Supplement to NATURE

No. 3293 DECEMBER 10, 1932

Electric Supra-Conduction in Metals*

By Prof. J. C. McLennan, O.B.E., F.R.S.

THE discussion at the York meeting of the British Association on the electric supra-conductivity of metals was opened by a reference to the classical experiments of Dewar and Fleming[1] made in 1893 on the electrical conductivity of metals cooled to very low temperatures by means of liquefied gases, including air and hydrogen. These yielded results suggesting that the electrical resistances of all pure metals would vanish at the absolute zero of temperature.

This suggestion, however, proved to be wrong, for in 1911, Kamerlingh Onnes at Leyden, while carrying out researches at low temperatures with the aid of liquefied helium, discovered that mercury, when cooled down and solidified with liquid helium, suddenly and abruptly at about 4·2° K. became what is now designated as a supra-conductor of electricity. At temperatures below 4·2° K., mercury offers no measurable resistance to the passage of a current. Currents of electricity started in a ring of a metal in the supra-conductive state will continue apparently undiminished in intensity while the metal is in that state. The duration of these persistent induced ring currents seems to be limited only by the length of time the cooling agent, liquid helium, will last. In the course of a lecture on the evening of June 3 last at the Royal Institution on supra-conduction in metals, I exhibited to the audience a closed ring of lead immersed in liquid helium and carrying a current of more than 200 amperes. The current had been started in the supra-conducting lead ring some six hours earlier in the afternoon by Prof. Keesom in Leyden, and it persisted undiminished in intensity while being transported in liquid helium by aeroplane from Leyden to London by Colonel the Master of Sempill.

SUPRA-CONDUCTIVE METALS

Metals in addition to mercury and lead that exhibit the supra-conductive property if made sufficiently cold are tin, indium, gallium, thallium, tantalum, titanium, thorium, and niobium. The transition temperature for the passing of a metal from the ordinary conducting to the supra-conductive state is not a constant but varies with the metal. For mercury it is 4·22° K., for lead 7·2° K., tin 3·7° K., tantalum 4·4° K., thallium 2·37° K., indium 3·37° K., gallium 1·05° K., thorium 1·5° K., titanium 1·75° K., and niobium 8·2° K.

ALLOYS AND CHEMICAL COMPOUNDS

Some alloys and chemical compounds of the metals also exhibit the supra-conductive property. Copper sulphate, for example, does so, though none of the constituent elements is a supra-conductor. The nitrides and carbides, borides and silicides of several of the metals, such, for example, as those of molybdenum, tungsten, tantalum, zirconium and niobium, are also supra-conductive at sufficiently low temperatures.

The addition of metals of the bismuth group to supra-conductive metals has been found, speaking generally, to raise their transition temperature. Bismuth added to lead raises the transition temperature from 7·2° K. to 8·8° K.; carbon raises that of niobium from 8·2° K. to 10·5° K. Gold

---

* From a discussion on electric supra-conduction in metals held in Section A (Mathematical and Physical Sciences) on Friday, September 2, at the York meeting of the British Association. Among those who took part in the discussion were Prof. J. C. McLennan, Prof. W. J. de Haas, Dr. W. Meissner and Prof. O. W. Richardson.

alloyed with bismuth becomes supra-conductive at 1·94° K., whereas neither constituent alone becomes supra-conductive even at the lowest temperatures obtainable.

With pure metals the transition from the ordinary conductive to the supra-conductive state generally occurs within a tenth or at most a few hundredths of a degree. With impure metals, with alloys or with chemical compounds, the transition is not generally so rapid. In the transition stages, in the case of most of the metals the variation of resistance can be readily followed by observing the vapour pressure of the liquid in which the metal is immersed. In the case of liquid helium, a variation in vapour pressure of about 40 mm. of mercury corresponds to about one tenth of a degree centigrade.

Recently McLennan, Allen and Wilhelm, in making a study of various alloys of the silver-tin, gold-tin, gold-lead systems, found three outstanding features to characterise the results. First, in alloys with the supra-conductive elements it was observed that gold and silver produced an effect on the transition temperature opposite to that produced by bismuth, antimony and arsenic. When one observes alloys containing the latter metals, one finds usually a pronounced elevation of the supra-conducting temperature, while in alloys with gold and silver one finds an equally pronounced depression of the supra-conducting temperature. Secondly, it was noted that a binary alloy system composed of a supra-conductor and a non-supra-conductor does not necessarily have a unique transition temperature. Thirdly, it was found that with the alloy systems, silver-tin, gold-tin, gold-lead, the transition temperatures were higher for eutectic mixtures than for chemical compounds of the two metals constituting the alloys. The data compiled in Table I will serve to illustrate these points. The element silver and the compound Ag_3Sn, it will be seen, have not been found to be supra-conductors at any temperature reached up to the present.

