REVIEWS OF MODERN PHYSICS

VOLUME 7 | OCTOBER, 1935 | NUMBER 4

Superconductivity

H. GRAYSON SMITH AND J. O. WILHELM, *The McLennan Laboratory, University of Toronto*

TABLE OF CONTENTS

Part I. Experimental

THE phenomenon of superconductivity is perhaps one of the most interesting, and certainly one of the most puzzling, of the properties of matter at extremely low temperatures, such as are attained only with the aid of liquid helium. Since the original discovery by Onnes in 1911, it has been the subject of a great number of experiments, first and mainly at Leiden, then at Toronto where a cryogenic laboratory has been operated since 1924, and recently also in other laboratories. Many theoretical physicists have attempted to find an explanation for the phenomenon, until recently with very little success, and from the theoretical point of view the problem is still far from an adequate solution.

It is not intended in the present review to give more than a brief outline of the earlier experiments and theories, which have been thoroughly discussed elsewhere. However, several important advances, both experimental and theoretical, have been made within the last two or three years. A discussion of these will form the main part of the present work, which is therefore to some extent a continuation of the monograph, *Superconductivity*, by E. F. Burton and others.[1]

1. The Phenomenon of Superconductivity

Fig. 1 shows typical curves between resistance and temperature for reasonably pure elements. At high temperatures the resistance is approximately proportional to the absolute temperature T. At very low temperatures it may be taken to be of the form $\rho = \rho_0 + Af(T)$ where ρ_0 is the resistivity extrapolated to 0°K, designated as the "residual resistance." According to Bloch's[2] wave-mechanical theory of metallic conduction the temperature-dependent portion is of the form AT^5 at sufficiently low temperatures, and is due to thermal vibrations of the perfect metallic lattice. The constant residual resistance ρ_0 is due to irregularities and foreign atoms in the lattice. This last contention is supported by the fact that ρ_0 is increased by further admixture of an impurity, and may become an important part of the total resistance at ordinary temperatures in the case of a mixed crystal alloy.

For certain metals the curve follows the normal course down to a definite low temperature, and then the resistance falls rapidly to an immeasurably small value, as shown in Fig. 2, which is reproduced from Onnes' original curve for mercury.[3] Such metals are known as superconductors, and are said to be in the superconducting state when the temperature is sufficiently low that the resistance is zero. The transition point is usually taken to be the temperature at the point A, where the resistance commences to fall, al-

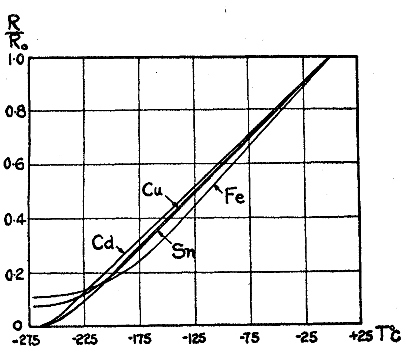


FIG. 1. Change of resistance with temperature.

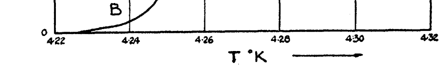


FIG. 2. Onnes' curve for mercury.

[1] E. F. Burton, *Superconductivity* (Univ. Toronto Press, 1934). W. Meissner, Ergeb. der exakt. Naturwiss. **11**, 218 (1932).

[2] R. Peierls, Ergeb. der exakt. Naturwiss. **11**, 264 (1932); J. C. Slater, Rev. Mod. Phys. **6**, 209 (1934).

[3] H. Kammerlingh-Onnes, Proc. Roy. Soc. Amsterdam **27**, 75 (1911); Leiden Comm. 142a.

though some writers have preferred to give the temperature at which the resistance becomes one-half of its normal value. The transition interval AB is usually a few hundredths of a degree for a pure element, but may be considerably larger in the case of an alloy. In the literature on superconductivity the term "residual resistance" has been used to designate the resistance just above the point A on the resistance curve. In the present paper this term will be retained, and when necessary the extrapolated resistance at 0°K will be referred to as the resistance due to irregularities.

The transition curves of superconductors have usually been studied by a potentiometer method, in which a known steady current is passed through the specimen, and the fall of potential across it is measured. The metal is assumed to be in the superconducting state when this potential difference becomes too small to measure. In Onnes' original experiment he was able to state that, whereas the residual resistance at 4.3°K was 0.084 ohm, at 3°K it was less than 3.10^{-6} ohm. The question immediately arises whether the metal in the superconducting state is entirely devoid of resistance, or whether there still remains a very small amount. In order to test this point Onnes and Tuyn[4] performed their famous experiment of setting up a persistent current in a superconducting ring of lead. The lead ring was cooled through its transition point (7.2°K) in the presence of an external magnetic field, and the field was then removed, setting up an induced current in the ring. The strength of the current was measured at intervals by observing its effect upon an external magnetometer, but no evidence of diminution of the current strength could be obtained. From the sensitivity of the magnetometer, Onnes concluded that the resistance of the ring must be less than 10^{-12} ohm. Many repetitions of this experiment have never disclosed any measurable decay of the persistent current as long as the entire circuit can be maintained at a temperature below its transition point. Consequently it may be concluded that the superconducting state is characterized by complete absence of electrical resistance.

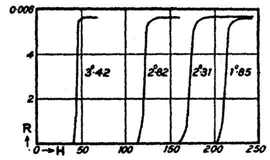


FIG. 3. Dependence of resistance on magnetic field.

In the search for other factors which might affect the superconducting property of a metal, or for other effects accompanying superconductivity, it was first found by Onnes and Tuyn[5] that the resistance could be restored by subjecting the specimen to an external magnetic field. The form of the curve between magnetic field and resistance, for a gradually increasing field strength, is similar to that between resistance and temperature, showing a similar rapid, but not immediate, transition (Fig. 3). The "threshold magnetic field" H_t is taken to be the magnetic field at which the resistance is restored to one-half of its normal value. As would be expected, it is a function of the temperature.

The only other properties of the metal which have been definitely shown to be affected by the transition to the superconducting state are the specific heat, the thermal conductivity, and the thermoelectric properties. Finite changes in the specific heat of tin, and in the thermal conductivity of indium, have been observed to accompany the transition. For other superconductors which have been studied the changes in these properties are limited to changes in slope of the temperature curves of the properties in question. However, distinct differences are found in all cases between the specific heat and thermal conductivity of a metal when it is allowed to become superconducting, and those of the same metal when superconductivity is prevented by placing it in a magnetic field. There is no discontinuity in heat content, analogous to a latent heat. These properties will be discussed in detail below.

It is not yet surely established that there is no change in crystal structure,[6] although any

[4] H. Kammerlingh-Onnes and W. Tuyn, Leiden Comm., **198** (1929); Supp. 50a (1924).

[5] H. Kammerlingh-Onnes and W. Tuyn, Leiden Comm. 174a (1925).

[6] W. H. Keesom, Int. Congress of Refrigeration **7**, 125 (1924).

such change must be of a secondary nature since there is no change in volume. There is no evidence of any abrupt change in the coefficient of thermal expansion.[7] There is no change in the photoelectric effect,[8] from which it may be concluded that there is no change in the surface work function. Other properties which have been found to be unchanged are the absorption of β-particles[9] and slow electrons,[10] and the torsion constant.[11]

From all this it may be concluded that the transition to the superconducting state is one which affects only the conduction electrons in the interior of the metal, and that changes in the metallic lattice are entirely secondary if they exist at all.

2. The Superconducting Metals

a. Elements

Among the pure elements, those given in Table I have to date been shown to become superconducting. Most of these have been known for some time, as all but some of the rarest of the metallic elements have been explored down to about 1°K. However, improvements in technique have now made it possible to attain a temperature of 0.71°K by the evaporation of helium at low pressure. The temperature can then be still further reduced by the method of adiabatic demagnetization of a paramagnetic salt, as suggested by Debye and Giauque. Using this method de Haas has recently attained a temperature (calculated) of 0.0044°K. The latter method has been applied on a sufficiently large scale to test a sample of metal down to about 0.3°K, but so far only a very few elements have been tried. The following elements are not superconducting at about 0.75°K: Cu, Ag, Au, Bi, W, Fe, Ni, Pt, Sn(gray).

TABLE I. *Superconducting elements.*

Element	Transition Point	Element	Transition Point
Mg	0.70°K	Ti	1.75°K
Zn	0.78	Th	1.5
Cd	c. 0.6	Sn*	3.71
Hg	4.22	Pb	7.2
Al	1.14	V	4.3
Ga	1.05	Nb	9.2
In	3.37	Ta	4.4
Tl	2.37		

* Tetragonal (white) tin only.

b. Alloys and compounds

In addition to the elements given in Table I, a large number of alloys and compounds are superconductors. A detailed discussion of these is beyond the scope of the present work, and must be seen in the original papers. The superconducting binary alloys may be divided into four groups:

(*i*) *Alloys of two superconductors.* These are apparently always superconducting, the transition point being a continuous function of the composition, and in some cases being considerably higher than the transition points of either of the components. The transition range is always very much wider than for a pure metal, and may become several degrees in the case of a mixed crystal. The transition point usually, and the transition range always, show sharp minima at the eutectic.

(*ii*) *Alloys of a superconductor with a nonsuperconductor.* Alloys of this type which contain free atoms of the superconducting component are superconducting, usually with only a slight change in transition point until the percentage of free superconductor becomes small. The transition range is usually a few tenths of a degree.

TABLE II. *Superconducting alloys and compounds.*

Alloy	Transition Point	Alloy	Transition Point
Bi_6Tl_3	6.5°K	TiN	1.4°K
Sb_2Tl_7	5.5	TiC	1.1
Na_2Pb_5	7.2	TaC	9.2
Hg_5Tl_7	3.8	NbC	10.1
Au_2Bi	1.84	ZrB	2.82
CuS	1.6	TaSi	4.2
VN	1.3	PbS	4.1
WC	2.8	Pb-As alloy	8.4
W_2C	2.05	Pb-Sn-Bi	8.5
MoC	7.7	Pb-As-Bi	9.0
Mo_2C	2.4	Pb-Bi-Sb	8.9

[7] J. C. McLennan, J. F. Allen and J. O. Wilhelm, Trans. Roy. Soc. Canada, **25**/III, 1 (1931).

[8] J. C. McLennan, J. H. McLeod and R. G. Hunter, Trans. Roy. Soc. Canada, **24**/III, 1 (1930).

[9] J. C. McLennan, J. H. McLeod, and J. O. Wilhelm, Trans. Roy. Soc. Canada, **23**/III, 269 (1929).

[10] W. Meissner and K. Steiner, Zeits. f. Physik **76**, 201 (1932).

[11] W. J. de Haas and M. Kinoshita, Leiden Comm. 187b (1927).

The eutectic may or may not be superconducting. In the latter case its transition point may be higher or lower than that of the pure superconductor, and the behavior with change of composition is similar to that of an alloy of two superconductors.

(*iii*) *Alloys of non-superconductors.* Only one case of this group has been found, the intermetallic compound Au_2Bi. The relation between transition point and composition has not been studied, but it may be presumed that it will act like an alloy with one superconducting component up to a considerable percentage on either side of the eutectic.

(*iv*) *Compounds with a nonmetallic element.* A number of carbides, nitrides, etc., both of superconductors and of non-superconductors, have been found to become superconducting. In this group the compound NbC has the highest transition point yet observed, 10.1°K.

Table II gives the transition points for some of the superconducting eutectics and compounds. A few lead alloys are also included, which are interesting on account of their high transition points.

c. Perfection of the crystal

Closely connected from the theoretical point of view with the effect on a superconducting element of the presence of foreign atoms is the effect of crystalline perfection of the sample. Fig. 4 shows results obtained by de Haas and Voogd[12] with different samples of very pure tin. The curve marked △ is for a single crystal, that marked O for a polycrystalline sample containing many large grains, and that marked □ for an ordinary polycrystalline wire. In the cases both of crystalline imperfection, and of admixture of foreign impurity, the primary effect seems to be a widening of the transition range. In the experiments of de Haas and Voogd this means a raising of the temperature at which the fall of resistance commences, while the temperature of complete superconductivity is practically unaltered. Steiner and Grassmann[13] have

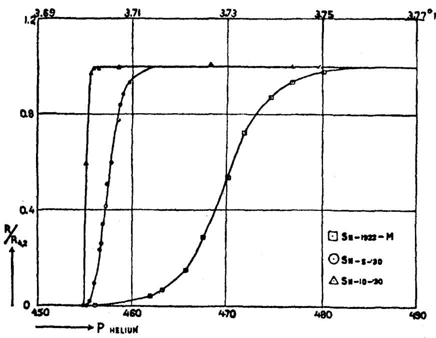


FIG. 4. Transition curves for monocrystalline and polycrystalline tin.

also compared small-grained polycrystals of tin of varying grain size, and have found in this case that the transition is uniformly shifted to slightly higher temperatures for the smaller grains. These authors conclude further from their experiments that effects of previous history of the sample, mechanical working, etc., are primarily due to changes in grain size. Although the effects of small quantities of impurities, grain size, etc., are not large in the case of a superconducting element, it may be stated as a general rule that they become much more important for a eutectic compound.

Onnes and Sizoo[14] have investigated the effects of mechanical tension and hydrostatic pressure on the transition points of tin and indium. Tension was found to raise the transition slightly, while compression lowered it.

d. Superconducting contacts

Two observations by Onnes,[15] which are allied to the question of superconductivity in a mixed crystal, should be noted here. It was shown, and the fact has been widely applied, that two different superconductors could be soldered with any Pb-Sn solder, and the contact would also be superconducting below the transition point of the lowest metal concerned. Still further, it was found possible to set up a persistent current in a

[12] W. J. de Haas and J. Voogd, Leiden Comm. 214c (1931).

[13] K. Steiner and P. Grassmann, Physik. Zeits. **36**, 516 (1935); **36**, 519 (1935).

[14] H. Kammerlingh-Onnes and G. J. Sizoo, Leiden Comm. 180b (1925).

[15] H. Kammerlingh-Onnes, Leiden Comm. 141b (1914).

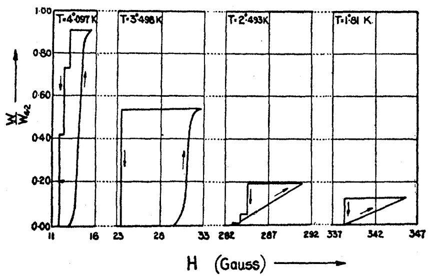


FIG. 5. Magnetic hysteresis in mercury.

circuit consisting of an open lead ring when the cut in the ring was temporarily closed by a tightly pressed lead plug. The ends of the cut were connected to an external ballistic galvanometer. Then after the current had been set up, the plug was withdrawn, and a momentary current passed through the galvanometer, showing that at least some of the current had been flowing around the circuit through the lead plug.

