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# Paramagnetic Effect in Superconducting Tin, Indium, and Thallium

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Measurements have been carried out on the longitudinal magnetization of pure rods in the intermediate state between normal and superconduction. The observed "paramagnetic" flux increase is dependent on the externally sustained current, external magnetic field, and temperature only. The dependence is much the same for the metals studied. There is a threshold current to be exceeded before the flux increase is observed. The threshold is linearly dependent on the external magnetic field; the slope of the threshold curve is the same for the metals studied. The results compare favorably with existing theory, except for the threshold. An upper limit has been placed on the relaxation time for the currents responsible for the flux increase. The effect of the physical purity of the sample has been observed.

## INTRODUCTION

IN the so-called paramagnetic effect[1–3] one finds that a solid rod of superconducting material may, under certain conditions, contain more magnetic flux than can be ascribed to external magnetic fields. If the rod carries a high current along its axis and is in a small external magnetic field parallel to that axis, then the longitudinal flux content will exceed the flux due to the applied field when the metal is in the transition region between the normal and superconducting states. The excess flux may be several times as large as the flux due to the external field. It has been established[2] that the extra flux is due to a circular component of the applied current and not to some basically atomic paramagnetism. Theoretical explanations have been proposed,[4,5] but are in need of further experimental data. For this reason results obtained earlier on tin[3] have been extended to two other superconductors: indium and thallium. Measurements of the flux content of the single-crystal specimen rods of pure metals have been made at constant values of current, external magnetic field, and temperature; thus assuring that measurements were made on equilibrium properties. We have also carried out experiments which place an upper limit on the relaxation time necessary for the extra longitudinal flux to establish itself or to die out.

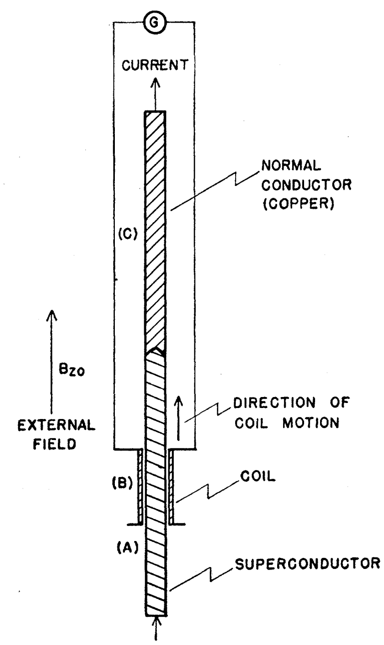


FIG. 1. Schematic diagram of sample and flux-measuring system. Samples of tin, indium, and thallium were used.

## MEASUREMENTS OF APPARENT PERMEABILITY

The longitudinal flux content of the cylindrical specimen ($A$) is measured by moving a concentric detection coil ($B$) from the sample to a normal conductor of known flux content ($C$) and observing the deflection of a ballistic galvanometer ($G$) connected to the coil. See Fig. 1. The experimental apparatus and procedure is essentially that described by Thompson and Squire.[3] The sample is initially established in the superconducting state (with zero frozen flux) and in a specified external magnetic field, less than the critical field. Then a small current is turned on and the flux content of the sample (i.e., galvanometer deflection) measured for various steady currents in the superconducting, intermediate, and normal states. See, for example, Fig. 2. Potentiometer measurement of the current in the specimen permits high accuracy; however, it was found that precision of 0.1 amp was adequate to obtain a smooth function as in Fig. 2.

It will be useful to talk in terms of apparent relative permeability,[2] $\tilde{K}=\tilde{\mu}/\mu_0$ when describing the effect. If $\delta$ is the galvanometer deflection when the coil is moved from the sample to the copper and $\delta_1$ is the deflection when the sample is in the pure superconducting state, then $\tilde{K}$ is given by

$$\tilde{K}=1+(\delta/|\delta_1|)$$

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[1] K. Steiner, Z. Naturforsh. **4a**, 271 (1949).
[2] Meissner, Schmeissner, and Meissner, Z. Physik **130**, 521, 529 (1951); **132**, 529 (1952); W. Meissner and R. Doll, Z. Physik **140**, 340 (1955); A. Sellmaier, Z. Physik, **141**, 550 (1955).
[3] J. Thompson and C. F. Squire, Phys. Rev. **96**, 287 (1954).
[4] H. Meissner, Phys. Rev. **97**, 1627 (1955).
[5] C. J. Gorter, Conference de Physique des basses temperatures, Paris, September, 1955 (unpublished), paper No. 126.

