On Temperature Dependence of Penetration Depth in Superconductors

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By use of the Gorter-Casimir thermodynamic theory of superconductivity, the form of the Sommerfeld relation for the specific heat of electrons, and the form of the acceleration theory expression for penetration depth, the relative number of superconduction electrons and the relative penetration depth are derived as functions of the temperature. When the parabola relationship for threshold magnetic fields is used, comparison with experiment shows good agreement. In the limit of the absolute zero temperature, it is concluded that all of the normal conduction electrons become superconduction electrons in the absence of applied magnetic fields. The parabola relationship for threshold magnetic fields is discussed.

1. INTRODUCTION

IN a paper entitled "Some remarks on supraconductivity and Fermi-Dirac statistics,"[1] Kok has shown how a combination of the Gorter-Casimir equations for the thermodynamics of superconductivity,[2] the Sommerfeld relation for the contribution of normal conduction eletrons to specific heat,[3] and a parabola relationship for magnetic thresholds, leads to an explanation of the specific heats of superconductors in the absence of magnetic fields and in the presence of greater than threshold magnetic fields. It is the purpose of this paper to extend Kok's work to determine theoretically the temperature dependence of the relative number of superconduction electrons and of the relative penetration depth.

2. CALORIMETRIC RELATIONS

In the Gorter-Casimir thermodynamic theory of superconductivity,[2] the difference in the atomic heat of a substance in the superconducting state, C_S, and of the same substance in the normal state, C_N, at a given temperature T°K, is related to the threshold magnetic field H, at that temperature, by

$$\Delta C = C_S - C_N = (JVT/8\pi)[d^2(H^2)/dT^2]. \quad (1)$$

V is the atomic volume at T°K and J is the factor (2.3889×10^{-8}) required to convert ergs to calories.

We shall assume that in the low temperature range of superconductivity, the atomic heat of the substance, when held in the normal state by a magnetic field greater than threshold value, has a T^3 term due to lattice vibrations plus a linear term $\gamma_N T$ due to electron contribution. Then,

$$C_N = D_N T^3 + \gamma_N T. \quad (2)$$

For the atomic heat C_S in the superconducting state, we shall further assume that the lattice contribution also follows a T^3 law and that the electron contribution to the atomic heat is due to those electrons which remain in the "normal" state when the material becomes superconducting. However, whereas γ_N in Eq. (2) was assumed constant, γ_S in the relation below will be a function of the temperature T, since it will be supposed that the number of normal electrons decreases with decreasing T. Thus we write

$$C_S = D_S T^3 + \gamma_S(T) T. \quad (3)$$

Substitution of (2) and (3) into (1) gives

$$(D_S - D_N)T^2 + (\gamma_S - \gamma_N) = (JV/8\pi)[d^2(H^2)/dT^2]. \quad (4)$$

At this point we introduce two relations. The parabola relationship for threshold magnetic fields, with H_0 denoting the value of H at 0°K, is

$$H = H_0(1 - T^2/T_c^2), \quad (5)$$

where T_c is the transition temperature when $H=0$. The second relation is that

$$\gamma_S(0) = 0. \quad (6)$$

From these and the earlier equations, it can be

[1] J. A. Kok, Physica **1**, 1103 (1933–34).
[2] C. J. Gorter and H. Casimir, Physica **1**, 306 (1934).
[3] A. Sommerfeld, Zeits. f. Physik **47**, 1 (1928).

shown that

$$\gamma_N=(JV/2\pi)(H_0^2/T_c^2), \tag{7}$$

$$(\Delta C)_{T_c}=2\gamma_N T_c, \tag{8}$$

and

$$C_S=[D_N+(3\gamma_N/T_c^2)]T^3. \tag{9}$$

Equations equivalent to (7), (8), and (9) were derived by Kok.[1]