TABLE I

Tin-Silver Alloys

Substance	Mixture	Percentage of Tin	Transition temperature
Tin	Pure	100	3·76° K.
Silver and tin	Eutectic alloy	96	3·52° K.
Ag_3Sn+Sn	Eutectic alloy	50	3·57° K.
Ag_3Sn+3 per cent Sn	Mixture	30	2·3° K.
Ag_3Sn	Compound	27	—
Silver	Pure	0·0	—

Mechanical Strains and Thermal Dilatation

The application of mechanical stresses such as those of torsion and tension raises the transition temperature of a supra-conducting metal, but observations made on the thermal dilatation of a lead rod showed no discontinuity when its temperature was lowered as it passed through the transition temperature, 7·2° K., from the ordinarily conducting to the supra-conductive state.

Action of a Magnetic Field

The application of a magnetic field delays the appearance of supra-conductivity and causes it to appear in a metal at a lower temperature than normally.

If a metal in the supra-conductive state be subjected to a gradually increasing magnetic field, a critical field strength is reached when electrical resistance re-appears in the metal. The strengths of the critical fields required for different supra-conductors vary; an alloy of bismuth and lead, for example, at 1·2° K. requires a magnetic field of 20,000 gauss to restore the property of electrical resistance, while metallic thallium at the same temperature requires a field of only 15 gauss.

Since the electrical resistance of supra-conductive metals is zero, no heat is produced when electrical currents are passed through them. Currents of high intensity can therefore be passed through supra-conductive wires of small diameter without melting them. Electric currents of more than 1,000 amperes have been so obtained in wires of small cross-section. The factor that imposes a limiting value upon the current strength is the magnetic field set up in the wire by the current itself. A critical value is reached when resistance is restored to the wire by the magnetic field.

Owing to the fact that metals in the supra-conducting state have no electrical resistance, currents of electricity induced in rings of metals in this state will persist with undiminished intensity so long as the metals remain supra-conductive. So far, it has been found impossible to detect with instruments of precision any diminution in the intensity of ring currents in supra-conductors even after the lapse of a period so long as thirteen hours.

Recently some experiments were carried out by McLennan, Allen and Wilhelm on the intensities of persistent currents of electricity induced in rings having the same dimensions of lead, tin and tantalum, brought into the supra-conductive state by the use of liquid helium. The currents in the rings were induced by the magnetic field provided by electric currents established in a circular coil of wire placed in turn coaxial with and close to each of the supra-conducting rings. The results of these experiments are represented by the graph shown in Fig. 1. It was found that, for the weaker magnetic fields, equal changes of flux produced currents of equal magnitude in each of the three supra-conductors. The magnitude of the persistent current developed depended not on the substance of the supra-conductive ring but only on its dimensions and on the magnitude and form of the inducing magnetic field.

The case of tin is very interesting, since the values of the current in it agree with those of the current in the others only up to fields of about 25 gauss. For inducing fields higher than this amount the strength of the persistent current dropped off. Above this point, then, part of the ring must have been in a magnetic field, the strength of which had reached the critical value where resistance re-appeared, that is, an inner layer of the ring must have become non-supra-conductive. As the field was increased above this point, one can suppose the outside supra-conductive portion of the ring became thinner and thinner until the whole ring became non-supra-conductive.

The fact that the same flux engenders the same persistent current in different supra-conducting metals having the same size and form follows from an application of the equation

$$L\frac{di}{dt} = \frac{dB_A}{dt} \quad \text{or } i = \frac{B_A}{L}$$

For rings of the same dimensions, the self-inductances would be identical; and in the supra-conducting state the resistances of the three metals would be vanishingly small. Self-induction and zero resistance were the two factors that made the magnitude of the induced current in different supra-conductors the same.

Looking at the matter in another way, we see that the induced currents in the three supra-conductors must be the same since the magnetic field of the persistent current must be equal in magnitude and distribution but opposite in direction to the flux of the exciting field.

