SUPERCONDUCTIVITY

BY

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Introduction

Recent years have seen a great expansion of research effort in low temperature physics. This has been brought about partly by the development of simpler and more available techniques, but also because of the intrinsic interest of the subject. This interest is two-fold ; on the one hand many phenomena become much simpler in character when kT is sufficiently small, so that more crucial tests of their theoretical bases become possible, while on the other hand quite new and unexpected effects turn up at low temperatures, which are particularly attractive because of the challenge they offer to the theoretical physicist. In this last category come the peculiar properties of liquid helium and superconductivity, both in a sense macroscopic manifestations of quantum theory, but neither as yet properly understood. Rather than attempt to cover the whole range of low temperature physics in outline I have decided to concentrate in these three lectures on the single problem of superconductivity. I propose to present a survey of the main characteristics of this phenomenon and to indicate how far theory is able to correlate them and explain them.

Superconductivity was discovered by Kamerlingh Onnes in 1911 about 3 years after he had opened up the new range of low temperatures below 4.2°K by his

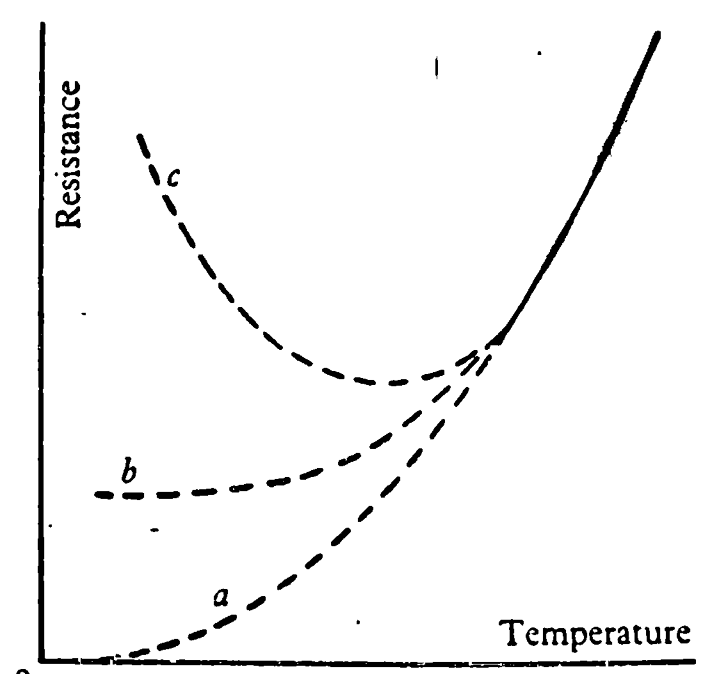


Fig. 1. Possible forms of temperature variation of resistance (schematic).

success in liquefying helium. One of the first problems he chose to study was the electrical resistance of metals. The theory was at that time rather sketchy

16679

and any one of the three modes of variation illustrated in fig. 1 seemed possible. Thus (*a*) would occur if the resistance was due entirely to obstruction of electronic paths by thermal vibrations, (*b*) would occur if obstruction by impurities and imperfections were important, while (*c*) would occur if the number of free electrons available to carry the current fell off rapidly at low temperatures due to "condensation" on the atoms.

The new experimental results (see fig 2) were presented by Onnes in an interesting paper to the Third International Congress of Refrigeration held in September, 1913 at Chicago : 'I already inclined to the idea that had been expressed by Dewar, that resistance wculd tend to vanish at the absolute zero itself, when the experiments with liquid helium brought quite a revelation. The resistance of very pure platinum became constant instead of passing through a minimum or of tending to vanish at the aboslute zero.' The constant value of the resistance turned out to depend strongly on the impurity content of the metal, and indeed such an impurity effect could have been anticipated, for nearly 50 years earlier, in 1864, Matthiessen had fcund that specimens of the same metal differing in purity differed in resistance by amounts which did not vary with temperature.

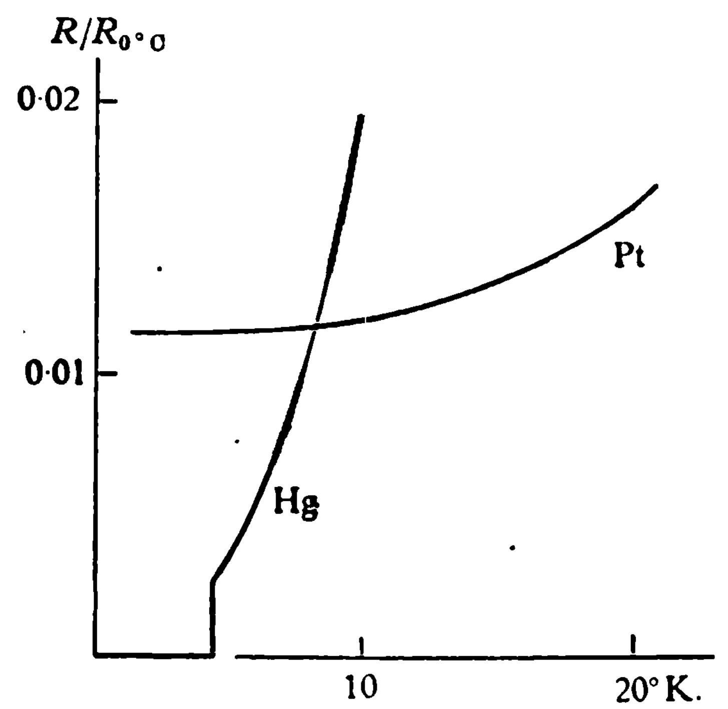


Fig. 2. Variation of $R/Ro°c$. (ratio of the resistance to resistance at o°C.) of platinum and mercury.

Onnes then explains that since it seemed as if it was only impurities which prevented the resistance of platinum and gold disappearing, even 'using the purest gold of any mint in the world', he decided to experiment with the 'only metal which one could hope to get into wires of a higher state of purity, *viz.*, mercury. . . it could be foretold that the resistance of a wire of solid mercury would be measurable at the boiling point of helium but would fall to inappreciable values at the lowest temperatures which I could reach. With this beautiful prospect before me there was no more question of reckoning with difficulties. They were overcome and the result of the experiments was as convincing as could be hoped. No doubt was left of the existence of a new state of mercury in which

H																	He
Li 0·08 (7) cub.	Be 0·06 (1) hex.											B 1·3 (23) hex.	C 1·2 (22) hex.	**N**	**O**	F	Ne
Na 0·09 (7) cub.	Mg 0·05 (15) hex.											Al 1·20 (13, 8) cub.	Si 0·07 (1) cub.	P 2·0 (15) orth.	S	**Cl**	**A**
K 0·08 (7) cub.	Ca 1·3 (23) cub.	Sc cub.	Ti 0·53 (20, 4) hex.	V 5·1 (25, 35) cub.	Cr 0·08 (1) cub.	Mn 0·15 (7) cub.	Fe 0·75 (14) cub.	Co 0·06 (26) hex.	Ni 0·75 (14) cub.	Cu 0·05 (15) cub.	Zn 0·91 (14, 8) hex.	Ga 1·10 (10, 8) orth.	Ge 0·05 (15) cub.	As 0·8 (12) rhom.	Se 1·3 (24) hex.	**Br**	**Kr**
Rb 0·8 (12) cub.	Sr 1·4 (23) cub.	Y 0·10 (7) hex.	Zr 0·70 (15) hex.	Nb 8 (21, 11) cub.	Mo 0·05 (26) cub.	Tc	Ru 0·47 (7) hex.	Rh 0·09 (1) cub.	Pd 0·10 (7) cub.	Ag 0·05 (26) cub.	Cd 0·56 (15, 8) hex.	In 3·37 (34, 28) tetr.	Sn 3·730 (30, 16) tetr.	Sb 0·15 (1) rhom.	Te 1·2 (24) hex.	**I**	Xe
Cs 0·8 (12) cub.	Ba 0·15 (7) cub.	La 4·37 (27, 32) hex.	Hf 0·35 (15) hex.	Ta 4·4 (18, 5) cub.	W 0·06 (26) cub.	Re 1·0 (2) hex.	Os 0·71 (7) hex.	Ir 0·10 (7) cub.	Pt 0·10 (7) cub.	Au 0·05 (15) cub.	Hg 4·152 (29, 16) rhom.	Tl 2·38 (31, 28) hex.	Pb 7·22 (30, 3) cub.	Bi 0·05 (15) rhom.	Po mono	**At**	Rn
Fr	Ra	Ac	Th 1·39 (19, 33) cub.	Pa	U 0·8 (2, 9) orth.		Transuranic:			Np	Pu	Am	Cm				

Rare earths

Ce 0·25 (7) cub.	Pr 0·25 (7) hex.	Nd 0·25 (7) hex.	Pm	Sm	Eu cub.	Gd hex.
Tb hex.	Dy hex.	Ho hex.	Er 0·8 (12) hex.	Tm hex.	Yb cub.	Lu hex.

Fig. 3. The superconducting elements in the periodic system. The superconducting elements are "boxed-in", and the figures indicate T_c in °K; since the diagram was prepared Tc has also been found superconducting with $T_c = 11$°K.

its resistance has practically vanished. . . .Mercury has passed into a new state, which on account of its extraordinary electrical properties may be called the superconductive state.'

It is curious that the discovery of superconductivity should have come about in this way, for Onnes himself soon showed that the confirmation of his predictions about the behaviour of mercury was only apparent. Thus he found that considerable impurities added to mercury did not in fact inhibit the drop to zero resistance, *i.e.,* that the zero resistance was not just a matter of using a very pure metal. At the same time more careful measurements showed that the resistance fell to zero much more sharply than the fall Onnes had foretold (which was according to a formula based on what is now known to be an unsound theory).

The discovery of superconductivity opened up a whole series of problems about the scope and nature of the new phenomenon. As regards the scope of superconductivity, it has been found that twenty-two metallic elements and a large number of alloys become superconducting, the transition temperature being characteristic of the particular metal, and varying from as low as 0.35° K. for hafnium up to about 11° for technetium (some alloys have higher transition temperatures, the highest known being about 15.5° K. for niobium nitride). The known superconducting elements fall roughly into two groups in the periodic system (see fig. 3) which suggests that superconductivity is probably not a universal property ; but since every new advance in the lowering of temperature has revealed new superconductors, we cannot yet be certain that superconductivity is, indeed, limited only to certain metals. Since it is impossible to reach the absolute zero, this question can be definitely settled only by the development of a theory of the origin of superconductivity ; unless, of course, further advances in lowering temperature should show that all metals do, indeed, become superconducting.

One fact that was established quite early on was that the resistance in the superconducting state was really negligibly small. Using the conventional potentiometer method it could be established only that the resistance was less than, say, 0.1% of its value immediately above the transition temperature (since this value is already very small) and Onnes developed the ingenious "persistent current" method to obtain a much lower limit. Imagine a closed metal ring of area A and self inductance L cooled down in a magnetic field H normal to its plane until it becomes superconducting and suppose the residual resistance is R. If now the field is reduced, a current i will be induced according to the equation

$$L \frac{di}{dt} + Ri = A \frac{dH}{dt} \tag{1}$$

If R is very small we can neglect the second term and on integration we find

$$L i_0 = - A H \tag{2}$$

if i_0 is the current left in the ring in zero field. This current should now decay according to the same differential equation, but with the right hand side zero, which gives—

$$i = i_0 e^{-Rt/L} \tag{3}$$

Thus the time of decay gives an immediate estimate of L/R, and hence of R, since L can be calculated. No experiment up to now has however indicated the least trace of decay of the so-called "persistent current" even over periods of many hours, and from the most delicate of such experiments it can be concluded that in the superconducting state the resistance is less than 10^{-12} of its value just above the transition. We may therefore safely assume that a characteristic feature of the superconducting state is that it cannot support any steady electric field : $E=0$.

