3. *Effects of impurities on the resistance of the intermediate state.*—An examination of the time effects in impure tin in both transverse and longitudinal fields shows definitely that the effect of impurities is to increase the resistance of the specimen in the intermediate state. Bismuth increases this resistance more than the other impurities, and consequently decreases the current the most rapidly. Thallium has the next greatest effect, and lead the least.

Equation (2) expressing the behavior of persistent currents in transverse fields does not hold for the impure samples as it does for large currents in pure tin. Nor is there any consistent linear relation between persistent current and applied longitudinal field as expressed in Eq. (3). This is hardly to be expected, for since the presence of a large locked-in flux considerably complicates any generalization, it is impossible to say just when penetration of the specimen by the field commences. Since the flux is locked in with each reading, penetration may commence as soon as the persistent current begins to be affected by the external field. If this is so, we would expect the current-carrying capacity of the intermediate state to be altered by impurities. Thus, the high transverse critical fields given by tin-lead and tin-thallium would indicate that owing to the presence of the superconducting impurities, the current-carrying capacity of the intermediate state is increased. Bismuth on the other hand must decrease it. Eqs. (2) and (3) however, are not valid over any portion of the curves.

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Relaxation Effects Connected with the Transition Between the Superconducting and Normal States

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Several authors have suggested that the relaxation effects frequently observed in experiments on the magnetic properties associated with superconductivity may be due to the slow decay, caused by a very small resistance, of eddy currents in the specimen. Similar relaxation effects have recently been observed by the authors and Wilhelm in experiments on persistent currents in a closed superconducting circuit. Viewed in the light of a marked parallelism in behavior of all time effects, these experiments definitely confirm the above suggestion. Further, a simple thermodynamic argument shows that the same cause will produce relaxation in the thermal equilibrium, and so will account also for the time effects in the calorimeter experiments of Keesom and van Laer.

INTRODUCTION

THE relaxation effects which have been observed in connection with the transition between the superconducting and normal states of a metal, when this takes place in the presence of a magnetic field, have given rise to much discussion. The effect in question can be described generally as a delay in attaining equilibrium when a change is made in either the external magnetic field or the temperature. In all cases so far reported, the relaxation effects have been found only with metals of high purity, in the transition region between the pure superconductor and the normal metal. It can reasonably be assumed, therefore, that the effects are associated with a mixture of superconducting and normal regions in a pure metal.

Different experimenters who have observed the effects have suggested various tentative explanations, but so far it has not been possible to present definite evidence of the cause, or even to show that all the effects are due to the same cause. Several authors have suggested[1–5] that the effects observed in experiments on the magnetic properties associated with superconductivity might be due to the slow decay, caused by a very small resistance, of eddy currents induced in the specimen by the changing magnetic field. If this is the case, the phenomenon must be an irreversible one, and so must be associated with a certain amount of hysteresis in the magnetic cycle, as pointed out by Mendelssohn and Pontius.[2, 3]

Similar relaxation effects have recently been observed by the authors and Wilhelm,[6] in experiments on the prevention of persistent currents in a closed superconducting circuit by a magnetic field. In these experiments, the current in the circuit was measured directly, independently of other magnetic effects, and the decay of the current strength with time was clearly due to the presence of a very small resistance when the specimen contained suitable proportions of superconducting and normal regions. The experiments showed, in agreement with those of de Haas, Voogt and Jonker,[7] that no resistance appeared until a certain portion of the metal had passed into the normal state, and then as the transition proceeded the resistance remained finite but small over an appreciable range of magnetic field strengths. The small effective resistivity in the earlier stages of the transition region is also indicated by the experiments of Shoenberg[8, 9] on a superconducting sphere in an alternating magnetic field, where the resistance to the eddy currents was shown by an out-of-phase component in the inductance of a coil surrounding the sphere.

The experiments described in *I* show that under certain external conditions the currents induced in a superconducting metal may take an observable time to decay, and it is the purpose of the present paper to advance the proposition that all the relaxation effects which have so far been observed are due to this relatively simple cause. It is significant that the manner in which equilibrium is approached, and the conditions under which the effects are observed, are very similar in the experiments *I*, in which the resultant current strength was actually measured, and in other experiments in which the magnetic or thermal properties have been studied.

Experiments in which relaxation effects have been observed can be divided into three classes:

A. Experiments, such as *I*, in which the effect is clearly due to the decay of the current circulating around a closed circuit.

