photovoltages. It is difficult to reconcile this with the opinion expressed in reference 3 that all individual elements contributing to the total photovoltage are lined up in one direction.

From Figs. 2, 4, and 7 we see that the negative and positive peaks can occur separately. This suggests that they may be due to independent mechanisms. For the positive peak, processes occurring in the bulk of the crystal are likely to be of major importance. The negative peak, occurring in the region of very high optical absorption, may be mostly governed by surface properties. It is also significant that whenever a crystal shows an abnormally large photovoltage both the negative and positive peaks are of the same order of magnitude. This shows that the mechanism responsible for the larger-than-band-gap voltages must be operative both in the bulk and at or near the surface.

In conclusion we should like to point out that the measurement of the anomalous photovoltaic effect can become a useful tool in the study of crystalline disorder in ZnS. Even at the present stage we can determine from the shape of the I_{sc} curve the predominant crystal structure and the presence of stacking faults. In order to put the correlation between disorder and photovoltaic effect on a more quantitative basis a much deeper understanding of both is necessary. We hope to continue these studies.

ACKNOWLEDGMENTS

The author wishes to express his sincere thanks to the following collaborators: Dr. H. Samelson for the supply and selection of crystals as well as for numerous suggestions; Mr. V. Brophy for the x-ray analysis; Mr. M. Adler for design of apparatus and Mr. S. Kellner for help in the measurement; Dr. D. R. Frankl, Dr. J. L. Birman, and Dr. G. Neumark for many hours of discussion. Thanks are due Dr. P. Keller for making available his results prior to publication.

PHYSICAL REVIEW VOLUME 113, NUMBER 5 MARCH 1, 1959

Penetration Depth in Impure Superconductors

PETER B. MILLER
Department of Physics, University of Illinois, Urbana, Illinois
(Received October 17, 1958)

The equation giving the current density as a functional of the vector potential for an impurity superconductor derived by Mattis and Bardeen is used to compute the temperature dependence of the penetration depth of impure superconductors. Results of calculations for different values of the ratio of the coherence distance to the mean free path and also for different values of the ratio of the coherence distance to the London penetration depth are given. The results are applied to tin as an example, and appreciable deviations from the $[1-(T/T_c)^4]^{-\frac{1}{2}}$ temperature dependence of the penetration depth are found for all values of the mean free path.

PIPPARD'S[1] experiments on penetration depths in tin-indium alloys show that there is a marked increase in penetration depth with decrease in the mean free path, l, from impurity scattering. Largely on the basis of this work, Pippard suggested that the London equation for the current density in terms of the vector potential,

$$\mathbf{j}(\mathbf{r}) = -(1/c\Lambda)\mathbf{A}(\mathbf{r}), \tag{1}$$

be replaced by the nonlocal relation

$$\mathbf{j}(\mathbf{r}) = \frac{-3}{4\pi c\Lambda(T)\xi_0}\int \frac{\mathbf{RR}\cdot\mathbf{A}(\mathbf{r}')J(R,T)e^{-R/l}}{R^4}d\mathbf{r}', \tag{2}$$

where $\mathbf{R}=\mathbf{r}-\mathbf{r}'$, $\Lambda(T)$ is the London parameter, and ξ_0 is the coherence distance. In both cases the gauge is to be chosen so that $\mathrm{div}\mathbf{j}=0$. In (1), this implies $\mathrm{div}\mathbf{A}=0$, and this is also true of (2) for most cases of practical interest. Pippard suggested that the kernel be taken as $J(R,T)=\exp(-R/\xi_0)$. To account for the fact that the penetration depth, λ, of even impure specimens seems to follow the empirical law

$$\lambda(t)/\lambda(0) = (1-t^4)^{-\frac{1}{2}}, \quad (t=T/T_c). \tag{3}$$

he also suggested that ξ_0 and Λ increase with t in a similar manner.