Influence of External Agents

The influence of various factors on superconductivity has been extensively studied. The most important of these are the following.

(1) Superconductivity is destroyed by a sufficiently large magnetic field known as the critical field, H_c, the resistance being restored quite sharply if the field is parallel to the length of the wire. The critical field is a function of temperature and some typical $H_c - T$ curves are shown in fig. 4. It will be seen that usually H_c is of the order of only a few hundred gauss, and that the curves are approximately parabolic, *i.e.*

$$H_c = H_0 \ (1 - (T/T_c)^2) \tag{4}$$

We shall see later that the $H_c - T$ curve of a superconductor has a thermodynamic significance rather like that of a p–T diagram for melting or boiling, and that much of the thermal behaviour of the superconductor may be deduced from it.

(2) A consequence of the existence of a critical magnetic field is that there is also a critical current, namely that current which produces the critical magnetic field at the surface. Curiously enough, this connection between between critical current and critical field was not realized by Onnes, and was first pointed out by Silsbee on the basis of Onnes' published data. Since for a round wire of radius a, $H = 2\,i/a$, it can be seen that the critical current is of order 100 amps for a wire 1 mm in diameter.

(3) A mechanical stress can change the transition temperature and the critical field slightly, but quite large stresses are required since dT_c/dp is only of order 10^{-100} K dyne^{-1} cm^2 and dH_c/dp of order 10^{-8} gauss dyne^{-1} cm^2.

(4) Addition of chemical impurities or plastic deformation modifies the superconducting properties in a complicated way, which will be referred to briefly later. (5) Reduction of specimen size below about 10^{-4} cm. modifies the superconducting properties in a manner which will be discussed later.

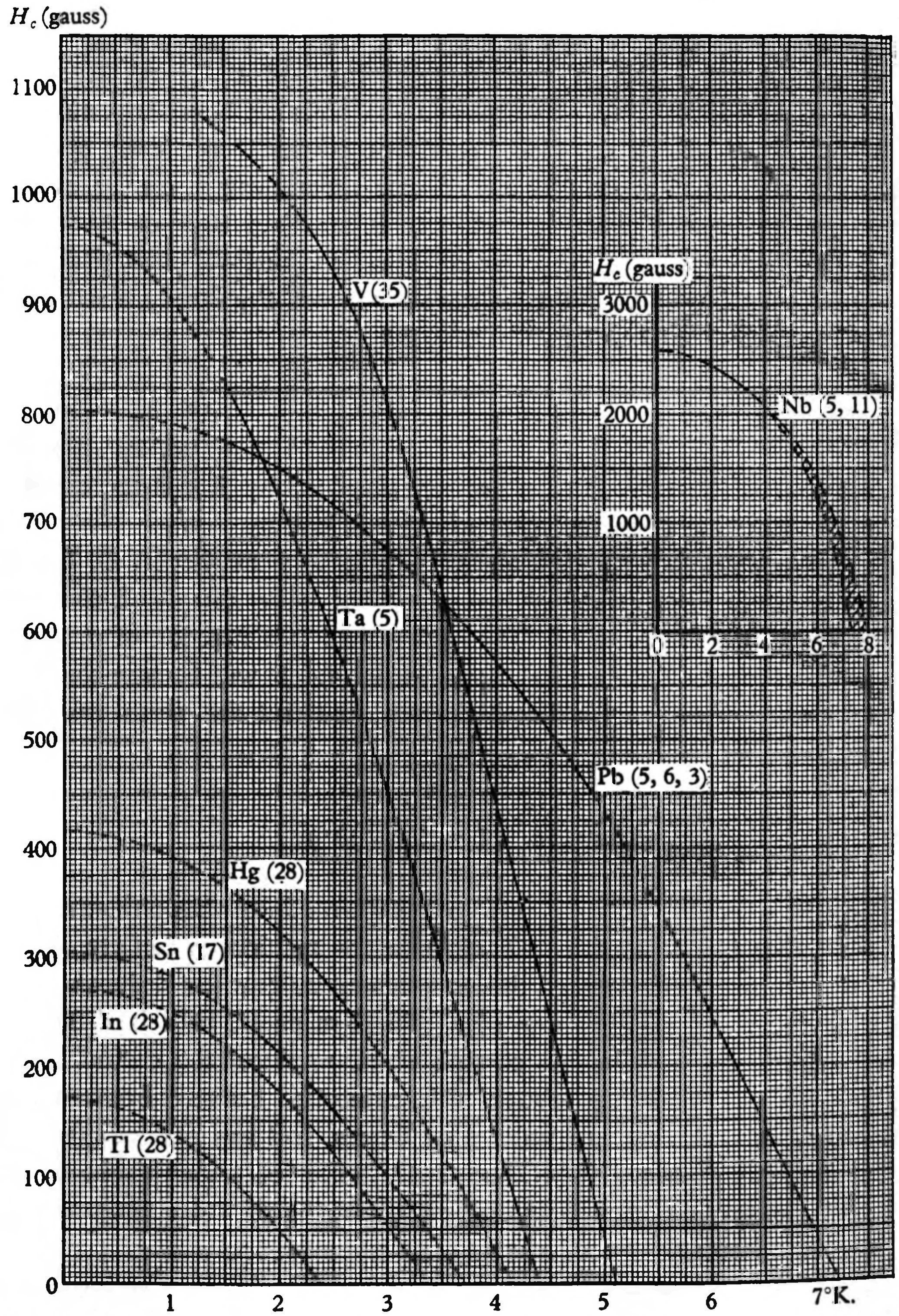


Fig. 4. $H_c - T$ curves for some superconducting elements (the numbers are references to the literature as given in the author's monograph "Superconductivity").

(6) The resistance of a superconductor is no longer zero at very high frequencies, as illustrated in fig. 5. Up to 10^7 cyc/sec., R is still practically zero at all tempera-

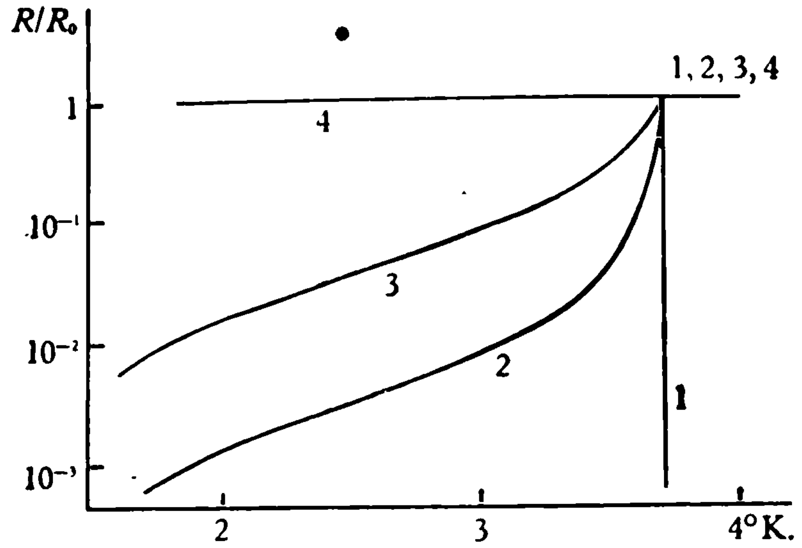


Fig. 5. Temperature variation of resistivity of tin at various frequencies. (1) d.c. (2) 1.2×10^9 cyc./sec. (3) 9.4×10^9 cyc./sec. (4) 2×10^{13} cyc./sec.

tures below T_c, but for 10^9 cyc/sec, H. London and later Pippard showed that there was a considerable resistance which tended to zero as T approached 0°K. This effect has been considerably studied by Pippard in recent years, and I shall refer briefly to its interpretation later on. For still higher frequencies, falling in the infra red range, Ramanathan has shown that the resistance does not drop at all below T_c, so it is probable that somewhere between centimetre waves and infra red, absorption sets in even at 0°K.

(7) About 3 years ago it was found that T_c was appreciably different for different isotopes of the same superconductor, and that roughly T_c varies as $M^{-\frac{1}{2}}$. We shall see later that this was predicted by Fröhlich's theory.

Changes of other properties accompanying the superconducting transition

(1) The magnetic properties undergo a change no less remarkable than the electrical properties. This will be discussed in detail in the second lecture.

(2) The specific heat shows a discontinuity at T_c (see fig. 6) and in presence of a magnetic field (but not otherwise) there is a latent heat of transition. We shall see that these effects as well as the small volume changes found in a magnetic field, find a detailed thermodynamic explanation in terms of the magnetic properties. This thermodynamic theory predicts also discontinuities in the thermal expansion and elastic properties, but these have not yet been observed owing to their very small magnitude. It is hoped to observe the jump in thermal expansion by a new sensitive method at present being developed at the National Physical Laboratory of India by Dheer and Surange.

(3) All the thermoelectric effects vanish sharply at T_c. This is on the whole not

surprising since it is unlikely that a temperature gradient would modify the superconductor's inability to maintain an electric field.

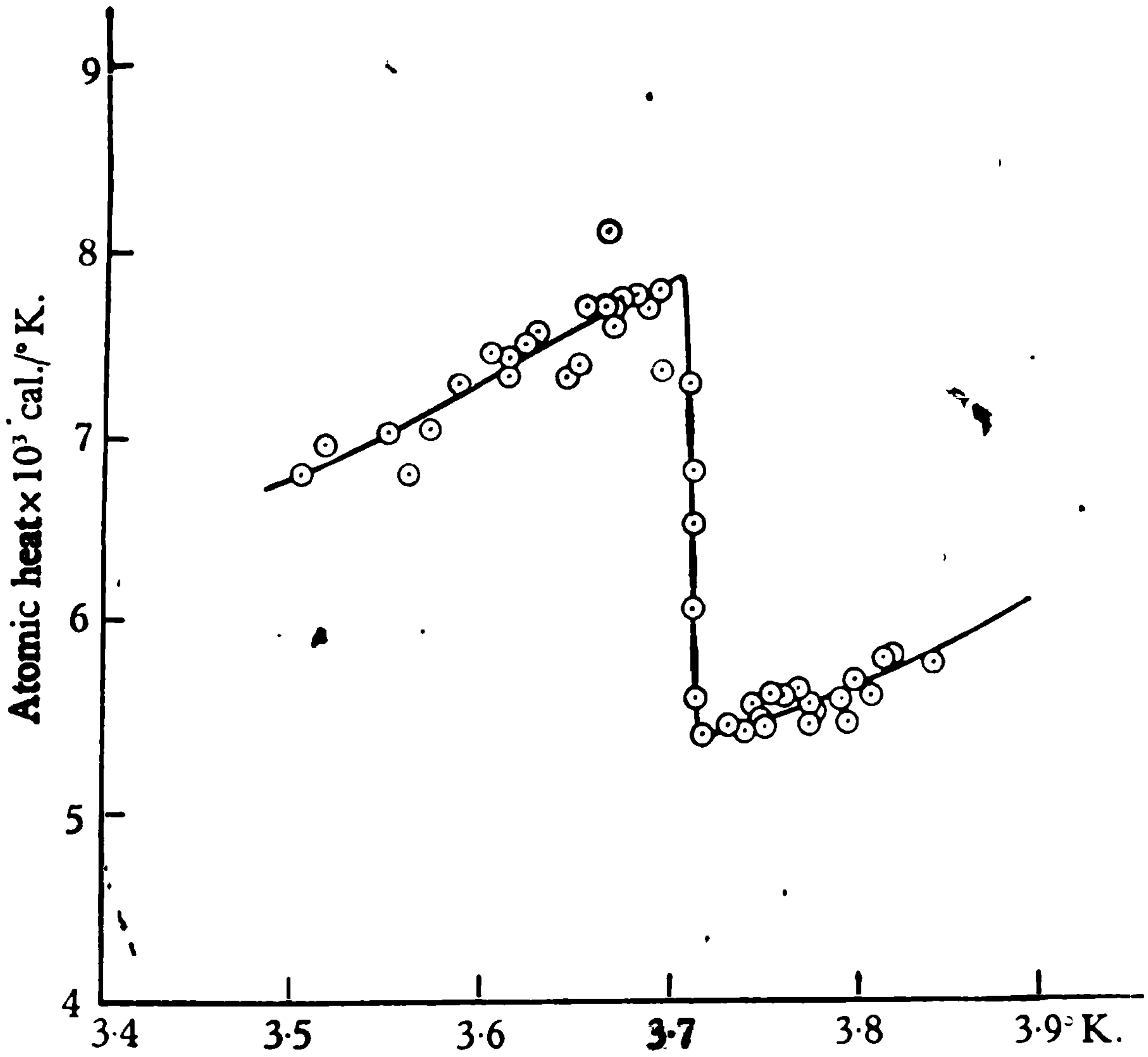


Fig. 6. Temperature variation of the atomic heat of tin.