The assumption of Eq. (6) is justifiable only if Eqs. (7), (8), and (9) agree with experiment. Thus, these equations have been derived on a semi-empirical basis. However, no assumption was made in this derivation concerning the relation between D_S and D_N. If we put $\gamma_S(T_c)=\gamma_N$ so that the discontinuity in atomic heat at the transition temperature is all ascribed to a lattice atomic heat change, the corresponding change in Debye characteristic temperature for tin would be about 20 percent. The modulus of rigidity for tin and mercury was measured by de Haas and Kinoshita,[4] and no change was observed on passing through the transition temperature. Unpublished results obtained in this laboratory by J. R. Clement on the velocity of sound in tantalum show no discontinuity in the velocity at the transition temperature. This suggests that $D_S=D_N$ and that all of the change in atomic heat is to be attributed to the electrons. Thus, with $D_S=D_N$, it follows that

$$\gamma_S=(3\gamma_N/T_c^2)T^2. \tag{10}$$

3. PENETRATION DEPTH

It will be assumed that those electrons which contribute to $\gamma_N T$ and to $\gamma_S T$ do so in accord with the Sommerfeld relation. Thus the variation of γ_S, with temperature, given by Eq. (10) will be attributed to a decrease in the number of normal conduction electrons with decrease in temperature, accompanied by a corresponding increase in the superconduction electrons. γ has been shown by Sommerfeld[3] to be proportional to the cube root of the number of electrons contributing to the specific heat. The constant of proportionality depends, among other things, on how "free" the electrons are. So we shall not use the relation literally, as Kok[1] did, but limit ourselves to the general form of the Sommerfeld relation. Thus, if k is the constant of proportionality,

$$\gamma=kn^{\frac{1}{3}}. \tag{11}$$

Therefore, if n_N is the number of normal electrons contributing to the atomic heat when the substance is in the normal state, n_S is the number of *normal* electrons remaining when the material becomes superconducting, and the constants of proportionality k_N and k_S are different, Eq. (10) becomes

$$(n_S/n_N)^{\frac{1}{3}}=(3k_N/k_S)t^2, \tag{12}$$

where $t=T/Tc$ is the "reduced" temperature.

Let σ represent that fraction of normal conduction electrons which have become superconduction electrons, that is, which no longer contribute to the atomic heat. Then

$$\sigma=(n_N-n_S)/n_N \tag{13}$$

or, using (12),

$$\sigma(t)=[1-(3k_N/k_S)^3t^6]. \tag{14}$$

When $t=0$, $\sigma(0)=1$. This is the consequence of Eq. (6) and thus the assumption of (6) implies that all of the normal conduction electrons become superconduction electrons at the absolute zero. If at $t=1$, the transition temperature, none of the normal conduction electrons have become superconduction electrons, then $\sigma(1)=0$ and $k_S=3k_N$, corresponding to a sudden change in the state of the normal conduction electrons on passing through the transition temperature. With this condition, $\sigma(1)=0$, (14) becomes

$$\sigma(t)=1-t^6. \tag{15}$$

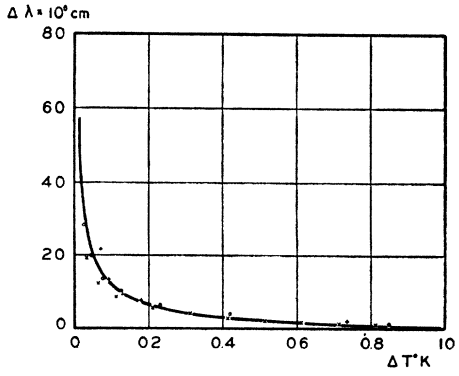

FIG. 1. Results for tin. ○, +, × from Laurmann and Shoenberg (see reference 6). The solid curve is a theoretical plot of Eq. (17) with $\lambda_0=0.75\times10^{-5}$ cm and $T_c=3.711$°K.

[4] W. J. de Haas and M. Kinoshita, Leid. Comm. No. 187 (1927).