3. Interruption of Superconductivity by a Magnetic Field

a. The magnetic threshold field

As already mentioned in §1, when a metal is in the superconducting state, its resistance can be restored to the normal value by means of an external magnetic field (see Fig. 3). When observed with increasing magnetic fields, the magnetic transition from the superconducting to the normal state takes place over a definitely reproducible range of field strength. However, the phenomenon is accompanied by more or less hysteresis (compare §4h). On decreasing the magnetic field again, the normal resistance persists to a field strength somewhat smaller than the critical value, and then disappears either suddenly, or in discontinuous steps (Fig. 5). For this reason the "threshold field" is defined as the field strength at which one-half of the normal resistance is restored, using a slowly increasing field.

With the above definition, the threshold field is a definite function of the temperature for any superconductor (Fig. 6). In the first experiments of Onnes and Tuyn[16] the experimental curve between threshold field H_t and temperature T agreed well with a law of the form

$$H_t = a(T_0^2 - T^2),$$

where T_0 is the normal transition point in the absence of a magnetic field. This law has frequently been quoted as the general empirical law of the threshold field. However, as will be seen from Fig. 6, the curves for lead and tin are almost linear. It appears more probable that no general law of this form can be given.

Concerning alloys we note here only that the threshold fields are in general very much larger than for the pure metals, a point which will be discussed in §10.

b. Direction of field

In the ordinary experiments, with polycrystalline wires, the threshold field strength has been found to be independent of the direction of the field with respect to the wire. However, de Haas and Voogd[17] have observed a dependence on the

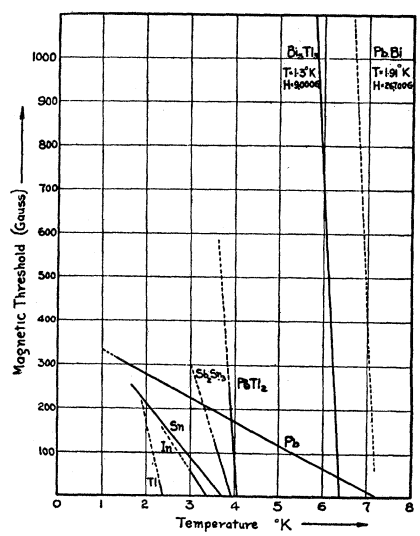


FIG. 6. Magnetic threshold fields for superconductors.

[16] H. Kammerlingh-Onnes and W. Tuyn, Leiden Comm. 174a (1925).

[17] W. J. de Haas, J. Voogd and J. M. Jonker, Physica 1, 281 (1934); Leiden Comm. 229c.

direction of the field in the case of a single crystal of tin. In this case the magnetic transition is the same as that usually observed for polycrystalline tin wires only when the field is parallel to the wire. For a transverse magnetic field, the resistance commences to return gradually for field strengths only about half the usual threshold field. Normal resistance is restored at about the same point in both cases. They have also performed some experiments with single crystal wires of elliptic cross section, and have found that the transverse threshold field then depends on the orientation of the field with respect to the axes of the ellipse.

c. Maximum superconduction current, Silsbee's hypothesis

Onnes discovered that the transition point of a superconductor was lowered when the current used to measure the resistance was increased. Subsequently he showed that a given superconducting wire at a given temperature could carry only a definite current (several hundred amperes in some of the experiments) without the reappearance of resistance, and the consequent generation of heat. That is, there is a threshold current strength analogous to the threshold magnetic field.

Silsbee suggested[18] that the interruption of superconductivity by large current strengths was due to the magnetic field produced by the current itself. According to this conception the maximum superconduction current I_t which can be carried without the generation of heat by a wire of radius r at a temperature T is related to the threshold magnetic field at that temperature by the equation $H_t = 2I_t/r$. This was found to be in good numerical agreement with the results of Onnes and with later experience in general. It can probably be accepted as valid for solid wires of most pure, or nearly pure, superconducting elements. Exceptions have, however, been observed where superconductivity is interrupted by smaller currents, in alloys (§10c), and in thin films (§9d).

[18] F. B. Silsbee, J. Wash. Acad. Sci. **6**, 597 (1916); Bur. Stand. Sci. Paper, No. 307, 1917; No. 556, 1927.

4. Distribution of Magnetic Field Around a Superconductor

a. Diamagnetism of the superconducting state

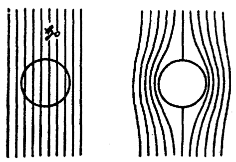
One of the most important experimental developments of the last three years has concerned the opposite effect to that of §3, the effect of a superconductor upon the distribution of an external magnetic field. A very simple corollary of Maxwell's law of induction

$$\text{curl}\,\boldsymbol{E} = -\frac{1}{c}\frac{d\boldsymbol{B}}{dt} = -\frac{\mu}{c}\frac{d\boldsymbol{H}}{dt}$$

first noticed by Maxwell himself, and discussed in connection with superconductivity by Lorentz,[19] is that the normal component of magnetic induction $\boldsymbol{B}$ must vanish at the boundary of a perfect conductor. For the tangential component of the electric field $\boldsymbol{E}$ must vanish, and so the normal component of curl $\boldsymbol{E}$. It follows from this in general that a magnetic field cannot penetrate a superconductor, but that due to any change in the external magnetic field, induced currents will be set up in the surface layers so that the normal component of induction remains zero. Or, if a magnetic field previously existed within the body, it cannot be altered by any change in the external field. Obviously this applies to a superconducting metal only as long as the external field is less than the threshold field. An alternative statement, useful in the discussion of experimental results, is that a superconducting body acts as if it had an effective magnetic permeability $\mu = 0$, that is, acts as a "perfect diamagnetic."

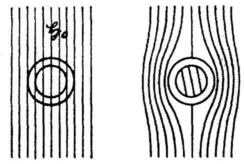
The effect of this on the distribution of magnetic field was applied by von Laue[20] in an attempt to explain the results of de Haas and Voogd on the magnetic interruption of superconductivity in transverse fields (§3b). In this experiment, when the magnetic field is parallel to the wire, the normal component is already zero, and the distribution of field is practically unaffected. However, with a transverse magnetic field, the problem is effectively that of a cylinder with magnetic permeability $\mu = 0$, and

[19] H. A. Lorentz, Leiden Comm., Supp. 50b (1924).
[20] M. von Laue, Physik. Zeits. **33**, 793 (1932).



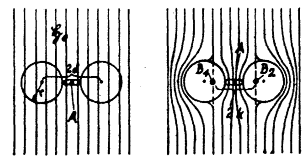
a b

FIG. 7. Cylinder in a magnetic field. (a) Normal. (b) Superconducting.



a b

FIG. 8. Hollow cylinder. (a) Normal. (b) Superconducting.



a b

FIG. 9. Parallel cylinders. (a) Normal. (b) Superconducting.

the distribution of field becomes that illustrated in Fig. 7b. At a point on the surface of the wire the magnetic field is tangential and is given by

$$H = 2H_0 \sin \theta,$$

where H_0 is the applied field at a distance. Superconductivity would then begin to be interrupted along the sides of the wire as soon as $H_0 = \frac{1}{2}H_t$ where H_t is the threshold field. According to de Haas and Voogd, the resistance actually began to reappear when the applied field was a little more than $\frac{1}{2}H_t$.

This explanation cannot be considered as entirely satisfactory in the particular case to which it has been applied, for one cannot understand why it should apply only to the case of a single crystal. In fact one would expect that even when the magnetic field starts to penetrate the body at the sides there would still remain a cylinder of elliptical cross section where the magnetic field is less than H_t. The observed resistance would remain zero as long as any such cylinder still existed, and actually there should be no difference between the longitudinal and transverse cases under the conditions of the ordinary experiment on the threshold field.

However, this discussion served to draw attention to the diamagnetic properties of superconductors. It may now be considered as definitely established experimentally that when a body is actually in the superconducting state it acts towards any change in a small magnetic field as if its magnetic permeability were zero, or as a diamagnetic substance with susceptibility $-\chi = 1/4\pi$. It is unnecessary to discuss in detail the many confirmations of this statement, as most of them have been incidental to the experiments to be considered below.

It would be expected that a superconductor would act as a perfect diamagnetic as long as the magnetic field at the surface nowhere exceeds the threshold field H_t. For larger fields the superconducting state is destroyed, and, since none of the ferromagnetic metals are known to be superconductors, the permeability may be taken equal to unity. This is true at least for the superconducting elements, Pb, Sn and Hg when fairly pure, and is probably true for most of the pure metals. It is not the case for certain alloys, or for tantalum, which have been shown to depart from the ideal perfect diamagnetism under magnetic fields very much smaller than the threshold field. We shall designate as a "normal superconductor" one for which the limiting field in the present sense coincides with the threshold field for the reappearance of resistance.

b. The Meissner effect

A clear distinction must be drawn between the diamagnetic properties described above, where the body remains throughout in the superconducting state, and those diamagnetic effects which appear when a metal passes from the normal to the superconducting state in the presence of an external field. The latter case may occur either:

(A) when the body is cooled through its transition point in a steady magnetic field (as in the original experiments on persistent currents); or

(B) when the temperature is kept constant and the field strength is reduced from a value greater than the threshold field.

Since the deduction of the diamagnetic effect from Maxwell's equations applies only to changes in the magnetic field we should expect, as shown by Lorentz:[19]

In case A: No change in the distribution of magnetic field.

In case B: The effect of superposing on a uniform field H_t an opposing field equal to $-H_t$ at a great distance, but distributed about the body as if the latter were a perfect diamagnetic. The body ought to become permanently magnetized, with a magnetic moment equal to that acquired by a perfect diamagnetic in a field $-H_t$.

The simple form of the Meissner effect is shown in case A, in a spontaneous readjustment of the magnetic field distribution. This diamagnetic effect, therefore, cannot be due to electromagnetic induction of surface currents, but must be the result of some characteristic property of the superconducting metal.

c. Redistribution of external field

In the first experiment performed by Meissner and Ochsenfeld[21] a cylindrical single crystal of tin, 10 mm in diameter and 130 mm in length, was placed in a uniform magnetic field with its axis perpendicular to the field, and was then cooled through its transition point. The field in the superconducting state was explored by means of a test coil 1.5 mm in breadth and 10 mm in length, connected to a ballistic galvanometer. The test coil was arranged so that it could be moved into various positions around the tin cylinder, and could be rotated about its own axis, without opening the cryostat.

In the superconducting state the magnetic field was found to be distributed as shown in Fig. 7(b), corresponding approximately, but not with exact numerical agreement, with the field distribution calculated on the assumption of a cylinder with permeability zero. There was no subsequent change in this field over a period of 2 hours. Further the field distribution was unaltered by rotating the tin cylinder, whose crystallographic axis made an angle of about 65° with the cylindrical axis.

In the second experiment a hole 6 mm in diameter was bored through the tin cylinder, and the field explored inside this hole as well. The remarkable fact was then observed that, while the field outside the cylinder was altered as before, that inside remained nearly constant, as illustrated in Fig. 8(b). By actual measurement, there was a slight change of direction (exaggerated in Fig. 8), and an increase in the average field strength of about 10 percent which was most pronounced near the inner boundary. The magnet was then removed, and the external field disappeared, while the internal field dropped to about 40 percent of the original strength. This residual internal field then remained constant as long as the cylinder was kept below its transition point. If the external field was once more applied, it again took the distribution shown in Fig. 8(b) outside the cylinder, but the residual field inside was only very slightly increased. Since the internal behavior might be expected to depend on whether the outside or inside surface first became superconducting, the experiment was repeated with the outer surface insulated so that the cooling proceeded from the center outwards. The results were exactly the same as before.

In a third experiment two parallel cylinders of monocrystalline tin were used, with the results illustrated in Fig. 9. The calculated flux through the test coil, assuming $\mu = 0$, was $1.77\varphi_0$ where φ_0 is the flux above the transition point. The observed flux was $1.70\varphi_0$. This last experiment was repeated with ordinary polycrystalline lead cylinders with the same result, the observed flux in this case being actually $1.77\varphi_0$.

d. Redistribution of current

Meissner and Ochsenfeld showed also that the spontaneous redistribution took place when the magnetic field was produced by a current flowing in the superconductor itself. This must indicate, therefore, that the current within the wire changes spontaneously from the uniform distribution characteristic of an ordinary direct current to the distribution near the surface which can be shown to be characteristic of any current introduced into a wire which is already superconducting (see §13).

The same parallel cylinders as those used in the third experiment above were connected together at one end, and a current of about 5 amp. passed through the two in series. The flux through the test coil placed between the cylinders was then measured above and below the transition point, showing an increase in the superconducting state. The field between the cylinders was roughly the same whether the current was introduced before or after the tin passed through its transition point, but was greater in both

[21] W. Meissner and R. Ochsenfeld, Naturwiss. **21**, 787 (1933); W. Meissner, Zeits. f. tech. Physik **15**, 507 (1934).

cases than that calculated on the assumption of surface currents.

e. Spontaneous expulsion of magnetic flux

Tarr and Wilhelm[22] have performed a series of experiments in which fixed search coils were wound in various positions around superconductors of various shapes and materials. Each coil was connected separately to a Grassot fluxmeter, and the changes in flux were observed:

(i) When the magnetic field was switched on and off with the metal above its transition point—φ.

(ii) When the field was switched on and off with the metal in the superconducting state—φ_s.

(iii) When the metal was cooled rapidly through its transition point in the presence of the field—φ_{rc}.

(iv) When the external field was removed after the cooling (iii)—φ_r.

$(\varphi-\varphi_s)/\varphi$ measures the extent to which the coil was shielded by the superconductor from changes in magnetic field which took place after the cooling. It is therefore the fractional change of flux to be expected when the body behaves as a perfect diamagnetic.

$\varphi_{rc}/(\varphi-\varphi_s)$ is then the fraction of the original flux which was spontaneously expelled from the superconductor during the cooling, and $(\varphi_r-\varphi_s)/(\varphi-\varphi_s)$ is the further fraction which was withdrawn on removing the external field. These three quantities, expressed as percentages, are given for various cases in Table III.