B. Experiments in which the effect is a delay in attaining equilibrium between the magnetic induction within the specimen and the external magnetic field.

C. Experiments showing a delay in attaining thermal equilibrium when the heat of transition is involved.

It is proposed to discuss these in order, and to show that there is a strong thread of continuity running through the entire series, with definite connecting links between the three types of experiment.

Delay in Establishing Magnetic Equilibrium

The largest number of observations of relaxation effects belong to class *B*, connected with experiments on the magnetic properties of simple superconducting bodies.[10] In all these cases the effect has been a delay, of very variable length, in attaining the final state of equilibrium of the magnetic induction within the body.[11]

The experiment performed by de Haas, Engelkes and Guinau[1] forms a direct link between the persistent current experiments *I* and other magnetic experiments. In this experiment the

[1] W. J. de Haas, A. D. Engelkes and O. A. Guinau, Physica **4**, 595 (1937); Leiden Comm. 247*e*.

[2] K. Mendelssohn and R. B. Pontius, Physica **3**, 327 (1936).

[3] K. Mendelssohn and R. B. Pontius, Nature **138**, 29 (1936).

[4] D. Shoenberg, Camb. Phil. Soc. Proc. **33**, 260 (1937).

[5] J. G. Daunt, Phil. Mag. **24**, 361 (1937).

[6] K. C. Mann, H. Grayson Smith and J. O. Wilhelm, Phys. Rev. **54**, 758 (1938). This paper will be referred to throughout as *I*.

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

[8] D. Shoenberg, Actes du 7e Congrès Internat. du Froid **1**, 492 (1936).

[9] D. Shoenberg, Camb. Phil. Soc. Proc. **33**, 559 (1937).

[10] References 1 to 5, 12, 13 and 15; also J. N. Rjabinin and L. W. Schubnikow, Physik. Zeits. Sowjetunion **6**, 557 (1934).

[11] The experiment performed by Daunt (reference 5) is included in class *B* because it is concerned with the magnetic equilibrium. However, the effect observed, a variation with time of the shielding properties of a hollow tin cylinder, depends rather upon the proportion and distribution of the superconducting regions. It follows from the thermodynamic arguments given below that the amount of superconducting material present varies with the time in the same way as the excess eddy current.

field strength was measured inside a canal bored through a tin sphere in the direction of the external field. On account of this canal, the body has to be considered as a closed circuit, in which circulating currents can be induced. In the light of the present evidence the relaxation effects were evidently due, as the experimenters themselves suggested, to the decay with time of these currents, and the experiment should be placed along with *I* in class *A*. This is further supported by the fact that no field was observed in the canal until the external field strength was appreciably greater than the value at which penetration of flux into the sphere commenced. Since it is now known that resistance does not usually begin to appear until an appreciable part of the body has passed into the normal state, the exclusion of the field from the canal was evidently due to a resistanceless persistent current set up around the closed circuit.

Now, de Haas, Engelkes and Guinau stated further that there was no essential difference in behavior, including the relaxation effects, between the field at the surface of the sphere with the canal, and that at the surface of a similar solid sphere. We can conclude, therefore, that the effect in the solid sphere is due to the same cause as that in the bored sphere, namely to the decay of eddy currents.

Insofar as details have been reported of the relaxation effects of class *B*, the behavior has been quite similar to that in the persistent current experiments *I*. In the first place, the decay with time definitely does not follow a simple exponential law, with a rate of decay proportional to the excess.[2, 4, 5, 12] Rather, the rate of approach to equilibrium is rapid at first, and then becomes much slower as the final state is neared. This agrees with *I*, and in the latter case the shape of the decay curve could be ascribed to the fact that the small resistance depends on the amount of current flowing, in excess of the equilibrium current which the specimen can carry without resistance.

The relaxation effects have been observed in general only with pure metals.[2, 13] In *I* it was found that the resistance in the early stages of the transition was very much greater for tin contaminated with various impurities than it was for pure tin.

In experiments on spheres, and on cylinders in transverse fields where the field is considerably distorted around the body and the penetration of field proceeds gradually, the relaxation effects have been found to be more pronounced, and the times to be longer, during the earlier stages of penetration.[14] In *I* also, the small resistance which made the decay of current slow enough to be observed was associated with the earlier stages of the transition.