The theory of superconductivity of Bardeen, Cooper, and Schrieffer,[2] as modified by Mattis and Bardeen[3] to take impurity scattering into account, gives a form similar to (2), but with ξ_0 a temperature-independent parameter and $J(R,T)$ a relatively slowly varying function of temperature. The temperature dependence of the penetration depth then comes almost entirely from a variation of Λ with T. It is of interest to compare predictions based on the B.C.S. theory with experiment, particularly in view of the fact that the relative independence of coherence distance with temperature differs qualitatively from Pippard's suggestion.

[1] A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).

[2] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957), referred to as B.C.S.

[3] D. C. Mattis and J. Bardeen, Phys. Rev. **111**, 412 (1958).

We find that for all values of l, the theory gives a dependence similar to (3) near T_c, with some departure at low temperatures.[4] When theoretical values of $\lambda(T)$ are plotted as a function of the parameter $y=(1-t^4)^{-\frac{1}{2}}$, a straight line is obtained for large y, but there is some bending below the line for $y\lesssim 1.5$.[5] The difference between the slope for large y and the intercept at $y=1$ is small, of the order of 10%.

The result of Mattis and Bardeen reduces at zero frequency to a form similar to (2), with the kernel $J(R,T)$ given by

$$J(R,T)=\frac{2\Lambda(T)\epsilon_0^2}{\pi\epsilon_0(0)\Lambda(0)}\int_0^\infty\left\{\frac{1-2f(\epsilon_0)}{\epsilon_0}-\frac{1-2f(E)}{E}\right\}\times\frac{\sin(2\alpha\epsilon)}{\epsilon}d\epsilon, \quad (4)$$

where $\alpha=R/\hbar v_0$. We use the same notation as B.C.S., in which ϵ_0 is the temperature-dependent energy parameter and f the ordinary Fermi function. The penetration depth is defined by

$$\lambda=\int_0^\infty H(x)dx/H(0). \quad (5)$$

It is convenient to use the Fourier transform of the current density and of the vector potential:

$$\mathbf{j}(\mathbf{r})=(2\pi)^{-\frac{3}{2}}\int d\mathbf{q}e^{i\mathbf{q}\cdot\mathbf{r}}\mathbf{j}(\mathbf{q}). \quad (6)$$

Define $K(q)$ by

$$\mathbf{j}(\mathbf{q})=-(c/4\pi)K(q)\mathbf{a}(\mathbf{q}), \quad (7)$$

where $\mathbf{a}(\mathbf{q})$ is the Fourier component of the vector potential. Once $K(q)$ is known, the penetration depth may be found from the general solution given by Pippard[1] and based on corresponding equations derived by Reuter and Sondheimer for the anomalous skin effect.[6] For random scattering, we have

$$\lambda=\pi\left\{\int_0^\infty \ln[1+q^{-2}K(q)]dq\right\}^{-1}. \quad (8)$$

To derive $K(q)$, use (4) and (7) to get

$$K(q)=\frac{3}{c^2\Lambda(T)\xi_0}\int_0^{2\pi}\int_0^\pi\int_0^\infty \sin^3\theta\sin^2\varphi \times e^{iqR\cos\theta}J(R,T)d\varphi d\theta dR. \quad (9)$$

Carrying out the φ integration, letting $u=\cos\theta$, and using (5), we get

$$K(q)=\frac{6\epsilon_0^2}{c^2\xi_0\Lambda(0)\epsilon_0(0)}\int_0^\infty\int_0^\infty\int_{-1}^1\left\{\frac{1-2f(\epsilon_0)}{\epsilon_0}-\frac{1-2f(E)}{E}\right\}\times\frac{\sin(2\alpha\epsilon)}{\epsilon}(1-u^2)e^{iqRu}e^{-R/l}dudRd\epsilon. \quad (10)$$