TABLE III. *Percent expulsion of flux on cooling with various superconductors.*

Description of Body	Shielding	Expulsion on Cooling	Expulsion on Removing Field
Cylinders with field perpendicular to axis, coil around a diametral plane			
Tin, hollow	85	41	—
Tin, solid	88	28	5
Tin, solid, coil embedded in a groove and covered with tin foil	100	65	16
Lead, hollow	92	65	0
Cylinders with field parallel to axis			
Tin, length 4 cm, diam. 1 cm	81	42	32
Tin, length 3.2 cm, diam. 2 cm	88	27	60
Tin, hollow, coil outside	91	26	16
Tin, hollow, coil inside	100	−23	0
Mercury in a hemispherical cup, coil embedded in metal			
Pure mercury	100	85	15
Emulsion of mercury in lard (50% Hg)	29	100	—
Mercury containing quartz pebbles	100	20	30
Flat pulleys with coil in groove around circumference			
Lead	95	12	25
Tin	97	10	38
Tantalum	93	1	3
Lead-tin alloys and Rose metal	97–100	0	0

[22] F. G. Tarr and J. O. Wilhelm, Can. J. Research **12**, 265 (1935); Trans. Roy. Soc. Canada **28**/III, 61 (1934).

The first experiments of Tarr and Wilhelm were performed with a hollow cylinder of commercial tin, and confirmed qualitatively Meissner's observations. Their later results with bodies of different shapes and materials are given in Table III. Commercial metals were used in all cases.

Although no accurate readings were made, Tarr and Wilhelm observed that the decrease in flux with decrease of temperature, as measured with the aperiodic fluxmeter, took place in a manner very similar to the decrease of resistance. As nearly as they could tell under the conditions of rapid cooling here necessary the transition temperature for change of flux coincided with the usual transition point. Meissner also attempted this test, observing the motion of the ballistic galvanometer connected to a fixed test coil while the temperature was being reduced, but was unable to draw a definite conclusion. It is probably legitimate to assume that the magnetic transition and the resistance transition coincide, although the point cannot be said to be firmly established.

Tarr and Wilhelm have also confirmed Meissner's conclusion in the case of a hollow cylinder that the results were identical whether the cylinder was cooled from the outside or the inside.

f. Permanent magnetic moment

An attempt was early made by Tuyn[23] to set up a persistent current in a solid lead sphere by the same process, cooling in a magnetic field and subsequent removal of the field, as was used to set up a current in the lead ring. According to the electromagnetic equations, surface currents should be induced by this process just sufficient to cause, as described in §4b, a permanent magnetic moment equal and opposite to that acquired in the given field by a body with permeability zero. On the other hand, if Meissner's spontaneous diamagnetic effect is complete, no current will be induced on removing the field. Onnes had actually found that the sphere acquired a magnetic moment in this process, but very much smaller than that predicted. He also

[23] W. Tuyn, Leiden Comm. 198 (1929).

found that the measured magnetic moment remained constant as long as the sphere could be kept cold, and was not affected by applying a magnetic field in a direction different from that of the original field.

There is no evidence in any of the experiments of this nature concerning the distribution of the currents which give rise to the magnetic moment observed, and indeed there is some reason on theoretical grounds to doubt whether a macroscopic circulation of current does take place in the case of a solid body as opposed to a ring. Hence it is better here to speak of the acquisition of a permanent magnetic moment.

This permanent magnetic moment appears again in the work of Tarr and Wilhelm, where it is represented by the magnetic flux which is still linked with the test coil after operation (iv). Again it is "permanent" as the observed change in flux when the magnetic field is again applied amounts only to the small defect of the "shielding" from 100 percent. As will be seen from Table III, these experiments show that the permanent moment acquired may vary all the way from zero to that predicted by electromagnetic considerations, just as the Meissner effect varies from complete to negligible.

Mendelssohn and Babbitt[24] have recently repeated the original experiment of Onnes with the sphere, using both solid and hollow spheres of lead. The observed magnetic moment for the solid sphere was about $\frac{1}{6}$ of that calculated on the assumption $\mu=0$, and for the hollow sphere $\frac{1}{3}$ to $\frac{1}{2}$.

It must be noted that the permanent magnetic moment described here does not necessarily correspond in the case of a hollow body to the flux observed within the hollow. In Meissner's second experiment described above, the field inside the hollow tin cylinder still retained about 40 percent of its original value, but no field was observed outside. Again in one of the experiments of Tarr and Wilhelm (lines 7 and 8 of Table III) only a part of the flux linked with a coil inside the hollow is shown by the test coil outside. Some or all of the lines of induction within the hollow must be joined inside the superconducting body, and, since this acts as a perfect magnetic shield, these internal closed lines of induction cannot be detected by an external device.

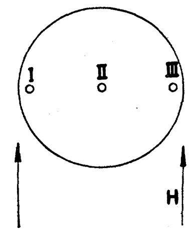


FIG. 10. Bismuth wires in a tin cylinder.

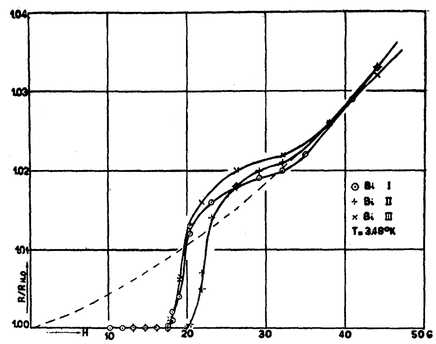


FIG. 11. Penetration of a magnetic field into a tin cylinder.

g. Penetration of magnetic field into a superconductor

De Haas and Casimir-Jonker[25] have studied the way in which a magnetic field penetrates into a superconducting wire as the field strength is gradually increased above the threshold value. Three bismuth wires were passed through holes in a monocrystalline cylinder of tin (Fig. 10), and the field strength at these points was indicated by the change in resistance of the bismuth. The field was first applied at right angles to the axis of the cylinder, and at right angles to the plane containing the bismuth wires, as shown in the figure. The curves obtained on plotting the resistance of the bismuth against the external field strength are shown in Fig. 11. The dotted curve is the calibration curve of the bismuth wire, showing the resistance in a uniform magnetic field of the given strength.

[24] K. Mendelssohn and J. D. Babbitt, Nature **133**, 459 (1934).

[25] W. J. de Haas and M. J. Casimir-Jonker, Physica **1**, 291 (1934); Leiden Comm. 229d.

The field reaches wires I and III (1 mm below the surface) at a strength slightly higher than that at which resistance begins to return. The field required to penetrate to the center was slightly greater, but still less than that for which resistance is completely restored. The fields rapidly rise to values somewhat greater than the applied field strength, and only agreed with the latter above 32 gauss, where the resistance attains its normal value.

Similar measurements were made with the magnetic field still at right angles to the cylinder, but in the plane of the bismuth wires. The results for wires I and II were practically the same as the previous result for wire II.

The same experimental arrangement was also cooled in a constant magnetic field, showing results similar to those of Meissner and Ochsenfeld. The field became zero at points I and III, and was somewhat increased at the center.

Experiments have also been carried out with certain alloys by this method, with quite different results. These will be discussed in §10b.

h. Magnetic hysteresis effects

A few experiments were carried out by Tarr and Wilhelm on the Meissner effect of type B, where, at a constant temperature, the magnetic field is increased to a strength greater than the threshold value, and then gradually decreased. A typical curve between observed flux and external field is shown in Fig. 12 (the units are arbitrary). On increasing the field strength the flux remained zero in all cases up to a definite point, and then fairly rapidly increased to normal. When the external field was decreased again, the flux began to decrease rapidly as soon as the threshold field was reached, but remained always higher than in increasing fields. In the case illustrated the flux became zero only for zero external field. In certain other cases, some flux remained when the external field was zero, showing that the body had acquired a permanent magnetic moment.

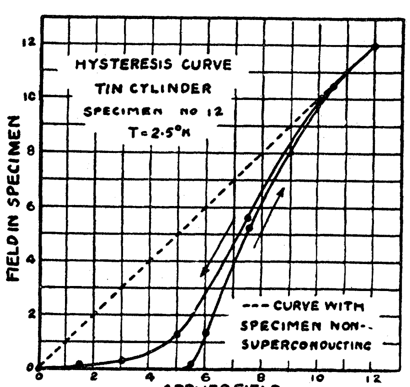


FIG. 12. Magnetic hysteresis curve for a tin cylinder.

Rjabinin and Schubnikow[26] have made a more detailed study of this case, but for one body only, a long cylinder of pure polycrystalline lead, with field applied parallel to the axis. Their most accurate results were obtained when the lead cylinder was arranged so that it could be moved parallel to its length, in and out of a fixed test coil. The external field was obtained by means of a long solenoid, and was uniform over the distance through which the lead cylinder moved. The deflection of the ballistic galvanometer on removing the cylinder from the test coil measures the difference between B and H.

Fig. 13 shows results obtained by this method. The sudden changes in B took place accurately at the threshold field strength, both in increasing and decreasing fields. The first sudden decrease

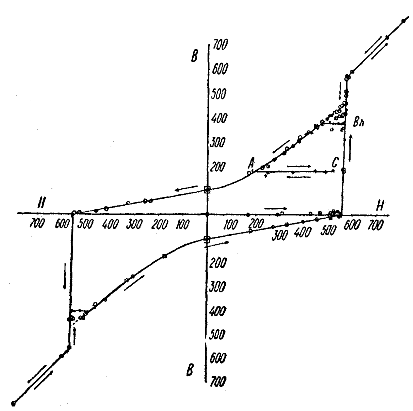


FIG. 13. Magnetic hysteresis in lead.

[26] J. N. Rjabinin and L. W. Schubnikow, Physik. Zeits. d. Sowjetunion **6**, 557 (1935).

in B with decreasing fields was not reproducible, but varied from 20 to 40 percent of the value before the sudden change. When a point on the continuous decreasing curve was reached the same curve was followed in all cases, giving the same value for the residual magnetization when the external field became zero.

If the cycle were interrupted at any point on the decreasing side, and the external field increased from that point, the induction was unaltered as long as the field did not exceed the threshold value.

i. General conclusions

In the above experiments the spontaneous diamagnetism of the Meissner effect seems to vary all the way from zero to fair agreement with that predicted on the basis $\mu=0$. However, recent careful repetitions of Meissner's original experiment[27] seem to show that in practice there is always a slight departure from perfect diamagnetism.

Nevertheless the effect has been shown to be nearly complete under favorable circumstances for the elements Pb, Sn and Hg, and it seems reasonable to assume that it can be complete for these metals under still more favorable circumstances, e.g., for smaller bodies. It seems to be absent, or at most partial, for the element Ta, and for the various alloys which have been tried. The possibility of a complete Meissner effect may therefore be assumed to be a second characteristic of a "normal" superconductor as defined above. These elements must, when in the superconducting state, possess some characteristic electronic structure which prevents the penetration of magnetic induction, quite apart from the induction of surface currents in a changing magnetic field. In other words, they act as if perfect diamagnetism, magnetic susceptibility $\chi=-1/4\pi$, were an intrinsic property (cf. §§14, 15).

A high degree of purity and crystal perfection seems to be the first requirement for a complete effect, although it is nearly complete under otherwise favorable conditions for commercial metals. Where a partial effect is observed for a metal of sufficient purity, the shape of the body seems to be the decisive factor, although the only definite conclusion in this regard is that the most favorable shape is a long narrow cylinder. It is definitely established that the distribution of temperature in the cooling body is unimportant.

The partial effects observed under certain conditions for normal superconductors are probably due, as suggested by Gorter[46] and by London,[47] to the inclusion of non-superconducting regions. As portions of the body pass into the superconducting state the magnetic flux is expelled from these parts and concentrated in intervening regions. Because of this process the local magnetic field may become large enough in places to prevent the transition to the superconducting state. We are then left with a superconducting body which is threaded by non-superconducting "holes." The flux which is left in these holes gives rise to the permanent magnetic moment, which is obviously "locked in" by the shielding effect of the surrounding superconductor. The formation of such holes will obviously be favored by the structural inclusion of foreign microcrystals, whether these are of non-superconducting impurities or of eutectic alloys which do not show the Meissner effect. There is some support for this view in the experiment by Tarr and Wilhelm on mercury containing pieces of quartz (Table III).

5. Current in a Closed Superconducting Circuit

a. Law of constant magnetic flux

Since the discovery of the Meissner effect and other magnetic effects associated with superconductivity, there has been some question as to the real nature of the so-called "persistent current" which can be set up in a superconducting ring. Until recently these currents have always been studied by measuring the magnetic moment of the ring with a magnetometer, and it was found by Onnes that almost as large a magnetic moment could be obtained with an open ring in which a narrow slot had been cut. In the latter case at least it is more appropriate to speak of permanent magnetization, rather than of persistent current.

[27] W. Meissner, Proc. Roy. Soc. (in press).

Recently, however, F. and H. London[28] have pointed out that there is an essential difference between simply and multiply connected bodies (in the mathematical sense). They give the law that for a multiply connected superconductor (ring or closed circuit) the flux through the non-superconducting region must be constant, and equal to the flux at the instant when the body became superconducting, regardless of the Meissner effect. If L is the self-inductance of the superconducting circuit, this leads at once to the equation

$$Li=\varphi-\varphi_0, \qquad (5.1)$$

where φ is the magnetic flux through the circuit due to external field, and φ_0 is the amount of this flux before the transition to the superconducting state. The current i is then actually a macroscopic circulation of current around the circuit, which we may describe as a "true current" as opposed to the unknown circulation which causes the magnetic moment in the case of a simply connected body.

This result is identical with that obtained by classical consideration of a resistanceless circuit, that the e.m.f. is always zero, or

$$d\varphi/dt-Ldi/dt=0. \qquad (5.2)$$

b. Superconducting galvanometer

In order to be able to measure persistent currents very much smaller than can be detected with a magnetometer, the authors and Tarr[29] have designed a superconducting galvanometer in which the moving coil and the leads are made of fine lead wire and are immersed in liquid helium. The preliminary tests of this instrument show definitely that the persistent current in a superconducting circuit is a true current in the above sense. The construction of the galvanometer is shown in Fig. 14. The suspension is in a tube attached to the top of the cryostat, practically at room temperature, and the moving coil of fine lead wire hangs from this on a long rigid rod. The magnetic coil in which the coil moves is provided by a pair of copper coils without any iron, and so can be accurately controlled. These coils are surrounded by a cylinder of sheet lead, which serves to shield the galvanometer proper from all external magnetic fields (up to the threshold field of lead at 4.2°K). For the preliminary experiments to be described here the galvanometer was connected to an "inducing coil," consisting of a few turns of tin wire in an external magnetic field.

