Sound waves of finite amplitude

where \( C_0 \) is chosen to enclose the points 0, \( \pm x \). If we invert the order of integration, we obtain

\[
\int_{0}^{x} (x^2 - r^2)^{N-1} F(r) r \, dr = \frac{1}{2m} \int_{C_0} 2^{2N} \Phi(z) \left( \int_{0}^{x} \frac{(x^2 - r^2)^{N-1}}{(x^2 - r^2)^{N+1}} r \, dr \, dz \right)
\]

\[
= \frac{x^{2N}}{4\pi i N} \int_{C_0} \frac{\Phi(z)}{z^2 - x^2} \, dz
\]

\[
= \frac{x^{2N-1}}{4N} \{ \Phi(x) - \Phi(-x) \},
\]

which proves the result when \( x \) is real. The truth of the lemma for complex values of \( z \) follows by analytical continuation.

**References**


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An experimental and theoretical study of the relation between magnetic field and current in a superconductor

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The penetration depth, \( \lambda \), in superconducting tin at 0° K has been found to be capable of variation by the addition of impurity, 3\% of indium causing it to be nearly doubled, although the thermodynamical properties such as \( T_c \) are hardly affected. It is suggested that this result throws doubt on the phenomenological theory of F. and H. London, and a new equation for the supercurrent is proposed, in which the current is related to an average of the vector potential over a region around the point considered. The size of the region is governed by a parameter \( \xi \), which is dependent, in a similar way to the mean free path in a normal metal, on the degree of purity. The new theory agrees in a satisfactory manner with the experimental results, and also provides an explanation of the magnitude of \( \lambda \) in a pure metal. It has been found that the unusual anisotropy of \( \lambda \) in pure tin is absent in tin + 3\% indium, and this too is in agreement with the prediction of the new theory. The fact that the temperature variation of \( \lambda \) appears to have the same form independent of the degree of purity implies that \( \xi \) depends on temperature in the same way as \( \lambda \); this result agrees with the observed behaviour of the interphase surface energy, \( \sigma_{\text{sur}} \), if \( \xi \) is regarded as determining the width of the interface between superconducting and normal regions. The paper ends with a discussion of the relation of the new theory to microscopic theories of superconductivity.

**Introduction**

On the basis of experiments on the variation of the penetration depth in a superconductor when a magnetic field, less than the critical field, is applied to its surface
(Pippard 1950c), and of considerations concerning the origin of the surface energy between superconducting and normal phases (Pippard 1951a), it was suggested that the behaviour of a superconductor is in some respects controlled by an interaction of rather long range (called the 'range of coherence') within the electron assembly, which restricts the rate of change from point to point of the parameters describing the local properties of the assembly. For example, the magnitude of the interphase surface energy may be understood if it is assumed that the degree of order or 'number of superconducting electrons' can change only gradually, so that the boundary between the phases is not clear-cut but diffuse. The view was expressed that this behaviour is analogous to the extended coherence of a wave-system in which scattering centres are few and far between, and that in a pure metal at low temperatures there is no scattering mechanism sufficiently potent to destroy close correlation between the properties of neighbouring regions. With this concept in mind it was natural to undertake an experimental inquiry into the influence of small amounts of impurity on the behaviour of a superconductor, to see whether the addition of impurity shortened the range of coherence. Positive results were obtained, as already briefly reported (Pippard 1951b), the penetration depth in impure tin being found to vary much more than in pure tin on application of a magnetic field. During the course of the work, however, a more striking phenomenon was disclosed, namely, that it is possible by the addition of impurity to alter considerably the penetration depth in zero magnetic field, without producing a corresponding change in the thermodynamical properties of the material. This discovery, which casts doubt on the London theory of superconductivity, led to a shelving of the original purpose of the investigation. The present paper describes a systematic study of the effect of impurity on the penetration depth, together with a new phenomenological theory which appears to describe the observations adequately. Further tests of the theory have on the whole been satisfactory and, among other things, an explanation is found for the absolute magnitude of the penetration depth and for its peculiar anisotropy in pure tin (Pippard 1950a). The paper ends with a discussion of the relation between the new phenomenological theory and recent microscopic theories of superconductivity.

**Experimental Procedure**

The aim in adding impurity to the superconductor was to introduce in a controllable manner scattering centres for the electrons, without at the same time altering the main characteristics of the metal. For this purpose it is desirable to use as impurity another metal which forms a substitutional solution with the principal constituent. Tin was chosen as the experimental material, since its superconducting properties are better known than those of any other metal, and indium was chosen as impurity. It is possible to form substitutional solutions with indium concentrations up to about 3%, which can be grown as single crystals having very nearly the same thermodynamical properties as pure tin. For example, the superconducting transition temperature is only slightly affected, being lowered on the addition of 3% In from 3·72 to 3·63° K, and the critical magnetic field is
similarly only slightly changed. On the other hand, the indium provides satisfactory scattering centres, as may be seen by its effect on the residual electrical resistance of the normal metal. In the purest available tin this is about $10^{-9}$ ohm cm, while addition of 3% In increases it by a factor of about 1200; correspondingly, the mean free path of the conduction electrons is reduced from $10^{-2}$ cm to less than $10^{-6}$ cm. Indium concentrations greater than 3% could not be used, since richer alloys exhibit superconductivity at 4.2°K, presumably as a result of the appearance of a new phase.

The technique for measuring the penetration depth, $\lambda$, was essentially similar to that described earlier (Pippard 1950a, hereafter referred to as 'A'), in that it involved a determination of the change in resonant frequency of a half-wave wire when superconductivity was destroyed by a magnetic field greater than critical. The specimens, as in A, were wires about 1.4 cm long (resonant frequency about 9400 Mc/s) and $\frac{1}{3}$ mm in diameter. On account of the anisotropy of tin it is necessary to use single crystals of controlled orientation to achieve reproducible results. Attempts to grow crystals of impure tin with the tetrad axis lying along the specimen were unsuccessful, but the next orientation tried, having the tetrad axis normal to the specimen axis, was easy to grow from a seed crystal; the specimens, of different impurity content, used in the first part of the investigation were all grown from the same seed, and were thus identically oriented within about one degree. The wires were recrystallized in the glass envelope in which they were originally cast, so that they remained circular; the glass was then dissolved in hydrofluoric acid, and the wires polished electrolytically. After cutting to the right length they were mounted on silica frameworks exactly as in A. The only change in the cryostat, compared with that used in A, was to replace the wave-guide leads to the resonator by coaxial lines, so as to save space and also to avoid soft-soldered joints in the region where they might become superconducting and distort the applied magnetic field. A new detailed procedure for measuring $\lambda$, however, had to be devised, since the earlier procedure is inapplicable to impure specimens. The chief reason is that it depends on assuming the law of temperature variation of $\lambda$ to deduce the absolute value of $\lambda_0$, the penetration depth at 0°K, and there is no guarantee that the same law applies to specimens of different impurity content; but there are technical difficulties as well, arising from the imperfect Meissner effect in impure tin.