From the rate of decay of the persistent currents in *I* an estimate can be made of the mean resistivity of the mixture of superconducting and normal material. Towards the end of the relaxation period this was about 3×10^{-12} ohm-cm for pure tin, but the estimate is very rough since the resistance varied as the decay proceeded. With such a resistivity, the relaxation time for Foucault currents flowing around the circumference of a cylinder of radius r would be of the order of $700r^2$ seconds. The order of magnitude of the resistance observed is therefore satisfactory, although this figure is somewhat less than the times which have been observed for long cylinders in a longitudinal magnetic field.[2, 12, 15]

The Time of Relaxation

In most cases the times of relaxation which have been reported are the times required for equilibrium to be attained within the limits of measurement, and these times have varied very much in different experiments. It is well known that the secondary phenomena associated with superconductivity are very sensitive to variations in the shape and purity of the specimens, and this, as shown in *I*, includes the small resistance. However, it can be shown that in different experiments where the purity and shape are similar, the observed relaxation times can still depend very much on the way in which the experiment was carried out, principally on the magnitude of the steps in which external conditions were altered.

[12] L. W. Schubnikow, W. I. Chotkewitsch, J. D. Schepelew and J. N. Rjabinin, Physik. Zeits. Sowjetunion **10**, 165 (1936); **10** (Supp.), 36 (1936).

[13] D. Shoenberg, Proc. Roy. Soc. **A155**, 712 (1936).

[14] References 1, 4, 5, and 13. However, Mendelssohn and Pontius (reference 3) observed relaxation effects throughout the transition for a short cylinder.

[15] K. Mendelssohn, Proc. Roy. Soc. **A155**, 558 (1936).

The experiments I, and the general shape of the decay curves, show that the resistance increases rapidly with the amount of excess current flowing. Consequently, when the field or temperature are varied in small steps so that the currents induced are small, the effective resistivity will be extremely small, and the time required for the current to decay to half-value will be comparatively long. It can easily be seen that the whole decay curve will be extended along the time axis. Then, since experiments in which small changes have been made are usually those in which a sensitive method of measurement has been used, the time to attain "effective equilibrium" is also likely to be long.

When different experiments are compared, the association of slow relaxations with small changes of field strength seems for the most part to be confirmed. Rapid relaxations, of the order of a few seconds, have been observed by Daunt[5] when the direction of the field was suddenly changed, by Keesom and van Laer[16] with changes of the order of a third of the transition range, by the authors in I where every observation represented a reduction of the total field through a large part of the transition range. Slow relaxations, of several minutes, have been observed only in detailed studies of the magnetic cycle, where the field was changed in small steps.[1, 2, 3, 12, 15] On the other hand, Shoenberg[4, 13] has observed rapid relaxations in studying the magnetic cycles of spheres and short cylinders.

The Delay in Thermal Equilibrium

In experiments on the heat of transition and specific heat of tin, in the presence of a magnetic field, Keesom and van Laer[16] observed relaxation effects as the tin was heated through its transition from superconducting to normal, indicating a delay in the absorption of the heat of transition. When the metal was in its transition region, and heat was added at a uniform rate, the initial rise of temperature was greater than it ought to have been if the heat of transition had been immediately absorbed. Then, after the heating ceased, the temperature dropped again to its final equilibrium value, with a relaxation time of 20 to 40 seconds.

On the other hand, no delay was observed in the cooling due to the magneto-caloric effect, when the magnetic field was increased adiabatically. Keesom and van Laer consider that a relaxation of the order of 5 seconds ought to have been observable, and for this reason they suggest that there is some essential difference in the two cases. However, the dependence of the relaxation time on experimental conditions could cause a variation by a factor of 5 or more. Moreover, the alternating current experiments of Shoenberg[9] indicate that there is a relaxation, in this case very rapid, in the magneto-caloric effect. Hence the authors see no necessity for concluding that the cause of relaxation is different in the two cases.

Mendelssohn has reported[2, 15] that similar delays were observed in establishing magnetic equilibrium whether the field strength was altered, or the temperature changed keeping the field constant. This is to be expected if the effect is due to eddy currents, for in the transition region a change of temperature will initiate a redistribution of the field, and this will induce currents of the kind postulated. It then follows that there ought to be a relaxation in the thermal equilibrium, as observed by Keesom and van Laer.