Applied to the circuit consisting of the inducing coil and the moving coil, condition (5.1) reads, for small deflections θ,

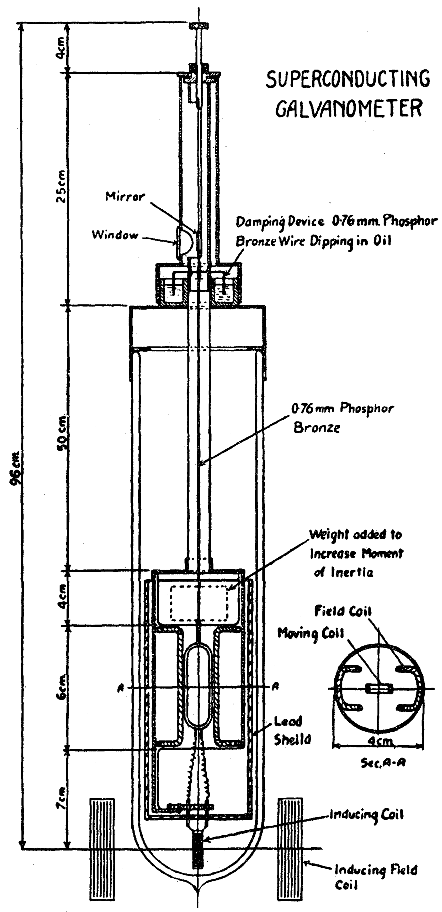


FIG. 14. Superconducting galvanometer.

[28] F. and H. London, Physica **2**, 341 (1935).

[29] H. Grayson Smith and F. G. Tarr, Trans. Roy. Soc. Canada **29**/III, 1 (1935).

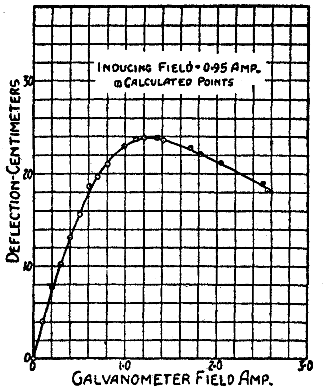


FIG. 15. Experimental test of superconducting galvanometer.

$$Li = \varphi - NAH\theta, \qquad (5.3)$$

where H is the galvanometer control field, N, A are the number of turns and average area of the moving coil, φ refers to the flux through the inducing coil, and i, φ, θ denote the changes in these quantities from their initial values. This current causes a torque $NAHi$ on the moving coil. Substituting this torque into the equation of motion of the coil, we have

$$\ddot{\theta} + \frac{k}{I_m}\dot{\theta} + \frac{N^2A^2H^2 + L\tau}{I_mL} = \frac{NAH}{I_mL}\varphi, \qquad (5.4)$$

where τ is the torsion constant, I_m the moment of inertia, and k the constant of mechanical damping. Eq. (5.4) represents displaced simple harmonic motion, with the center of oscillation, and so the final galvanometer deflection, given by

$$\theta = \varphi NAH/(N^2A^2H^2 + L\tau) \qquad (5.5)$$

and the period by

$$T = 2\pi\left(\frac{N^2A^2H^2}{I_mL} + \frac{\tau}{I_m} - \frac{k^2}{4I_m^2}\right)^{-\frac{1}{2}}. \qquad (5.6)$$

It will be noticed that electromagnetic damping is entirely absent, and so artificial mechanical damping had to be introduced in order to obtain stable deflections of the coil when operated under boiling helium.

Two corrections, which are themselves of interest, had to be applied. First, the galvanometer control field is strongly affected at liquid helium temperatures by the presence of the superconducting lead shield. The ratio NAH/I, where I is the current in the control coils, had therefore to be treated as an unknown parameter. Second, the diamagnetism of the superconducting lead in the moving coil introduces an additional torque, which is proportional to the deflection and to the square of the control field. Allowance was made for this effect by writing

$$\tau = \tau_0 + \beta I^2 \qquad (5.7)$$

where τ_0 is the observed torsion constant (at liquid helium temperature) without control field, and β is another unknown parameter.

Fig. 15 shows the relation between the observed deflection and the control current I, for a given change of flux φ. The good agreement between the experimental results and the predictions of Eq. (5.5), when corrected as above, confirms satisfactorily this method of treating a closed circuit. Fair agreement was also found with the relation (5.6) between the period of vibration and the control field. The necessity for the correction (5.7) shows that the true current and the local currents which give rise to the diamagnetic effect exist simultaneously and independently in the superconducting wire of the moving coil.

These conclusions have been confirmed by recent experiments of Steiner and Grassmann[30] on the behavior of a closed superconducting ring in a magnetic field.

One practical characteristic of the superconducting galvanometer should be noted, namely, that the initial current set up in the circuit is reduced by the motion of the galvanometer coil. The deflection really indicates the final persistent current, and therefore has to be multiplied by a certain factor, which can easily be calculated when the constants are known, in order to find the "impressed current," or the current which would flow in a fixed circuit of the same self-inductance. As seen from Fig. 15, the deflection for a given impressed current actually becomes a maximum for a certain control field, and falls off with higher fields. At the optimum

[30] K. Steiner and P. Grassmann, Physik. Zeits. **36**, 520 (1935).

field (about 5 gauss) the persistent current is a little more than one-half of the impressed current, and 1 mm deflection corresponds to an impressed current of about 10^{-4} amp.

c. Divided circuits

Von Laue[20] pointed out that in the absence of resistance a current will divide between parallel superconducting circuits in such a way as to make the magnetic energy $\frac{1}{2}\Sigma p_{ik}I_iI_k$ a minimum, where I_i is the current in the ith branch, p_{ii} is the self-inductance of the ith branch, and p_{ik} the mutual inductance of the ith and kth branches. From this we obtain the equation

$$\sum_k p_{ik}I_k = \int_0^t Edt \tag{5.8}$$

to determine the currents. This applies strictly only to currents introduced into the circuit when it is already in the superconducting state. If, as apparently shown by the experiments on the superconducting galvanometer, the true current in a closed circuit is not affected by the Meissner effect, the current determined by Eq. (5.8) will be superposed on any current which flowed in the circuit at the instant of the transition.

This has been qualitatively confirmed by an experiment performed by Sizoo.[31] Two superconducting coils, of approximately equal dimensions, but of different sized wire, were arranged in parallel with their magnetic fields opposed. The difference between the currents in the two coils could be calculated from the magnetic field produced by the combination. When the current, from an external circuit, was introduced after the transition to the superconducting state no field could be detected, showing that the current had divided equally, and was independent of the size of wire. Applying von Laue's general condition, we have approximately $p_{12} = -p_{11} = -p_{22}$, and therefore the magnetic energy

$$\tfrac{1}{2}(p_{11}I_1^2 + p_{22}I_2^2 + 2p_{12}I_1I_2) \sim \tfrac{1}{2}p_{11}(I_1 - I_2)^2$$

becomes very small when $I_1 = I_2$.

If a current was passed through the parallel coils before they became superconducting it divided according to their resistances, and a magnetic field was observed. This field was not altered by the passage to the superconducting state, showing the absence of Meissner effect for the true current. The field remained unaltered when the external circuit was later broken. But the breaking of the circuit really amounts to introducing an equal current in the opposite sense, and this reverse current divides equally as in the first experiment. There remains a persistent current around the superconducting part of the complete circuit, just sufficient to maintain the magnetic field.

[31] G. J. Sizoo, Dissertation (Leiden, 1926).

6. Thermoelectric and Thomson Effects

Borelius and collaborators[32] studied the thermoelectric effects between lead and a silver alloy, tin and silver alloy, and from the results they concluded that there is no thermal e.m.f. between lead and tin when both are superconducting. Meissner, and Steiner and Grassmann[33] found that a thermocouple of lead and tin gave no thermoelectric effect when both were superconducting. This has been confirmed by Burton, Tarr and Wilhelm[34] using the superconducting galvanometer (§5b). When the lead is superconducting, but the tin is not, a thermal e.m.f. is observed.

From these experiments it follows that, when both metals are superconducting,

$$\sigma_{\mathrm{Sn}} - \sigma_{\mathrm{Pb}} = Tde/dT = 0,$$

where σ is the Thomson coefficient. According to the measurements of Borelius, this difference has a negative value just above the transition temperature of tin, and changes to positive above the transition point of lead. Since the Nernst theorem predicts that the Thomson effect is zero at 0°K, it is probable that $\sigma_{\mathrm{Sn}} = \sigma_{\mathrm{Pb}} = 0$ in the superconducting state. It seems likely, but is not yet proved, that the disappearance of the Thomson coefficient is abrupt, accompanying the disappearance of resistance.

[32] G. Borelius, W. H. Keesom, C. H. Johansson and J. O. Linde, Leiden Comm. 217c (1931).

[33] W. Meissner, Zeits. f. d. gesamte Kalte Ind. **34**, 197 (1927); K. Steiner and P. Grassmann, Physik. Zeits. **36**, 527 (1935).

[34] E. F. Burton, F. G. Tarr and J. O. Wilhelm, Nature **136**, 141 (1935).

7. Specific Heats

a. Normal specific heat

Keesom[35] and his collaborators have made extensive investigations of the calorific properties of certain of the superconducting elements. In the case of pure tin, allowed to cool naturally and pass into the superconducting state without external disturbance, a marked increase in the specific heat occurs at the electrical transition temperature. The latest curve for this element is shown in Fig. 16. A similar, but somewhat smaller, increase in specific heat has also been found for thallium. In neither case, however, is there any evidence of a heat of transition with undisturbed cooling.

On the other hand, the measurements have failed to reveal any discontinuity in the calorific properties of lead. Here some allowance must be made for the fact that it is very difficult to control the temperature accurately in the neighborhood of the transition point of lead (7.2°K), where helium boiling under reduced pressure cannot be used. Consequently it has come to be generally accepted that a change in specific heat, without measurable heat of transition, is a characteristic phenomenon accompanying the normal transition to the superconducting state, at least for the normal superconductors.

It has been shown by Rutgers,[55] and by Gorter and Casimir[46] that there should be a close connection between the specific heat anomaly ΔC and the threshold magnetic field H_t. This is expressed in Rutgers' equation (see §12a):

$$\Delta C = \frac{T_0 V}{4\pi}\left(\frac{dH_t}{dT}\right)^2_{T=T_0},$$

where T_0 is the transition temperature, and V the molar volume. The calculated and experimental values of ΔC are shown in Table IV, whence it will be seen that the agreement is very satisfactory.

Table IV. *Calculated and observed specific heat anomaly.*

Element	T_0°K	dH_t/dT (gauss/°K)	ΔC cal./°K/mole calc.	exp.
Tin	3.71	151.2	0.00229	0.0024
Thallium	2.36	137.4	0.00144	0.00148

[35] W. H. Keesom, Zeits. f. tech. Physik. **15**, 515 (1934).

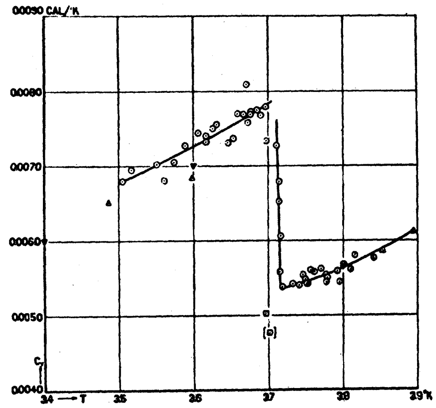


Fig. 16. Undisturbed (no external field) specific heat of tin.

b. Calorific properties in a magnetic field

Since the transition point for resistance is lowered by a magnetic field, the specific heat anomaly should also be affected when the cooling is carried out in an external field. Fig. 17 shows the specific heat curve for thallium, when cooled in a field of 33.6 gauss. The dotted curve gives the undisturbed specific heat, showing the sudden increase at the normal transition point. In the magnetic field the curve is continuous with that in the normal state until the transition temperature appropriate to the field strength is reached. The change is then accompanied by a heat of transition, after which the specific heat curve coincides with the curve for undisturbed cooling.

From these experiments there can be derived as functions of temperature the difference ΔC between the specific heats in the normal and

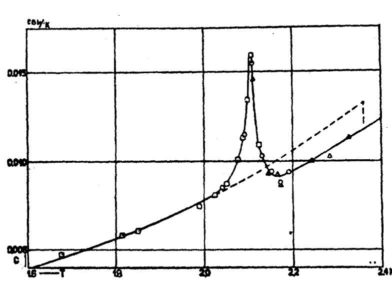


Fig. 17. Specific heat of thallium in a magnetic field.

superconducting states, and the heat of transition Q. In general $\triangle C$ is finite at the transition point, then decreases at lower temperatures, and may change sign. Q is zero at the transition point, and increases uniformly with the increase in threshold field at lower temperatures. Both $\triangle C$ and Q are given quite accurately by equations derived by Gorter and Casimir,[46] involving the threshold field (see §11b).

c. Magneto-caloric effect

The close connection between the magnetic and thermal properties of superconductors should also be made evident in a magneto-caloric effect on adiabatic magnetization or demagnetization. Preliminary experiments have been carried out on this effect by Mendelssohn and Moore,[36] using a cylinder of tin in both longitudinal and transverse fields. As expected, they observed a cooling when the external field was increased to a value greater than the threshold field at the temperature in question, and a heating on the reverse change. The cooling on magnetization is zero at the normal transition point, and increases very considerably with the increase in threshold field at lower temperatures, but the numerical values are subject to error due to heating by eddy currents while the body is in the nonsuperconducting state.

This effect may prove to be of very great assistance in the study of the magnetic and thermal properties at extremely low temperatures, below those attainable with boiling liquid helium. The cooling effect on magnetization of the superconductor is comparable with that observed on demagnetization of a paramagnetic salt, and the magnetic fields required are considerably smaller.

8. Thermal Conductivity

It is readily understood that the thermal conductivity of a superconductor should be affected by the change in electronic structure which produces the superconducting state, and an effect of this kind has been found for several superconductors by de Haas and Bremmer.[37]

[36] K. Mendelssohn and J. R. Moore, Nature **133**, 413 (1934).

[37] W. J. de Haas and H. Bremmer, Leiden Comm. 214d (1931); 220bc (1932).

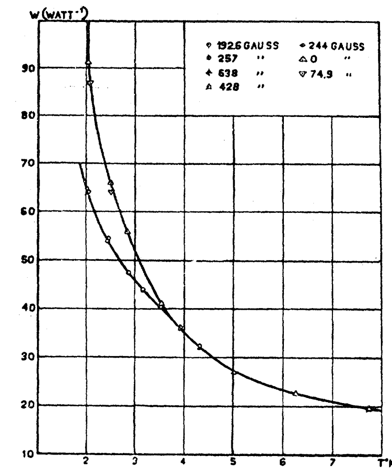


Fig. 18. Thermal resistance with and without magnetic field.

However, it is very difficult to draw definite conclusions from their measurements, other than the qualitative statement that the thermal conductivity of a normal superconductor is reduced by the onset of electrical superconductivity.