(4) The thermal conductivity is different in the normal and superconducting states, but as figs. 7 and 8 illustrate, the phenomena are complex, and different super-

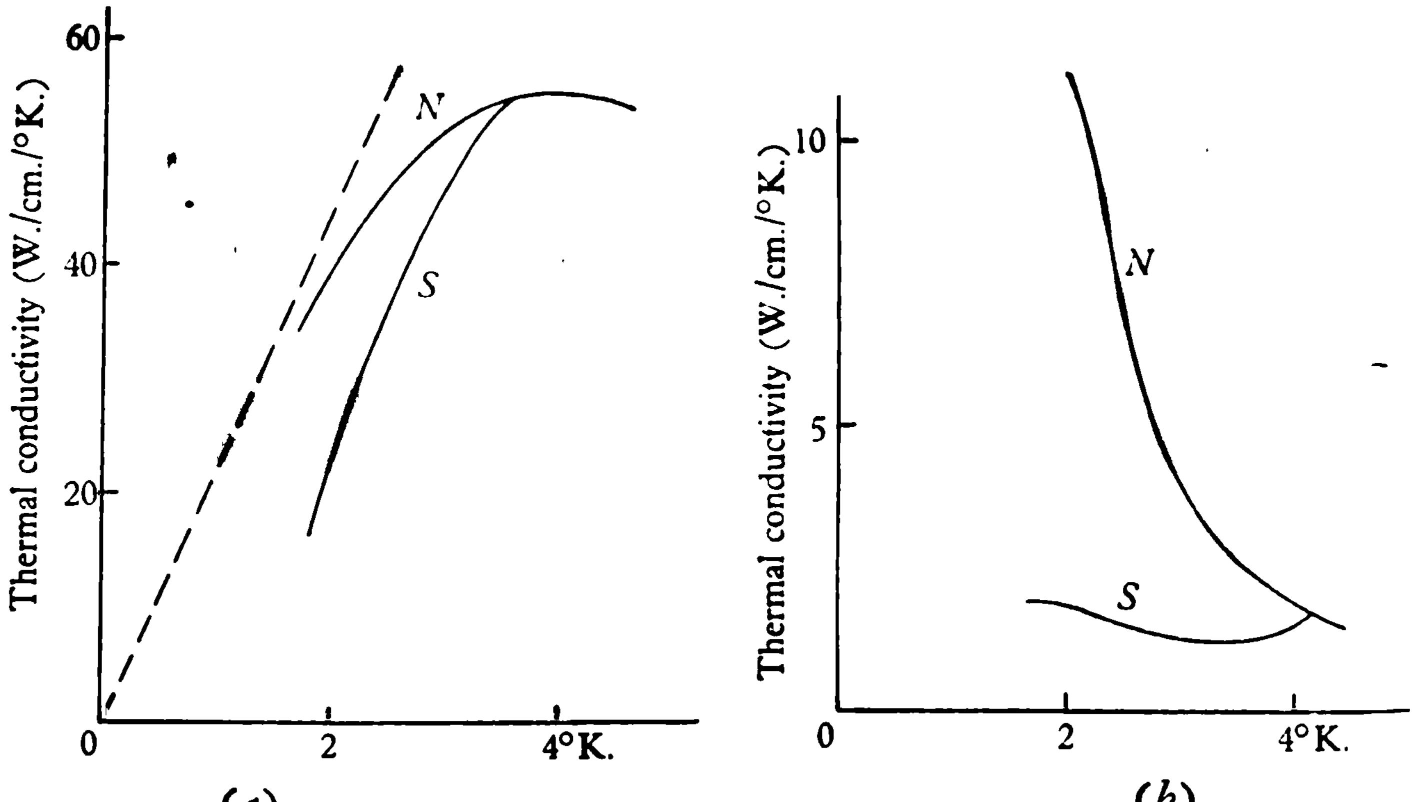


Fig. 7. Temperature variation of thermal conductivity in the normal (N) and superconducting (S) states (a) tin (b) mercury.

conductors behave differently. Most striking is the fact that for some alloys the thermal conductivity is higher for the superconducting than for the normal metal, while the reverse holds for pure metals. All this complexity is not very surprising, because of the variety of mechanisms for transport of heat in a metal. These various mechanisms are differently affected by the onset of superconductivity, and are of differing relative importance in different metals.

(5) Finally I should mention that no change has been found in the X-ray diffraction pattern of a metal when it becomes superconducting. This indicates

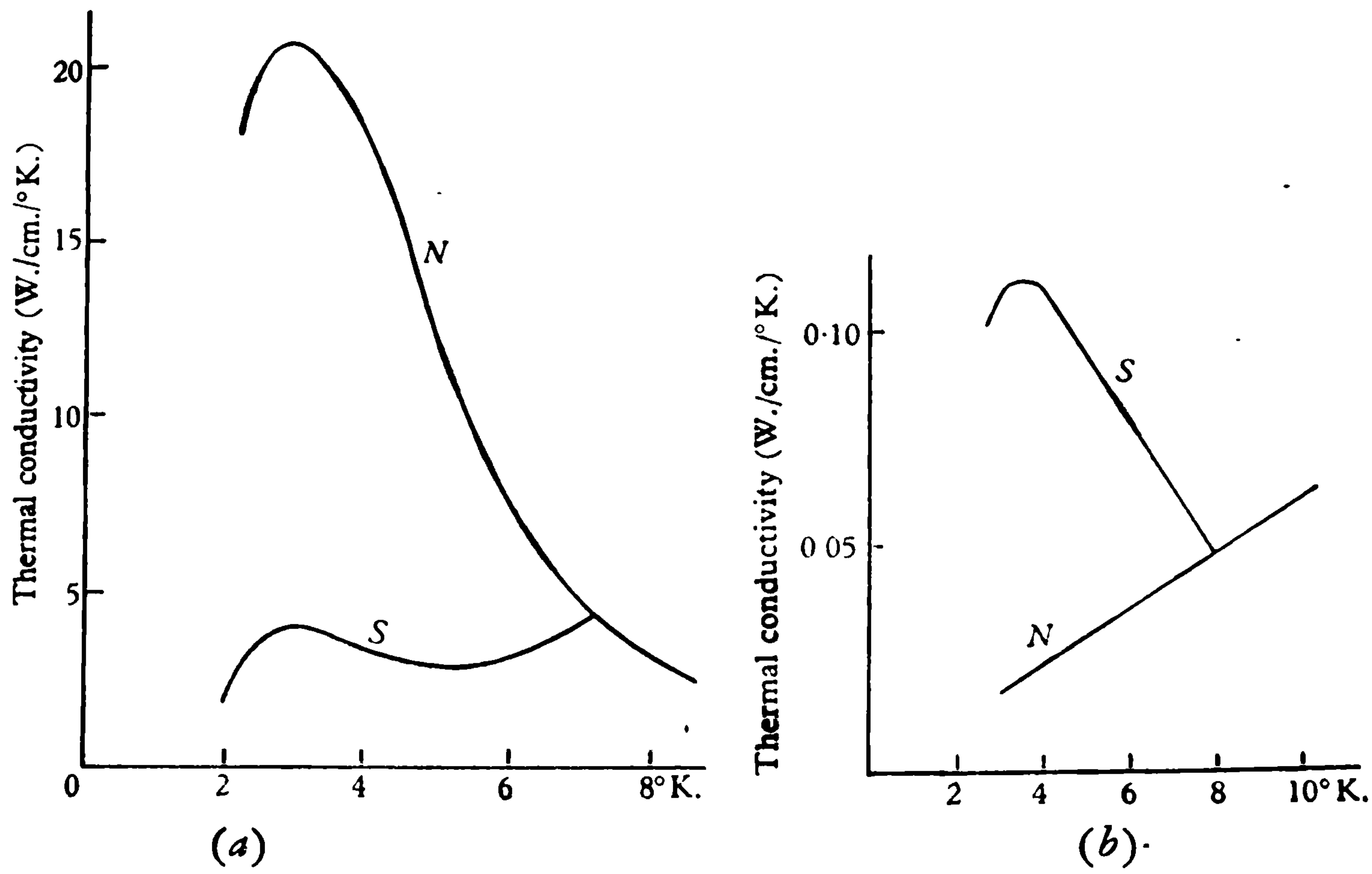


Fig. 8. Temperature variation of thermal conductivity in the normal (N) and superconducting (S) states (a) lead (b) alloy of $Pb + 10\%\ Bi$.

clearly that the change is one which does not affect the lattice structure appreciably and indeed, if any change is to be found, it should be looked for in fine details associated with the electronic structure.

Magnetic Properties

For a long time after the discovery of superconductivity it was thought that the magnetic behaviour of a superconductor could be deduced from its zero resistance alone. It was only in 1933 when Meissner and Ochsenfeld first put the matter to experimental test that it was found that the magnetic properties had an independent status.

First I shall show what magnetic properties should result from zero resistance alone, and then I shall contrast them with the actually observed properties. To do this, imagine a long rod of metal with a search coil wound on it and placed inside a long solenoid. We can then measure changes of B corresponding to changes of the applied field H_e, in the same way as is done for a rod of iron, by observing the throws of a galvanometer connected with the search coil. Since the metal is supposed to be a perfect conductor, the currents induced by a change of field will not die away and will maintain the field B inside the metal at exactly the same value H_0 as it had when the metal first lost its resistance. In other words

$$\frac{dB}{dt} = 0 \qquad B = H_0 \tag{5}$$

The induced currents themselves must be surface currents (since any body currents would cause a non-uniform field in the metal) and their strength per unit length is given by the jump in field across the surface *i.e.* by

$$g = (H_0 - H_e)/4\pi \tag{6}$$

Returning now to our imaginary experiment, we can predict the variation of B with H_e in various circumstances (see fig. 9). First suppose H_0 is zero, *i.e.*, the