Let $b=\epsilon/\epsilon_1$, $\epsilon_1=\frac{1}{2}q\hbar v_0$, $b_0=\epsilon_0/\epsilon_1$, $a=1/ql$, and define $g(b)$ by

$$g(b)=q\int_0^\infty\int_{-1}^1 \sin(bRq)(1-u^2)e^{-R/l}e^{iqRu}dudR. \quad (11)$$

Evaluation of the integral gives

$$g(b)=2b-\frac{b^2}{2}\ln\left[\frac{(1+b)^2+a^2}{(1-b)^2+a^2}\right]+\frac{1+a^2}{2}\ln\left[\frac{(1+b)^2+a^2}{(1-b)^2+a^2}\right]+2ab\left[\arctan\left(\frac{2a}{1-b^2-a^2}\right)-\pi\right]. \quad (12)$$

That branch of the arc tangent between 0 and π must be taken. We need to find

$$\int_0^\infty\left\{\frac{1-2f(\epsilon_0)}{\epsilon_0}-\frac{1-2f(E)}{\epsilon_1(b^2+b_0^2)^{\frac{1}{2}}}\right\}\times\left\{\left[2b-\frac{b^2}{2}\ln\left(\frac{(1+b)^2+a^2}{(1-b)^2+a^2}\right)\right]+\frac{1+a^2}{2}\ln\left[\frac{(1+b)^2+a^2}{(1-b)^2+a^2}\right]+2ab\left[\arctan\left(\frac{2a}{1-b^2-a^2}\right)-\pi\right]\right\}\frac{db}{b}. \quad (13)$$

The product of the first term in each curly bracket is integrated directly and gives

$$[1-2f(\epsilon_0)]\pi a/\epsilon_0. \quad (14)$$

The other terms will be integrated in various limits and values of $K(q)$ valid in the intermediate region will be found by graphical interpolation. Consider the region where $ql\gg1$ and $\epsilon_0(0)\pi q\xi_0/2\epsilon_0\gg1$. In this region we neglect all terms of higher order than a or b_0 compared to 1. The first term in curly bracket one of Eq. (13), multiplied by the second term of curly bracket two, gives a contribution

$$[1-2f(\epsilon_0)][\tfrac{1}{2}\pi^2-\pi a]/\epsilon_0. \quad (15)$$

The second term in bracket one multiplied by the sum of the first two terms of bracket two is integrated by the same method as used by B.C.S. We need the further

[4] J. Bardeen, *Proceedings of the Kamerlingh-Onnes Memorial Conference on Low-Temperature Physics, Leiden, Holland, 1958* [Physica 24, 5–27 (1958)].

[5] A similar departure from the empirical law has been observed by A. L. Schawlow (to be published), contrary to results of Pippard and co-workers.

[6] G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) A195, 336 (1948).

restriction that $\frac{1}{2}\pi q\xi_0 \gg 1$. The result is

$$-(4/\epsilon_1)\ln[qhv_0/\epsilon_0(0)]. \tag{16}$$

The sum of the first two terms in bracket one multiplied by the third term of bracket two is integrated by use of the approximation

$$\left[\arctan\left(\frac{2a}{1-b^2-a^2}\right)-\pi\right]\begin{matrix}=0 & \text{for } b>1,\\ =-\pi & \text{for } b<1.\end{matrix} \tag{17}$$

The corrections to this approximation are negligible. The result is

$$-2a\pi[1-2f(\epsilon_0)]/\epsilon_0. \tag{18}$$

Adding all the contributions, we get, for $ql \gg 1$ and $\pi q\xi_0/2 \gg 1$,

$$K(q)=\frac{3\pi^3\epsilon_0}{qc^2\Lambda\hbar v_0}\left\{1-2f(\epsilon_0)-\frac{16\epsilon_0}{\pi^2 q\hbar v_0}\ln(\pi q\xi_0)-\frac{4}{\pi ql}[1-2f(\epsilon_0)]\right\}. \tag{19}$$

This reduces to the result of B.C.S. as $l\to\infty$.