It was therefore decided to concentrate on measuring $\lambda$ at one temperature only as low as convenient, and 2.2°K was chosen. The actual quantity measured is the difference between $\delta_i$, the penetration depth in the normal metal, and $\lambda$; if $\delta_i$ can be deduced from the surface resistance of the normal metal, which is easily determined experimentally, then an absolute value of $\lambda$ is obtainable. The problem of determining $\delta_i$ is discussed in an appendix, and no more need be said here about the method adopted than to point out that it depends partly on the theory of the anomalous skin effect (Reuter & Sondheimer 1948) and partly on guesswork; it is most reliable in the least pure specimens, for which the classical theory of the skin effect is nearly correct, and $\delta_i$ is given very nearly by $R/4\pi\omega$, where $\omega$ is the angular frequency.
Apart from errors arising from the determination of $\delta_\lambda$, the values of $\lambda$ may be affected by an insidious source of error in the measurements, which was absent when the earlier technique was used. Any imperfections of impedance matching in the leads connecting the resonator to the oscillator and detector can produce an apparent shift in the resonant frequency, of a magnitude depending on the width of the resonance peak, and thus different in the normal and superconducting states of the specimen. This source of error is important only when absolute values of $\delta_\lambda - \lambda$ are required, and is automatically eliminated in the earlier technique in which only the temperature variation of $\delta_\lambda - \lambda$ is determined. No direct means has been found for allowing for this effect, which is probably highly dependent on frequency; from internal evidence it probably does not in the present experiments introduce errors greater than $\pm 5\%$.

Finally, it is important to justify the assumption which will be made throughout all that follows, that the values of $\lambda_0$ obtained by the present high-frequency method are the same as would be obtained by static measurements. That this is a reasonable assumption may be seen by applying the Kramers-Kronig (Kramers 1927; Kronig 1926) relation to the surface impedance of a superconductor; in this way the penetration depth measured at a frequency $\omega$ may be expressed in terms of the high-frequency resistance, $R$,

$$\lambda(\omega) - \lambda(0) = \frac{1}{\pi} \int_0^\infty \delta_r \left( \frac{\mu}{\mu^2 - \omega^2} - \frac{1}{\mu} \right) d\mu,$$

where $\delta_r$ is the resistive skin depth, $R/2\pi\omega$. Now measurements of $R$ at 9400 Mc/s, presented in $\Lambda$, show that it is extremely small at 0° K, probably less than 0.1% of the normal resistance. It is likely that $R$ is as small as this, or even zero, at all frequencies up to 9400 Mc/s, and possibly up to 25,000 Mc/s and higher (Grebenkemper & Hagen 1952). Let us assume, then, that $\delta_r = 0$ for frequencies less than $3\omega$ ($\omega$ being the frequency of the present experiments, 9400 Mc/s), and, for example, let us put $\delta_r = \text{constant}$ for frequencies greater than $3\omega$. Then we find, on performing the integration, that $\lambda(\omega) - \lambda(0) \sim \delta_r/50$, so that even on the extreme assumption that $\delta_r$ is as great as the skin depth in the normal metal, which is the same order of magnitude as $\lambda_0$, the assumption that the measured value of $\lambda_0$ is the same as the value at zero frequency will only involve an error of a small percentage.

**Experimental results**

Measurements were made on eight specimens, containing from 0 to 3% In, all single crystals with the same orientation. The measured values of $\lambda$ at 2.2° K have all been reduced by 7% to give values of $\lambda_0$. The degree of purity of each specimen is conveniently defined by the mean free path, $l$, which is inversely proportional to the residual resistance; on account, however, of the difficulty of mounting the small specimens for resistance measurements, and of doubts about the uniformity of indium concentration in them, $l$ was determined from the high-frequency resistance in the normal state, as explained in the appendix. Figure 1 shows how $\lambda_0$ varies with $l$ for those six specimens which contained the highest concentrations of indium; as explained in the appendix, the results for the two purest specimens
could not be used. In spite of the shortcomings of the experimental technique and the method of analysis, the points lie well on a smooth curve. Whether or not it is the correct curve is open to doubt, but at any rate the extremities are fairly free from suspicion. On the one hand, when \( l \) is very long, in pure tin, \( \lambda_0 \) is known to take a value near \( 5 \times 10^{-6} \) cm (Laurmann & Shoenberg 1949; Pippard 1950a; Lock 1951); the value \( 5.3 \times 10^{-6} \) cm, taken from \( A \), has been adopted here. On the other hand, when \( l \) is much less than the skin depth, as in those specimens which contained \( 3 \% \) In, the classical skin-effect theory is very nearly correct, and the evaluation of \( \delta \) is not likely to be seriously wrong. There is thus good evidence for a marked dependence of \( \lambda_0 \) on \( l \), even if the exact form of the dependence is uncertain.

**Discussion**

(a) Development of a new phenomenological theory

The problem raised by these results may be most easily understood by reference to the phenomenological theory of superconductivity developed by London & London (1935) and comprehensively presented by F. London (1950). In essence the theory postulates a dependence of supercurrent on magnetic field which takes the form

\[
\text{curl} (\Lambda \mathbf{J}) + \mathbf{H} = 0,
\]

or, in a more compact form, in terms of an appropriately gauged vector potential

\[
\Lambda \mathbf{J} + \mathbf{A} = 0. \quad (1)
\]

This equation, as is well known, leads to an exponential decay of magnetic field within a plane-surfaced superconductor, according to the law

\[
H = H_0 \exp \left( -\frac{x}{\lambda} \right), \quad \text{where} \quad \lambda^2 = \frac{\Lambda}{4\pi}. \quad (2)
\]
London shows that (1) may be interpreted microscopically by the assumption that
the electron structure is rigid against perturbation by an applied magnetic field.
The quantum expression for current density (see London 1950, p. 147),
\[
J(R) = \sum_{a=1}^{N} \left\{ \frac{\epsilon h}{4\pi lm} [\Psi^* \nabla_{\alpha} \Psi - \Psi \nabla_{\alpha} \Psi^*] - \frac{e^2}{m} \lambda(r_a) \Psi \Psi^* \right\} \delta(R - r_a) \, dr_1 \ldots dr_N,
\]
vanishes in a stationary state if the magnetic field, and hence \(\lambda\), is zero. Now if
\(\Psi\) remains unperturbed by the application of a field, the first term in the integral
still vanishes, leaving only a contribution from the second term, which may be
written, after performing the integration,
\[
J = -\frac{ne^2}{m} \lambda,
\]
in which \(n\) is the number of superconducting electrons per unit volume. This
expression is identical with (1), if \(\lambda\) is put equal to \(m/ne^2\). Here \(m\) is the real
electron mass, but it may be shown (private communication from Professor J.
Bardeen) that the effect of the periodic lattice may be taken into account by
treating \(m\) as an effective mass, as in standard metal theory.