ALTERNATING FIELDS

Since the discovery of the phenomenon of supra-conductivity in metals by Kamerlingh Onnes in 1911, researches in this field have been until recently almost invariably carried out by the use of unidirectional electric currents. No systematic attempt appears to have been made hitherto to investigate the phenomena of supra-conductivity with alternating electric currents of high, medium and low frequencies.

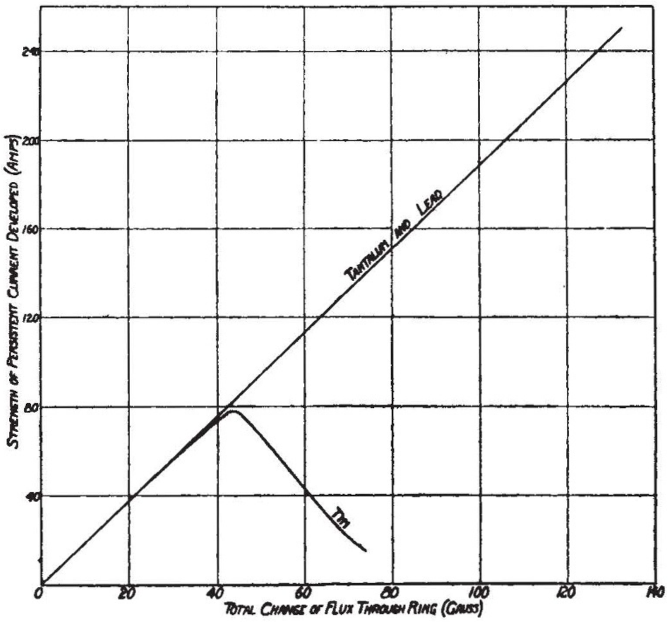

Fig. 1.

Some of the theories[2] put forward to explain supra-conductivity suggest that an orientation of some kind is involved in the production of the supra-conducting state in metals. If this suggestion should prove to be correct, one would expect some modification of the phenomenon for currents of high frequency. It need only be mentioned that all 'orientation' effects are considerably modified in an oscillating field with a time-period of the order of, or less than, the 'time of relaxation' of such orientation. A well-known example is that of the dielectric constant, which rapidly diminishes in value for very high-frequency electric fields. As to 'relaxation times', it will be recalled that in the case of ice, experimental evidence shows that the relaxation time is of the order of 10^{-6} sec. at 0° C. and rapidly increases as the temperature is lowered.[3] It would not seem unreasonable then to expect to find 'relaxation times' exhibited by metals in the supra-conducting state, provided one used in one's experiments alternating fields of suitable and adequate frequencies. A short time ago an investigation was initiated in this direction by McLennan, and through a set of researches carried out successively with the collaboration of a number of his associates, namely, Niven, Wilhelm, Burton, Allen, Smith, McLeod and others, the work recently culminated in the discovery that such metals as lead, tin and tantalum can be made to exhibit, when in the supra-conducting state, characteristic phenomena that point to their possessing 'relaxation times' roughly of the order of 10^{-7} sec. or 10^{-8} sec.

ABSORPTION OF β-RAYS BY SUPRA-CONDUCTORS

In the first of these researches[4] the absorption of β-rays by a thin sheet of lead was investigated when the lead was gradually cooled from a temperature a few degrees above to a few degrees below the critical transition temperature of 7·2° K. The β-rays used were those emitted by mesothorium and the lead sheet had a thickness sufficient to absorb, at ordinary room temperature, 50 per cent of the β-rays issuing from the mesothorium. In these experiments no measurable variation or discontinuity was detected in the absorption coefficient as the temperature of the lead was lowered through the critical value 7·2° K. The high-velocity electrons from the mesothorium apparently encountered just as much resistance in their passage through the lead with the latter in the supra-conducting state as when the lead possessed the normal conductivity exhibited at the higher temperatures. This investigation gave definite proof that although resistance in the supra-conducting state is zero, or a very low value for currents carried by slow-moving electrons, it is not zero but maintains a normal value for currents carried by high-speed electrons.

Looking at the matter in another way, this result indicates, if the de Broglie wave equation $p = h/mv$ applies, that lead at the lowest temperatures cannot exhibit supra-conductivity when subjected to alternating electric fields with frequencies of the order of 10^{21} per sec.

