Differential Paramagnetic Effect in Superconductors

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The magnetic moment and the differential magnetic susceptibility of two spherical samples of tin and tantalum have been measured as a function of magnetic field and temperature. The differential paramagnetic effect (DPE) is observed in both ac and dc mutual inductance measurements provided the sample exhibits a good Meissner effect. For a superconducting sample in which the infinite conductivity behavior dominates the Meissner effect, the DPE does not appear in the ac measurements but does, under certain conditions, show up in dc measurements. The results of the dc mutual inductance measurements are used to classify the DPE as reproducible or nonreproducible. The former is characteristic of ideal Meissner-type superconductors while the latter is more characteristic of superconductors whose macroscopic magnetic properties are dominated by the classical infinite electrical conductivity behavior. The superconducting-to-normal transitions obtained by the three techniques are compared and the data discussed in view of (a) occurrence of the DPE; (b) magnitude of the DPE; (c) ability of these data to give information about the volume participation of the sample; and (d) relation of the "characteristic magnetic fields" determined by these transitions and the bulk critical field of the sample.

INTRODUCTION

DIRECT current mutual inductance techniques[1] have been widely employed to study the magnetic properties of superconductors at temperatures below 1°K. Daunt and Heer[2] used such a method to determine the critical magnetic fields of Al and Zn. Chips of Al or Zn were imbedded in the paramagnetic salt "pill" used to cool the specimens to temperatures below 1°K. Critical magnetic fields were determined by observing the differential magnetic susceptibility of the composite sample, i.e., metal chips plus salt, as it warmed in the presence of an externally produced magnetic field. The differential susceptibility is defined here as $(\Delta M/\Delta H)_{H_a}$. ΔM is the change in magnetic moment accompanying the application or removal of a small incremental magnetic field ΔH. ΔH is longitudinal to the larger applied magnetic field H_a, which is maintained constant. These particular warmups displayed a new feature. They indicated that the metal samples, when in an applied magnetic field less than critical, exhibited, over a finite range of temperature, an "excessive paramagnetism." Daunt and Heer attributed this region of "excessive paramagnetism" to the presence of multiply-connected superconducting regions. Steele[3] pointed out that this effect should also occur for singly-connected superconductors as it is due to the fact that in the intermediate state $\Delta M/\Delta H$ is positive.[4] We refer to this phenomenon of "excessive paramagnetism" as the differential paramagnetic effect and denote it as the DPE. For this effect to be observed, the external magnetic field must have a measurable component longitudinal to the axis of the secondary coils.[5]

For the purpose of establishing that a given material is a superconductor, the results of magnetic measurements are felt to be more trustworthy that are those of direct electrical resistance measurements.[6] This feeling has led to the relatively wide use of ac and dc mutual inductance methods to study the magnetic properties of superconductors. The belief that the observed diamagnetism is a property of the sample as a whole, and is not the result of some superconducting impurity, is often conveyed through statements to the effect that 100% superconductivity was observed or that the entire volume was superconducting. These statements, when based only on the observation of the correct magnitude for the diamagnetic susceptibility, are open to serious criticism. Such an observation is only a necessary and not a sufficient observation from which to conclude that the entire volume of the sample was superconducting. Hudson[7] has shown that small amounts of superconducting impurities can lead to a large apparent volume participation in dc mutual inductance measurements. Therefore, the question arises: Can ac or dc mutual inductance measurements reveal information about the actual volume of the sample which is superconducting? Steele's explanation of the DPE indicates that this effect may be of use in answering this question.

There is, however, a rather disturbing inconsistency between theory and experiment as far as the DPE is concerned; namely, the failure of dc mutual inductance measurements to exhibit a DPE in hard superconductors like Ti,[8,9] Zr,[9] and U.[10] The failure to observe this effect in Ti was attributed to the nonideal superconducting properties of the specimen.[8] This explanation is incomplete as all superconductors, ideal or otherwise, exhibit magnetization curves which possess a positive $\Delta M/\Delta H$ over some range of magnetic fields. This should manifest itself as a DPE in any superconducting-to-normal transition which takes place in the presence of a

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[2] J. G. Daunt and C. V. Heer, Phys. Rev. **76**, 1324 (1949).
[3] M. C. Steele, Phys. Rev. **87**, 1137 (1952).
[4] D. Shoenberg, Proc. Cambridge Phil. Soc. **33**, 559 (1937).
[5] H. B. G. Casimir, *Magnetism and Very Low Temperatures* (Cambridge University Press, Cambridge, England, 1940), pp. 20–21.
[6] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, England, 1952), p. 55.
[7] R. P. Hudson, Phys. Rev. **79**, 883 (1950).
[8] M. C. Steele and R. A. Hein, Phys. Rev. **92**, 243 (1953).
[9] T. S. Smith and J. G. Daunt, Phys. Rev. **88**, 1172 (1952).
[10] R. A. Hein, W. E. Henry, and N. M. Wolcott, Phys. Rev. **107**, 1517 (1957).

properly oriented applied magnetic field. Since this was not the case with the above mentioned superconductors, what is the relationship between such dc inductance data and the slope of the magnetization curve?