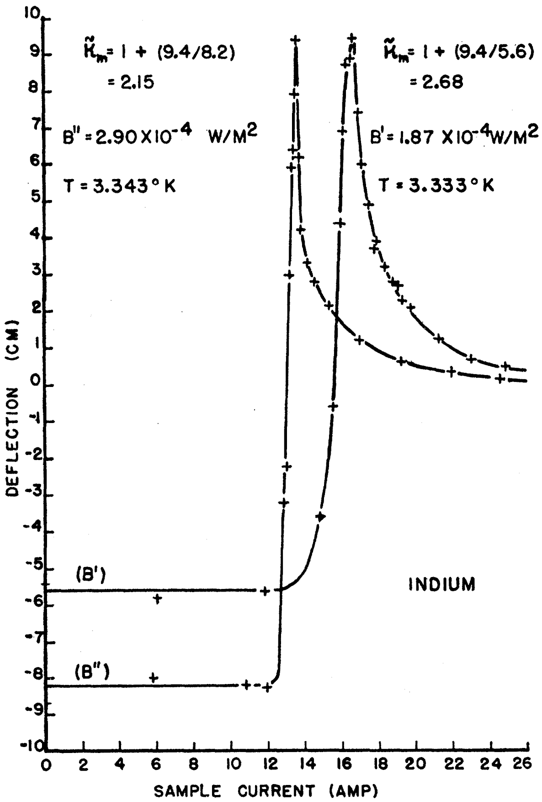


FIG. 2. Typical transition curves, these are for indium. Similar curves obtain for tin and thallium. Deflections were obtained at constant $B$, $I$, $T$ by moving the coil from position $(A)$ to position $(C)$ as indicated in Fig. 1.

and is a function of the current and field at which $\delta$ is obtained. See Fig. 2. Thus $\tilde{K}$ is zero in the superconducting state, unity in the normal state, and greater than unity in the paramagnetic region. We shall give special notice to the maximum value, $\tilde{K}_m$.

Both horizontal and vertical components of the earth's field were compensated or taken into account in field calculations. Temperature was determined from vapor pressure of the helium bath, and was regulated to $\pm 0.001$ K deg near the tin and indium critical temperatures, and within $\pm 0.002$ K deg for the thallium data.

## MEASUREMENTS OF RELAXATION TIME

The curves labeled $B'$ and $B''$ in Fig. 2 are the transitions one obtains at two different external fields, $B'$ and $B''$, and at slightly different temperatures. It is apparent that the flux content at a given current is quite different, e.g., there is more flux in the sample at the low field, $B'$, at 17 amp than at the higher field at the same current. Transition curves taken at the same temperature show the same general behavior as Fig. 2 though the peaks are closer together. In the following discussion we will always be dealing with curves taken at the same temperature, but will refer to Fig. 2 for illustration. One might inquire if the field were quickly increased from $B'$ to $B''$, would the galvanometer deflection obtained when the change occurs ever indicate a flux decrease in the sample? The answer was found to be yes and the relaxation time found to be quite short. Experiments were carried out to ascertain the behavior of the flux change with such field changes. First, two transition curves were taken at some fixed temperature. Then the current was set at some value, the external field switched from $B'$ to $B''$, and the galvanometer deflection recorded (called initial deflection below). About seven seconds after the field was changed the coil was lifted from the sample to the copper and the flux measured. This flux measurement was repeated if the flux content did not correspond to curve $B''$ until the proper value was reached. Next, the process was reversed, the field quickly changed from $B''$ to $B'$, and flux measured at field $B'$ until equilibrium was again reached. This procedure was repeated at various currents, yielding the flux change in the coil when a field change occurs. The net change in the sample alone may be determined by correcting for: the leakage flux in the superconducting state due to the gap between the coil and the sample; and the frozen flux which may occur if a field decrease puts the sample in the superconducting state. In the superconducting state the flux change is zero, and in the normal state the flux change is simply due to the external field change. The corrected data are shown by the crosses in Fig. 3. By referring to the original transition curves we can predict what this change should be for any current by noting the difference in the galvanometer deflection obtained by moving the coil in the constant