From this brief survey of the London theory the important point emerges that
\(\lambda\) depends only on constants of the metal, and not on any parameter which may be
greatly modified by the addition of small amounts of impurity. The fact that
addition of indium modifies the thermodynamic properties of tin to only a trivial
extent is evidence that there is no significant modification of \(m\) or \(n\). It seems
therefore that the London theory as it stands is unable to account for the observed
variation of \(\lambda_0\).

As a starting point in our search for a phenomenological theory which will
contain our results, it is instructive to notice that the rapid variation of \(\lambda_0\) with
\(l\) begins at about the point where \(\lambda_0\) and \(l\) become comparable, and this suggests
an analogy with a free path effect in normal conductors, the anomalous skin effect.
In a normal conductor so long as \(l\) is short, so that the electric field may be treated
as constant over a region comparable to \(l\), it is permissible to express the dependence
of current density on electric field as a linear point-relation
\[
J = \sigma E.
\]
This expression is, however, only a limiting case of a more general space-relation,
in which \(J\) is related to an appropriate average of \(E\) over a region comparable in
dimensions with \(l\):
\[
J = \frac{3\sigma}{4\pi l^2} \int \frac{r(r \cdot E) e^{-r^2}}{r^4} \, dr.
\]
Here \(E\) is the electric field within a volume element \(dr\), and \(r\) is the radius vector
from \(dr\) to the point at which \(J\) is to be evaluated. The integral is to be taken over
the whole volume of the metal.† If \(E\) be assumed constant (5) reduces to (4), except

† I am indebted to Dr R. G. Chambers for showing me how to derive the correct form of
(5) for a Fermi gas. Strictly, (5) is valid for a degenerate isotropic electron gas, on the
assumption that the electrons are diffusely scattered on collision with the surface of the metal.
near the surface. It is the application of (5) to the theory of the high-frequency skin effect which leads to Reuter & Sondheimer's (1948) theory of the anomalous skin effect, while (4) leads to the classical theory of the skin effect.

In Reuter & Sondheimer's theory, which has been experimentally verified (Chambers 1952), as $l$ is increased, the frequency being constant, the skin depth $\delta$ first decreases as $l^{-1}$ so long as (4) is applicable, and thereafter less rapidly, tending eventually to a constant value. This behaviour of $\delta$ is similar to what we have found for $\lambda$, and it suggests that London's equation should be subjected to the same transformation as leads from (4) to (5). There is, however, one by no means trivial modification needed in (1) before the transformation can be applied successfully. In (4) the conductivity $\sigma$ is proportional to $l$, while in (1) $\Lambda$ is a constant of the metal. It appears appropriate therefore to use instead of (1) the equation

$$\mathbf{J} = -\frac{\xi}{\xi_0 \Lambda} \mathbf{A}, \quad (6)$$

in which $\xi$ will be treated as analogous to $l$, and dependent on the degree of purity of the metal, and $\xi_0$ is a constant, having the dimensions of length. We may now transform (6) into a form analogous to (5):

$$\mathbf{J} = -\frac{3}{4\pi \xi_0 \Lambda} \int \frac{r(r \cdot A) e^{-r\xi}}{r^4} \, dr. \quad (7)$$

We shall now discuss the consequences of this equation for the supercurrent, and the evidence which favours its being regarded as the basis of a new phenomenological theory of superconductivity, superseding the London theory.

Combining (7) with Maxwell's equations, i.e. putting $\nabla^2 \mathbf{A} = -4\pi \mathbf{J}$, we have immediately an equation for $\mathbf{A}$:

$$\nabla^2 \mathbf{A} = \frac{3}{\xi_0 \Lambda} \int \frac{r(r \cdot A) e^{-r\xi}}{r^4} \, dr. \quad (8)$$

There is only one special case in which the solution of this equation is known, but fortunately it is this case which corresponds to the conditions of the present experiments, namely, when the superconductor may be treated as a semi-infinite solid having a plane surface. If the $z$-axis be taken normal to the surface, and $\mathbf{H}$ parallel to the surface and directed along the $y$-axis, $\mathbf{A}$ and $\mathbf{J}$ have only $x$-components, and (8) may be written

$$\frac{d^2 A_x}{dz^2} = \frac{3\pi}{\xi_0 \Lambda} \int_0^\infty k \left( \frac{z-t}{\xi} \right) A_x(t) \, dt, \quad (9)$$

in which

$$k(u) = \int_1^{\infty} \left| \frac{1}{\sin s} - \frac{1}{\sin u} \right| e^{-s|\sin u|} \, ds.$$ 

We may rewrite (9) in dimensionless co-ordinates, putting $x = z/\xi$, $y = t/\xi$ and $f(x) = A_x(z)$,

$$f''(x) = \frac{3\pi \xi_0 \xi^3}{\xi_0 \Lambda} \int_0^\infty k(x-y) f(y) \, dy. \quad (10)$$

This equation is analogous to equation (A15) of Reuter & Sondheimer (1948), but is simpler in that it involves only real quantities. The solution of (10) yields the
magnetic field distribution within the superconductor, and hence the penetration depth, which we define by the equation

$$\lambda = \frac{\int_{0}^{\infty} H_y \, dz}{H_y(0)} = -\frac{\xi}{f^* h} \Bigl|_{x=0},$$

(11) since A and f must be gauged so as to vanish as $x \to \infty$. The solution of (10) proceeds in the same manner as in appendix II of Reuter & Sondheimer's paper, and yields an analogous result:

$$\lambda = \pi \xi \int_{0}^{\infty} \ln \left[ 1 + \frac{\beta \kappa(t)}{t^2} \right] \, dt,$$

(12) in which

$$\beta = \frac{3 \pi \xi^2}{\xi_0 \Lambda},$$

and

$$\kappa(t) = \frac{2}{t^3} (1 + t^2) \tan^{-1} t - t).$$

Equation (12) may be simplified in the two limiting cases when $\beta$ is very small ($\xi \ll \lambda$) and very large ($\xi \gg \lambda$). In the former $\kappa(t)$ may be replaced by $4/3$ and in the latter by $\pi/t$, and the integrations may then be easily effected, to give the results:

$$\beta \text{ small: } \lambda = \sqrt{(\xi_0 \Lambda/4 \pi \xi)};$$

(13)

$$\beta \text{ large: } \lambda = 3^4 (\xi_0 \Lambda)^{1/2} \pi = \lambda_\infty \text{ (say).}$$

(14)

The result for small $\beta$ follows directly if (7) is replaced by (6); it will be observed that $\lambda$ varies as $\xi^{-1}$, while when $\beta$, and hence $\xi$, is great $\lambda$ is independent of $\xi$, in accord with the experimental results. Values of $\lambda$ for intermediate values of $\beta$ may be obtained by numerical quadrature of the integral in (12). The result is shown in figure 2, in which $\lambda_\infty/\lambda$ is plotted against $\sqrt{(\xi/\lambda_\infty)}$. Following Chambers (1952), a simple and accurate interpolation formula has been constructed for the upper part of the curve, having the form

$$\lambda/\lambda_\infty = 1 + 1.1007 (\xi/\lambda_\infty)^{-0.8301}.$$  

(15)

This formula agrees with the exact expression (12) within $\frac{1}{3}$ % for $\sqrt{(\xi/\lambda_\infty)} > 1.3$, and within 0.01 % for $\sqrt{(\xi/\lambda_\infty)} > 2.0$; it may be seen from figure 2 that with (13) it enables most of the curve to be represented by simple functions.