When the cooling proceeds normally without an external field, the effect for lead and tin is shown only by a change in slope of the curve between thermal conductivity and temperature. Indium seems to show a very small increase of thermal conductivity at the undisturbed transition, accompanied by a change in slope similar to that for lead and tin. In all three cases, however, if the electrical superconductivity is interrupted at any temperature below the transition point, by the use of a magnetic field, there is a distinct increase in thermal conductivity. When superconductivity is thus prevented, the curve obtained between thermal conductivity and temperature is a continuous extension of the curve above the normal transition point. Fig. 18 shows the thermal resistances of tin in the two states, as given by de Haas and Bremmer.

The difficulty in interpretation of the results arises when the difference between the two values of the thermal conductivity at a given temperature, in the normal and superconducting states, is considered as a function of the temperature. This difference presumably indicates the heat which, in the normal state, is carried by the superconduction electrons. For tin, it is quite small for some distance below the transition point, then increases rapidly. The difficulty here is probably connected with the general difficulties which have been encountered in comparing thermal conductivities at low temperatures with theory. Grüneisen and Reddemann[38] have shown that at very low temperatures an appreciable part of the thermal conductivity is due to conduction by the metallic lattice. Both the lattice conduction and the electronic conduction are limited by two factors, the perturbation of the lattice by thermal vibrations, and the perturbation by foreign impurities and irregularities. There is therefore an analogy with the separation of electrical resistance into the temperature dependent part due to thermal agitation and the residual resistance due to irregularities. However, in the case of the thermal conductivity the effect of irregularities is apparently much more serious, as is shown by many measurements at very low temperatures, and the separation of the different effects is very difficult. It can probably be assumed, since superconductivity does not appear to have any effect on the metallic lattice, that only the electronic conduction of heat is affected by the transition to the superconducting state. It is probably useless, however, to attempt more than a qualitative discussion until the different factors which affect the thermal conductivity in the normal state can be clearly separated.

9. Superconductivity in Thin Films

a. Transition points of thin films

A series of experiments has been carried out at Toronto[39] using thin films of tin and lead which show clearly that there is a minimum thickness for the existence of normal superconductivity in these metals. The first experiments concerned

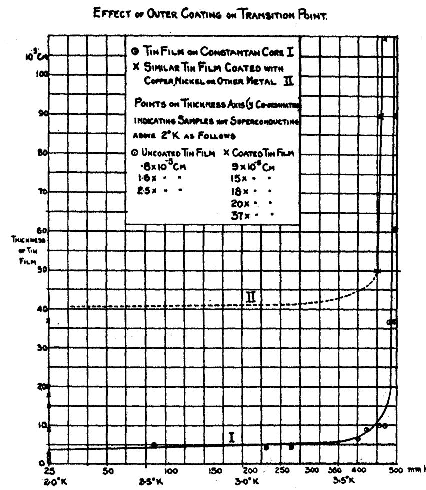


FIG. 19. Transition points of thin films of tin.

the normal transition points of films of various thicknesses, deposited on a non-superconducting wire. Different supporting wires were used, constantan, copper and nickel, and different methods of depositing the films, electrolytic, chemical, and wiping with molten metal. The transition temperature was found to be unaffected by using different supports or different methods of deposit, and to depend only on the average thickness. Most of the experiments have therefore been made with electrolytic films on constantan.

Fig. 19 (curve I) shows the normal transition points for films of tin as a function of the thickness. While there is a slight lowering of the transition point for thicker films, it will be seen that superconductivity suddenly begins to be seriously hindered with a thickness of about 1.0μ, and the transition range is widened. Films thinner than 0.4μ could not be made superconducting at 2°K, the lowest temperature attainable in these experiments. 1.0μ may therefore be accepted provisionally as the critical thickness for the restriction of superconductivity in tin, although it is probably in reality an upper limit on account of some still unknown action at the surfaces. Lead films behaved in an exactly similar manner, with a critical thickness at about

[38] E. Grüneisen and H. Reddemann, Zeits. f. tech. Physik **15**, 535 (1934).

[39] E. F. Burton, J. O. Wilhelm and A. D. Misener, Trans. Roy. Soc. Canada **28**/III, 65 (1934); A. D. Misener and J. O. Wilhelm, Trans. Roy. Soc. Canada **29**/III (1935).

0.8μ. In their experiments on the magnetic effects in superconductors (§4e), Tarr and Wilhelm[22] attempted to find a critical dimension for mercury by using small particles suspended in lard. They found that particles about 1μ in diameter became superconducting in the normal manner.

b. Double-coated films

Further experiments were performed in which tin films of the same nature were again coated on the outside by an electrolytic deposit of nickel or copper. The transition point was again independent of the nature of the coating metal, and also independent of the thickness of the outer coating down to 0.7μ. This outer coating caused a further slight lowering of the transition point for comparatively thick films, and the critical thickness was now attained for films of between 4 and 5μ (Fig. 19, curve II). No effect was found by using outer coatings of an insulator.

No interpretation has yet been offered for this experiment, other than to say that the contact with a non-superconducting metal must have some inhibiting effect on the superconductivity. A considerable percentage of copper in alloy with tin does not greatly affect the transition temperature, although it probably affects the associated magnetic properties. In any case, the independence of the nature of the supporting and coating metals, along with other general evidence on thin films, suggests that there is not much formation of alloy in these experiments. Even if the idea of some inhibiting cause of this kind is accepted, there must still be a special property of the double-coated films, for these require a thickness at least four times that of the single-coated films in order to show superconductivity.

c. Threshold magnetic field[40]

The behavior of superconducting films of tin in a magnetic field was found to be quite different from that of the massive metal, even for a film as thick as 31μ, which has a normal transition point indistinguishable from that of solid tin. Fig. 20 shows typical results for a film of thickness 4.2μ. The abscissa $\triangle T$ is the temperature

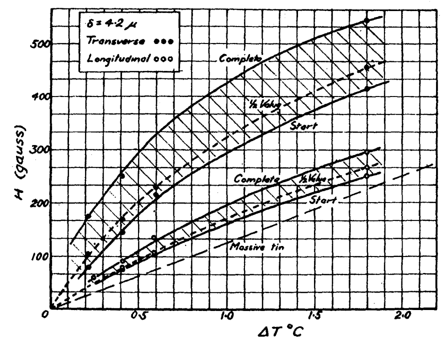


FIG. 20. Threshold fields for thin films of tin.

difference below the normal transition point for the film in question. The solid curves give, for both longitudinal and transverse fields, the (increasing) magnetic fields at which the first sign of resistance appears, and at which normal resistance is restored. The shaded areas therefore represent the transition regions. While a smooth curve was obtained on plotting the normal transition points of the films against the average thickness, the magnetic properties for different films were rather irregular. This may be due to distortion of the magnetic field by irregularities in the highly diamagnetic film, and, as might be expected if this is correct, is very much worse in transverse fields. For this reason it is possible at present to make only the following qualitative statements:

(i) The magnetic field required to restore the resistance was very much greater than for the massive metal, and the transition range was wider.

(ii) The transverse field required was considerably greater than the longitudinal, and the transition was still more gradual. Where any difference between longitudinal and transverse fields has been found for solid wires (as for single crystals of tin, §3b), the transverse threshold field is smaller.

(iii) The curve between the field required and the temperature $\triangle T$ below the normal transition point was definitely not linear, and it has not been possible to find a satisfactory empirical law. The difference between the critical fields for the films and for the massive metal only increased slowly when $\triangle T >$ about 0.5°.

(iv) There was marked hysteresis in increasing and decreasing fields, especially for transverse fields.

(v) The difference between film and massive metal was still considerable for the thickest film used (31μ), but was

[40] A. D. Misener, H. Grayson Smith and J. O. Wilhelm, Trans. Roy. Soc. Canada 29/III (1935).

evidently decreasing with increasing thickness. The field required also decreased somewhat for films of less than the critical thickness (1.0μ). It is obviously zero for very thin films which never become superconducting.

d. Sensitivity to increase of current

It was found in the earliest experiments on these films that the superconductivity was very easily disturbed by an increase in the current used in measuring the resistance. In Fig. 21 is plotted against the thickness the ratio of the external magnetic field H_t which would cause a given lowering of the transition point (in massive tin) to the field $H=2I_t/r$ which actually exists at the surface of the film when the transition point is lowered the same amount by an increase of current. According to Silsbee's hypothesis that the sensitivity to current strength is due to the magnetic field caused by the current, these fields should be equal. In the case of the films, therefore, the disturbance of superconductivity by increase of current strength is a direct effect of the current, and cannot be ascribed to the magnetic field produced (see §10c). Actually the discrepancy between these results and Silsbee's hypothesis is greater than is indicated in Fig. 21, for according to the experiments described above a field considerably greater than H_t is required to disturb the superconductivity of the films.

The only conclusion possible from this experi ment is that there is a definite limit to the current which can be carried by the superconduction electrons in a body, but that ordinarily this current is never attained because of the interruption of superconductivity by the magnetic field. It must be admitted, however, that the obvious assumption of a uniform limiting current

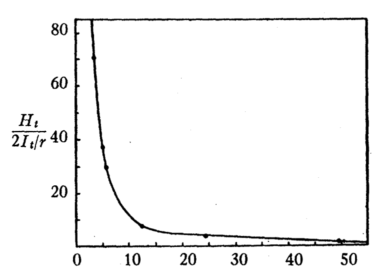


FIG. 21. Sensitivity of thin films to current.

density does not agree with the experimental results.

10. Anomalous Superconducting Alloys

a. Normal and anomalous superconductors

Attention has already been drawn to the fact that certain superconducting alloys have properties quite different from those of the common superconducting elements, lead, tin, etc., which have been defined above as "normal superconductors." The first difference to be noticed between alloys and pure metals was that the former, in general, have very high threshold magnetic fields for the restoration of resistance (§3a, Fig. 6). However, that this is in some way connected with an essential difference in their properties has only been recognized since the magnetic behavior of superconductors in general has been more fully understood.

There is really very little justification as yet for the use of the terms "normal" and "anomalous" for the two groups into which it is now found necessary to classify the superconducting metals. The authors' choice has arisen from the facts that the pure elements which have been most extensively studied are "normal," and that theoretical discussions have been almost entirely limited to this group.

In the present sense, a normal superconductor possesses the following properties:

(i) When in the superconducting state it acts as a "perfect diamagnetic" towards any external magnetic field less than the threshold field as determined by experiments on the resistance.

(ii) The Meissner effect can be complete under favorable conditions, e.g., for a body of suitable shape and sufficient purity.

(iii) Silsbee's hypothesis applies to the interruption of superconductivity by heavy currents, at least in massive wires.

(iv) The specific heat anomalies are connected with the threshold magnetic fields by the thermodynamic equations of Rutgers and of Gorter and Casimir.

Since these properties appear to be connected, it is assumed for the present that if a metal is proved to be normal in one respect it is normal in all. The following metals are therefore placed in the normal group, and are assumed to have the above properties when reasonably pure:

Tin—all properties proved.
Mercury—(ii) proved.
Thallium—(iv) proved.
Lead— (i), (ii) and (iii) proved.

Any element or eutectic compound which, when reasonably pure, definitely disobeys one of the above rules is placed in the anomalous group. The exceptions to the rules, and the properties which are displayed, will be discussed below. Alloys of a mixed-crystal nature appear in general[41] to be anomalous to a varying extent, but it seems possible to explain their behavior on the assumption of non-superconducting or anomalously superconducting inclusions. These will not be considered in detail.

b. Magnetic properties

In the experiments of Tarr and Wilhelm[22] (§4e) a lead-tin eutectic (and other mixed alloys) showed no Meissner effect. Tantalum showed only a small effect.

De Haas and Casimir-Jonker[25] have studied the penetration of a transverse magnetic field into cylindrical rods of Bi_5Tl_3, and of a lead-thallium alloy approximating to $PbTl_2$, measuring the field at the center of the cylinder by means of a bismuth wire (see §4g). As for any other superconductor, a weak external field did not penetrate the cylinder, but penetration commenced under a certain definite critical field very much smaller than that required to restore the resistance. On removing the external field again, a large part of the magnetic flux was left "locked in."

Practically the same results were obtained by Rjabinin and Schubnikow[42] with $PbTl_2$ and an alloy Pb65%−Bi35%, measuring the magnetic induction in the superconducting state by the method described in §4h. As the external field H was increased, the mean induction B remained zero until H was equal to a certain critical value H_{k_1}. With fields greater than H_{k_1}, B showed at first a sudden increase to a value somewhat less than H, then gradually attained sensible equality with H, in a field still very much less than the critical field H_{k_2} at which the electrical resistance returns. The relation between the critical fields H_{k_1} and H_{k_2} and the temperature is shown for $PbTl_2$ in Fig. 22.

Similar results for tantalum have been obtained by Mendelssohn and Moore,[41] but with a very much smaller difference between H_{k_1} and H_{k_2}.

c. Sensitivity to current strength

It was first reported by Keesom[43] that superconductivity was interrupted in a lead-bismuth eutectic by a current sufficient to give a magnetic field at the surface of only 308 gauss, whereas the external threshold field at the same temperature was about 16,000 gauss.

This question of the maximum current strength was also studied by Rjabinin and Schubnikow[42] for $PbTl_2$, with similar results. These workers used several wires of different diameters, and found that the critical current at a given temperature was proportional to the diameter. Therefore this direct sensitivity to current, apart from the magnetic field produced, is not an indication of a maximum current density throughout the wire, but rather of a maximum surface density. Or, if the maximum current is proportional to the diameter, the magnetic field produced by the current at the surface of the wire is the same for all diameters. Rjabinin and Schubnikow take the view that the restoration

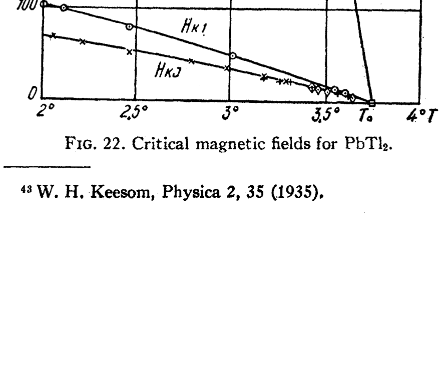


FIG. 22. Critical magnetic fields for $PbTl_2$.

[41] K. Mendelssohn and J. R. Moore, Nature 134, 773 (1934).

[42] J. N. Rjabinin and L. W. Schubnikow, Physik. Zeits. d. Sowjetunion 7, 122 (1935).