PHOTOELECTRIC AND LIGHT ABSORPTION EXPERIMENTS

In a second series of experiments,[5] thin films of lead were deposited on plates of glass and of quartz, sometimes by cathode spluttering and at other times by vaporisation of metallic lead. These films were subjected to a series of decreasing temperatures commencing a few degrees above 7·2° K. and ending at the temperature of liquid helium, 4·2° K. The photoelectric effect and the absorption of visible light were in turn investigated with these films and measurements were taken approximately by steps of a fraction of a degree as the temperatures of the films were lowered. In these experiments no measurable discontinuity was observed in the results of the measurements on the photoelectric effect, or in the results of those on the coefficient of absorption of the light waves when the lead films traversed were passed through the transition temperature of 7·2° K. These results were taken therefore to indicate that supra-conductivity with lead is a phenomenon that cannot be exhibited when electric fields alternating with a frequency approximately equal to or greater than 10^{14} per second are used.

It is clear, however, since supra-conductivity can be brought into evidence by the use of unidirectional fields, that is, with fields of zero frequency, that there must exist some critical alternating field with a frequency between zero and 10^{14} per second, by the use of which supra-conductivity should just be detectable.

EXPERIMENTS WITH ELECTRIC FIELDS OF RADIO-FREQUENCIES

Through the development which has taken place in recent times, it is a comparatively simple matter to arrange combinations of oscillating valve systems capable of providing alternating electric fields with frequencies so high as 10^7 or even 10^8 per second. Some experiments were therefore made with radio fields having frequencies approximating to 10^7 cycles per second and corresponding to a wave-length of about 30 metres. With fields of this frequency, it was thought that the phenomenon of supra-conductivity might appear with lead at a lower temperature than 7·2° K., might even be only partial, or might not appear at all. The experiments[6] and apparatus used, together with the theory applicable, have been fully described elsewhere and it will suffice to give here only a summary of the results obtained.

It was found that with currents of frequency $1{\cdot}1 \times 10^7$ per second a coil of lead wire showed an abrupt loss of resistance, of relatively large amount, at a temperature that appeared to be slightly lower than the critical temperature 7·2° K. characteristic of the transition to supra-conductivity, found for the same wire with direct current.

In a series of repeated experiments with a coil of tin wire, drawn to a diameter of 0·3 mm., it was found that with direct currents the resistance of the coil began to decrease abruptly at 3·76° K. and disappeared completely at 3·70° K. Experiments with the same coil with currents of frequency $1{\cdot}1 \times 10^7$ per second gave for the corresponding temperatures 3·67° K. and 3·61° K., that is, supra-conductivity did not begin to appear until a temperature was reached that was below the one at which it was complete in the case of the direct current experiments. Further experiments with higher frequencies revealed depressions of the critical transition temperature increasing in amount with the frequency. Extrapolation of the transition temperature – frequency curve, which appeared to be linear for the higher frequencies, gave 10^9 per second for the frequency corresponding to 0° K.

With tantalum wires and with wires of a bismuth-lead alloy, results were obtained similar in character to those found with wires of tin and of lead. Experiments with tin wire coils showed that the observed depression of the critical temperature was not dependent upon the magnitude of the high-frequency currents in the coils and was therefore attributable neither to the heating of the coils above the temperature of the surrounding liquid helium, nor to the effect of the magnetic field of the currents. Experiments with wires of different sizes made with currents of the same frequency showed that the depression of the transition temperature was not a direct function of the skin effect. It would appear, then, to be a function of the frequency of the current in the metal alone.

EXPERIMENTS WITH SIMULTANEOUS DIRECT AND ALTERNATING CURRENTS

Some interesting results have been obtained by passing direct and alternating currents simultaneously through supra-conductors.

In one of these experiments a tantalum conductor in the form of a solid wire was used. The graph given in Fig. 2 shows the results obtained. The magnitude measured was the direct current resistance, and the curves show that the presence of the high-frequency currents delayed the initial appearance of the approach to the supra-conducting state and enhanced the direct current resistance in the transition stages. The temperature at which supra-conductivity was complete according to the D.C. measurements was not, however, affected by the presence of the high-frequency current in the wire. This was due, of course, to 'skin effect', for the disturbing action of the high-frequency currents when the wire was at a sufficiently low temperature to be supra-conducting for D.C. measurements was confined entirely to the outer layers of the wire.