We are now in a position to consider the agreement between (12) and the experimental results. First, we shall regard $\xi$ as determined entirely by the concentration of scattering centres and hence proportional to, but not necessarily equal to, $l$. If we write $\xi = \alpha l$, a good fit of the experimental points to the theoretical curve, as may be seen from figure 3, is obtained by choosing $\alpha = 0.93$ and $\lambda_\infty = 5.61 \times 10^{-6}$ cm. The agreement is in fact much better than could reasonably have been expected, and some indication that the appearance of perfect agreement is in fact illusory is given by the fact that the required value of $\lambda_\infty$ is some 6 % higher than that obtained in $\Lambda$; this discrepancy, however, is not so great as to be seriously disturbing.

† I am grateful to Dr E. H. Sondheimer for verifying this solution.
The field equation of a superconductor

A somewhat different view of the connexion between $\xi$ and $l$ may also be considered. There is evidence (Pippard 1950c) that even in a pure superconductor the degree of order may change appreciably in a distance of $10^{-4}$ cm, much smaller than $l$. Possibly there is a limit to the range of coherence fixed, for example,

![Figure 2](image1)

**Figure 2.** Theoretical dependence of $\lambda$ on $\xi$. – , equation (12); ----, equation (13); . . . . , equation (15).

![Figure 3](image2)

**Figure 3.** Comparison of theory and experiment. ○, assuming $\xi = \alpha l$; +, assuming equation (16).

by interactions among the electrons themselves, and independent of impurity scattering; and, as we shall see later, there is reason to believe that the limiting value of $\xi$ is closely related to the new constant $\xi_0$ which we have introduced. From this point of view we might expect $\xi$ to be related to $l$ by an equation of the type

$$\frac{1}{\xi} = \frac{1}{\xi_0} + \frac{1}{\alpha l},$$

(16)
the interelectronic and impurity types of scattering being treated as independent. If, for example, we choose $\xi_0 = 1.2 \times 10^{-4}$ cm and $\alpha = 0.80$, a good fit between theory and experiment is obtained, as shown in figure 3, $\lambda_\infty$ being taken as $5.28 \times 10^{-6}$ cm. It must be remembered, however, that according to (16) $\xi$ cannot exceed $\xi_0$, so that $\lambda_\infty$, corresponding to an infinite $\xi$, is unrealizable. In fact the minimum value for $\lambda$, as $l \to \infty$, is now $5.72 \times 10^{-6}$ cm. This second view of the relation of $\xi$ to $l$ thus disagrees with experiment slightly more than the first, but the difference is so small in comparison with the possible errors of the experimental points that no decision can be made between the two views. It is worth pointing out, however, that on either view it is necessary to choose $\alpha$ very near unity, and this is some confirmation of the general principles on which the new theory is based.

(b) Anisotropy of the penetration depth

The penetration depth in pure tin has been found (A, figure 6) to exhibit a remarkable form of anisotropy, in that it takes about the same value for currents flowing parallel or perpendicular to the tetrad axis, but is some 25% greater for currents flowing at angles around 60° from the tetrad axis. Such behaviour cannot be understood in terms of the London theory if it is extended to anisotropic materials by treating $\Lambda$ as a second-order tensor, since $\lambda$ must then vary monotonically with orientation. On the other hand, the present theory can encompass much more elaborate anisotropies, as has been discussed in A with reference to the anisotropy of the anomalous surface conductance in the normal metal; there is, indeed, a close correlation between the latter and the anisotropy of $\lambda$, for which the present theory provides a qualitative explanation. The possibility of a nontensorial type of anisotropy in the anomalous skin effect arises because when $l$ is very long the greater part of the current is carried by the small proportion of electrons moving nearly parallel to the surface (see appendix and A, p. 106). For different orientations of the tetrad axis relative to the surface different groups of electrons come into play, and as a result any complicated anisotropy of the Fermi surface is reflected in the surface impedance. So in the present theory, when $\xi \ll \lambda$, there is a similar preponderating influence of electrons moving nearly parallel to the surface; as can be seen from (7), the greatest contribution to $J$ comes from those volume elements for which $r$ is nearly parallel to the surface, since it is only for these that $A$ maintains its magnitude over a distance much greater than $\lambda$. When $\xi \ll \lambda$, however, electrons having all directions of motion contribute more or less equally to $J$. Thus (13) and (14) are somewhat misleading when applied to an anisotropic metal, in that $\xi_0 \ Lambda$ is not necessarily the same in both. In (13) $\xi_0 \ Lambda$ is an average over all electrons, which we shall write as $\xi_0 \ Lambda$, but in (14) it is an average over only those electrons moving nearly parallel to the surface, which we shall write as $\xi_0' \ Lambda'$. While therefore we expect (by analogy with $\sigma$) that $\xi_0 \ Lambda$, and hence $\lambda$ in very impure specimens, will exhibit only a simple anisotropy, $\xi_0' \ Lambda'$, and hence $\lambda_\infty$, may be much more elaborately anisotropic.

† This value of $\xi_0$ has been chosen arbitrarily; an equally good fit can be obtained, by suitable choice of $\alpha$, for any value of $\xi_0$ between $10^{-4}$ cm and $\infty$. 

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This expectation may be tested experimentally by studying the anisotropy of \( \lambda \) in very impure specimens, and accordingly measurements were made on a number of specimens, each containing nominally 3 \% In, for which the angle \( \theta \) between the tetrad axis and the specimen axis took values between 18\(^\circ\) and 90\(^\circ\). The analysis of the experimental results is described in the appendix, and \( \lambda_0 \) is shown in figure 4 as a function of \( \sin^2 \theta \). The scatter of the points is unfortunately too great to allow a decision on whether the best straight line through the points, which is horizontal as drawn, really represents the behaviour of \( \lambda_0 \) in impure tin, or whether there is indeed a slight dip at intermediate angles. The uncertainties in the method of analysis are such that this dip might well be spurious, but at any rate it is fairly certain that the hump exhibited in pure tin is absent.