Consider the opposite limit of $ql \ll 1$. The value of $g(b)$ then is

$$g(b)=4b/3(a^2+b^2). \tag{20}$$

We need to find

$$\frac{4}{3}\int_0^\infty\left\{\frac{1-2f(\epsilon_0)}{\epsilon_0}-\frac{1-2f(E)}{E}\right\}\frac{db}{a^2+b^2}. \tag{21}$$

At $T=0$ we get for $ql \ll 1$

$$K(q)=\frac{2l}{\pi\lambda_L^2(0)\xi_0}\begin{cases}\dfrac{\pi}{2}-\dfrac{1}{[1-(\pi\xi_0/2l)^2]^{\frac{1}{2}}}\times\arctan\left\{\dfrac{2l}{\pi\xi_0}\left[1-\left(\dfrac{\pi\xi_0}{2l}\right)^2\right]^{\frac{1}{2}}\right\}\\[2ex] \dfrac{\pi}{2}-\dfrac{1}{[(\pi\xi_0/2l)^2-1]^{\frac{1}{2}}}\times\ln\left\{\dfrac{\pi\xi_0}{2l}+\left[\left(\dfrac{\pi\xi_0}{2l}\right)^2-1\right]^{\frac{1}{2}}\right\},\end{cases} \tag{22}$$

where the upper form holds for $\pi\xi_0/2l<1$ and the lower form for $\pi\xi_0/2l>1$. At $T=T_c$ the first term in the curly bracket of (21) gives

$$\tfrac{1}{3}\pi ql\beta_c. \tag{23}$$

The second term in the curly bracket of (21) is integrated by contour integration with the path chosen along the x axes from $-\infty$ to $+\infty$ and a semicircle of infinite radius in the upper half z plane. Poles are located at

$$b=ia \quad\text{and}\quad b=i\pi(2n+1)/\beta_c\epsilon_1,\quad n=0,1,2,\cdots\infty, \tag{24}$$

TABLE I. Values of $\lambda(T)/\lambda_L(T)$ as a function of the ratio $\xi_0/\lambda_L(T)$ for various values of $2l/\pi\xi_0$. The upper half of the table is for $t=0$, the lower half for $t=1$.

$\xi_0/\lambda_L(T)$ \ $2l/\pi\xi_0$	∞	2.5	1.0	0.5	0.25	0.125	0.0625
0.0	1.00	1.14	1.32	1.57	2.11	2.56	3.45
0.2	1.06	1.21	1.37	1.60	2.14	2.60	3.46
2.0	1.29	1.43	1.58	1.80	2.27	2.71	3.52
7.3	1.62	1.75	1.87	2.09	2.45	2.87	3.63
20	2.06	2.20	2.30	2.50	2.77	3.14	3.84
50	2.68	2.83	2.89	3.08	3.26	3.62	4.20
100	3.36	3.40	3.47	3.60	3.78	4.15	4.61
0.0	1.00	1.07	1.20	1.36	1.78	2.19	2.91
0.2	1.05	1.11	1.24	1.40	1.81	2.22	2.93
2.0	1.24	1.30	1.41	1.55	1.92	2.32	3.01
7.3	1.53	1.57	1.66	1.81	2.10	2.48	3.11
20.0	1.91	1.95	2.03	2.16	2.40	2.76	3.27
50.0	2.46	2.50	2.56	2.66	2.86	3.18	3.59
100	2.97	3.00	3.07	3.15	3.34	3.66	4.05

and they give a contribution to the integral of

$$-\frac{4ql^2}{\xi_0\epsilon_0(0)}\tan\left[\frac{\beta_c\epsilon_0(0)\pi\xi_0}{4l}\right]-\tfrac{4}{3}q\beta_c^2\epsilon_0(0)\pi\xi_0\cdot\sum_{n=0}^{\infty}\left\{(2n+1)\left[\left(\frac{\beta_c\epsilon_0(0)\pi\xi_0}{2l}\right)^2-(\pi(2n+1))^2\right]\right\}^{-1}. \tag{25}$$