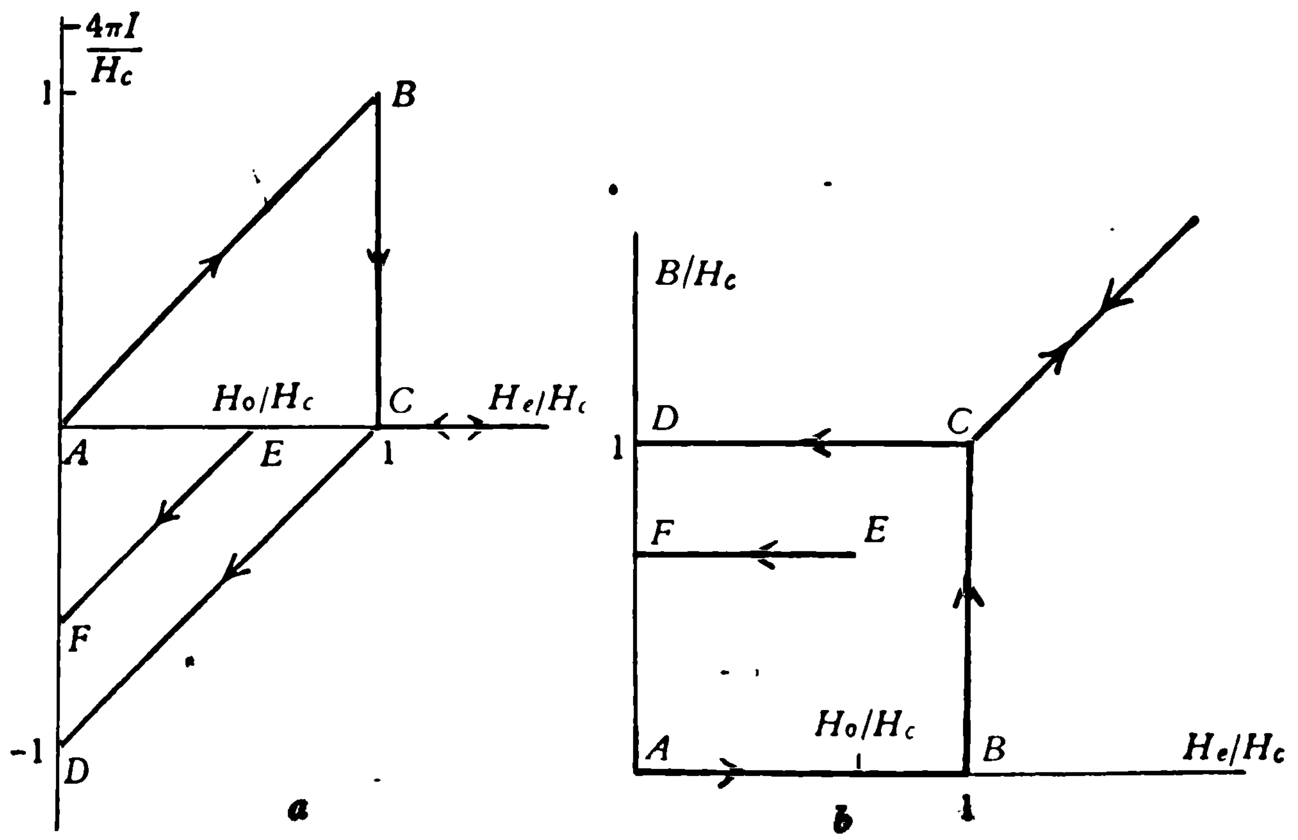


Fig. 9. Magnetic behaviour of perfectly conducting long cylinder.
(*a*) Magnetization curves. (*b*) $B - H_e$ curves.

metal is cooled in zero field, and that increasing fields H_e are applied by the solenoid. We should then expect B to remain zero right up to the critical field ; at this point the resistance is restored, and as the field enters inside, the galvanometer should give a kick proportional to H_c. For higher values of H_e, we should expect to find $B = H_e$ as for any ordinary non-magnetic substance (changes of H_e will of course induce eddy currents, but these will die away almost instantaneously and produce no kicks on a long-period galvanometer). If now the field is again reduced, the metal will again lose its resistance at $H_e = H_c$ and thereafter B should remain constant and equal to H_e. When H_e is zero the rod should in fact behave like a permanent magnet with circulating surface currents of strength per unit length given by

$$g = H_c/4\pi \tag{7}$$

It is instructive also to consider a second imaginary experiment in which the rod is cooled in a steady field H_0. The value of B will then remain H_0 and no change should be observed when the metal loses its resistance. If the field is then reduced to zero, B should still be maintained constant by the induction of surface currents, and as before, in zero field it will behave like a permanent magnet with surface currents of strength per unit length given by

$$g = H_0/4\pi \tag{8}$$

All this behaviour can, of course, equally well be described in terms of I the magnetic moment per unit volume. This magnetization can be thought of as produced by the surface currents and is evidently given by

$$I = g = -(H_c - H_0)/4\pi \tag{9}$$

or equally well as $(B - H_e)/4\pi$ which gives, of course, the same answer. The predicted results of our various imaginary experiments are shown in terms of I on the left of fig. 9.

These predictions of irreversible magnetization curves were regarded as so obvious that no direct experimental tests were undertaken for a long time, and in many of the early Leiden Communications references are made to "frozen-in fields" in specimens which had been cooled in an applied field or to which a field greater than critical had been temporarily applied. To everyone's surprise, when Meissner and Ochsenfeld first made a direct experimental test in 1933 they

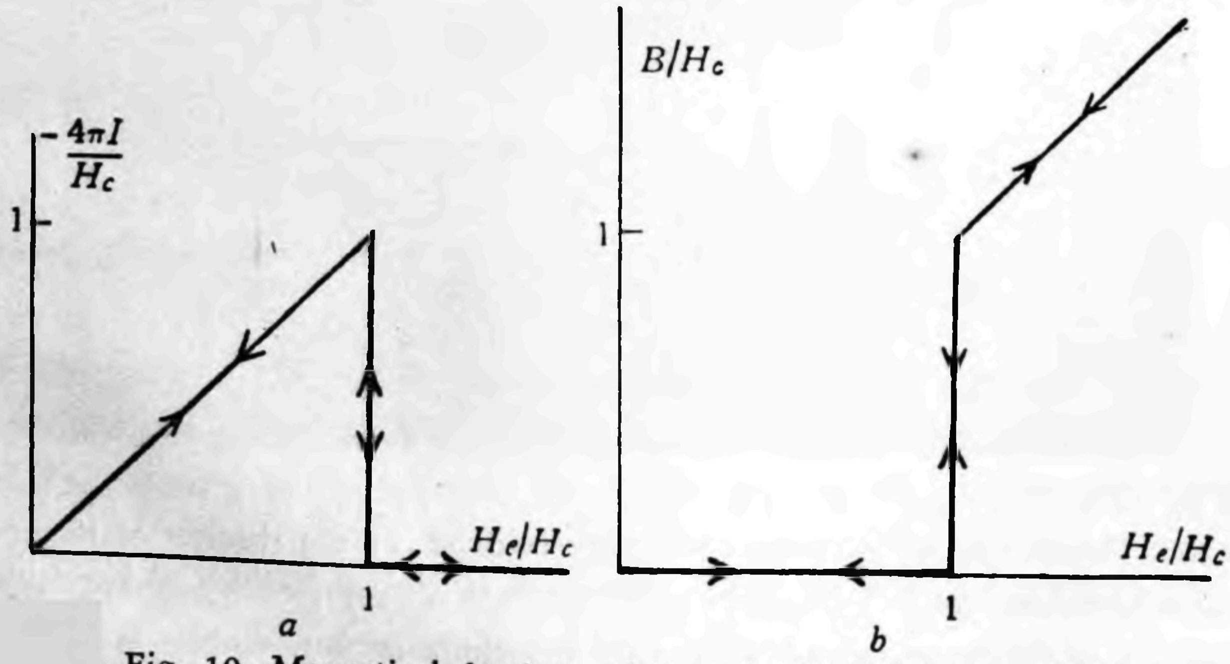


Fig. 10. Magnetic behaviour of superconducting long cylinder. (*a*) Magnetization curve. (*b*) $B - H_e$ curve.

did not find these irreversible effects at all in pure metals. Actually their experimental arrangement was rather more complicated than that of our imaginary experiment, but in terms of our arrangement, what they found is illustrated in fig. 10. In the first experiment the curves for an actual superconductor follow the same course as for a perfect conductor for increasing fields, but for decreasing fields the curve is retraced without hysteresis, *i.e.*, on passing below H_c the galvanometer gives a kick equal and opposite to the kick it gave when the flux entered on the destruction of superconductivity. Even more astonishing is the behaviour on cooling the metal in an applied field H_0. Here again, although the applied field is held constant, the galvanometer gives a kick corresponding to complete expulsion of all the flux which was in the metal before it became superconducting.

This inability to hold any magnetic flux, or in other words the strong diamagnetism of a superconductor, can be described by the equations

$$B = 0 \qquad I = g = -H_e/4\pi \tag{10}$$

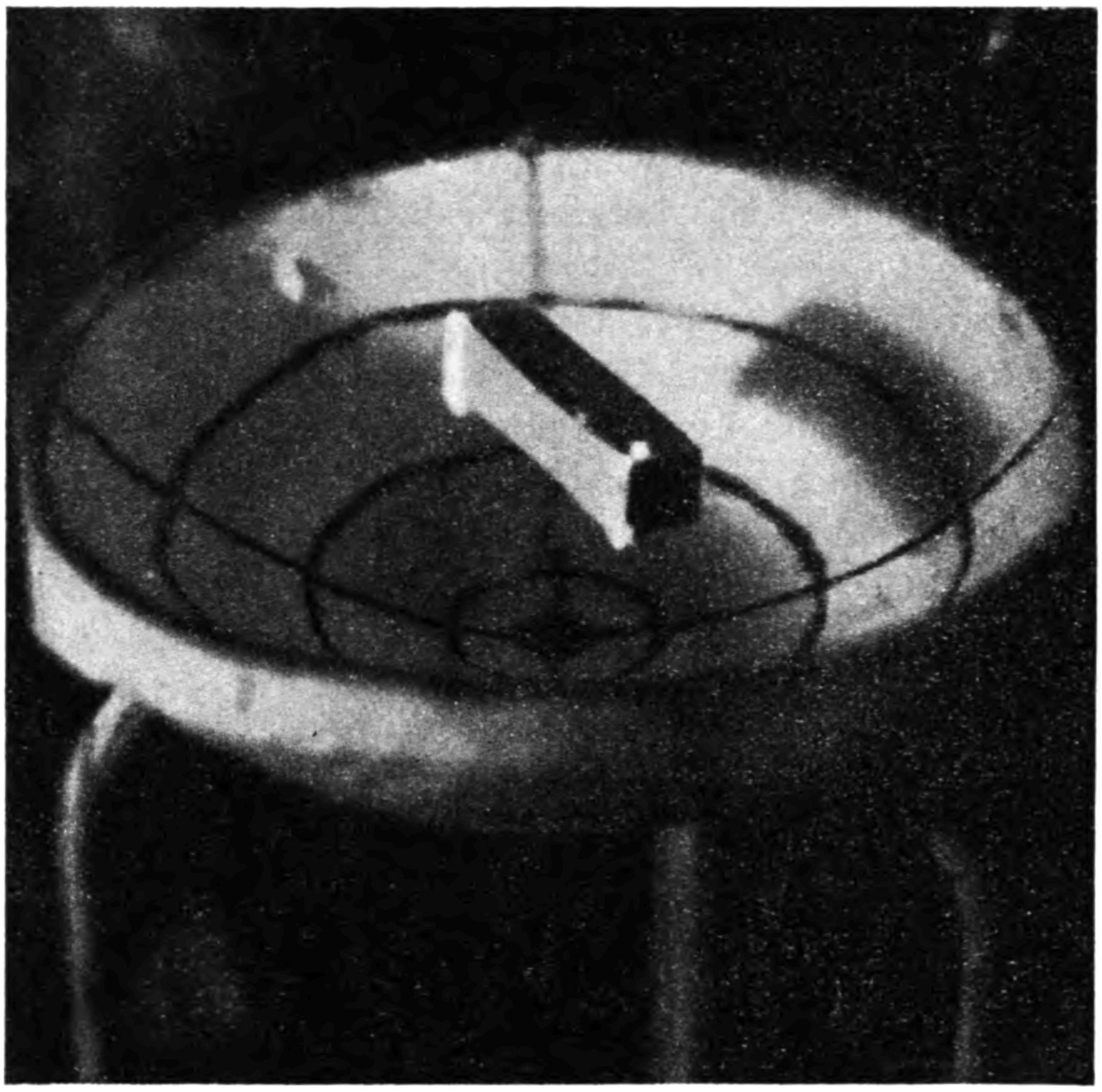


Fig. 11. The floating magnet. The short bar magnet is floating in helium gas nearly half an inch above the bottom of the superconducting lead bowl ; the shadow of the magnet is visible on the right-hand side of the bowl. The bowl is painted white with black lines on it to bring out the perspective and is standing on three copper legs which dip into liquid helium to keep it superconducting (the liquid helium is not visible in the picture). The white specks on the magnet and in the bowl are small pieces of solid air (the air is a slight impurity in the helium).

nd is known as the Meissner Effect. It must be regarded as a new and indepen-
ent characteristic of a superconductor.