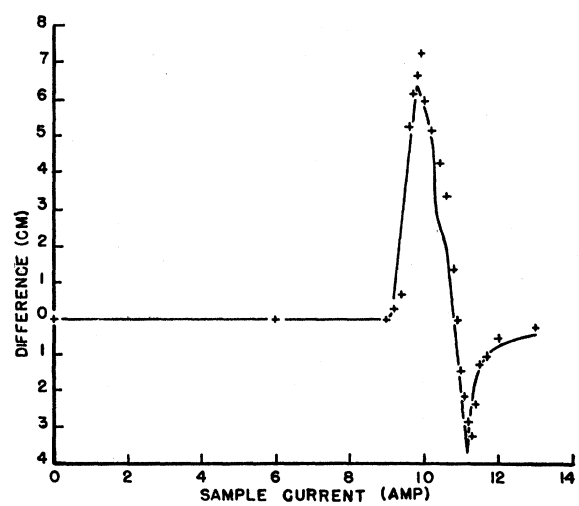


FIG. 3. Comparison of expected and measured deflections after corrections. Field change from $2.37\times10^{-4}$ weber/meter$^2$ to $4.89\times10^{-4}$ weber/meter$^2$ with the coil fixed about the superconductor. The solid curve is the expected deflection, the crosses are the actual deflection obtained. A positive sign indicates that the flux change went in the same direction as the external field change.

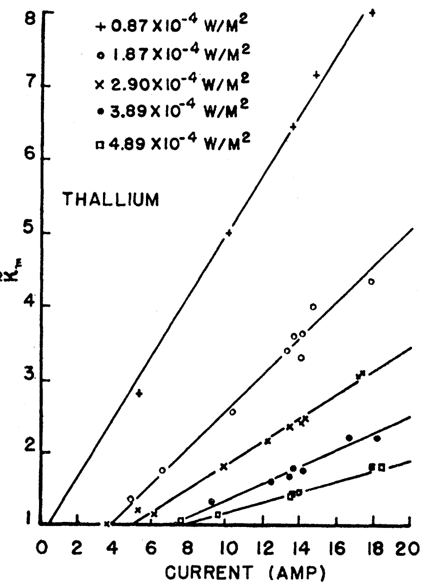


FIG. 4. Magnitude of the peak paramagnetism as a function of the current and field at which it was obtained for thallium. Solid lines are fitted to the experimental points by least squares. Results for tin and indium are similar.

fields, $B'$, $B''$. Here we must remember the fact that the deflection obtained in the superconducting state depends on the external field even though the induction in the sample is zero. Results of the comparison are shown in Fig. 3 for thallium, and a flux increase in the sample is found when the external field is decreased in the neighborhood of 11 amp.

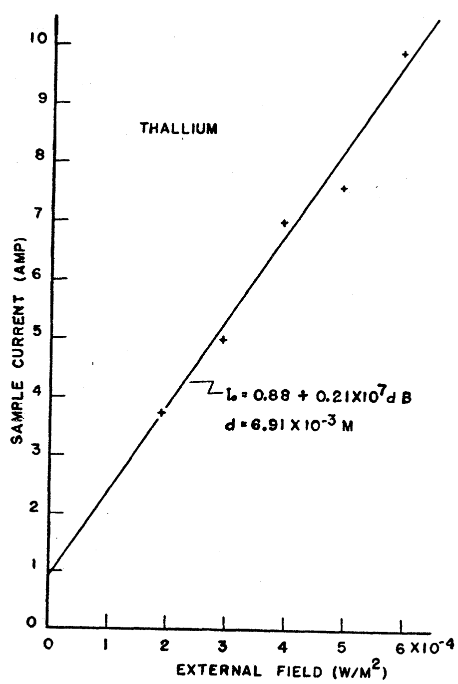


FIG. 5. Threshold for the paramagnetic effect in thallium. For currents at the transition above $I_0$ extra flux is observed, for currents less than $I_0$ only the usual transition. Each point is obtained from Fig. 4 by extrapolation to unit permeability. Similar lines result for tin and indium.