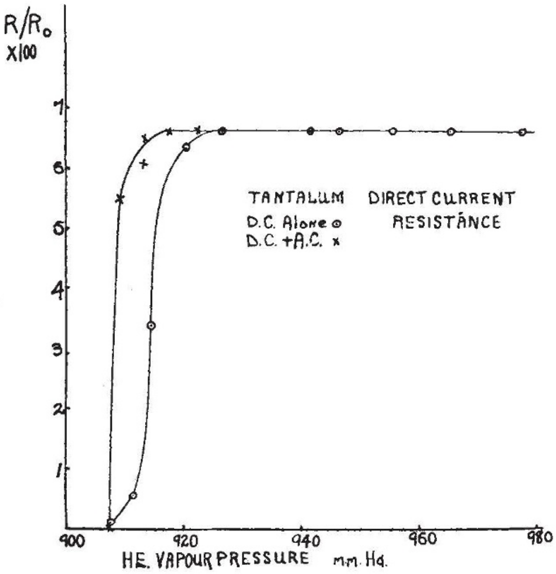

FIG. 2.

In another experiment which was rather instructive, a conductor was constructed by wiping' a layer of block tin upon a constantan wire, of diameter 0·016 cm. The tin skin was of average thickness about 1/500 mm., and its presence decreased the resistance of the wire at room temperature by about seven per cent. Calculation shows that at the low temperatures just above the supra-conducting point the resistance of the constantan was then about thirty times that of the tin.

The results of measurements made with this wire are shown by the graphs of Fig. 3, which represent the relation between the direct current resistance ratio R/R_0 and the temperature, both without high-frequency currents present, and with the high-frequency and direct currents flowing simultaneously in the metal.

It can be seen that when, in addition to the direct current, high-frequency currents were passed through the wire, the resistance was changed so that the curve *AB* first obtained was shifted to lower temperatures, becoming the curve *A'B'*. The switching on and off of the high-frequency generator changed the resistance reversibly from the point *A* to *A'*, *B* to *B'* and so on. The magnitudes of the shifts *A* to *A'* and *B* to *B'* increased, as the curves show, with an increase in the ratio of the strength of the high-frequency current to that of the D.C. one. Even when the resistance had become zero on the undisturbed curve it could be partially restored to the tin layer by switching on the alternating current. Moreover, the curves clearly show that the presence of alternating high-frequency currents in the tin coating on the wire had the effect of lowering the temperature at which with D.C. measurements the tin layer became supra-conducting.

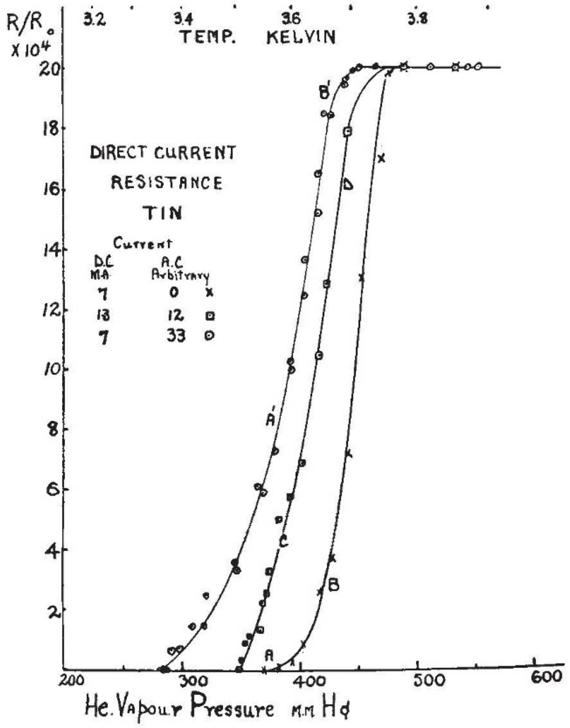

FIG. 3.

It may be of interest to state that when observations were made with this tin-coated wire on the resistance it offered to high-frequency currents, it was found that the addition to it of a direct current had the effect of removing partially or wholly the high-frequency resistance. The graphs in Fig. 4 illustrate this point.

The results of the experiments with high-frequency alternating currents would seem to justify the conclusion that a polarisation or orientation phenomenon of some kind must be involved in the production of the supra-conducting state in metals.