The strong diamagnetism of a superconductor may be demonstrated in other vays than that of the search coil method. Perhaps the most beautiful demonstra-ion is that of the floating magnet originally devised by Arkadiev. If a small ›ermanent magnet is lowered over a superconducting surface—a lead bowl in the llustration (fig. 11)—the diamagnetism of the superconductor repels the magnet trongly enough to overcome its weight, and the magnet floats.

I must now confess that I have somewhat oversimplified my description of the nagnetic behaviour of superconductors and though it is not possible to go into all he complications in detail on this occasion, I think I should at least mention ;ome of them. What I have said is almost true provided the geometry is just as [described it and the metal is quite pure and free from strains.

If, however, the specimen shape is not a long thin cylinder parallel to the applied ìeld, complications at once arise due to the strong diamagnetism. As can be ;een from fig. 12 which shows the lines of force of a field applied *transversely* to a

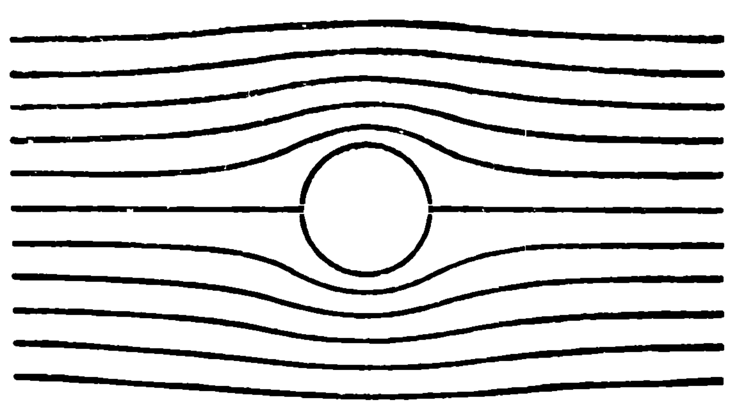


Fig. 12. Lines of force round a superconducting cylinder in a transverse field.

long cylinder, the lines of force of an originally uniform field are much distorted by the cylinder because they cannot pass through it. Consequently the field at the surface varies from zero at the poles to double its original value at the equator of the section. If now we consider the magnetization curves, this means that the field at the equator already reaches H_c when the applied field is only $\frac{1}{2}$ H_c, and consequently destruction of superconductivity is spread over the range $\frac{1}{2}$ H_c to H_c. This is illustrated in fig. 13 (which, however, is for a sphere so that the factor $\frac{1}{2}$ for a transverse cylinder must be replaced by 2/3). The details of how the gradual destruction of superconductivity takes place are of considerable interest. If we suppose that a normal region forms at the equatorial part of the surface we are led immediately into a paradox. The boundary between this normal region and the superconducting core would presumably be determined by the condition that the field is just critical on it, but being necessarily a convex boundary, the field must decrease as we go outwards from the superconducting core into the normal region. Why then should this region be normal, if the field in it is less than critical? The resolution of this paradox was first proposed by

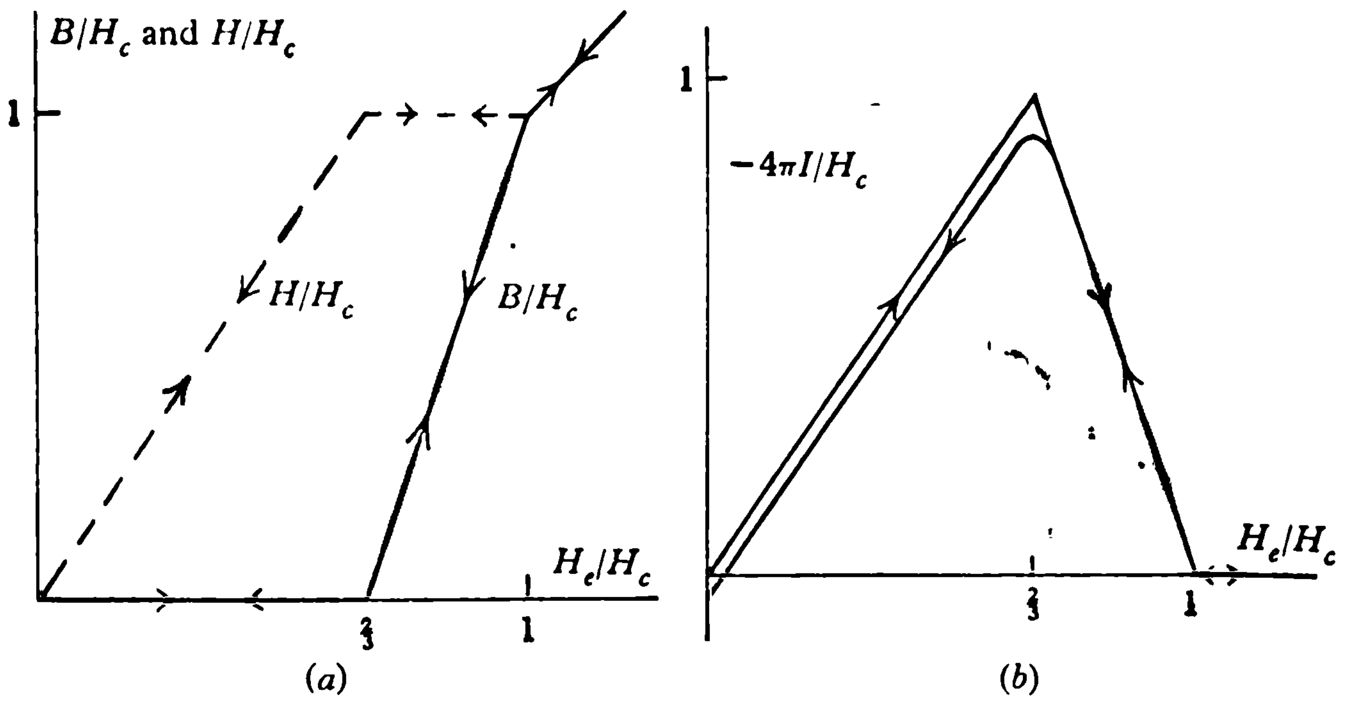


Fig. 13. Magnetic behaviour of a superconducting sphere (*a*) $B - H_e$ and $H - H_e$ curves for tin (H is the field at the equator of the sphere). (*b*) $I - H_e$ curve for lead (the slight hysteresis is due to impurities—see remarks on alloys).

F. London and worked out by Landau who showed that in this so called "intermediate state" the metal splits up into a fine mixture of normal and superconducting regions, the proportion of the former increasing as the field is increased. The regions are in the form of thin laminae or filaments and the flux passes through the normal ones. The scale of this structure depends on the value of the surface energy at a boundary between a normal and a superconducting region, and also on the absolute dimensions of the specimen. Although the detailed structure of the intermediate state has not yet been quite completely worked out, it is possible to estimate the surface energy from an experimental determination of the structure and also from certain detailed modifications of the simple magnetization curves of fig. 13, which occur when the specimen dimensions are sufficiently reduced (below about 1 mm).

Shalnikov has studied the structure directly by an ingenious method in which a minute bismuth probe (whose resistance provides a measure of the local field) is moved about in a narrow gap between two tin hemispheres in an applied field sufficient to maintain the whole sphere in the intermediate state. Some of his curves are shown in fig. 14 and it can be seen that they leave no doubt as to the reality of the fine structure. The individual domains are of order a fraction of a millimetre thick for a sphere of 2 cm radius, and from this it can be deduced that the surface energy α per unit area, which is most appropriately expressed as a length ∇ given by

$$\nabla = 8\pi\alpha/H_c^2, \qquad (11)$$

is of order 10^{-4} cm.

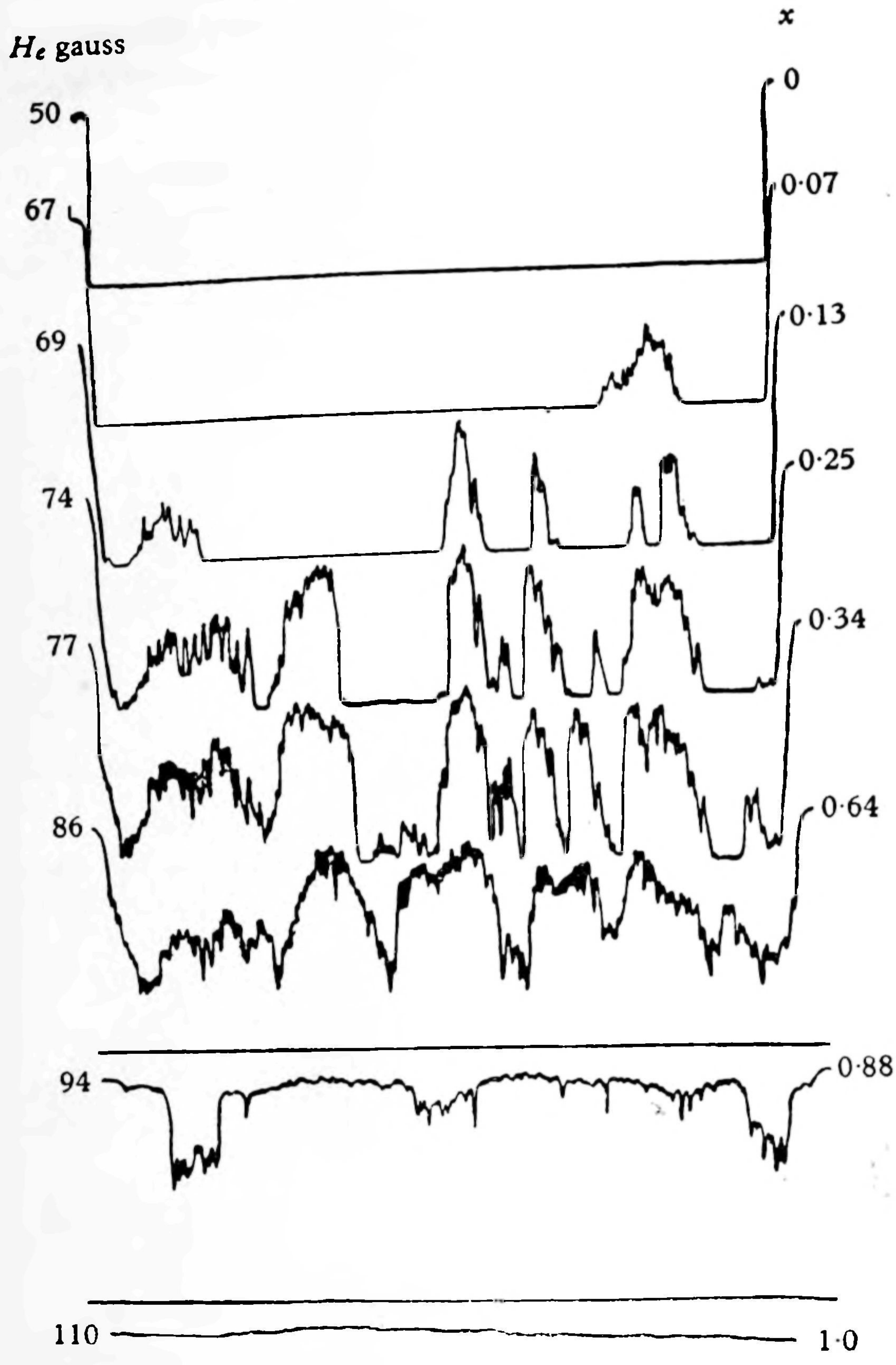


Fig. 14. Field variation across diameter in a gap 0.12 mm. wide between two tin hemispheres (4cm. diam.). x indicates the theoretical proportion of normal phase, and the presence of normal regions is indicated by the rises above the zero level characteristic of the superconducting regions.