## RESULTS

We carefully ascertained that the maximum flux content, i.e., $\tilde{K}_m$, exists when the total field due to the current and to the external solenoid equals the critical field. The magnitude of the effect for each metal was determined at various fields, temperatures, and currents. The magnitude of the maximum paramagnetism was found to increase linearly with current for a given external field, once some threshold current dependent on the field had been exceeded. The curves of $\tilde{K}_m$ *versus* current using different fixed external fields are shown in Fig. 4 for thallium; similar curves obtain for tin and indium. The lines drawn through the points are fitted by the method of least squares. Each point corresponds to a different temperature or current and external field combination where the total field equals the critical field.

The intercept of the line of $\tilde{K}_m$ *versus* current for some field gives the threshold current characteristic of that field. These current intercepts with their associated fields yield the threshold curve shown in Fig. 5 for thallium. The considerable scatter is due to the derived nature of the quantities involved. One may represent the threshold curve by[2]

$$I_0 = I_g + \gamma dB,$$

where $d$ is the sample diameter, all quantities in mks units. Paramagnetism is observed for currents greater than $I_0$. Experimental values of $\gamma$ and $I_g$ are given in Table I, with values reported by other workers. With thallium there exists a sharp discrepancy between our results and those reported by Meissner *et al.*[2]; we indicate that thallium is more like the other superconductors.

Meissner[4] has developed a theory attempting to explain the paramagnetic effect in terms of the intermediate state structure postulated by London[6] and

TABLE I. Parameters of the threshold curve $I_0 = I_g + \gamma dB$ for various superconductors.

| Specimen | $I_g$ (amp) | $\gamma$ (meters/henry) | Reference |
|---|---|---|---|
| Tin | 1.6±0.7 | $(0.21\pm0.05)\times10^7$ | present work |
| | 1.2 | $0.17\times10^7$ | a |
| | 1.2 | $0.23\times10^7$ | b |
| Indium I | 0.3±0.2 | $(0.21\pm0.01)\times10^7$ | present work |
| III | 0.2±0.3 | $(0.21\pm0.01)\times10^7$ | present work |
| | 0.6 | $0.17\times10^7$ | a |
| Thallium | 0.9±0.3 | $(0.21\pm0.01)\times10^7$ | present work |
| | 0.6 | $0.09\times10^7$ | a |

[a] See reference 2.
[b] Y. Shibuya and S. Tanuma, Phys. Rev. 98, 938 (1955).

[6] H. London, *Superfluids* (John Wiley and Sons, Inc., New York, 1950), Vol. I, p. 120.

