values.

Only for lead is there a large disagreement with the experimental values, but lead usually agrees less well with the simple BCS theory than the other metals. This is probably due to the stronger electron-phonon coupling in lead,[34] which renders the weak-coupling BCS theory inapplicable. It is then less likely that the entropy will have a simple volume dependence.

6. CONCLUSION

Values of γ^{en} obtained directly by the thermal-expansion method are more accurate than those obtained by the magnetic method. Unless improved techniques are developed for generating very closely isotropic pressures of accurately known magnitude at low temperatures, the magnetic method will remain unsatisfactory.

For the four metals studied here γ^{es} appears to be negative at all temperatures. The assumption that the functions f, g, and h are independent of strain leads to theoretical values of γ^{es} which are consistent with experiment for indium, tantalum, and tin, but not for lead. The disagreement for lead may arise because it is a strong-coupling superconductor (though f, g, and h may also be strain dependent in weak-coupling superconductors).

According to the BCS theory, the relative magnitudes of γ^{es} for different metals depend on their re-

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spective values of $d\ln T_c/d\ln V$, and at the critical temperature the same conclusion follows from thermodynamic arguments. The theory also predicts[9]

$$T_c \propto \Theta \exp(-1/NA), \tag{24}$$

where Θ is a Debye characteristic temperature,[37] N is the density of electronic states for one spin at the Fermi level, and A is an electron-phonon interaction parameter. Then

$$d\ln T_c/d\ln V = -\gamma^l + (1/NA)[\gamma^{en} + d\ln A/d\ln V], \tag{25}$$

where we have put $\gamma^l = -d\ln\Theta/d\ln V$, an approximation strictly valid only at 0°K. So ultimately γ^{es} depends on both γ^l and γ^{en} as well as on the volume dependence of the interaction. A discussion of the interaction and its volume dependence is beyond the scope of this paper, and the reader is referred to recent theoretical papers on the topic.[38]

Experimental or theoretical values of γ^{es} as a function of temperature can be used to calculate the volume dependence of quantities related to S^{es} such as C^{es}. The theoretical values can also be used to calculate values of $\beta^n - \beta^s$ for direct comparison with experiment. For noncubic metals the present work could be extended to calculations of the directional Grüneisen functions $\gamma_\lambda{}^{es}$, which describe the strain dependence of their properties more completely than γ^{es} alone, but the necessary experimental data are not yet available.

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APPENDIX A: CHANGE OF LATTICE PROPERTIES ON TRANSITION

For *indium*, Bryant and Keesom[28] found that C^{ln} was greater than C^{ls}, while measurements on *tin* in the same apparatus gave the usual result $C^{ln} = C^{ls}$. These findings were confirmed by O'Neal and Phillips,[19] who made a careful study of indium again using tin for comparison. They concluded that although calorimetric data alone could not entirely exclude the possibility that C^{ln} and C^{ls} were the same for indium, the elastic constant data tended to support the conclusion that they were significantly different. However, from careful critical field measurements Finnemore and Mapother[11] concluded that there was no evidence for a difference between the entropies S^{ln} and S^{ls}. They referred to a "disagreement" between their data and the calorimetric data, but in fact they showed that the difference was within the expected range of accuracy of the calorimetric measurements. Since the magnetic and calorimetric data were consistent with another, the different conclusions drawn from the two sets of data presumably arise from differences of analysis and interpretation (unless one set of measurements contains a consistent error).

The magnetic data were analyzed by calculating thermodynamically from $(\partial H_c{}^2/\partial T)_p$ values of $S^n - S^s$, which were shown graphically to have the linear behavior in T at low and intermediate temperatures expected for $S^{en} - S^{es}$ alone. However, in this graph (Fig. 9 of Ref. 11) the experimental values of $S^n - S^s$ seem to lie slightly above the linear extrapolation at about $T = 0.2T_c$, subsequently falling below the line. Such behavior is consistent with the presence of a small positive curvature in $S^n - S^s$ as found by the calorimetric method. For a strict comparison with the calorimetric data a rigorous analysis would have been necessary in which $(S^n - S^s)/T$ was plotted against T^2: the intercept would then have given Γ and the limiting slope the coefficient of T^3 in $S^{ln} - S^{ls}$. In the absence of such an analysis, the magnetic data cannot be regarded as disproving the calorimetric result $C^{ln} \neq C^{ls}$.