[43] W. H. Keesom, Physica 2, 35 (1935).

of resistance by current is here, as for normal superconductors, an effect of magnetic field, but that for some reason the critical field required is very much smaller when caused by internal currents than when applied externally. They have therefore calculated a third critical field H_{k_j}, somewhat less than the critical field H_{k_1} for penetration of external field, which is shown as a function of temperature in the lowermost curve of Fig. 22.

d. Specific heat and thermal conductivity

Schubnikow and Chotkewitsch[44] measured the specific heat of a lead-bismuth alloy, and found no evidence of an anomaly near the transition point, although the discontinuity predicted by Rutgers' formula should have been many times the probable error of measurement. The possibility remains that there may be a very much smaller discontinuity, determined by the critical field H_{k_1} for penetration rather than by the critical field H_{k_2} for resistance.

De Haas and Bremmer[37] found that the thermal conductivity of $PbTl_2$ in the superconducting state was affected by an external magnetic field much smaller than the critical field at the temperature in question. The effect was very irregular but, contrary to the pure elements, there was a decrease of thermal conductivity on passing from the superconducting to the normal state.

e. Metals of the anomalous group

As a result of the above experiments the following superconductors can be placed in the anomalous group:

Tantalum—Exception to rules (i) and (ii)
$PbTl_2$—Exception to rules (i) and (iii)
Bi_5Tl_3—Exception to rule (i)
Pb_2Bi—Exception to rules (i), (iii) and (iv)
PbSn—Exception to rule (ii)

Part II. Theoretical

11. Theories of Superconductivity

a. Introduction

It is evident, firstly, that the change which takes place at the transition to the superconducting state affects only the conduction electrons in the metal, and possibly only a small fraction of the total number of conduction electrons. Secondly, in the superconducting state the superconduction electrons, which are responsible for the phenomenon, must be in some condition such that they can move through the metallic lattice, but cannot exchange energy with it. This does not necessarily mean complete freedom of the electrons, but may mean some form of binding with the lattice as a whole rather than with particular atoms. Exchange of energy between electrons and lattice must take place at any finite temperature according to all "free electron" theories of conduction, and further considerations must be sought at once.

There is no advantage in discussing here the many classical and semiclassical theories which have been proposed.[45] They have nearly all aimed at devising a metallic model, in which, at sufficiently low temperatures, the exchange of energy which is responsible for electrical resistance would not take place. None have proved satisfactory, and it now appears certain that the solution is not to be found through any special assumption of this kind. For we know that it is already necessary to appeal to quantum mechanics, as in the Bloch theory of conduction,[2] in order, for example, to obtain the correct dependence of resistance on temperature at very low temperatures, and to explain the anomalous Hall effect.

However, when the existence of superconductivity is accepted as an experimental fact, and the known principles of thermodynamics and electrodynamics are applied to the discussion of the phenomena associated with it, considerable progress can be made towards finding the form which the eventual solution must take. With this end in view the principles of thermodynamics have been applied with considerable success

[44] L. W. Schubnikow and W. J. Chotkewitsch, Physik. Zeits. d. Sowjetunion, **6**, 605 (1935).

[45] E. F. Burton, reference 1, §49.

by Gorter and Casimir[46] and classical electro dynamics by F. and H. London[47] and by one of the authors.[48] It must then be left to quantum mechanics to account for the essential fact, the absence of electrical resistance at a finite temperature. Two quantum-mechanical treatments have been given along somewhat different lines, by Brillouin[49] and by Schachenmeier[50] from which it appears, at least, that superconductivity is not definitely excluded from the quantum-mechanical theory of metals, as it is, for example, from Sommerfeld's theory. The application of these treatments to the varied experimental phenomena is limited, however, by the fact that they are implicitly applied to an infinite metallic crystal, and that the interactions between the superconduction electrons are neglected.

b. Older suggestions

Two only of the semiclassical models should be mentioned briefly; the electron lattice or electron chain theory of Bohr and Kronig;[51] and the spontaneous current theory of Bloch, Landau[52] and Frenkel.[53] Kronig suggested that in the superconducting state some or all of the conduction electrons might be "frozen" into a rigid "electron lattice" which existed within the metallic lattice, but more or less independent of the latter, and unaffected by the thermal vibrations. When analysis showed that it would be impossible for a three-dimensional electron lattice to move as a whole through the metallic lattice, Kronig modified his idea to that of a system of one-dimensional "electron chains."

In the spontaneous current theory it is supposed that the conduction electrons can be in a state in which more or less of them move in parallel streams, as Frenkel terms it, a state of "collectivized motion." At sufficiently low temperatures this state is assumed to be more stable than the state of random motion of the electron gas. According to this view, in any region of a superconductor, small compared to the dimensions of the body, but large enough to contain many atoms, there is a resultant current density at all times. Obviously it has to be assumed that the local currents form closed circuits within the body in the absence of an external electric or magnetic field; and further that these circuits, which the author has called "current orbits," are sufficiently small and are balanced against one another so that the body causes no observable magnetic field. The observed currents and magnetic moments are then the resultant effects of distortions of the current orbits by external fields.

Before the announcement of the Meissner effect this suggestion was discussed by Landau[52] and by Frenkel,[53] both of whom attempted to show that it is thermodynamically possible; that is, that the state with resultant current can have, under suitable conditions, a smaller free energy than the state of random motion. As Frenkel pointed out, this may be considered possible by analogy with ferromagnetism, where the stable state, the state of spontaneous magnetization, is that in which all electron spins are oriented in the same direction. In the present case the angular momenta are parallel.

Landau showed that it is possible to find a balanced system of local currents which will be electrodynamically stable, but his assumption of a uniform saturation current density is probably untenable. Frenkel showed that if a sufficient number of electrons take part in the organized motion their apparent momentum can be greatly increased by the effect of mutual induction, without an increase in energy. He argued from this that the local currents might be stable with respect to the thermal vibrations of the lattice and so give rise to the phenomenon of superconductivity.

Frenkel suggested further that if the local current theory is correct, a superconducting body must be highly diamagnetic, and since the discovery of the spontaneous diamagnetism of the Meissner effect his conception has been

---

[46] C. J. Gorter and H. Casimir, Physica **1**, 305 (1934).
[47] F. and H. London, Proc. Roy. Soc. **A149**, 71 (1935); Physica **2**, 341 (1935).
[48] H. Grayson Smith, Univ. Toronto Studies, Low Temp. Series, No. 76, 1935.
[49] L. Brillouin, J. de phys. et rad. **4**, 334 (1933); **4**, 677 (1933).
[50] R. Schachenmeier, Zeits. f. Physik **74**, 503 (1932); **89**, 183 (1934).
[51] R. de L. Kronig, Zeits. f. Physik **78**, 744 (1932); **80**, 203 (1933).
[52] L. Landau, Physik. Zeits. d. Sowjetunion **4**, 43 (1933).
[53] J. Frenkel, Phys. Rev. **43**, 907 (1933).

favored by many writers. H. G. Smith has discussed it in detail in the light of other recent developments,[48] and its consequences will be considered further in §15. This conception has, in common with that of an "electron lattice," a certain analogy with the solid state of matter, as opposed to the "electron-gas" of Sommerfeld's theory. A primary requisite for the existence of either is strong interaction between the electrons.

12. Thermodynamics

a. Rutgers' equation

Since the transition to the superconducting state is not accompanied by latent heat or change of volume, but only by a change in specific heat, it may be considered analogous to a "phase change of the second order." Ehrenfest's equation[54] for the change of specific heat in such a phase change reads

$$\Delta C = -T\cdot\frac{\Delta(\partial v/\partial t)^2}{\Delta(\partial v/\partial p)}. \qquad (12.1)$$

Rutgers[55] suggested that if v and p in Ehrenfest's theory are replaced, respectively, by the external magnetic field H and the magnetization, the equation might be applicable to superconductivity. If we assume that the magnetization is that of "perfect diamagnetism," then $\partial p/\partial v$ corresponds to the susceptibility per gram, and is equal to $-1/4\pi d$ where d is the density. This leads to Rutgers' equation for the specific heat change associated with superconductivity:

$$\Delta C = (T/4\pi d)(dH/dT)^2 \qquad (12.2)$$

valid at the transition point T_0, and in which $H(T)$ is taken to be the threshold magnetic field. This equation has since been derived directly by Rutgers.[56] It is very satisfactorily confirmed numerically for tin and thallium (see §7a).

b. The cycle of Gorter and Casimir

Gorter and Casimir[46] placed Rutgers' equation upon a more satisfactory basis by discussing *ab initio* the thermodynamics of superconductivity.

[54] P. Ehrenfest, Leiden Comm., Supp. 75b (1933).
[55] Appendix to Ehrenfest, reference 54.
[56] A. J. Rutgers, Physica 1, 1055 (1934).

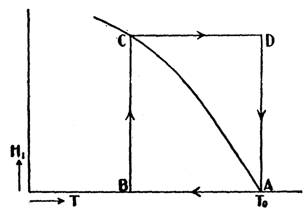


Fig. 23. Thermodynamic cycle of Gorter and Casimir.

Consider the case of a long ellipsoid in an external magnetic field H (so that the critical field can be taken to be the sharply-defined longitudinal threshold field H_t, and the polarization factor can be ignored in the calculations), and suppose this to be taken around the cycle illustrated in Fig. 23, where AC represents the curve between magnetic threshold and temperature. The only assumptions made are:

(i) That the body acts as a perfect diamagnetic, so that the magnetization per gram is given by $\sigma = -H/4\pi d$;
(ii) That under the ideal conditions mentioned the processes are reversible, and the second law of thermodynamics can be applied.

By experiment there is no heat of transition at the normal transition point A. If we denote by Q the heat of transition at C, and by H_t, σ_t, the critical field and magnetization at C, the first law of thermodynamics gives

$$-\int_T^{T_0}\Delta C\cdot dT + Q = -\int_0^{\sigma_t} H d\sigma + H_t\sigma_t$$

or

$$Q = \int_T^{T_0}\Delta C\cdot dT - H_t^2/8\pi d. \qquad (12.3)$$

With Eq. (12.3) the second law gives

$$H_t^2/8\pi d = \int_T^{T_0}\Delta C\cdot dT - T\int_T^{T_0}(\Delta C/T)\cdot dT. \qquad (12.4)$$

If we consider a small interval of integration in the immediate neighborhood of T_0, Eq. (12.4) reduces directly to Rutgers' Eq. (12.2). Eq. (12.4), however, goes further, for by differentiation and combination with (12.3) we find:

$$\Delta C = (T/8\pi d)\cdot(d^2(H^2)/dT^2), \qquad (12.5)$$

$$Q = -(T/8\pi d)\cdot(d(H^2)/dT). \qquad (12.6)$$

Eqs. (12.5) and (12.6) have also been very well confirmed experimentally, at least for tin and thallium (§7b).

Rigorously, this has been applied only to the case of a long ellipsoid, but Gorter and Casimir have shown that in other cases, although the cycle cannot be taken in such a simple form, the magnetic term in the equation is still $H_t^2/8\pi d$. The result should therefore be general, in agreement with experiment.

c. Entropy in the superconducting state

Some further remarks by Gorter and Casimir[57] on the thermodynamics of superconductivity are also of interest. For mercury they have calculated from Eq. (12.5) the entropy difference $\triangle S$ between the normal and superconducting states, the magnetic measurements having been carried to very low temperatures for this metal. As shown in Fig. 24, $\triangle S$ increases rapidly as the temperature is reduced just below the transition point, but at the lowest temperatures is plainly approaching zero at 0°K, and is approximately proportional to the absolute temperature, in agreement with the Nernst law. The lower part of the curve agrees with $\triangle S = 3.5.10^{-4}/T$ cal. per mole-degree. According to the Sommerfeld electron theory the entropy of the free electrons in a metal at very low temperatures is given by

$$S = 3.2.10^{-5}\,(A^2w/d)^{1/3}\,(1/T),$$

where A is the atomic weight, w the number of electrons per atom and d the density. This is in fair numerical agreement with the above experimental figure for mercury, which suggests that at these lowest temperatures the entropy of the electrons in the superconducting state is zero. This fits in with the idea, often expressed, that in a superconductor the electrons must be in some ordered arrangement analogous to the solid state of matter. This ordered state, whether one thinks more definitely of the solid analogy or of something like the local currents of Frenkel, would in some way be excluded from disturbances by the thermal vibrations of the metallic lattice.

If Z is the thermodynamic potential we have at the transition point $\triangle(dZ/dT)=0$ and only $\triangle(d^2Z/dT^2)\neq 0$. The Z curves representing the two states in the entropy-temperature diagram therefore do not intersect at $T=T_0$, but are tangent. The superconducting state should then

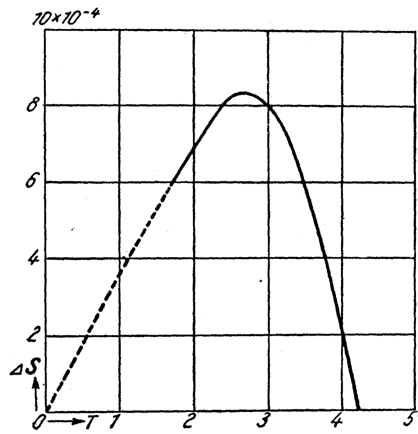


FIG. 24. Entropy difference between normal and superconducting states for mercury.

be stable at any temperature, from which Gorter and Casimir conclude that it is not merely unstable at temperatures higher than T_0, but actually cannot exist. This, together with the shape of the upper part of the entropy curve (Fig. 24), suggests that at temperatures somewhat below the transition point we have to do with a "two-phase system," in which a gradually increasing proportion of the conduction electrons pass into the superconducting phase as the temperature is reduced.

13. ELECTRODYNAMICS

a. The acceleration theory

From the macroscopic point of view we have for a superconductor, as shown in §4a, both $\boldsymbol{E}=0$ and $\boldsymbol{B}=0$ (or rigorously $\dot{\boldsymbol{B}}=0$). The ordinary electromagnetic equations then become indefinite, and no further progress can be made along this line without additional consideration. Becker, Heller and Sauter[58] have shown that in order to be able to apply classical electrodynamics one must take into account the inertia of the electrons. The necessary mathematics are included in their treatment of a special problem, but H. G. Smith has given elsewhere[59] a simpler

[57] C. J. Gorter and H. Casimir, Zeits. f. tech. Physik 15, 539 (1934).

[58] R. Becker, G. Heller and F. Sauter, Zeits. f. Physik 85, 772 (1933).

[59] H. Grayson Smith, reference 48, §3.

and more general derivation of the essential equations.