It is probable therefore that the anisotropy of \( \lambda_0 \) in pure superconducting tin is to be ascribed to the same cause as the corresponding effect in the high-frequency resistance of normal tin, and this view receives further support from a more detailed comparison of the two effects. In the normal metal, as \( l \to \infty \), the surface resistance at a frequency \( \omega \) tends to a value \( R_\infty \) given by the equation

\[
R_\infty = 1.76 (\Lambda'_n v' \omega^2)^{\frac{1}{2}},
\]

in which \( \Lambda'_n \) is written, by analogy with London's \( \Lambda \), for the quantity \( m'/\hbar e^2 \) in the normal metal, and \( v' \) is the Fermi velocity; the primes have the same significance as before. This expression may be compared with the expression for \( \lambda_\infty \) (equation (14)),

\[
\lambda_\infty = 0.28 \xi_0 \Lambda'.
\]

In the absence of detailed knowledge of the electronic structure of tin no allowance can be made for variations in \( v' \) and \( \xi_0 \), but if we assume that \( \Lambda'_n \) and \( \Lambda' \) are quantities of the same kind, if not actually identical, and that they are responsible
for the major part of the anisotropy, then clearly we must expect similar aniso-
tropic behaviour in $R_\infty$ and $\lambda_\infty$. These two quantities are compared in figure 5, the
data being taken from $\Lambda$. The general similarity of the curves encourages the belief
that we have here in principle the explanation of the anisotropy of $\lambda_\infty$, and in
consequence additional evidence of the essential correctness of (7).

![Graph showing $R_\infty$ and $\lambda_\infty$ in pure tin.](image)

**Figure 5.** Anisotropy of $R_\infty$ and $\lambda_\infty$ in pure tin. Both quantities are expressed
in terms of their values when $\theta = 90^\circ$.

(c) **Temperature variation of penetration depth**

So far we have considered only the penetration depth at $0^\circ$ K, but we must now
turn to the temperature variation of $\lambda$, since this raises an important point in the
interpretation of $\Lambda$ and $\xi$. In pure tin (see, for instance, $\Lambda$), for a given orientation,
$\lambda_\infty$ varies with temperature according to the law

$$
\lambda_\infty = \lambda_{\infty,0}(1 - t^4)^{-\frac{1}{4}}, \quad \text{where} \quad t = T/T_c.
$$

Comparison of (18) with (14) shows that $\xi_0\Lambda$ must vary as $(1 - t^4)^{-\frac{1}{4}}$. Thus when
sufficient impurity is added for (13) to apply, the temperature variation of $\lambda$ may
be written

$$
\lambda \propto (1 - t^4)^{-\frac{1}{4}} \xi^{-\frac{1}{4}}.
$$

A study therefore of the temperature variation of $\lambda$ in impure tin can give information
about the dependence of $\xi$ on temperature.

It has already been mentioned that the imperfect Meissner effect in impure tin
makes a determination of the temperature dependence of $\lambda$ difficult, and for this
reason a thorough investigation of this point has not been practicable. A certain
amount of information, however, has been obtained which makes it clear that $\xi$
not independent of temperature. Values of $\delta_i - \lambda$ were determined for each of two
specimens, containing 3% In, at 2·2 and 3·0° K, corresponding to values for $(1 - t^4)$
of 0·866 and 0·527.† If (18) were still applicable to the impure specimens, $\lambda$ would

† A more sensitive test could be obtained by measuring $\lambda$ nearer the transition temperature,
but this is not possible with the present technique, since the measured values are modified
by the high-frequency resistance of the superconductor (Pippard 1950b).
have changed by 29 % of its value at 2-2° K, while if $\xi$ were taken as constant in (19) the change would have been 47 %. These two possibilities are readily distinguishable experimentally, and the actual changes observed were $32 \pm 3$ % for one specimen and $30 \pm 2$ % for the other. Thus it is highly probable that an equation of the type (18) is applicable under all conditions of impurity, and consequently $\xi$ must be taken to vary as $(1-t^4)^{-1}$, in the same way as $\lambda$ itself. The physical reason for the temperature-dependence of $\xi$, which was introduced originally as an analogue of the temperature-independent free path, is obscure; but the dependence seems empirically necessary, and, moreover, such evidence as is available concerning the interphase surface energy supports it, as we shall see later. A similar obscurity will confront us in our consideration of the temperature variation of $\lambda$ in colloidal particles, and it may be that the correct approach to the microscopic theory of superconductivity will clarify both points simultaneously.

Although we must assume $\xi$ to vary with temperature, it is likely that $\xi/\xi_0$ is temperature-independent, since $\xi$ and $\xi_0$ are quantities of the same kind introduced more or less equivalently into the theory. It follows then from the present experimental results and from (13) that $\lambda$ varies as $(1-t^4)^{-1}$, which is the same variation as is required according to the London theory. The present theory, therefore, like the London theory (Daunt, Miller, Pippard & Shoenberg 1948), may be linked to the two-fluid model (Gorter & Casimir 1934) to give a correct account of the temperature variation of the penetration depth.

(d) Field distribution within the superconductor

So far we have confined ourselves to evaluating the penetration depth from the solution of (10) without considering the detailed form of the solution. Unfortunately, the field distribution derived from (10) is awkward to evaluate, but there is a very similar equation for which the computation is relatively simple, and which will serve to illustrate the difference between the present theory and that of London. The anomalous skin effect was treated by Reuter & Sondheimer in two special cases, according as electrons striking the surface were scattered diffusely or reflected specularly. The former appears to accord with experimental findings (Chambers 1952), and has been assumed to apply in the formulation of the present theory, but the latter gives a simpler result when applied to a plane surface; the results for the surface impedance in the two cases are so similar that it is likely the field distributions also are similar. The analogous treatment of a superconductor, assuming specular reflexion, leads to an expression for the vector potential as a function of depth below the surface of the form (cf. Reuter & Sondheimer 1948, equation A.7),

$$f(x) = \int_0^\infty \frac{\cos xt}{t^2 + \beta \kappa(t)} \, dt,$$

in which the symbols have the same meaning as before. The magnetic field, which is proportional to $df/dx$, has been computed as a function of $x$ for the case $\beta = 2000$ (corresponding to $\lambda = 0-0432\xi$). The computation was carried out by expressing $1/(t^2 + \beta \kappa(t))$ as a sum of analytical functions whose Fourier transforms are known, and the resulting curve for $H$ is shown in figure 6, together with an exponential
curve (as given by the London theory) corresponding to the same penetration depth. It will be seen that in the new theory $H$ falls at first rather less rapidly than in the old, and becomes negative at depths greater than about $3.5\lambda$. The magnitude of the negative field is, however, small (at its maximum about 3 % of the field at the surface), and the field becomes very small indeed at depths considerably less than $\xi$. The negative field is an essential part of the behaviour when $\xi \gg \lambda$, since it is only through its influence that the field can fall to a low value in a distance smaller than $\xi$; its existence does not depend upon the special form of (7), but only on the general hypothesis that $J$ depends on some sort of space-average of $A$ over a region large compared with $\lambda$. It is unlikely that any direct experimental demonstration of its existence can be devised.