Summing all the contributions and using,[7] near $T=T_c$,

$$\Lambda/\Lambda_T=0.20\epsilon_0^2\beta_c^2, \tag{26}$$

we get for $ql \ll 1$

$$K(q)=\frac{3l}{\lambda_L^2(T)0.40\pi\beta_c\epsilon_0(0)\xi_0}\times\left\{\frac{\pi}{3}-\frac{4l}{3\xi_0\beta_c\epsilon_0(0)}\tan\left(\frac{\beta_c\epsilon_0(0)\pi\xi_0}{4l}\right)-\frac{4}{3}\frac{\beta_c\epsilon_0(0)\pi\xi_0}{l}\times\sum_{n=0}^{\infty}\left\{(2n+1)\left[\left(\frac{\beta_c\epsilon_0(0)\pi\xi_0}{2l}\right)^2-\pi^2(2n+1)^2\right]\right\}^{-1}\right\}. \tag{27}$$

A simple form for (27), valid only when $l/\xi_0 \ll 1$, gotten by simple integration of (21), is

$$K(q)=\frac{2l}{\lambda_L^2(T)\beta_c\epsilon_0(0)0.20\pi\xi_0}\times\left\{\frac{\pi}{4}+\frac{2l}{\pi\xi_0}\frac{1}{\epsilon_0(0)\beta_c}\ln\left(\frac{l}{\pi\xi_0}\right)\right\}. \tag{28}$$

The values of $K(q)$ in the intermediate region of q are found by graphical interpolation of the above results.

[7] A more accurate value for the numerical coefficient in (26) has recently been found to be 0.21.

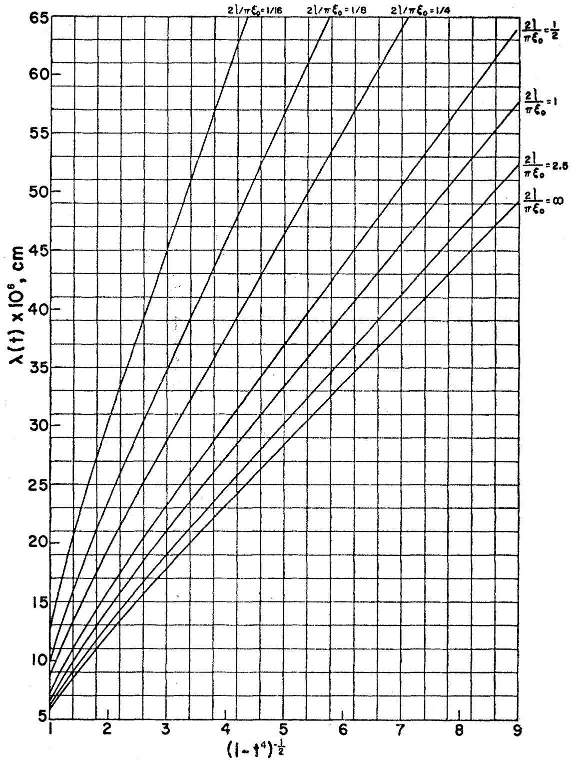

FIG. 1. Calculated values of $\lambda(t)$ for Sn *vs* $(1-t^4)^{-\frac{1}{2}}$ for various values of $2l/\pi\xi_0$.

The penetration depth is found by numerical integration of (8). The results of this integration are shown in Table I for various values of the parameter $2l/\pi\xi_0$. The results show that the ratio $\lambda(T)/\lambda_L(T)$ is almost the same at $t=0$ as at $t=1$, and therefore results for intermediate temperatures may be found by interpolating between the values at $t=0$ and $t=1$.