It is assumed that, while the electric field $\boldsymbol{E}$ vanishes in the steady state, it cannot do so while the current is changing. The acceleration of the electrons is then connected with the field by the ordinary classical relation

$$\dot{\boldsymbol{v}}=(e/m)\boldsymbol{E}. \quad (13.1)$$

This requires later modification according to quantum mechanics, which, however, affects only the numerical factor in the final equations (see §16d). We write the density of the supercurrent

$$\boldsymbol{i}=qN\cdot e\boldsymbol{V}, \quad (13.2)$$

where N is the number of atoms per cc, q the average number of *superconduction* electrons per atom (which from the classical point of view may have to be considered small), and $\boldsymbol{V}$ their mean velocity. The fundamental equation for the acceleration of current is then

$$\dot{\boldsymbol{i}}=(qNe^2/m)\boldsymbol{E}. \quad (13.3)$$

It is further assumed that from this microscopic point of view we can put $\mu\sim K\sim 1$. We then substitute (13.3) into the electromagnetic equations

$$\text{curl } \boldsymbol{H}=4\pi \boldsymbol{i}/c, \quad \text{curl } \boldsymbol{E}=-\dot{\boldsymbol{H}}/c, \quad (13.4\text{a, b})$$

neglecting the displacement current (Gaussian units are used throughout). (13.4b) then gives

$$-(1/c)\dot{\boldsymbol{H}}=(m/qNe^2)\text{ curl } \dot{\boldsymbol{i}}. \quad (13.5)$$

From this we obtain by integration

$$\text{curl } (\boldsymbol{i}-\boldsymbol{i}_0)=-(qNe^2/mc)(\boldsymbol{H}-\boldsymbol{H}_0), \quad (13.6)$$

where $\boldsymbol{i}_0$ and $\boldsymbol{H}_0$ are the current density and field when the body was still above its transition point, and can be put equal to zero in many cases.

By eliminating $\boldsymbol{H}$ between (13.4a) and (13.5), using div $\boldsymbol{i}=0$, curl $\boldsymbol{H}_0=4\pi\boldsymbol{i}_0/c$, we obtain with complete generality

$$\nabla^2(\boldsymbol{i}-\boldsymbol{i}_0)=\beta^2(\boldsymbol{i}-\boldsymbol{i}_0), \quad (13.7)$$

where $\beta^2=4\pi qNe^2/mc^2 \quad (13.8)$

and similarly $\nabla^2(\boldsymbol{H}-\boldsymbol{H}_0)=\beta^2(\boldsymbol{H}-\boldsymbol{H}_0). \quad (13.9)$

b. Distribution of current

Eq. (13.7) determines the distribution of that part of the current which is set up after the body passes into the superconducting state, and is to be solved subject to the general conditions:

$\boldsymbol{i}$ is single-valued and finite throughout the body, div $\boldsymbol{i}=0$ everywhere, and
the normal component of $\boldsymbol{i}$ vanishes at the boundary.

It is well known that these conditions are not sufficient to give a unique solution. This can be obtained in some cases by assuming symmetry conditions, e.g., in the case of an infinitely long cylindrical wire. In other cases the unique solution can be found by assuming that the *external* magnetic field is the same as would be found if the body had magnetic permeability zero, and that the tangential component of $\boldsymbol{H}$ is continuous at the boundary.

However, only the asymptotic solution for a body with dimensions large compared with $1/\beta$ is of practical interest. In this case the solution depends on the normal distance ζ from the surface only through the factor $i/i_0=\epsilon^{-\beta\zeta}$, where i_0 is the current density at the surface. Therefore, for sufficiently large bodies the current density falls to $1/\epsilon$ of its value at the surface in a distance $d=1/\beta$, and we can take this distance as a measure of the effective thickness of the current layer. Because of the uncertainty in the factor q (13.2), it is possible without further evidence only to give a probable lower limit to the value of d. For tin, where $N=3.72.10^{22}$ atoms per cc,

$$d=2.76.10^{-6}/q^{\frac{1}{2}} \text{ cm}, \quad (13.10)$$

so that if we assume $q<1$, $d>3.10^{-6}$ cm. Eq. (13.9) shows that d also measures the depth of penetration of an external magnetic field of strength less than the threshold field.

c. Special problems

It is unnecessary to give the mathematical details of certain special problems which have been treated by this method. Becker, Heller and Sauter[58] have considered the two problems: (i) of the possibility of setting up a persistent current in a superconducting sphere by stopping a rapid rotation, analogous to the experiments of Tolman and Stewart with ordinary conductors; (ii) of the current induced in a sphere by a changing magnetic field. As regards problem (i), if a superconduction current were distributed throughout the body like an ordinary current it would be possible to set up a considerable current in this way. On the other hand, if it is a purely surface current as would be implied by the older "$\boldsymbol{B}=0$" conception, the current set up by rotation would be very small. Exact analysis by the present method leads to a current in the surface layer of depth d, but probably too small to measure by the magnetometer methods commonly used.

Becker *et al.* gave the exact solution of problem (ii) as a simple extension of problem (i). However, the magnetic moment produced, the only observable quantity, is appreciably different from that calculated on the basis of $\boldsymbol{B}=0$ and surface currents only for very small dimensions, comparable with d.

Braunbek[60] has applied these ideas to a discussion of the penetration of an electromagnetic wave into a superconductor (which, according to a direct application of Maxwell's equations, should act as a perfect reflector). The depth of penetration of a plane wave into a superconducting medium, for any frequency less than about 10^{15}, is identical with the depth d (13.10). However, consideration of the incident, reflected and transmitted waves shows that the transmission through a sheet of this thickness would be immeasurably small at any practical frequency. The transmission into the space shielded by two thin sheets was also calculated, and found to depend on the thickness of the shielded space. It might be measurable if the latter were sufficiently small.

14. The London Theory

a. Failure of the acceleration theory

The electrodynamical treatment outlined in the last section, which, following London, we shall refer to as the "acceleration theory," probably leads to the correct results as regards any changes in current, magnetic field, etc., which take place after the body has passed into the superconducting state. However, it is definitely in disagreement with experiment, in general, when the transition takes place in the presence of an external magnetic field or an internal current. For according to Eqs. (13.7) and (13.9) the original current $\boldsymbol{i}_0$ and field $\boldsymbol{H}_0$ should remain unaltered through the transition, which is contrary to the experimental evidence of the Meissner effect (§4).

In view of this discrepancy F. and H. London[47] have developed a new system of electromagnetic equations for superconductors, in which they abandon the fundamental Eq. (13.3) of the acceleration theory, but retain the result (13.9) in the stronger form

$$\nabla^2\boldsymbol{H}=\beta^2\boldsymbol{H}. \tag{14.1}$$

This now applies to the whole field, including that present before the transition, and agrees with the experiments on the Meissner effect (at least for "normal" superconductors). This, and the equation

$$\nabla^2\boldsymbol{i}=\beta^2\boldsymbol{i}, \tag{14.2}$$

which necessarily accompanies it, can be considered to arise by assuming the general truth of the equation

$$\Lambda \text{ curl } \boldsymbol{i}=-\boldsymbol{H}/c,$$

where
$$\Lambda=m/qNe^2=c^2/4\pi\beta^2 \tag{14.3}$$

in place of (13.5) which applies only to the time derivatives of these vectors. Eq. (14.3) is therefore taken as the fundamental equation by which the ordinary electromagnetic equation must be supplemented in a superconductor. Now, however, Eq. (13.3) holds only in the differential form

$$\text{curl } (\Lambda\dot{\boldsymbol{i}}-\boldsymbol{E})=0 \quad \text{or} \quad \Lambda\dot{\boldsymbol{i}}-\boldsymbol{E}=\text{grad } \mu \tag{14.4}$$

where μ is an undetermined function.

The six components of the electromagnetic field form an antisymmetrical tensor in relativity theory with

$$H_x,\ H_y,\ H_z,\ E_x,\ E_y,\ E_z\equiv f_{23},\ f_{31},\ f_{12},\ if_{14},\ if_{24},\ if_{34};$$

and the three components of current density $\boldsymbol{i}$

[60] W. Braunbek, Zeits. f. Physik **87**, 470 (1934).

are the space-like components of a four-vector of which the time-like component is $ic\rho$ where ρ is the charge density. Therefore the six equations

$$\Lambda \operatorname{curl} \mathbf{i} = -\mathbf{H}/c; \quad \Lambda(\mathbf{i} - \operatorname{grad} \mu/\Lambda) = \mathbf{E}$$

can be combined into one invariant tensor equation if we put $\mu/ic\Lambda = ic\rho$. With this (14.4) becomes

$$\Lambda(\dot{\mathbf{i}} + c^2 \operatorname{grad} \rho) = \mathbf{E}, \tag{14.5}$$

which is taken as a second fundamental equation.

It follows very simply from (14.5) that the electric field and charge also obey the distribution equations

$$\nabla^2 \mathbf{E} = \beta^2 \mathbf{E}, \quad \nabla^2 \rho = \beta^2 \rho. \tag{14.6}$$

If we introduce the potentials $\mathbf{A}$ and φ, the relations

$$\mathbf{E} = -\operatorname{grad} \varphi - \mathbf{A}/c, \quad \mathbf{H} = \operatorname{curl} \mathbf{A}$$

are satisfied by putting, within the superconductor,

$$\mathbf{A} = -\Lambda c \mathbf{i}, \quad \varphi = -\Lambda c^2 \rho \tag{14.7}$$

(14.5) can now be written

$$\Lambda \mathbf{i} = \mathbf{E} + \operatorname{grad} \varphi. \tag{14.8}$$

The difference in the results of this treatment and of the acceleration theory, as modified to allow for the Meissner effect (see §15), is comprised in Eq. (14.6) and (14.8). In the acceleration theory there cannot be an electric field within the superconductor in the steady state. According to the London theory, however, the electric field penetrates to the same depth as the magnetic field, and is balanced by an accumulation of charge in the surface layer. That part of the electric field which arises from the scalar potential does not accelerate the current, which is fundamentally connected with the magnetic field alone by Eq. (14.3) and (14.7).

b. The transition curve

In order to discuss the transition state F. and H. London considered a cylindrical wire of radius a, carrying a current I somewhat greater than the critical current $I_t = 2acH_t$ where H_t is the threshold magnetic field. It is assumed that the wire can be divided into an internal superconducting region of radius R where $H < H_t$, and an external region where $H > H_t$, and that the total current I can be divided into two corresponding parts

$$I = I^{(i)} + I^{(e)}, \quad \text{where} \quad I^{(i)} = 2cRH_t. \tag{14.9}$$

The current and electric field outside the radius R are connected by the ordinary relation for a metal of conductivity σ, and therefore

$$\sigma E \cdot \pi(a^2 - R^2) = I^{(e)} = I - I_t \cdot R/a, \tag{14.10}$$

which gives the field E in the non-superconducting region. This field penetrates slightly into the superconducting region, but, since it is derived from a scalar potential, does not accelerate the inner current.

Because of this feature of the London theory it is possible to have parallel superconducting and non-superconducting regions in equilibrium, both carrying a current. Previously it was usually supposed, in order to account for the existence of stable states with resistance intermediate between zero and the normal, that different parts of the wire became superconducting at slightly different temperatures, so that the current passed through superconducting and non-superconducting regions in series.

Assuming uniform distribution of current in the non-superconducting region, the magnetic field there cannot everywhere exceed H_t unless

$$R > R_0 = a(I/I_t - [(I/I_t)^2 - 1]^{\frac{1}{2}}). \tag{14.11}$$

For given I and I_t this same value of R is further selected by the property that it makes the heat developed a minimum. R_0 is therefore taken to be the equilibrium radius of the superconducting region. The apparent resistance per unit length can then be calculated with the result

$$\omega = \tfrac{1}{2}\omega_0(1 + [1 - (I_t/I)^2]^{\frac{1}{2}}), \tag{14.12}$$

where ω_0 is the normal resistance.

According to Eq. (14.12), as the temperature is reduced so that I_t increases from 0 to the given I, ω decreases from ω_0 to $\frac{1}{2}\omega_0$, this first drop being very rapid for a small I. When $I_t > I$, the entire metal is of course superconducting, and the resistance therefore drops discontinuously from $\frac{1}{2}\omega_0$ to 0 at this point.

This theory naturally applies to the ideal metal, and therefore it is significant that the closer the approach to an ideal crystal, and the smaller the measuring current, the more rapid is the transition. Departure from ideality may be presumed to bring with it the commonly accepted conception that different regions pass into the superconducting state at slightly different temperatures. In an actual metal I_t is probably not constant throughout the wire.

We shall return again to the London theory in §17, after discussing other recent theories.

15. The Spontaneous Current Theory

a. Modification of the acceleration theory

H. G. Smith's recent discussion[48] of the spontaneous current theory arose from an attempt to see how far one can go in the treatment of superconductivity by applying accepted physical principles, both classical and quantum mechanical. The acceleration theory (§13a) was therefore accepted as correct in principle. If this is done, the only explanation of the discrepancy between Eq. (13.9) and the Meissner experiments is to assume that the microscopic electronic structure of a "normal" superconductor is such that it has a macroscopic diamagnetic susceptibility $-\chi = 1/4\pi$, in the absence of an external field. This view is supported by the success of the thermodynamical treatment of Gorter and Casimir, an essential point of which is the reversibility of the transition in a magnetic field (§12b). A diamagnetic susceptibility of this order of magnitude can only arise if the classical orbits described by the electrons are very large compared with the dimensions of an atom. A classical discussion should therefore be approximately correct.

From the classical point of view the only possible conception is that the electrons in a superconductor pass spontaneously into a state of orderly motion in long resistanceless paths, whose order is maintained in a magnetic field less than the threshold field by mutual interactions between the electrons. Since the paths must be closed in general it is convenient to speak of them as "current orbits," or "vortex currents." No theory was offered to account for the setting up of the current orbits, or to explain their stability in the face of the thermal vibrations in the lattice. This must come from the eventual complete quantum-mechanical treatment.

Continuing the classical calculation as a first approximation, it was assumed that the acceleration theory was locally valid. The distribution of current density must therefore satisfy Eq. (13.7). It must also be balanced so that there is neither a resultant current, nor an observable magnetic moment. This leads to a system of related local vortices, so that there is a strong analogy between this conception and that of spontaneously magnetized "aggregates" in a ferromagnetic body. It seems likely then that in a polycrystalline metal independent vortex systems would be set up in different crystallites, since the grain boundaries, like alloys, are probably not "normal" superconductors. The author attempted to give an explanation on this basis of the sharp transition in a single crystal, and of the widening of the transition range in a polycrystal. Stark[61] has recently given a slightly different explanation of the effect of grain size on the transition point, using the language of the electron lattice theory, which for this purpose is equivalent since both theories involve the analogy with solidification. These arguments are not entirely satisfactory, and so will not be repeated here.

b. Objection to the spontaneous current theory

Bloch[62] has offered a very general objection to any conception which depends upon the assumed stability of spontaneous local currents. This was originally expressed in quantum-mechanical language as an objection to Brillouin's theory, but has been translated into equivalent classical terms by Brillouin.[63] In the latter form the argument is as follows: Suppose that an element of volume in the metal is carrying a current I. Let an electric field be applied such as to increase the current and let the potential difference across the element be V. The energy

[61] J. Stark, Physik. Zeits. **36**, 515 (1935).