In the discussion, Prof. W. J. de Haas expressed the view that it seemed probable that the electrons go over into a new phase when the metals become supra-conductive, and in order to support this view certain experiments had been carried out by him and his associates on the conductivity of single crystals. Formerly the region of disappearance of resistance was about 0·03°, but he had found that for good single crystals and small measuring currents this region did not exceed 0·0005°. He and his associates had investigated the influence of the crystal lattice on grey and white tin, which differ only in this respect that grey tin does not show supra-conductivity, while white tin does. Gold-bismuth alloys show the same influence—the alloy becomes supra-conductive though neither of the components do. X-ray experiments, however, showed that this alloy has a crystal lattice of its own.

Investigations of the thermal conductivity of supra-conductors shows an influence of the supra-conductive state. At the transition point, indium shows a small sudden increase of thermal conductivity. When the supra-conductivity is disturbed by a magnetic field, the thermal conductivity is increased for pure metals. The results for $PbTl_2$ are very complicated, probably as a result of the lack of homogeneity of the alloy. The specific heat of tin increases when the metal becomes supra-conductive. In a magnetic field high enough to disturb supra-conductivity, this increase disappears.

Prof. O. W. Richardson pointed out that there is some resemblance, even though it may be only superficial or accidental, between supra-conductivity and ferromagnetism. Following this idea, Keesom and his associates at Leyden have measured the specific heat of supra-conductors in the neighbourhood of the critical point, where one might expect an abnormality similar to the abnormality in the specific heats of ferromagnetic substances in the neighbourhood of the Curie point; but no such effect could be detected. This, however, is not entirely conclusive. The number of electrons concerned in the supra-conductive phenomenon may be too small a fraction of the total number, or of the number of atoms present, to exert any appreciable influence on the specific heat, or, alternatively, there may be some compensating effect on the atoms which may counterbalance any changes in the specific heat of the whole substance arising from changes in the energy of the electrons.

Dorfman has pointed out that a test which is in some respects a more direct one of this particular issue can be made if the specific heat of electricity (Thomson effect) in the supra-conductive region of temperature is considered. The magnitude of this effect can be deduced from the thermoelectric measurements of Keesom and his associates which refer to lead and tin. These show that there is such an abnormality in the Thomson effect. It is true that it does not occur exactly at the supra-conductive critical temperature. For example, in the case of lead this critical temperature is 7·2° K.; whereas the anomaly in the Thomson effect sets in at about 5° K. and rises to a maximum at a little above 10° K.. after which it falls. This anomaly is quite similar to the corresponding anomaly in the case of ferromagnetic substances near the Curie point.

If it is admitted that this anomaly in the Thomson effect is associated with the establishment of supra-conductivity, it is a natural inference that it is a result of the change in the energy of an electron connected with this phenomenon. On this basis, the thermoelectric data enable the difference ΔW_0 between the energy of a supra-conducting and a non-supra-conducting electron to be estimated. The interesting fact then emerges that, approximately,

$$\Delta W_0 = \mu H_0 = h\nu_0$$

where μ is the spin moment of the electron, H_0 the magnetic field necessary to destroy the supra-conductivity, h is Planck's constant, and ν_0 McLennan's destructive frequency; ΔW_0, H_0 and ν_0 are all extrapolated to the absolute zero of temperature. In other words, the magnetic energy and the vibrational energy required to break up the supra-conductive structure are each approximately equal to the energy of the structure itself.

Dr. W. Meissner described experiments in which very slow-moving electrons are made to impinge upon a sheet of tin-foil at temperatures both above and below the transition temperature of tin, 3·7° K. His object was to see whether the foil when supra-conductive is transparent to such slow-moving electrons. It was found not to be so, although by his experimental arrangements the velocities of the impinging electrons after their entrance into the tin-foil were probably not greater than the velocities with which the conducting electrons in the metal, according to recent theories, are supposed to be endowed.