To find the temperature dependence of the penetration depth for a specific metal, we need to know $\lambda_L(0)$ and ξ_0 for that metal. For tin, values of $\lambda_L(0)$ and v_0 have been estimated from experimental data.[8] The value of ξ_0 is given by the B.C.S. theory as

$$\xi_0=0.18\hbar v_0/kT_c. \tag{29}$$

For tin, $\lambda_L(0)=3.5\times10^{-6}$ cm and $\xi_0=7.3\lambda_L(0)$. The temperature dependence of the penetration depth for tin is plotted in Fig. 1, with the abscissa being $(1-t^4)^{-\frac{1}{2}}$. The results of Fig. 1 are rather insensitive to the exact interpolation procedure used in Table I. Figure 1 shows appreciable deviations for all values of $2l/\pi\xi_0$ from the straight line described by (3).

A comparison of the experimental data with our theoretical results is shown in Fig. 2. There is good qualitative agreement between experiment and theory, which is all that can be expected in view of the simplifications made in the theory and the appreciable uncertainties in the experimental data.

The penetration depth for smaller values of the ratio $2l/\pi\xi_0$ than those shown in Table I is found by forming the $K(q)$ values of (22) and (28) in the limit $l/\xi_0\rightarrow0$. Assuming also that $l/\lambda_L(T)\ll1$, corresponding to the London limit, one gets[9]

$$\lambda(0)=\frac{\lambda_L(0)(\xi_0/l)^{\frac{1}{2}}}{[1-(4l/\pi^2\xi_0)\ln(\pi\xi_0/l)]^{\frac{1}{2}}},\quad \text{at}\quad T=0 \tag{30}$$

and

$$\lambda(T)=\frac{\lambda_L(T)(\xi_0\beta_c\epsilon_0(0)/l)^{\frac{1}{2}}}{[\frac{5}{2}-(20l/\pi^2\beta_c\epsilon_0(0)\xi_0)\ln(\pi\xi_0/l)]^{\frac{1}{2}}},\quad \text{at}\quad T=T_c. \tag{31}$$

For finite small values of $2l/\pi\xi_0$ one makes a plot of the ratio of the exact penetration depth as given by Table I to the limiting value of the penetration depth given by (30) or (31) as a function of $2l/\pi\xi_0$. Such a plot approaches the asymptotic value 1.00 as $2l/\pi\xi_0$ approaches zero and gives accurate values of the penetration depth for small values of $2l/\pi\xi_0$.

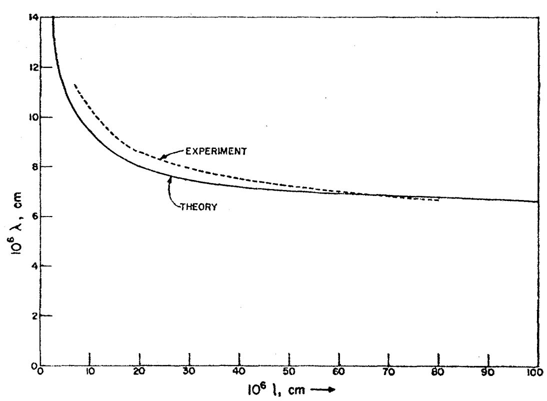

FIG. 2. Comparison between experiment and theory for Sn. λ is plotted *vs* l at $t=0.6$. The arrows at the right refer to the value at $l=\infty$.

ACKNOWLEDGMENT

The author is indebted to Professor J. Bardeen for suggesting this problem and for his guidance in this work.

[8] T. E. Faber and A. B. Pippard, Proc. Roy. Soc. (London) A231, 336 (1955).

[9] Several similar formulas for $K(q)$ values and penetration depths recently have been obtained by A. A. Abrikosov and L. P. Gor'kov, Zhur. Eksptl. i Teoret. Fiz. **35**, 1558 (1958); **36**, 319 (1959).