The same parameter ∇ enters into another complication of the magnetization curve, namely the existence of a kind of supercooling found in very pure specimens and illustrated in fig. 15. When the field is reduced from below the critical value, the specimen stays completely in the normal state until at a much lower field it suddenly and abruptly becomes superconducting again and ejects the flux from itself. The explanation of this effect is very similar to that of supercooling in ordinary phase transitions, namely that the creation of the superconducting phase in a normal matrix must start from a nucleus, and the nucleus can only grow if it is greater than a certain size, because the surface energy at its boundary

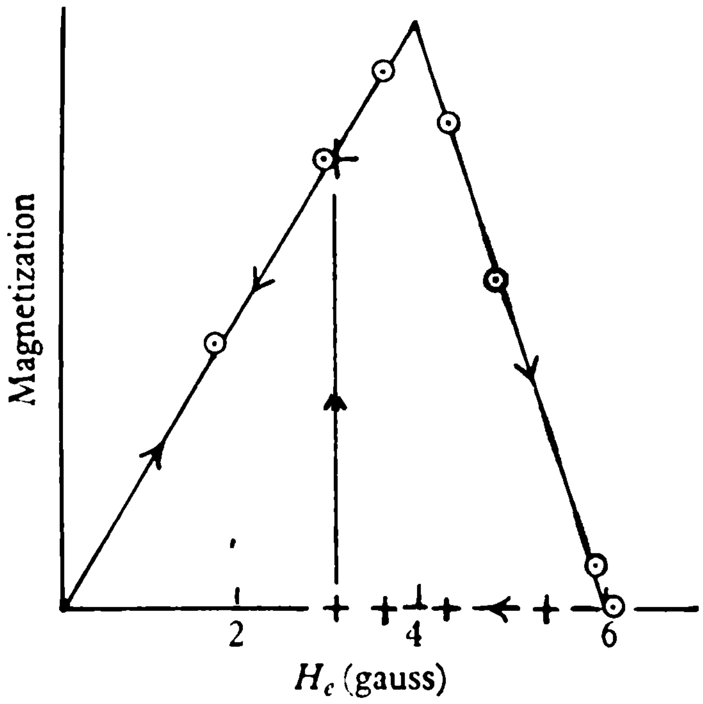


Fig. 15. Magnetization curve of an aluminium sphere at 1.16°K illustrating large supercooling effect. ⊙ increasing fields ; + decreasing fields.

does not allow it to expand when it is too small. Faber in a series of ingenious experiments has been able to follow the creation and growth of such superconducting nuclei and has shown that the parameter ∇ has indeed just the order of magnitude estimated from intermediate state experiments.

Finally, I should mention the complications brought about by impurities. In impure or alloy specimens the Meissner effect is far from complete, and the transition far from sharp, as can be seen from the typical $B - H_e$ curve illustrated in fig. 16. This behaviour can be qualitatively explained partly in terms of the inhomogeneities of an alloy and partly in terms of the assumption that the surface energy may be negative over parts of the alloy. Such parts would retain superconducting regions within them even above H_c and if they were connected in closed circuits could trap flux into the normal regions they embrace, when the applied field was reduced (rather like the trapped flux in a superconducting ring). It will be noticed that this type of explanation, first suggested by Mendelssohn and H. London, implies that a good deal of an alloy remains in the normal state even when the field has been reduced to zero, and this has been confirmed by Mendelssohn calorimetrically.

Thermodynamical Theory

Leaving aside all the complications I have just been describing, we can draw some important thermodynamic conclusions from the ideal magnetic behaviour of a pure long cylinder in a parallel field. Let the free energies per unit volume of the superconductor be G_n and G_s in the normal and superconducting states when the field is zero. Then evidently $G_n < G_s$ for $T < T_c$ since the super-

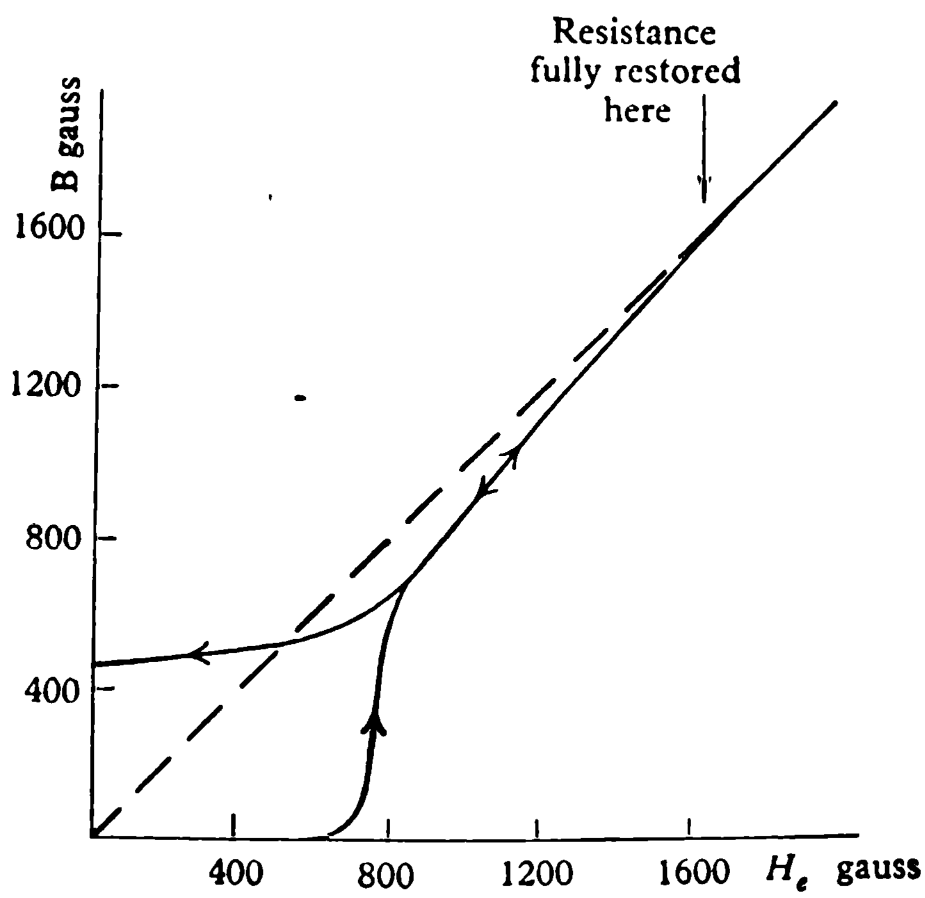


Fig. 16. $B - H_e$ curve for the alloy $Pb + 2\%$ In at $T = 1.95°K$.

conducting state is the stable one. If a magnetic field H is applied, the free energy of the normal state is not affected, since the metal is practically non-magnetic, but owing to the expulsion of the field from the metal in the superconducting state, G_s is increased by $H^2/8\pi$ and if H is big enough, the two free energies may become equal, and superconductivity will then be destroyed. Since this happens for $H = H_c$, we see that

$$G_n - G_s = H_c^2/8\pi\,. \tag{12}$$

It follows at once that the entropy difference per unit volume is

$$S_n - S_s = -\frac{H_c}{4\pi}\frac{dH_c}{dt} \tag{13}$$

(since $S = -dG/dt$) and it is at once obvious why there is no latent heat in the absence of a field (for then $H_c = 0$). One more differentiation gives the difference of specific heats per unit volume

$$C_s - C_n = \frac{T}{4\pi}\left(H_c\frac{d^2H_c}{dT^2} + \left(\frac{dH_c}{dT}\right)^2\right) \tag{14}$$

This does not vanish even for $H_c = 0$ because dH_c/dT is finite, and the jump of specific heat at $T = T_c$ is given by

$$C_s - C_n = \frac{T_c}{4\pi}\left(\frac{dH_c}{dT}\right)^2 \tag{15}$$

a formula first proposed by Rutgers. This is just the jump already mentioned in my first lecture and the measurements confirm the formula very well. Experimentally it is found that the specific heat, which above T is given by

$$C_n = aT + bT^3, \qquad (16)$$

(the first term due to the electrons and the second to the lattice vibrations) below T_c becomes approximately

$$C_s = bT^3 \qquad (17)$$

as if the electrons had somehow condensed into a lattice. By integration of the difference C_n—C_s it can easily be deduced that these formulae automatically imply that

$$H_c = H_0 \left(1 - (T/T_c)^2\right)$$

which as I mentioned earlier is approximately true (see equation (4)).

In the thermodynamics I have just outlined the volume V of the superconductor was treated as fixed. If however it is regarded as a variable it is not difficult to generalize the results and obtain a formula for V_n—V_s (quite analogous to the Clapeyron-Clausius equation) in terms of dH_c/dp which agrees well with the measurements of Lazarew and his school (see fig. 17). Formulae for the

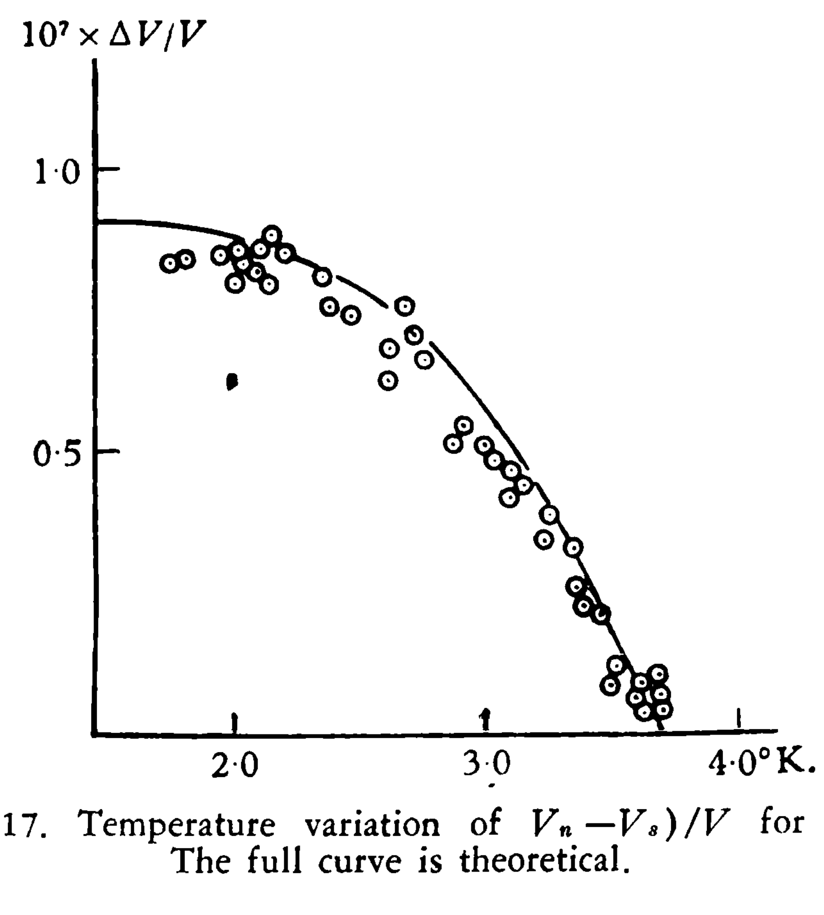


Fig. 17. Temperature variation of $(V_n - V_s)/V$ for tin. The full curve is theoretical.

jumps of thermal expansion and compressibility are easily derived by differentiation, and it turns out that although the jump in compressibility is probably too small to be ever observed, there is some chance of observing the jump in thermal expansion, and as I have already mentioned, we are hoping to do this at the National Physical Laboratory of India.