![Figure 6. Variation of magnetic field with depth. (a) present theory, (b) London theory.](image)

(e) Implications of the theory

When we seek a microscopic interpretation of (7) it is useful to start with a numerical estimate of $\xi_0$, such as is provided by the limiting value of $\lambda_0$ in pure superconductors. In this connexion it is instructive to note that there is no need to suppose that $\Lambda_0$, the value of $\Lambda$ at $0^\circ$ K, in the superconducting state is different from the corresponding $\Lambda_n$ in the normal state, and thus a difficulty inherent in London’s theory is absent here. For example, from (17) and the results of anomalous skin-effect measurements in pure tin (see A), $\Lambda_{0^\circ}^p v'$ for the $90^\circ$ crystal orientation is found to be about $5 \times 10^{-3}$; the Fermi velocity in tin is not known, but is unlikely to be very different from $5 \times 10^7$ cm/s, so that $\Lambda_{n^\prime}$ may be estimated to be about $10^{-10}$. If, in the London theory, $\Lambda_{0^\prime}$ is equated to $\Lambda_{n^\prime}$,

$$\lambda_0 = \sqrt{(\Lambda_{0^\prime}^p / 4\pi)} = 2.8 \times 10^{-6} \text{ cm},$$

i.e. about half the experimental value of $5.3 \times 10^{-6} \text{ cm}$. To obtain agreement it is necessary to assume either that the Fermi velocity has the improbably low value of $1.4 \times 10^7 \text{ cm/s}$, or that $\Lambda_0$ and $\Lambda_n$ are quite different quantities. On the other
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hand, if (14) be taken to give \( \lambda_{\omega 0} \), we may put \( \Lambda_0' \) and \( \Lambda_n' \) equal and obtain agreement with experiment by choosing \( \xi_0 = 7 \times 10^{-5} \) cm at 0\(^\circ\) K.

This value for \( \xi_0 \) is suggestive, for a distance of the order of \( 10^{-4} \) cm enters into the behaviour of superconductors in several ways, of which the one which concerns us here owes its origin to simple quantum considerations. In the theories of Fröhlich (1950) and Bardeen (1951a) and probably in any theory of superconductivity, the transition to superconductivity is associated with an ordering in momentum space of those electrons particularly whose energies lie within \( kT_c \) of the Fermi surface. Thus the moment of the wave functions is rather precisely specified, and correspondingly, by the uncertainty principle, the extension in co-ordinate space must be large; a simple calculation gives \( 10^{-4} \) cm as an approximate lower limit to the dimensions of a single-electron wave function. There may therefore be some justification for interpreting \( \xi_0 \) as this characteristic length, and this impression is strengthened by a deeper inquiry into the fundamental nature of superconductivity.

Following London, we shall assume that the primary manifestation of superconductivity is the Meissner effect, of which perfect conductivity is a corollary, and we shall postulate a model of a superconductor in which the Meissner effect is a thermodynamic necessity. If we suppose that the superconducting state, which without further particularizing we shall refer to as a condensed state of the electrons, is one for which the condensation mechanism is highly sensitive to the presence of an extended magnetic field, then in the presence of an applied field the superconductor has the choice of two types of behaviour. Either it can allow the penetration of the field, which will destroy the condensation, or it can remain condensed and exclude the field by means of surface currents. Which of these alternatives is preferred will depend on whether the free energy of condensation, \( f_a - f_o \), is less or greater than the field energy \( H^2 / 8\pi \). London's model may be interpreted as an extreme example of this model, in which fields less than critical are excluded from all but the penetration layer, and the condensed phase is so rigid as to remain unperturbed even by the field in the penetration layer. Under these conditions (3) applies, and a point–relation obtains between \( \mathbf{J} \) and \( \mathbf{A} \), which is the London equation.

But in order to realize the Meissner effect it is not necessary to postulate perfect rigidity of the condensed state—indeed, it is difficult to see how a state so sensitive to extended fields could remain unperturbed by the field in the penetration layer, and correspondingly there is no reason to suppose that the surface currents produced by the interaction of the magnetic field with the partially rigid structure will be as great as required by London's model. This provides a qualitative explanation of why the penetration depth is greater than would be expected from London's expression for \( \lambda \), and suggests also that the effect of adding impurity is to decrease the rigidity of the condensed phase. We shall leave the latter point to a later stage of the discussion, and consider for the moment only the pure superconductor. The concept of coherence, which is closely allied to the extension of the wave function required by the uncertainty principle, as already discussed, may now be introduced as an argument for regarding the perturbation produced by the fields as im-
perfectly localized. If it were possible to apply a perturbing force at one point only of the condensed phase we should expect the corresponding reaction to be spread over a region at least as large as the dimensions of the wave function. Consequently, if the perturbing force is extended, the reaction at any point will be an integrated effect depending on the magnitude of the perturbing force within a finite region surrounding the point considered. This is perhaps the physical behaviour underlying the integral form of (7); it should be noted that although it bears a superficial similarity to the free-path effect in normal conductors it is in fact a quite different mechanism, so that the precise form of (7) may well be incorrect. There are many different forms which would lead to the same type of behaviour, but the experimental results are not nearly accurate enough to allow a decision to be made between any of the possibilities.

If this picture be taken as the explanation of the general form of (7), it seems reasonable to suppose that in a pure superconductor $\xi$, which determines the effective size of the region of integration, is of the order of magnitude of $\xi_0$ rather than of $l$, which may be 100 times greater. It is for this reason that in our analysis of the experimental results we considered the possibility that $\xi$ tends to $\xi_0$ as $l$ tends to infinity. Perhaps an even more convincing argument may be adduced by employing a device due to Heisenberg (1949), that of treating the velocity of light as a variable. If, as appears probable, the origin of the superconducting state is to be traced to electron interactions with the ionic lattice, then the condensation mechanism is electrical in nature, and not affected by a variation of $c$. On the other hand, the magnetic effects of a current may be decreased indefinitely by an increase of $c$, so that the penetration depth may be regarded as similarly variable. This being so, there is no apparent reason why we should not imagine a circumstance in which $\lambda$ is so much greater than $\xi$ that $\Lambda$ may be treated as constant over a region comparable to $\xi$. Then (6) will apply, in pure as in impure superconductors. We can now see that if $\xi > \xi_0$ the current produced by a given $\Lambda$ will be even greater than in the London theory. While this is not impossible it is highly improbable, since London's theory represents a model of extreme rigidity, and we shall therefore suppose $\xi \geq \xi_0$. It is not obvious from this argument that $\xi = \xi_0$ in a very pure superconductor, but it is perhaps reasonable to make this assumption in the absence of any experimental evidence.