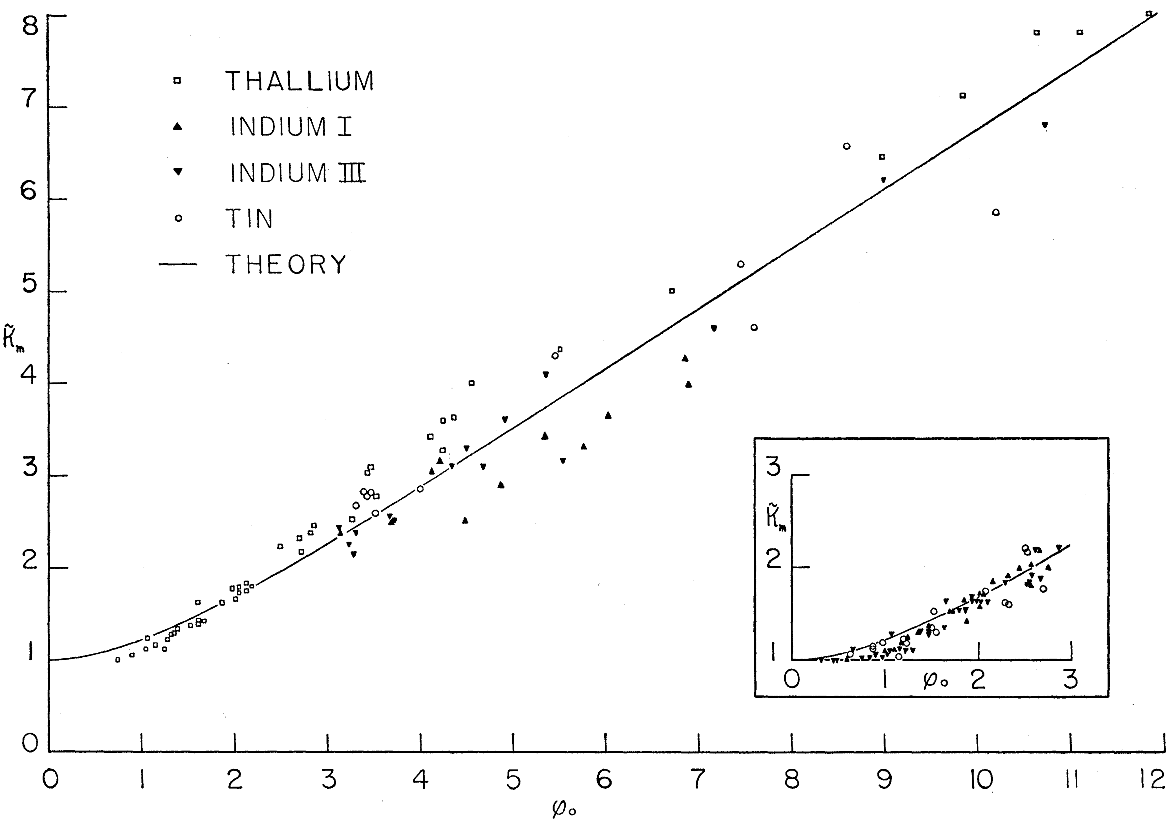


FIG. 6. Comparison of experimental data and theory due to Meissner.[4] The abscissa is $\varphi_0=\mu_0 I/\pi d B_{z_0}$. The equation of the line is $\tilde{K}_m=(\frac{2}{3})\varphi_0^{-2}[(1+\varphi_0^2)^{\frac{3}{2}}-1]$. $I$ is the sample current, $B_{z0}$ the external field, and $d$ is the sample diameter.

Pippard.[7] The model assumes that the intermediate state is made up of grains of superconducting material in a matrix of normal metal. The grains tend to line up with the long axis parallel to the total magnetic field, which is spiral in the system studied. Thus the path of least resistance is a spiral and the spiraling current acts like a solenoid to produce the extra flux. This theory yields a value of the maximum permeability, $\tilde{K}_m$, for a given transition as a function of the ratio: $\varphi_0=B_{\varphi 0}/B_{z0}$, where $B_{\varphi 0}=\mu_0 I/\pi d$, $I$ is the current, and $B_{z0}$ the external field at the point of the maximum. A parameter of the theory is the ratio of the length, $l$, to the diameter, $a$, of the superconducting grains less one, i.e., $C=(l/a)-1$. Thus $C=\infty$ corresponds to long thin grains and $C=0$ to spherical grains. The theoretical curve of Fig. 6 is based on $C=\infty$, which is also equivalent to a uniform current distribution. Lower values of $C$ displace the curve shown down and to the right.

A comparison of the data reported here and the theoretical curve is given in Fig. 6. Note that the theory gives the same result for all superconductors, and implies that there is no threshold current to be exceeded before the effect is observed. The experiments seem to support the contention that the effect is the same in all superconductors; however, the data indicate that a threshold probably exists.

A comparison of the deflection obtained when the field is changed from one value to another and the expected deflection indicates that the flux change occurs just as expected. This is true for all the samples tested, if the crystals were pure and homogeneous.[8] The relaxation time for the currents responsible for the extra flux is estimated to be less than 0.1 second as a result of the experiments on good single crystals, and quite probably much less. We are presently investigating this point. Thus even when a *decrease* of the external field causes an *increase* in the flux in the sample, the currents causing the flux increase are set up quite rapidly.

[7] A. B. Pippard, Phil. Mag. 41, 243 (1950).

[8] For one imperfect indium sample, the time variation of the flux content after the field was changed indicated an exponential decay (or increase) of the form $\exp(t/40)$, $t$ in sec. The points were taken over several transition sequences and indicate that the long delay was reproducible. Another sample was grown and particular paints taken to insure its chemical and physical purity; it was also annealed after mounting. For that crystal the relaxation time was short as in the cases of the original tin and thallium crystals. Both indium samples gave the same results for the magnitude of the paramagnetism at a given current and field. The long relaxation time for the imperfect crystal is probably due to flux trapping by grain boundaries similar to that which occurs in frozen flux experiments.