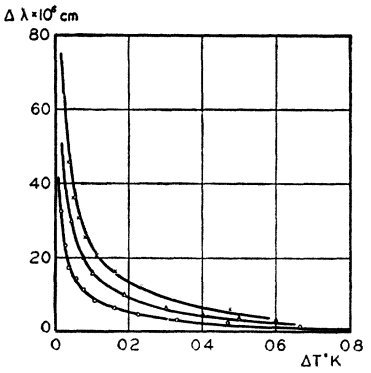

FIG. 2. Results for mercury. ○, Δ, × from Laurmann and Shoenberg (see reference 6). The solid curves are theoretical plots of Eq. (17), using $T_c=4.167$°K and the following values for λ_0: Upper curve, 1.37×10^{-5} cm; middle curve, 0.95×10^{-5} cm; lower curve, 0.54×10^{-5} cm.

To obtain an expression for the penetration depth λ, we use the *form* of the equation given by the acceleration theory[5] (for similar reasons which led us to use only the form of the Sommerfeld relation, Eq. (11)),

$$\lambda \propto \sigma^{-\frac{1}{2}}. \tag{16}$$

If λ_0 represents the penetration depth at 0°K,

$$\lambda=\lambda_0(1-t^6)^{-\frac{1}{2}}. \tag{17}$$

As the Gorter-Casimir thermodynamic equations were derived neglecting the penetration depth, Eq. (17) holds for those superconducting bodies for which λ is much smaller than the linear dimensions of the body.

4. COMPARISON WITH EXPERIMENT

In a recent article, Laurmann and Shoenberg[6] have collected data on change of penetration depth with change in temperature for tin and mercury. The linear dimensions of the cylinders used were large compared with λ, so that it would be expected that Eq. (17) should apply to their results. The change in penetration depth $\Delta\lambda$ is defined by $\Delta\lambda=\lambda(T)-\lambda(2.1\text{°K})$ and the change in temperature, ΔT, as the temperature difference from the transition temperature. The data for tin are plotted in Fig. 1. The solid curve was computed from Eq. (17) with $T_c=3.711$°K and $\lambda_0=0.75\times10^{-5}$ cm. In Fig. 2 are shown three sets of data for mercury. The solid curves were computed from Eq. (17) with $T_c=4.167$°K. For the upper curve, $\lambda_0=1.37\times10^{-5}$ cm; for the middle curve, $\lambda_0=0.95\times10^{-5}$ cm; for the lower curve, $\lambda_0=0.54\times10^{-5}$ cm. Laurmann and Shoenberg attribute the differences in the curves for mercury to anisotropy, the middle curve representing polycrystalline mercury.

Although Eq. (17) is not intended to hold for thin films, it is interesting to compare Eq. (17) with the experimental results of Appleyard *et al.*[7] The curve shown in Fig. 3 is a plot of Eq. (17) relating λ/λ_0 with the reduced temperature t. The solid circles represent experimental data obtained from Fig. 6 of the paper by Appleyard *et al.* on the superconductivity of thin mercury films. Their data have been adjusted so that the point corresponding to $t=0.6$ ($T=2.5$°K) is made to fit Eq. (17). The agreement is almost as satisfactory as for bulk materials.

Since Eq. (17) contains the assumption $\sigma(0)=1$, it is important to examine the validity of this assumption in view of reported values ranging from 0.01 to 0.1. If it is assumed that $\sigma(0)=0.1$, it can be shown that γ_N increases by a factor of about 90, while if $\sigma(0)=0.01$, this factor becomes 900. Unfortunately, calorimetric data for γ_N are not available for mercury. However, Keesom and van Laer[8] have made precise

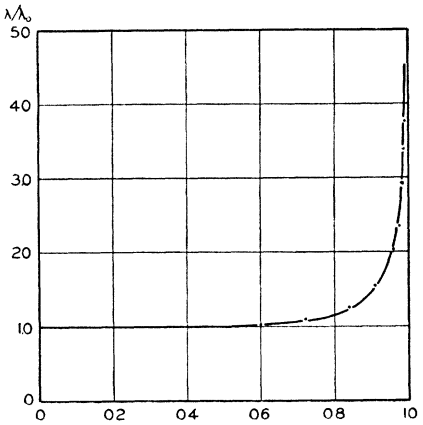

FIG. 3. The curve is a plot of Eq. (17) relating relative penetration depth λ/λ_0 with reduced temperature t. The solid circles are experimental points taken from Appleyard *et al.* (see reference 7).