The Penetration Depth

We have seen that when a superconductor is placed in a magnetic field no field is able to pass through. Thus in crossing the surface the field changes abruptly from its external value to zero, the abrupt change being caused by the currents flowing on the surface. No real change is however perfectly abrupt and *a priori* it would be reasonable to expect that the field penetrated the superconductor to some small depth λ and that the surface currents were really distributed through this penetration depth. Since measurements on specimens a centimetre or so in size give $B = O$ with quite high accuracy, it is clear that the penetration depth λ must be much less than say 10^{-2} cm, and I shall now describe briefly how λ can be determined experimentally, for as I shall explain later, it is a quantity of considerable theoretical interest.

The most obvious approach is to measure the magnetic behaviour of very small particles, for if their sizes are comparable with or smaller than λ, it is clear that the field will penetrate a much greater proportion of their volume than for a large specimen. Fig. 18 shows how the diamagnetic susceptibility of a mercury

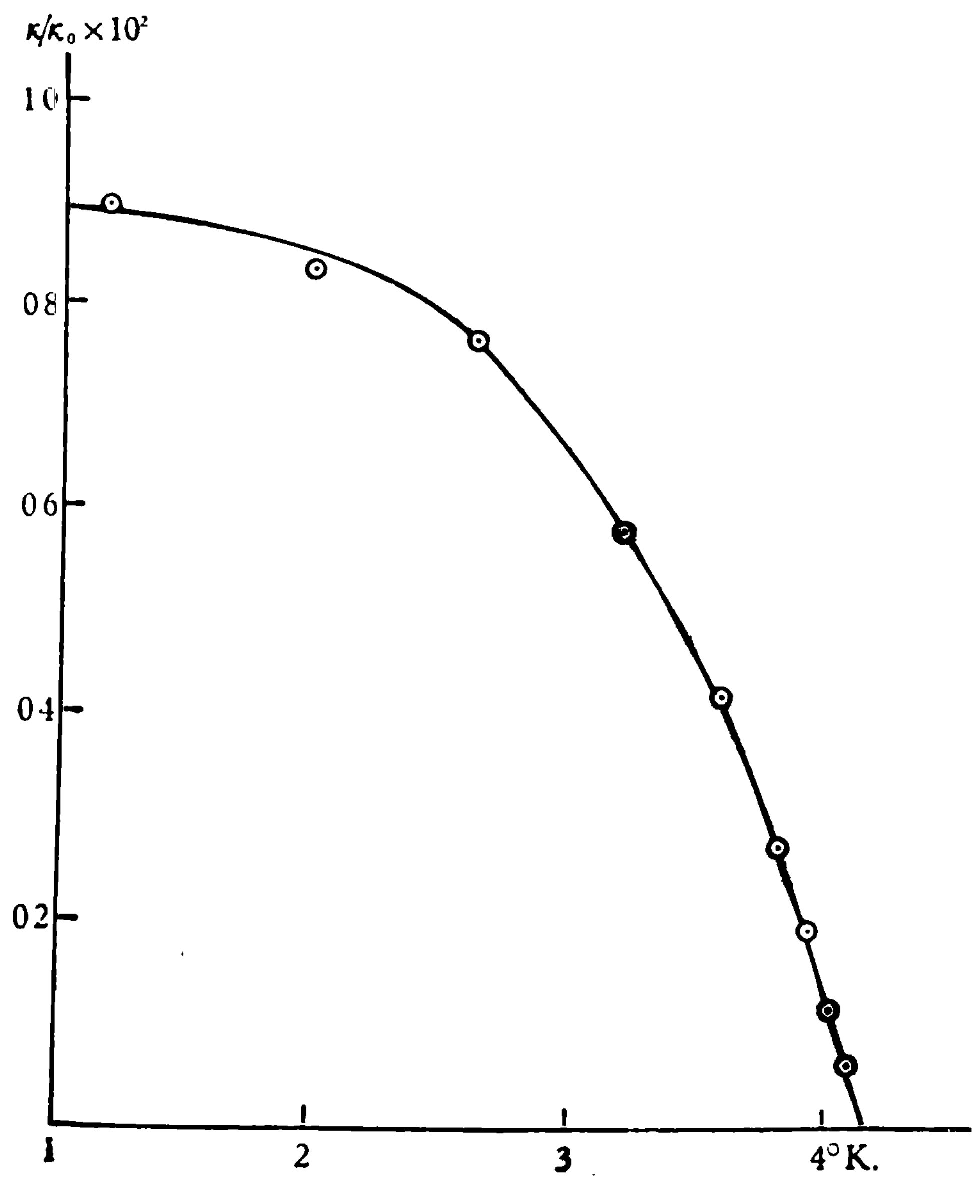
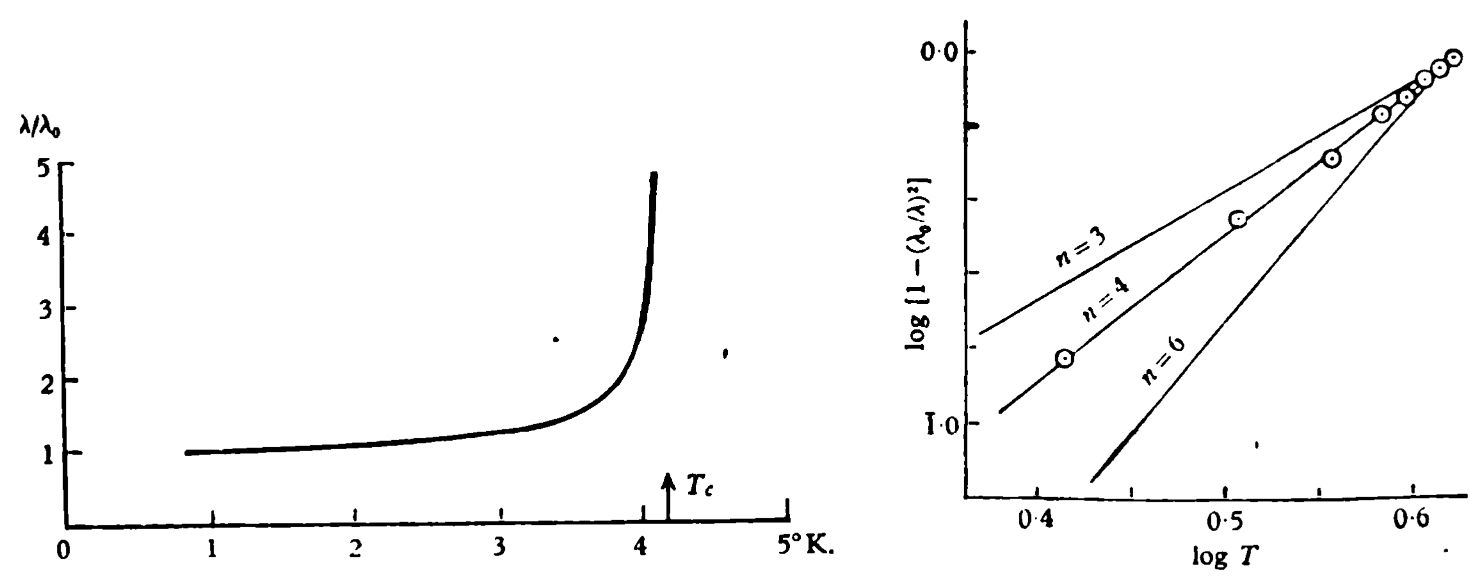


Fig. 18. Temperature variation of κ/κ_0 for a mercury colloid (κ_0 is the volume susceptibility of a macroscopic superconducting sphere, and κ of the colloidal sphere).

colloid (particle size of order 10^{-6} to 10^{-5} cm) varies with temperature. Two points are immediately evident—first that the susceptibility is now only of order 1% of the "bulk" susceptibility (corresponding to complete exclusion of field), so that the particle size is indeed comparable with or smaller than λ, and second that the susceptibility varies with temperature, becoming zero at T_c. This last



(*a*) (*b*)

Fig. 19. (*a*) Temperature variation of λ/λ_0 as deduced from fig. 18. (*b*) Plot illustrating the validity of equation (18).

result can mean only that λ itself is temperature dependent, becoming rapidly larger as T_c is approached. A simple dimensional argument enables λ/λ_0 to be deduced as a function of temperature (λ_0 is the value of λ at a low temperature) and the results are shown in fig. 19, from which it can be seen that the temperature variation is very well represented by the formula

$$(\lambda/\lambda_0)^2 = 1/(1 - T/T_c)^4) \qquad (18)$$

which as I shall explain later has some theoretical basis.

The absolute value of λ cannot easily be determined by the colloid method since it would require a very precise knowledge of the particle sizes in the colloid, and moreover, would involve special theoretical assumptions. It has however recently been found possible to determine it by delicate experiments on macroscopic specimens. In one method (devised by Casimir and successfully used by Laurmann and Shoenberg) the specimen forms the core of a mutual inductance and the very minute changes of the mutual inductance due to the changes of field penetration with temperature are observed. This gives essentially λ—λ_0 and by combining this with the known variation of λ/λ_0 the absolute values of λ are obtained. An ingenious variant of the same general principle was used by Pippard, who measured very precisely the resonant frequency of a cavity resonator containing a short piece of superconductor. As the penetration depth varies with variation of temperature the effective geometry of the resonator is slightly modified and the resonant frequency changes by an amount proportional to the change of λ. These and other methods agree quite well, and give accurate values of λ of the order of magnitude already indicated by the colloid results.

I should like to mention here one other feature of the behaviour of superconductors whose dimensions are comparable with λ. This is that the critical field, h, for destruction of superconductivity becomes larger, and even much larger, than H_c, the value for the bulk material. This is illustrated by fig. 20 which