[62] Appendix to L. Brillouin, J. de phys. et rad. **4**, 334 (1933).

[63] L. Brillouin, Proc. Roy. Soc. (in press).

of the electrons will be increased by an amount $VIdt$. But if the field is applied in the opposite direction the energy will be decreased by the same amount. Hence it is argued that the current cannot be stable.

However, it is not considered in this argument that it is essential to any form of spontaneous current theory that the current orbits must be closed in the absence of an external field. A small metallic crystal has to be treated as a unit, and then it is very easily seen that any distortion of the current orbits which gives a resultant current through the crystal causes an increase in the total energy.

c. Minimum dimensions for normal superconductivity

It is now possible to calculate the minimum size of current vortex which will satisfy the criterion $-\chi \geqq 1/4\pi$ for normal superconductivity. The ordinary theory of diamagnetism of electrons in stationary orbits is directly applicable, and we have

$$-\chi = (qNe^2/6mc^2)\overline{r^2} = \overline{r^2}/24\pi d^2 \geqq 1/4\pi, \qquad (15.1)$$

where $\overline{r^2}$ is the mean square radius vector of the current orbits, and d is the effective depth of the current layer (13.10).

From the solution of (13.7) we find for a square vortex of side a

$$\overline{r^2} = 0.129a^2 \qquad (15.2)$$

independently of the value of β or of the total number of vortices in the system.

Finally therefore we must have

$$a > a_{\text{min.}} = 6.83d = 18.8.10^{-6}/q^{\frac{1}{2}} \text{ cm for tin.} \qquad (15.3)$$

It was suggested that this minimum dimension might be approximately identified with the critical thickness of thin film (§9a) at which superconductivity begins to be seriously affected, or rather that the measured critical thickness should be a fairly close upper limit to $a_{\text{min.}}$, on account of the unknown action at the surface in contact with a non-superconducting metal. This allows an estimate to be made of a fairly close lower limit for the factor q, with the results:

Tin—$q > 0.035$; Lead—$q > 0.06$.

Values of this order are probably not unreasonable in the neighborhood of the transition point.

16. Quantum-Mechanical Treatments

Only a very brief outline of the quantum-mechanical theories of superconductivity will be attempted here. For the mathematical details references must be made to the original papers.

a. Brillouin's theory[49]

Brillouin studied by the method of the self-consistent field the energy E of the electron waves in the three cubic lattices as a function of the quantum number vector $\boldsymbol{a}$, where $h\boldsymbol{a}$ is the quantum-mechanical analog of the momentum vector. It was concluded that for "almost bound" electrons the curve between E and a component of $\boldsymbol{a}$ could, except for a simple cubic lattice, take the peculiar form shown in Fig. 25 in the lowest energy zone. The existence of superconductivity was associated with the existence of secondary minima, as at A, A', in the energy-momentum curve. In three dimensions one must, of course, think of secondary regions of minimum energy in the momentum space (i.e., in the space of the vector $\boldsymbol{a}$).

The process responsible for the ordinary temperature-dependent resistance is the scattering of the electron waves by the thermal vibrations of the lattice. Brillouin showed that this scattering cannot take place for electrons which satisfy the condition

$$|\text{grad}_a E| < hW, \qquad (16.1)$$

where grad_a denotes the gradient in momentum space, and W is the velocity of the elastic waves into which the thermal vibrations can be analyzed. At sufficiently low temperatures electrons in the secondary minima of the energy distribution satisfy (16.1) and so cannot be transferred to the other states by interaction with the thermal vibrations. Some of the electrons are so to speak "trapped" in metastable states.

In the absence of an external electric field, the distribution of electrons in momentum space is symmetrical, with no resultant current.* An

* It must be noted that the group velocity of an electron wave, and therefore the current carried by it, is not simply related to the momentum vector $h\boldsymbol{a}$. The current carried

electric field displaces the entire distribution in the direction of the field, destroying the symmetry, and causing a resultant current. Ordinarily, when the field is removed the distribution is rapidly restored to its steady symmetrical state by interaction with the thermal vibrations (and lattice irregularities), and the current disappears. But if the regions A, A' are metastable, the mechanism which restores the symmetry breaks down, the distribution remains asymmetrical, and the current, once started, persists without an external electric field.

Some doubt has been expressed, most recently by Brillouin himself,[63] whether a metastable electron distribution is adequate to explain the complete stability of the persistent currents of superconductivity. Further, no explanation was offered for the disappearance not only of the resistance due to thermal agitation, but also of the residual resistance due to irregularities.

by an electron at a given point in momentum space is proportional to grad$_a$ E. Consequently one must not think of the metastable electrons as actually carrying the persistent current, but rather of the persistence of an asymmetrical distribution.

b. Schachenmeier's theory[50]

Schachenmeier took as the zeroth approximation for his calculation a system consisting of N "series" electrons bound each to a particular metallic ion but under the influence of the periodic potential of the complete lattice, and one free "conduction" electron moving in the periodic potential field. The interaction between conduction and series electrons was then worked out as a first perturbation. Interaction between different conduction electrons was neglected. The combined eigenfunctions of the $N+1$ electrons were still degenerate, and this degeneracy was removed by considering as a second perturbation the effect of the thermal vibrations of the lattice. Certain eigenfunctions in this result apparently correspond to a periodic exchange between conduction and series electrons with a certain frequency ν, which depends on the temperature. Schachenmeier maintained that they also represent a transport of electricity without scattering by lattice irregularities, that is, superconductivity, as long as $\nu > \nu_m$ where ν_m is the so-called "maximal frequency" of specific heat theory. The transition temperature would therefore be determined by the condition $\nu = \nu_m$, and a numerical estimate of ν gave the correct order of magnitude for the transition point. These particular eigenfunctions represent states near the upper limit of the first energy zone. Since by the Pauli principle each zone contains $2N$ electrons, the states in question could be occupied only in metals of valence 2 or greater. This is in agreement with the existing evidence that there are no monovalent superconductors.

Schachenmeier's treatment has been very severely criticized by Bethe,[64] both in general and in detail. We need mention here only the general criticism that the distinction between "series" and "conduction" electrons is not permissible even in the zeroth approximation, since both have the same origin as valence electrons, and both are subject to the same potential field, namely, that of the metallic lattice as a whole.

c. Papapetrou's theory

One other quantum-mechanical treatment should be mentioned, that of Papapetrou.[65] In this it was suggested that superconductivity might be due to the presence of an almost filled energy zone in the metal, for electrons very near the upper limit of a zone should satisfy Brillouin's condition (16.1). Again monovalent metals could not become superconducting. Papapetrou concluded that metastable states would occur near the upper limit of a zone at low temperatures, without the necessity of any special energy distribution. These electrons, which at ordinary temperatures contribute only very slightly to the conductivity, he considered to be responsible for superconductivity.

There are, however, two processes which have not been considered in this treatment, and which make it appear doubtful whether the stability of a persistent current can be explained in this way. First, if there is to be a nearly filled energy zone at very low temperatures, it must be overlapped slightly by the next higher zone. It is not shown that transitions are impossible between the two zones. Second, electrons near the

[64] H. Bethe, *Handbuch der Physik*, Vol. 24/2, p. 333; Zeits. f. Physik **90**, 674 (1934).

[65] A. Papapetrou, Zeits. f. Physik **92**, 513 (1934).

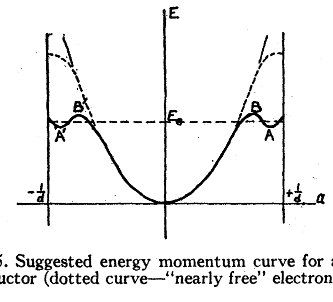


FIG. 25. Suggested energy momentum curve for a superconductor (dotted curve—"nearly free" electrons).

upper limit of an energy zone are known to be liable, when displaced by an external field, to have their momentum reversed by reflection in the lattice planes. Brillouin considered it necessary in order to avoid this process to postulate energy minima which did not extend to the boundary of the energy zone in momentum space (Fig. 25).

d. Bearing of quantum mechanics on the acceleration theory

Kikoin and Lasarew[66] have remarked that the known superconducting metals almost all have, at ordinary temperatures, very small (usually positive) values of the Hall coefficient R. This is especially true of the more familiar "normal" superconductors with comparatively high transition points. With the exception of magnesium (transition point 0.70°K) the remaining superconductors still have Hall coefficients considerably less than the classical values.

According to the wave-mechanical theory of conduction,[67] anomalous values of the Hall coefficient arise through the fact that the acceleration of an electron under a force $\boldsymbol{F}$ is given, not by the classical Eq. (13.1), but by

$$dv_x/dt = (e/h^2)\cdot(\partial^2 E/\partial a_x^2)F_x, \quad \text{etc.} \quad (16.2)$$

Therefore in regions where the second derivatives of E become negative—regions where the energy-momentum curve is concave downwards—there is a negative "apparent mass," or the electrons move as if positively charged. For free electrons (16.2) reduces to (13.1), and otherwise always $(1/h^2)(\partial^2 E/\partial a_x^2) < 1/m$, or the partial binding with the metallic lattice involves an apparent increase of inertia.

The observed Hall coefficient of a metal depends upon averages over the electrons involved of the second derivatives of E. The small Hall coefficients of most of the superconductors therefore indicate that in these metals the energy-momentum curves depart radically from the simple form for "nearly free" electrons (dotted curve, Fig. 25) such as is characteristic, for example, of the alkali metals. In fact, the curve supposed by Brillouin would give exactly a very small positive or negative Hall coefficient, since even at ordinary temperatures only electrons in the neighborhood of the level E_0 (representing the maximum electron energy at 0°K) need to be considered, and in this neighborhood small positive and negative curvatures nearly balance.

These considerations have an important bearing on the decisive quantity β of the acceleration theory (13.8) (which is presumably to be carried over also into the London theory). For here also the reciprocal mass has to be replaced by an average of the second derivatives of the energy. Concerning this, all that can be said at the present time is that the quantum-mechanical value of β must be very much smaller than the classical value, especially for those superconductors which have very small Hall coefficients. In view of this quantum-mechanical correction the simple relation (15.3) between the minimum dimension $a_{\min.}$ for normal superconductivity and the depth of penetration d is no longer valid. d may become more nearly comparable with, or greater than, $a_{\min.}$.

17. Discussion

In the preceding sections have been outlined those theoretical treatments of superconductivity which seem to have any value in the light of the most recent experiments. Of these only the thermodynamical developments (§12) really reach a satisfactory conclusion in the experimentally confirmed connection between magnetic properties and specific heat. There is still a long way

[66] I. Kikoin and B. Lasarew, Physik. Zeits. d. Sowjetunion **3**, 351 (1933); B. Lasarew, ibid. **4**, 567 (1933).

[67] R. Peierls, reference 2, 21. D. Blochinzew and L. Nordheim, Zeits. f. Physik **84**, 168 (1933).

to go before a clear atomic theory can be given to explain all the facts. Certain very general features of such a theory can, however, be indicated. It is fairly evident that interactions between the conduction electrons must play an important part, so that in the superconducting state the electronic structure presents certain analogies with the solid state. Again, the electrical considerations and the tin film experiments show that the behavior near the boundary of the body is of particular importance. The final solution must obviously be quantum mechanical, but those quantum-mechanical treatments which have been given up to the present, in which the crystal is treated as infinite in extent and the electron interactions are ignored, must be inadequate. The only result which can reasonably be expected from such a treatment is the formulation of some energy condition, e.g., based on the relation (16.1), which must be satisfied before resistanceless motion of the electron waves is possible. A definite proof that the motion is stable is probably impossible with these approximations. It seems probable that it will be necessary in order to obtain a satisfactory atomic theory to solve the quantum-mechanical problem of a finite crystal, taking into account the electron interactions and the lattice vibrations. This is obviously a matter of the greatest mathematical difficulty, even in a rough approximation.

Lacking a complete quantum-mechanical theory, the best available approach seems to be through phenomenological semiclassical theories in which the absence of resistance is accepted as a fact. In this respect the present choice seems to lie between the London theory and the vortex current theory. There is really less difference between these two views than appears on the surface. The vortex theory undoubtedly involves too concrete a picture of the electronic structure, concerning which we really know very little. The view which should logically be taken may be expressed as follows: The electronic structure is to be considered as made up of aggregates which behave like diamagnetic atoms of sufficient size to make the body as a whole a perfect diamagnetic; on account of the size of these aggregates classical theory should give a fair first approximation to their properties and behavior; the discussion given in §15 then follows, and is valid to this approximation. On the other hand, the Londons themselves showed that their theory is equivalent to considering the body as a single large diamagnetic atom. By applying this view to a topologically multiply-connected body they arrived precisely at the results attained through the classical view of "true current" in a closed circuit (see §5).

The only essential difference between the two views is that in the London theory the current depends entirely upon the magnetic field, and that part of the electric field which arises from a scalar potential is incapable of causing a current. In the vortex theory the local validity of the current acceleration Eq. (13.3) has to be retained. With this feature the London theory is relativistically invariant, and is probably to be preferred for that reason. However, there seems to be no way of distinguishing between the two views experimentally, since there is no way of applying a *constant* electric field under circumstances which might cause an observable superconduction current.

On the other hand, consider a superconducting circuit containing a soldered contact. Solder is not a "normal" superconductor, and therefore the London theory in its present form cannot apply in this part of the circuit. The acceleration theory has then to be invoked in order to explain the continuity of the current across the contact. It seems to the authors that the same consideration applies to the grain boundaries in a polycrystal, which would mean that the London theory is applicable only to a single crystal.

The example just given brings up the whole question of "normal" and "anomalous" superconductors. Until the present year the anomalous behavior of certain alloys, etc., was usually ascribed to the presence of non-superconducting inclusions. The realization that this is inadequate, and that there is a real distinction between, e.g., a pure metal and a pure intermetallic compound, is so recent that the point has not yet been seriously considered from the theoretical point of view. Here again there are two possible views. We may imagine two distinct kinds of superconductivity, one obeying the London theory, and one obeying the classical acceleration theory. Or we may imagine a difference in degree, say in the size of the aggregates in the vortex current theory. In connection with the latter of these views a remark by Gorter[68] should be mentioned. He has suggested that the absence of Meissner effect and the high threshold field for an alloy might be explained if in it the smallest possible superconducting region is smaller than the depth of penetration of the magnetic field. This is in line with the author's calculation of the smallest aggregate for normal superconductivity (Eq. (15.3)).

---

[68] C. J. Gorter, Physica 2, 449 (1935).