[5] R. Becker, G. Heller, and F. Sauter, Zeits. f. Physik **85**, 772 (1933).
[6] E. Laurmann and D. Schoenberg, Nature **160**, 747 (1947).
[7] E. T. S. Appleyard, J. R. Bristow, H. London, and A. D. Misener, Proc. Roy. Soc. **170**, 540 (1939).
[8] W. H. Keesom and P. H. van Laer, Physica **5**, 193 (1938).

calorimetric measurements with tin. Their values of γ_N and $(\Delta C)_{T_c}$ are 4.0×10^{-4} and 2.90×10^{-3}, respectively. If we take H_0 for tin to be 300 gauss, as given by de Haas and Engelkes,[9] T_c to be 3.72°K and the atomic volume V to be 15.8, corrected for thermal expansion, Eqs. (7) and (8) give $\gamma_N=3.91\times10^{-4}$ and $(\Delta C)_{T_c}=2.91\times10^{-3}$. The agreement with experiment is very good. Even if there had been a disagreement of 10 percent, $\sigma(0)$ would still be 0.99997 or 1.00004. Calorimetric experiments also show that C_S for tin follows a T^3 law in accord with Eq. (9).

5. DISCUSSION OF THE PARABOLA RELATIONSHIP

If we put $h=H/H_0$ and $t=T/T_c$, the parabola relationship given by Eq. (5) becomes

$$h=1-t^2. \tag{18}$$

Let us examine the experimental results for mercury obtained by independent investigators. In 1934, Kok[1] cites the following empirical formula

$$H=433.0-89.1T^2+60.59T^3 -18.608T^4+1.8774T^5. \tag{19}$$

His accompanying remark is: "For Hg and Pb it is impossible to assume a parabola for the curve of the threshold values." In 1937, Daunt and Mendelssohn[10] give their smoothed data but no empirical formula. Their accompanying remark regarding the equilibrium curves for mercury and the other elements studied is: "None of these curves is a parabola . . . ." In 1940, Misener[11] gives the following empirical formula for mercury

$$H=412.58-19.50T^2-2.133T^3+0.266T^4. \tag{20}$$

Now these polynomial representations, Eqs. (19) and (20) and the data of Daunt and Mendelssohn, can be described by the expression

$$h=(1-t^2)f(t) \tag{21}$$

where $f(t)$ is a "correction factor" to the parabola relationship. For example, $f(t)=1$ for the range $0<t<1$ would indicate that the data could be represented by a parabola, i.e., by Eq. (18). $f(t)$ for the three successive groups of data (in chronological order) is plotted in Fig. 4 and labeled I, II, and III, respectively. Even a cursory inspection will show that the "better" the data the smoother the function $f(t)$. Had a parabola been used to smooth the data for I and II, instead of drawing conclusions concerning the "impossibility" of fitting a parabola to the data, the agreement would have been closer to Misener's results than that which was attained.

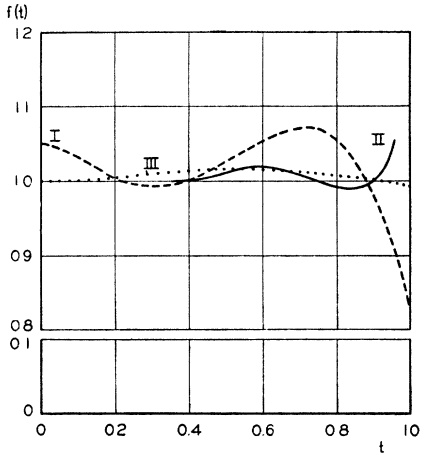

FIG. 4. The correction factor $f(t)$ plotted for Eq. (19) labeled I; Daunt and Mendelssohn's data, II; Eq. (20), III.