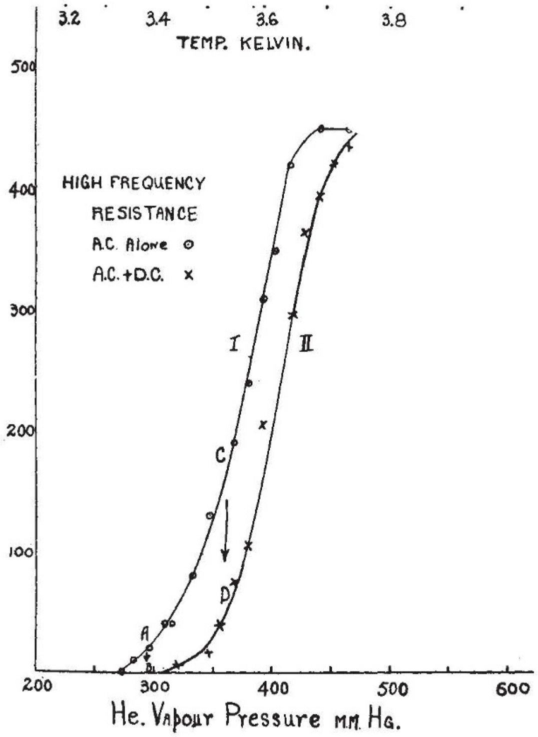

FIG. 4.

ELECTRON LATTICE THEORY

Interest in the problem of supra-conduction in metals has been stimulated recently by a view put forward independently by Prof. Niels Bohr, of Copenhagen, and by Prof. R. de L. Kronig, of Groningen, in communications to McLennan. The essential feature of this view is that the conducting electrons in a metal are supposed to form a crystal lattice of their own in addition to that formed by the atom-ions of the metal.

According to quantum mechanics, it appears that this electron lattice can move through the wire lattice without dissipation of energy even when the wire lattice is in thermal agitation. In other words, the metal will be supra-conducting whenever the electron lattice exists.

On this view of supra-conductivity, the transition point or temperature at which the metal passes from the supra-conductive state to the ordinary conducting one may be interpreted as the melting point of the electron lattice. The view that the conducting electrons in metals may build a lattice has already been put forward by Prof. F. A. Lindemann[7] and the suggestion was made both by him and by Sir J. J. Thomson that this idea may provide a basis for an explanation of the phenomenon of supra-conduction in metals. Without the aid of quantum mechanics, however, it was not clear that an electron lattice of the type now invoked could be stable and could be given a translatory motion without dissipation of energy through the wire lattice of a metal endowed with thermal agitation.

The electron lattice theory is a promising one, for it affords a direct and ready explanation of a number of the phenomena associated with supra-conduction in metals. The final verification of the theory will probably be reached through a study of the conductivity of single crystals of metals at the lowest temperatures. As de Haas has indicated, investigations have been begun already in this direction.

---

[1] *Phil. Mag.*, 5, **36**, 271; 1893.

[2] For example, Sir J. J. Thomson, *Phil. Mag.*, 6, **30**, 192; 1915; and Richardson, *Phil. Mag.*, 6, **30**, 295; 1915. Ashworth, *Phil. Mag.*, 6, **27**, 357; 1914; and *Phil. Mag.*, 6, **36**, 351; 1918.

[3] Errera, *J. Phys.*, 6, **5**, 304; 1924; J. Granier, C.R. Acad. Sci., **179**, 1,314; 1924; Debye and Wentsch, see "Polar Molecules", by Debye, p. 102, pars. 20 *et seq.*

[4] McLennan, McLeod and Wilhelm, *Trans. Roy. Soc. Canada*, 3, **23**, Sect. III, 269; 1929.

[5] McLennan, Hunter and McLeod, *Trans. Roy. Soc. Canada*, 3, **24**, Sect. III, p. 3; 1930; McLennan, Burton, Pitt and Wilhelm (Footnote), *Phil. Mag.*, 7, **12**, 708; 1931; McLennan, Smith and Wilhelm, *Phil. Mag.*, 7, **12**, 835; 1931.

[6] McLennan, Burton, Pitt and Wilhelm, *Phil. Mag.*, 7, **12**, 707; 1931; *Trans. Roy. Soc. Canada*, 3, **24**, Sect. III, 191; 1931; NATURE, **128**, 1004; 1931; and *Proc. Roy. Soc.*, A, **136**, 52; 1932. *Proc. Roy. Soc.*, A, **138**, 245; 1932.

[7] *Phil. Mag.*, 6, **29**, 127; 1915.

PRINTED IN GREAT BRITAIN BY FISHER, KNIGHT AND CO., LTD., ST. ALBANS