We shall assume that when a change in external conditions is made, either of magnetic field or of temperature, the immediate change $\delta'\sigma$ in the magnetization of the superconductor is numerically less than the change $\delta\sigma$ in the equilibrium value. Then there must be a further delayed change, the relaxation, amounting to $\delta''\sigma$, where

$$\delta'\sigma+\delta''\sigma=\delta\sigma,$$

and where $\delta''\sigma$ is a function of the time, determined by the decay of the eddy currents.

In any change the external work done is $H\delta\sigma$, and if the heat absorbed is δQ we have

$$H\delta\sigma+\delta Q=\delta U+\delta U_i, \tag{1}$$

where δU_i is the kinetic, or self-inductance energy of the eddy currents. Since δU_i is always positive when an equilibrium state is disturbed by altering external conditions, the magnetic cycle as a whole may be irreversible. But the process can be said to be instantaneously

[16] W. H. Keesom and P. H. van Laer, Physica **3**, 173 (1936); Leiden Comm. 240*c*; Physica **4**, 499 (1937).

reversible in the sense that, if the time required to alter conditions is small compared with the time of relaxation, an immediate reversal will destroy the eddy currents and restore the initial conditions. Therefore, for a rapid initial change, δU_i can be treated as a part of the internal energy. Then, during the slow decay, this energy is exactly recovered as heat, and so the decay represents merely a change in the form of the internal energy, and it is permissible to apply thermodynamic relations to the problem.

Ignoring the distinction between the energy of the eddy currents and other forms of internal energy, we obtain from (1), as a fair approximation to the actual conditions,

$$\delta Q = T\delta S = C_v \delta T - T(dH/dT)_\sigma \delta\sigma. \quad (2)$$

In this relation we can put, at least approximately,

$$(dH/dT)_\sigma = dH_c/dT,$$

where H_c is the critical field for the interruption of superconductivity, for throughout the transition region the field within the body must be nearly equal to the critical field, independent of σ.[17]

Consequently, in the first experiment of Keesom and van Laer, heating in a constant field, the rise of temperature during the heating period will be given by

$$C_v \delta' T = \delta Q + T(dH_c/dT)\delta'\sigma. \quad (3)$$

Since dH_c/dT is a negative quantity, and $\delta'\sigma$ is positive and less than the equilibrium value $\delta\sigma$, the temperature increase $\delta' T$ must be greater than the equilibrium increase, in agreement with experiment.

After the heating is complete, we have, according to the eddy current hypothesis, a further change $\delta''\sigma$ in the magnetization, and hence a further change in temperature, given by

$$C_v \delta'' T = T(dH_c/dT)\delta''\sigma. \quad (4)$$

This represents a delayed cooling, as observed, which follows exactly the variations in the magnetization.

[17] Theoretically, the internal field should be everywhere equal to H_c, if the distribution of normal and superconducting regions is regular: F. London, Physica **3**, 450 (1936).

Equation (4) gives also the cooling to be expected in the adiabatic magneto-caloric effect, and shows that in this case also the changes of temperature should follow the course of the magnetization, and exhibit the same kind of relaxation as has been observed in purely magnetic experiments.

The heat of transition from the superconducting to the normal state is given by[18]

$$L = -VT(H/4\pi)(dH_c/dT) = -T(dH_c/dT)\sigma, \quad (5)$$

where $\sigma = VH_c/4\pi$ is the total change in magnetization from pure superconductor to normal metal. Eq. (2) can now be written

$$\delta Q = C_v \delta T + L\delta\sigma/\sigma.$$

But, if the mixed phase interpretation of the transition region is accepted,

$$\delta Q = C_v \delta T + L\delta r,$$

where δr is the increase in the fraction of the material which is in the normal state. From this it can be argued that the transition of the material from one state to the other in local regions also follows the changes in magnetization, and so also proceeds slowly as the excess eddy currents die out. The same presumably applies to the distribution of the normal regions, insofar as this is determined by the direction of the external field, and so the eddy current hypothesis can also account for the relaxation effects observed by Daunt.[5, 11] This suggests that the process may be similar to that suggested by Mendelssohn and Pontius,[3] that in a decreasing field the regions in which the eddy currents are located contract as the currents decay, and allow the transition to the superconducting state to proceed.

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[18] C. J. Gorter and H. Casimir, Physica **1**, 305 (1934); W. H. Keesom and P. H. van Laer, Physica **4**, 487 (1937).