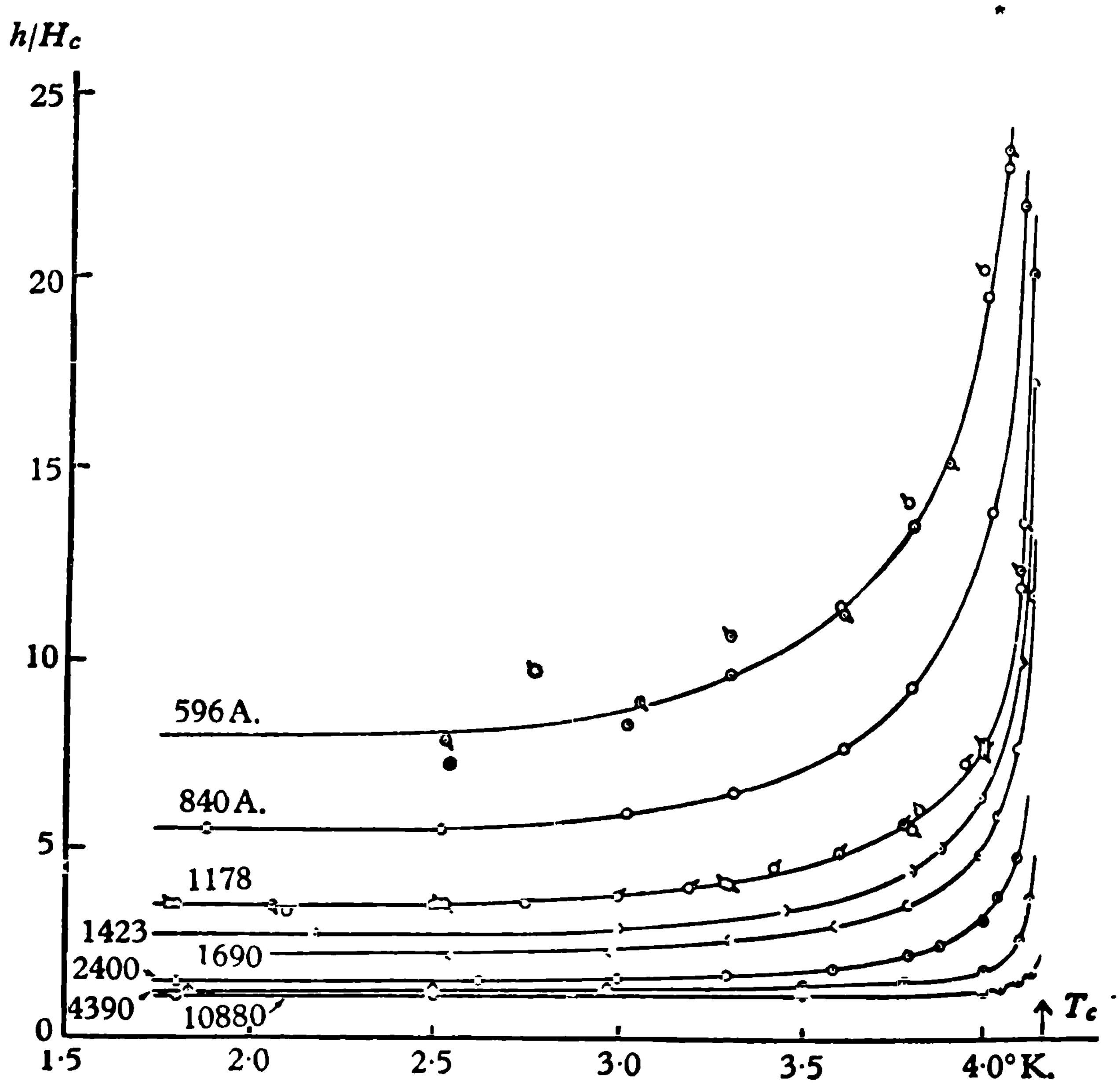


Fig. 20. Temperature variation of h/H_c for mercury films of various thicknesses ; the thicknesses are given in Angstroms.

shows the results of Appleyard, Bristow, Meissner and H. London for thin mercury films ; high values of h/H_c were found also in the colloid measurements. Qualitatively, the increased critical fields are easy to understand. Our thermodynamic result

$$G_n - G_s = H_c^2/8\pi \qquad (19)$$

was based on complete exclusion of flux ; if appreciable penetration occurs, then for a thin specimen we would have

$$G_n - G_s = \alpha h^2/8\pi \qquad (20)$$

where α is some factor less than 1, depending on the degree of penetration. Thus a greater value of h is necessary to reach the free energy difference characteristic of the bulk material, and clearly*

$$h/H_c = 1/\alpha^{\frac{1}{2}} \text{ i.e. } > 1 \tag{21}$$

The theories of F. and H. London and of Casimir and Gorter

The time has now come to give some sort of theoretical synthesis of the facts I have been presenting. So far no satisfactory fundamental theory has yet been worked out, though as we shall see later Fröhlich and Bardeen have made gallant attempts. It is however possible to connect together in a much more coherent form the various experimental facts, on the basis of the electrodynamic equations of F. & H. London combined with the "two-fluid model" of Casimir and Gorter.

The London brothers set out from the older "acceleration" theory of Becker, Heller and Sauter. They had considered what would happen if an electric field E were applied to an electron in a superconductor. Since there is no resistance the electron would accelerate according to the equation

$$eE = m\dot{v} \tag{22}$$

or since

$$nev = J \tag{23}$$

(n=number of electrons/unit volume, J=current density)

$$E = \frac{4\pi\lambda^2}{c^2}\dot{J} \tag{24}$$

where

$$\lambda^2 = mc^2/4\pi ne^2 \tag{25}$$

If now we take curls on both sides and use Maxwell's equation

$$\text{curl } E = -\dot{H}/c,$$

we find

$$\frac{4\pi\lambda^2}{c}\text{ curl }\dot{J} + \dot{H} = 0. \tag{27}$$

and substituting the other Maxwell's equation

$$\text{curl } H = 4\pi J/c \tag{28}$$

we finally obtain

$$\nabla^2\dot{H} = \dot{H}/\lambda^2. \tag{29}$$

Physically this means that $\dot{H}$ disappears exponentially inside the surface of the metal over a distance of order λ. Well beyond this penetration depth, $\dot{H}$ is zero, which is the same result as was obtained earlier for perfect conductor.† In the previous discussion of a perfect conductor, the electric field associated

* This argument ignores the possibility that $G_n - G_s$ may itself be size-dependent, but this does not affect its qualitative validity.

† In this analysis H is used for what we previously called B, since here the currents are explicitly recognized, while previously the magnetic behaviour was described by distinguishing between B and H.

with the acceleration of the electrons was ignored, and so the simpler result $\dot{H} = 0$ was obtained rather than the present one, which shows that there is a penetration depth in which $\dot{H}$ falls to zero. Just as $\dot{H} = 0$ led on integration to $H = H_0$ where H_0 could be arbitrary, in contradiction to the experimentally obsered Meissner Effect which shows that $H_0 = 0$, so too the new equation on integration gives

$$\nabla^2(H - H_0) = (H - H_0)/\lambda^2 \tag{30}$$

which would mean that the metal could have an arbitrary field H_0 inside it.

The Londons made the ingenious suggestion that since the macroscopic theory for a perfect conductor makes correct predictions for a superconductor if $H_0 = 0$, the Becker, Heller and Sauter theory might also apply, if H_0 was always assumed zero. In other words they proposed to adapt the Becker, Heller and Sauter theory by simply removing the dots from equations (27) and (29), thus getting

$$\nabla^2 H = H/\lambda^2 \tag{31}$$

This automatically describes the Meissner Effect for a macroscopic specimen, but goes further in predicting the existence of a penetration depth λ, which if one electron per atom is assumed, is indeed of almost the order of magnitude observed.

In order to interpret the temperature variation of as well as its absolute value, we must now combine the Londons' results with the two-fluid model of Casimir and Gorter. Essentially the idea of the two-fluid model is to suppose that below T_c the metallic electrons are divided between two groups of energy levels. A fraction (1—x) of the electrons occupies the lower group of levels, and these electrons can be called condensed or "superconducting", while the remainder stay uncondensed or "normal". By making some special, but plausible, assumptions about the form of the free energy of the assembly, Casimir and Gorter deduced that if

$$x = (T/T_c)^4 \tag{32}$$

the specific heat in the superconducting state would come out to be proportional to T^3 which, as we have seen, is just what is observed. In terms of this model the rise of the specific heat curve above the normal state value is easy to understand, for as the temperature rises, extra heat is needed to "evaporate" superconducting electrons from their state of lower energy, as well as in increasing the kinetic energy of the normal electrons. When, however, the transition temperature is reached, x has become just unity and all the electrons are "normal" so the extra specific heat disappears abruptly.

If now we combine this model with the Londons' theory by supposing that the number of superconducting electrons per unit volume in the Londons' theory is just the fraction (1—x) of the total number of free electrons per unit volume, we see immediately that we should have

$$(\lambda/\lambda_0)^2 = 1/(1-(T/T_c)^4)$$

which as I explained earlier is just what has been observed experimentally, (see equation (18)) and that now

$$\lambda_0^2 = mc^2/4\pi ne^2 \quad (33)$$

which agrees roughly, though not exactly, with the data if n corresponds to one electron per atom.

The presence of "normal" electrons requires a modification of the Londons' electrodynamics when non-stationary processes are considered (*e.g.*, in alternating fields). If in fact an electric field is present it will not only accelerate the superconducting electrons, but also cause a current of normal electrons. The simplest assumption about the normal electrons is that they obey Ohm's law, *i.e.*,

$$J_n = \sigma E \quad (34)$$

The current J_s of superconducting electrons may on the other hand be assumed to obey Londons' equations

$$H = -\frac{4\pi\lambda^2}{c^2} \text{ curl } J_s$$

$$E = \frac{4\pi\lambda^2}{c^2} J_s$$

while the total current to be used in Maxwell's equation is

$$J = J_n + J_s \quad (36)$$

On this basis it is easy to provide a qualitative explanation for the high frequency behaviour of superconductors which I outlined in my first lecture. The two systems of electrons may be thought of as behaving rather like a pure inductance without resistance connected in parallel with a pure non-inductive resistance. For D.C. or low frequency A.C., almost all the current goes through the inductance (*i.e.*, is carried by the superconducting electrons), and the system has zero resistance. For sufficiently high frequencies, however, the impedance of the inductance becomes appreciable and some current goes through the resistance (*i.e.*, is carried by the normal electrons), so that the system behaves as if it no longer had zero resistance. The falling off of the R.F. resistance to zero as the temperature approaches 0^0K is also understandable since the fraction x then approaches zero, *i.e.*, no normal electrons are left to produce any resistance. Detailed analysis of the problem, although supporting this qualitative explanation, does not however fit the facts in full detail, particularly as regards the frequency variation of resistance.

The two-fluid model gives also a qualitative explanation of why the thermal conductivity is lower in the superconducting than in the normal state (the theory for an alloy is more complicated). It is simply that the superconducting electrons carry no entropy and so are withdrawn from the heat transport mechanism as they "condense". Here no complete quantitative theory has been worked out as the two-fluid model by itself is not sufficient to give more than this general explanation, and more knowledge of the superconducting state is required to carry out any quantitative calculation.

I have already mentioned that the high frequency behaviour is not fully in accord with theory and detailed considerations by Pippard suggest that it is the two-fluid model which is at fault. No less serious doubt has recently been thrown on the detailed form of the Londons' equations by Pippard's experiments on the variation of λ with impurity, and both Pippard himself and Ginsburg and Landau have suggested how the equations might be improved. However, in spite of its defects, the phenomenological theory comprised by the Londons' equations combined with the two-fluid model, still retains its usefulness in providing a fairly simple working picture of what goes on in a superconductor.

Fundamental theories

From more detailed discussion of the Londons' equations than I can give in these lectures, it can be inferred that the currents flowing on the surface of a superconductor are rather like the currents flowing in an atom, *i.e.*, quantum manifestations on a macroscopic scale. It is also clear that this quantum current is carried by electrons which have undergone some sort of condensation out of the whole assembly of metallic electrons when the metal is cooled below its transition temperature. The task of a fundamental theory is to explain why this condensation takes place and why in the condensed phase the current obeys (at least approximately) the Londons' equations. So far there has been little progress in producing such a theory. The most encouraging attempts have been the recent theories of Fröhlich and Bardeen, which are rather similar to each other. Fröhlich considers a rather indirect interaction between the electrons : an electron slightly polarizes the lattice in its passage through it and this polarization in turn reacts on the other electrons. He suggests that this interaction leads to the required condensation process, and is able to obtain a reasonable order of magnitude for T_c. Owing to mathematical difficulties he has not yet however, been able to prove convincingly that condensation does really occur or to show that it is a superconducting condensation if it does occur. The main success of the theory has been that since the lattice enters into the interaction, the mass of the atoms enters into the formula for T_c in precisely the way indicated experimentally by the isotope effect I mentioned earlier. This success was all the more striking as in fact Fröhlich predicted the isotope effect just before it was observed experimentally.

You will see then that superconductivity is still an attractive subject for the experimental physicist, for since then is no really clear theory as yet, he can never tell when he may not be on the threshold of some exciting new discovery, rather than feeling that he is merely dotting the i's and crossing the t's of other existing knowledge as is so often the case in other branches of physics.

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