Now the addition of impurity to the superconductor decreases $\xi$ and hence the range over which a perturbation exerts its influence, according to (7), while at the same time, by the arguments of the last paragraph, the local perturbation is greater, since (6) predicts a smaller current as a consequence of the application of a given $\Lambda$. We may refer then to the effect of impurity as softening the condensed state so far as its resistance to a magnetic field is concerned by shortening the range of coherence of the wave functions. It appears strange at first that the properties of the wave function may be modified by the addition of impurity without altering the condensation energy, but this is probably a very similar phenomenon to that discussed by Bardeen (1951b), who has shown that there is nothing unreasonable in the experimental observation (e.g. Shoenberg 1940) that the transition temperature, and hence condensation energy, of particles much smaller than $\xi_0$ is the
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same as for the bulk material, although the wave function necessarily takes a different form.

The concept of a coherence range of the order of $10^{-4}$ cm, possibly shortened by the addition of impurity, may be used to provide a qualitative picture of the origin of the interphase surface energy, $\alpha_{\text{ns}}$ (Pippard 1951a). It is likely that the surface energy arises because the interface between a normal and a superconducting region is not a geometrically sharp boundary, but is spread over a region about $10^{-4}$ cm thick; the magnitude of the surface energy, which may conveniently be written as $\Delta \times H_c^2/8\pi$ ($H_c$ being the critical field), is then obtained by expressing $\Delta$ as the difference between a quantity of the order of magnitude of the thickness of the boundary and the effective penetration depth of a magnetic field in the boundary region. If we regard the thickness of the boundary in pure superconductors as closely related to $\xi_0$, we should expect $\Delta$ to vary with temperature in the same way as $\lambda$, since we have found $\xi_0$ and $\lambda$ to have the same temperature variation. This prediction accords fairly well with experiment (Désirant & Shoenberg 1948; Faber 1952). Moreover, when the range of coherence is reduced by the addition of impurity, it is to be expected that the thickness of the boundary will be governed by $\xi$, and in particular for very impure superconductors, in which $\xi < \lambda$, $\Delta$ may become negative. This expectation appears to be justified, since the peculiarities of magnetic behaviour in alloys—imperfect Meissner effect, absence of supercooling, spread out magnetic transitions—are all symptomatic of a negative interphase surface energy.

Further evidence of a coherence range of the order of $10^{-4}$ cm, which is decreased by the addition of impurity, comes from the variation of the penetration depth on application of a field less than critical. In pure tin (Pippard 1950c) the change is small, and is consistent with the hypothesis that the shift in equilibrium produced by the field is distributed over a depth at least as great as $10^{-4}$ cm. In impure tin preliminary results (Pippard 1951b) show that the change in $\lambda$ is greater for a given field, and this implies that the distribution of the shift in equilibrium is over a smaller depth. At present the data are not sufficient, nor has the necessary theory been developed, to allow a quantitative interpretation of these results, but at any rate they do not seem to be at variance with the present theory.

To sum up the preceding discussion, there is evidence from several sources that a parameter having the dimensions of length, and of order $10^{-4}$ cm, must be introduced into the theory of superconductivity. From surface-energy considerations this parameter, the range of coherence, is expected to vary with temperature in a similar manner to the penetration depth. Its function in the theory is to measure the distance over which the effects of a perturbing force are appreciable, and hence it is natural to expect it to enter into the equation defining the supercurrent. Its introduction in the form of equation (7), combined with the hypothesis that the addition of impurity decreases the range of coherence, leads to an explanation of the magnitude of the penetration depth, its variation with impurity content, and its anisotropy in the pure metal.

At this point it must be mentioned that a detailed discussion of the interphase surface energy and the variation of penetration depth with field has been given
by Ginsburg & Landau (1950), from a rather different standpoint. Instead of regarding the range of coherence as a lower limit to the distance within which a significant change of electronic structure can take place, they prefer to suppose that any rate of change is in principle possible, but that additional energy is required, similar in nature to zero-point energy, which makes rapid changes energetically unfavourable. It is quite possible, as Bardeen has pointed out (private communication), that there is no real conflict between these points of view. It should be noted, however, that if the supercurrent is given by an equation of the type of (7), rather than by London’s equation, the numerical calculations of Ginsburg & Landau may be in error. For in estimating the magnitude of the additional energy they supposed that $\Lambda$ was related to the penetration depth by London’s relation, $\Lambda = 4\pi\lambda^2$, so that their value of $n/m$ for the superconducting electrons may differ by a factor 4 from the true value. No attempt will be made here to modify the theory of Ginsburg & Landau in the light of (7), since the abandonment of the London picture leads to considerable fundamental difficulties in formulating the theory.

To conclude we shall touch briefly on two points arising from the theory. The first is a difficulty which is apparent when (7) is applied to very small particles, such as the mercury colloids studied by Shoenberg (1940). A strict application of the equation leads, as may be seen with little trouble, to a predicted temperature variation of the effective value of $\lambda$ for these particles as $(1 - t^4)^{-\frac{5}{2}}$, while according to Shoenberg’s results, $\lambda$ varies as $(1 - t^4)^{-\frac{1}{2}}$ (Daunt et al. 1948). It is possible to make an ad hoc modification of the theory by assuming that in small particles $\xi_0$ becomes dependent on the size of the particle, eventually, in the smallest particles, being proportional to the radius and independent of temperature. Other changes are possible which yield the same result, but we do not propose to discuss the justification of modifying the equation, since we cannot produce any convincing argument to compel or to preclude any such procedure.

The second point concerns the magnitude of $\lambda_0$ in different pure metals. The uncertainty principle argument by which we introduced $\xi_0$ as a fundamental parameter suggests that it should vary in the opposite sense to the critical temperature $T_c$, since those metals for which $T_c$ is high have a greater range for condensation in momentum space. Correspondingly, from (14), the penetration depth at 0° K should vary in the opposite sense to $T_c$, though the rate of variation may be quite slow. An exact correlation is not to be expected, since $\Lambda_0$ takes different values for different metals, but it is interesting that Lock (1951) has noted a tendency of this sort in lead, tin and indium. It remains for experiments to be performed on metals of low transition temperature to decide whether this prediction is really justified.

I am glad to express my indebtedness to Dr D. Shoenberg for his continued interest in this work, and to him as well as to Professors J. Bardeen, F. London and L. Onsager and Drs R. G. Chambers and E. H. Sondheimer for many valuable discussions. My thanks are also due to Mr F. Sadler and Mr W. A. R. Whitmore for help in the design and construction of apparatus.
Appendix

The high-frequency properties of a metal surface are determined by the surface impedance $Z (= R + iX)$. In the present experiments the value of $R$ for the normal metal is directly measured, but it is $\delta_\parallel (= X/4\pi\omega)$ which is needed to evaluate the penetration depth; thus a knowledge of the ratio $X/R$ is required. According to the classical theory of the skin effect $X/R = 1$, but when the mean free path $I$ of the electrons becomes comparable with or greater than the skin depth, $X/R$ increases and becomes dependent upon $I$. Reuter & Sondheimer (1948) have calculated $R$ and $X$ as functions of $I$ for an isotropic free electron gas, and from their results $X/R$ may be tabulated as a function of $R/R_\infty$, where $R_\infty$ is the limiting value of $R$ as $I$ tends to infinity; the value of $R_\infty$ is determined by the quantity $n/mv$, in which $n$ is the number of conduction electrons per unit volume, $m$ is the effective mass and $v$ the Fermi velocity.