For *lead*, Keesom and van der Hoeven[21] found that C^{ln} and C^{ls} differed, C^{ln} now being the smaller. They also found that for a sufficiently concentrated lead-indium alloy the difference disappeared. However, Phillips *et al.*[39] found that any discrepancy between C^{ln} and C^{ls} was within experimental error and certainly smaller than for indium. Since the primary data agreed with those of Keesom and van der Hoevel within experimental uncertainties (apart from the presence of a contribution due to frozen-in normal-state material) the difference is presumably in the analysis. Elastic constant measurements in both states[2] show that the cubic terms in $C^n - C^s$ should differ by only 14 parts per million, supporting the findings of Phillips *et al.* White[14] found that the lattice contributions to the thermal expansion differed by 20% for lead, but here the analysis is even more uncertain than for the heat capacity.

There is, therefore, evidence that for indium our assumptions are not valid to the accuracy we require. However, the evidence applies only to very low tem-

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peratures where C^{es} and β^{es} are negligible, and provides no means of estimating these quantities at higher temperatures. Consequently, in order to obtain values of γ^{es} we are obliged to retain our assumptions, which have the virtues of generality and simplicity.

APPENDIX B: THEORETICAL CALCULATION OF $(\partial H_c^2/\partial p)_T$

We obtain the following expression for $(\partial H_c^2/\partial p)_T$ using the theory described in Sec. 5:

$$\left(\frac{\partial H_c^2}{\partial p}\right)_T=\frac{8\pi\Gamma T_c^2}{V}h\left[-\chi(\gamma^{en}-1)+\frac{d\ln T_c}{dp}\times\left(2-\frac{T}{T_c}\frac{h'}{h}\right)\right].\qquad\text{(B1)}$$

From Eq. (17), we see that $h\propto H_c^2$ and $h'\propto(\partial H_c^2/\partial T)_p$. It can be shown, using Eq. (B1), that when H_c^2 approaches its limiting behavior (i.e., Q is flattening off), $(\partial H_c^2/\partial p)_T$ also approaches its limiting behavior with R flattening off.

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Critical-Field Ratio H_{c3}/H_{c2} for Pure Superconductors Outside the Landau-Ginzburg Region. I. $T\simeq 0°\text{K}$*†

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In this paper and a subsequent one (Paper II) we study the nucleation of superconductivity near a sample surface at temperatures outside the Landau-Ginzburg region. We develop a generalized image method to solve for the normal electron temperature Green's function for a semi-infinite sample with a specularly reflective plane boundary in an external magnetic field. Gor'kov's linearized gap equation is then obtained and studied for such a sample geometry. The pair wave function Δ is found to obey the Landau-Ginzburg boundary condition at all $T<T_c$, even though this boundary condition was originally suggested only for the Landau-Ginzburg region (i.e., when $T_c-T\ll T_c$). However, we also find that merely adding the boundary condition to the differential equation appropriate to the bulk case does not give the correct solution to the problem, except when $T_c-T\ll T_c$. At $T=0°\text{K}$, the integral gap equation is solved by a variational approach, yielding the critical-field ratio $H_{c3}/H_{c2}\geq 1.925$. This should be compared with Saint-James and de Gennes's result, ~ 1.7, for T in the Landau-Ginzburg region. The small-T correction to the ratio near $T=0°\text{K}$ is found to be proportional to $T^2\ln T$ with a small coefficient. An upper bound is also found for the $T=0°\text{K}$ ratio to be 5.22, which is useful mainly in proving the existence of a ground state, so as to help justify the use of a variational approach.

I. INTRODUCTION

THE phenomenological Landau-Ginzburg (L-G) equation[1] is, because of its simplicity, a very powerful tool for studying the various phenomena of superconductivity.[2] It is well known,[2] however, that except for extremely dirty superconductors[3] this equation is applicable in only a limited temperature range near the critical temperature T_c, and for very pure superconductors this limitation becomes rather restrictive. In order to extend the description of superconducting phenomena beyond the "L-G region" (the temperature range in which the L-G equation is applicable), it is necessary to use the microscopic BCS[4] theory or Gor'kov's[5] generalization of it to space- and time-dependent cases. A recent example of such an extension is the elegant calculation by Helfand and Werthamer[6] of the bulk nucleation critical field H_{c2} for all impurity concentrations and all temperatures below T_c. The

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