In fitting a polynomial of the fourth degree to data, there is a danger in being misled as to the quality of fit of a parabola. To illustrate, Misener's formula for mercury given in Eq. (20) can be written in "reduced" form as

$$h=1-0.82068t^2-0.37407t^3+0.19475t^4. \tag{22}$$

(The last coefficient was changed from 0.19439 to force the polynomial through $h=0$ at $t=1$.) One might at first believe that a parabola could not be fitted because 0.82 is 18 percent less than unity and the other coefficients are certainly not negligible. The drop in the coefficient of the t^2 term is necessary in order to compensate for the t^3 and t^4 terms. In the form of Eq. (21), Eq. (22)

[9] W. J. de Haas and A. D. Engelkes, Physica **4**, 325 (1937).
[10] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. **160**, 127 (1937).
[11] A. D. Misener, Proc. Roy. Soc. **174**, 262 (1940). Misener claims that his formulae for Hg, In, and Tl represent his data within 0.3 gauss and 0.001°K. However, it is curious to note that his curve for Tl passes through $H=0$ at 0.013°K below the transition temperature which he gives as 2.392°K. The error in H corresponding to this would be 1.8 gauss or 6 times his allowed error of 0.3 gauss.

becomes

$$h=(1-t^2)[1+0.17932t^2-(0.37407t^2/1+t)]. \quad (23)$$

The last two terms in the parenthesis compensate so well that they scarcely differ by 0.015 at the worst.

σ is very sensitive to the second derivative of H^2. For example, a deviation of only 1.5 percent in H between the parabola relation and the polynomial, given by Misener for indium, causes σ to fluctuate as much as 100 percent from the values computed from Eq. (15). It seems, therefore, that the error which still remains in the best available data is too great for a reliable use of the various polynomials in finding σ, and therefore, λ/λ_0.

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Artificially Radioactive Se^{73} and Se^{75}

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A radioactive isotope of 7.1-hour half-life has been produced by alpha-particle bombardment of germanium. Assignment of the isotope is made to Se^{73}. Absorption measurements indicate the presence of a positron end point of 1.29 Mev. Aluminum x-ray absorption measurements indicate an x-ray emission with a mass absorption coefficient of 22.1 cm^2/g, corresponding to 1.17A. Bombardment with alpha-particles of Ge^{70}, enriched electromagnetically from 21.2 percent to 90 percent, further confirms the assignment of the activity to Se^{73}. The half-life of Se^{75} is found to be 127 ± 2 days over a decay period of 1000 days. In this activity K-capture and gamma-radiations of 0.22 Mev and 0.43 Mev are observed.

A SELENIUM activity of 160-days half-life has been reported;[1] several electron groups were observed of energies less than 300 kev, corresponding to internally converted gamma-rays. This activity was the result of the bombardment with deuterons of the stable arsenic isotope of mass 75. The decay period of Se^{75}, produced by an (n,γ) reaction of selenium irradiated in the Argonne pile, has been observed[2] to be 115 ± 5 days. This activity was found to decay by K-capture to stable As^{75}, accompanied by a 0.4-Mev gamma-ray. A period of 125 days has also been reported[3] as the half-life of the Se^{75} isotope. The decay is by K-capture with the emission of conversion electrons and gamma-rays of 0.18 Mev and 0.35 Mev.

Inasmuch as the long period in selenium has not been reported in the literature as resulting from alpha-particle bombardment of germanium, such a bombardment was done. As a result of these experiments a strong activity of short half-life was found in selenium in addition to the long period. It is the purpose of this paper to report the characteristic radiations of this short period. Observations, extending over a period of some three years, on the decay and characteristic radiations of the long period will also be described.

I. THE 7.1-HOUR Se^{73} ISOTOPE

The germanium targets were prepared for alpha-particle bombardment by placing finely ground Hilger germanium powder in a thin-bottom copper target holder and carefully heating until a eutectic with the copper was formed.

Figure 1 shows the decay curves of the selenium fraction obtained from the Ge+α-

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[1] C. V. Kent, J. M. Cork, and W. G. Wadey, Phys. Rev. 61, 389 (1942).
[2] H. N. Friedlander, L. Seren, and S. H. Turkel, Phys. Rev. 72, 23 (1947).
[3] Isotope Committee, Science 103, 697 (1946).