It is certain that the long tail of the peak extends far beyond the critical field, so that there is extra flux in the sample after the sample has become normal conducting according to the Silsbee hypothesis. London[6] found a similar tail for the resistance approach to normal resistance when the transition is made with current alone in zero field. Theoretical description of the paramagnetic flux behavior beyond the peak is not available.

In conclusion one notes the similarity in behavior of the superconducting metals tested, and the agreement with Meissner's theory, at least beyond the threshold. These facts support the argument that the effect is a property of the intermediate state. The fast response time coupled with the reversible nature of the transition again emphasizes the dependence on current and field, not on method of measurement or history of the specimen.

### ACKNOWLEDGMENTS

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# Ordering and Antiferromagnetism in Ferrites

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The octahedral sites in the spinel structure form one of the anomalous lattices in which it is possible to achieve essentially perfect short-range order while maintaining a finite entropy. In such a lattice nearest-neighbor forces alone can never lead to long-range order, while calculations indicate that even the long-range Coulomb forces are only 5% effective in creating long-range order. This is shown to have many possible consequences both for antiferromagnetism in "normal" ferrites and for ordering in "inverse" ferrites.

## I. LATTICE OF OCTAHEDRAL SITES

THE ferrites are a class of oxides of iron-group metals, many of them of technical importance as ferromagnets, which crystallize in the spinel structure or structures closely related to it. The ideal ferrite has the formula $AB_2O_4$ (e.g., $NiFe_2O_4$) and the smaller metal ions $A$ and $B$ occupy certain interstices between the large oxygen ions, which latter are arranged in an approximation to the cubic close-packed structure.

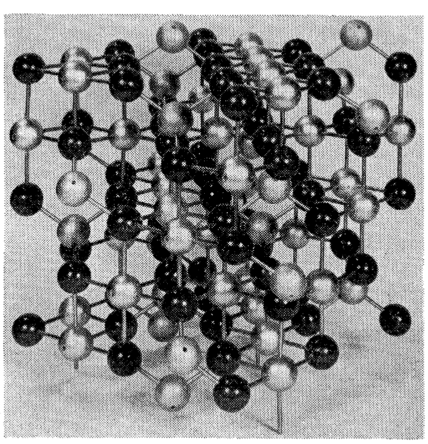

FIG. 1. Photograph of a model of the spinel lattice. The dark balls are oxygen; the tetrahedral sites are connected to their neighboring oxygens by four diagonal bonds, the octahedral by six vertical and horizontal ones.

The structure is shown in Fig. 1.[1] The distortion of the lattice of oxygen ions is such that a cell of 32 oxygens has cubic symmetry again. There are, for each oxygen, one interstice surrounded by an octahedron of oxygen and two surrounded by a tetrahedron; half of the former and only one-eighth of the latter are occupied by metal ions. This means that in the unit cell there are 8 "tetrahedral sites" and 16 "octahedral sites."

In a "normal" spinel, the 8 $A$ ions occupy the 8 tetrahedral sites, the 16 $B$ ions the octahedral ones. In an "inverse" spinel, 8 of the $B$ ions occupy the tetrahedral sites, the other 8 and the 8 $A$'s occupying the octahedral sites. Ferrites are known which range all the way from purely normal to purely inverse. We are here interested in two problems, both having to do with ordering on the octahedral sites: (a) the problem of atomic ordering in inverse ferrites; (b) in normal ferrites with small or no magnetic moments on the $A$ ions, the problem of antiferromagnetic ordering of spins.

To attack these problems we need to study carefully only the crystal lattice of the magnetic ions, particularly that of the octahedral sites. The occupied tetrahedral sites form a diamond-type lattice, the octahedral sites (see Fig. 2) a somewhat more complex cubic lattice which could be generated from this tetrahedral site lattice by displacing it through half the cube edge and then placing an atom at the center of each bond,

[1] T. F. W. Barth and E. Posnjak, Z. Krist. 82, 325 (1932).