If tin were isotropic it would probably be quite safe to rely on Reuter & Sondheimer’s results for calculating $X/R$ from $R$, since Chambers (1952) has shown that the variation of $R$ with $I$ for several metals follows the theoretical curve very closely. Unfortunately, however, the measurements in single crystals presented in A show that tin is highly anisotropic; it appears that there are larger concentrations of electrons moving parallel and perpendicular to the tetrad axis, and smaller concentrations at intermediate angles. This anisotropy may be seen to affect the dependence of $X/R$ on $R$. For the value of $R$ is determined not by the average value of $n/mv$ taken over the whole Fermi surface, but by an average which is weighted in proportion to the effective contributions of different groups of electrons to the current. Thus when $I$ is short all the electrons contribute, but when $I$ is very long almost all the current is carried by those electrons which are moving nearly parallel to the surface. Consequently in an anisotropic metal we may expect the effective value of $n/mv$, and hence of $R_\infty$, to depend to some extent on $I$. In the absence of detailed knowledge of the Fermi surface and of any theory of the anomalous skin effect in anisotropic metals no rigorous treatment of this problem is possible, and the evaluation of $X/R$ and $\delta_\parallel$ has necessarily depended upon approximate methods whose accuracy is hard to judge.

The method adopted has been to estimate from experimental results the effective value of $R_\infty$ for two specimens of tin, both having the tetrad axis normal to the axis of the specimen, but with widely different impurity contents, and to interpolate between these values by means of a reasonable smooth curve. At one extreme, when $I < \delta$, the effective value of $\Sigma_\infty (= 1/R_\infty)$ has been taken as 178 ohm$^{-1}$, the average over all orientations of the crystal axis relative to the surface (see A). For the other extreme a specimen containing 0·05 % In was chosen, for which $I$ could be calculated with sufficient accuracy from the residual resistance. This specimen was found to have a value of $R$ consistent with $\Sigma_\infty$ equal to 199 ohm$^{-1}$. In figure 7 curves for $X/R$ are shown as functions of $\Sigma (= 1/R)$ for these two values of $\Sigma_\infty$, the values being taken from Reuter & Sondheimer’s results. For specimens containing more than 0·05 % In the effective value of $\Sigma_\infty$ presumably lies between these extremes, and a suggested interpolation curve is drawn in figure 7 from
which $X/R$ may be read off for any value of $\Sigma$. The interpolation curve lies half-way between the two extreme curves at a value of $\Sigma$ at which $l$ is two or three times the skin depth; it is reckoned that about here the change-over occurs between the state of affairs ($l \ll \delta$) in which all electrons contribute more or less equally and that ($l \gg \delta$) in which there is a dominant contribution from electrons moving nearly parallel to the surface.

![Graph](image)

**Figure 7.** Variation of $X/R$ with $\Sigma$. (a) theoretical for $\Sigma_\infty = 178$ ohm$^{-1}$; (b) theoretical for $\Sigma_\infty = 199$ ohm$^{-1}$; (c) assumed interpolation curve.

No attempt has been made to treat specimens of tin containing less than 0.05% In, since for pure tin crystals with the tetrad axis normal to the specimen axis the value of $X/R$ is greater than $\sqrt{3}$, the limiting value according to Reuter & Sondheimer (see A). The origin of this high value of $X/R$ is not understood, but there is some scanty evidence that it arises only in very pure tin, and it may be associated with the fact that $\sigma$ is comparable with unity in pure tin at the frequency used, although in an isotropic metal, according to Reuter & Sondheimer, relaxation effects are not to be expected until much higher frequencies. Whatever the reason for this behaviour, however, the method adopted for determining $X/R$ is inapplicable in the purest specimens, for which absolute values of $\delta_i$ cannot be determined by the present method.

In addition to $X/R$, the value of $l$ is also needed in the analysis of the experimental results, and this too can be obtained from $R$, since according to Reuter and Sondheimer the value of $\Sigma/\Sigma_\infty$ is determined by $l$. A similar interpolation is required for $\Sigma/\Sigma_\infty$ as for $X/R$, and this is shown in figure 8, in which the assumed value of $\Sigma_\infty$ is plotted against $\Sigma$. The fixed points on this curve, as before, correspond to values
for $\Sigma_{\infty}$ of 178 ohm$^{-1}$ for very impure tin and 199 ohm$^{-1}$ for tin containing 0.05% In, for which $\Sigma$ was found to be 179 ohm$^{-1}$. The curve has been drawn so that $\Sigma_{\infty}$ is changing most rapidly when $l$ is two or three times $\delta$. The exact form of the curve is particularly unreliable at the higher values of $\Sigma$, since it is here that the peculiar behaviour of pure tin shows itself, but fortunately the values obtained for $l$ in the less pure specimens are not very sensitive to the particular form chosen.

Similar problems arise in the analysis of the results on the angular dependence of $\lambda$ in tin containing 3% In, since it is not possible to assume, even in such impure specimens, that $X/R$ (which is about 1.04 according to the free-electron theory), is independent of the orientation of the tetrad axis. Very rough calculations, based on simplified models, suggest that $(X/R - 1)$ may be greater at intermediate orientations than at those in which the tetrad axis is parallel or perpendicular to the axis of the specimen, perhaps by as much as 20%. A correction of this magnitude has been applied to the values of $X/R$ estimated in the way already described. This correction alters the estimated values of $X/R$, and hence of $\delta$, only to the extent of 1% at most, but since in the impure specimens $\delta_i \sim 5\lambda_0$ the effect of the correction on $\lambda_0$ may be as much as 5%.

![Figure 8. Assumed variation of $\Sigma_{\infty}$ with $\Sigma$.](image)

A further correction to the experimental results on specimens of different orientations is needed to allow for small variations in the indium content of different specimens. Measurement of $R$ enables the residual d.c. resistance of the specimen to be calculated, and to be compared with the value expected for a standard impurity content. An appropriate correction may then be applied to the measured value of $\lambda$, to obtain the value of $\lambda$ in a specimen containing the standard amount of impurity; the correction needed was never more than a small percentage. In order to apply this correction it is necessary to know the anisotropy of the residual resistance of tin containing 3% In. Measurements at 4°K on
a single crystal plate (carried out with the help of Mr T. E. Faber) showed that the ratio of the residual resistivities parallel and perpendicular to the tetrad axis is $1.14$; this is much less than the resistivity ratio in pure tin at room temperature, which is $1.44$.

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