The experiments quoted so far have all been performed below 1°K with samples which were not of simple geometry and therefore a quantitative analysis of the DPE observed for (Al, Zn),[2] Th,[11] and Cd [8] is difficult. The present work was undertaken to put the basic ideas of the DPE to a quantitative check as well as to study the effect in nonideal superconductors. Ac and dc mutual inductance measurements, as well as magnetic moment measurements, were performed as a function of magnetic field and temperature, on spherical specimens of Sn and Ta.

EXPERIMENTAL DETAILS

The dc mutual inductance method employed here is of the standard type.[1,12] The coil system consisted of two equal turn coaxial secondaries (1.3 cm long) placed in series opposition. The secondaries were spaced a center-to-center distance of 4.5 cm, and were equally spaced from the ends of a thin coaxial primary winding 9.2 cm long and 3.4 cm in diam. The sample to be investigated was placed in the center of one of the secondaries.

For all these measurements the applied field, H_a, was supplied by a nitrogen cooled solenoid, 51 cm long, with an i.d. of 6.0 cm and an o.d. of 19 cm. The field, H_a, was constant within 0.2% over the distance through which the sample was displaced in the magnetic moment measurements.

Magnetic moment measurements were made by observing the deflection of the galvanometer produced when the specimen was displaced from the center of one secondary coil to the center of the other. The galvanometer and a decade resistance box were connected in series with the secondaries. The series resistance was necessary to keep the deflections on scale.

Direct current mutual inductance measurements were made by observing the deflection of a galvanometer, connected in series with the secondaries, when a current was initiated or interrupted in the primary winding. The magnetic field of the primary winding is referred to as the incremental field, ΔH, and was equal to 1.8 gauss. In these measurements data were obtained with two different galvanometers. One was a 6.6-sec period galvanometer; the other was a 20-sec period galvanometer. When the sample was in the superconducting state, the deflections were adjusted to a convenient value by means of an external variable mutual inductance. Therefore, the change in the observed deflections, with either external magnetic field or temperature, is proportional to the change in the differential magnetic susceptibility of the specimen; i.e., the galvanometer deflection plus a constant is proportional to the susceptibility. This assumes that the change in the magnetic moment occurs in a time which is short compared to the period of the galvanometer.

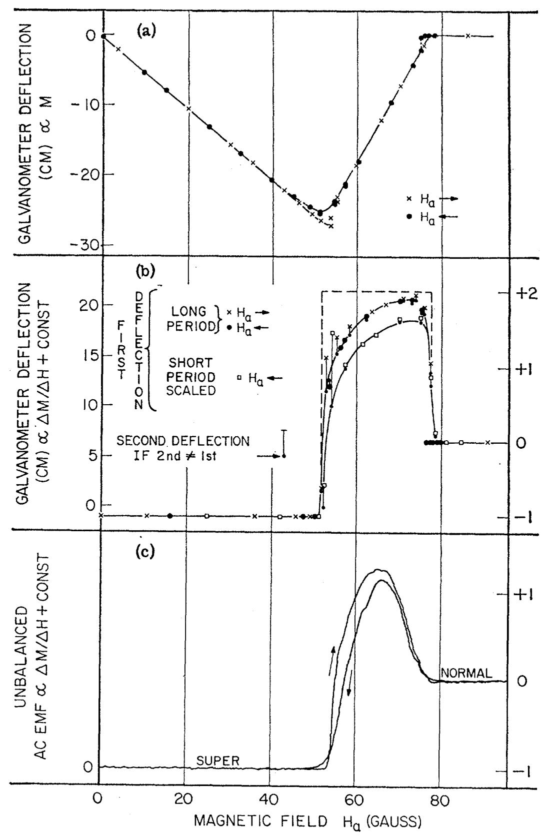

FIG. 1. Magnetic field dependence of (a) the magnetic moment, (b) the dc susceptibility, and (c) the ac susceptibility of the tin sphere at 3.17°K.

In the course of this paper we will have occasion to refer to first and second deflections as well as the "off" deflection. This terminology was arrived at in the following manner. After adjusting H_a to a constant value, current is initiated through the primary, and the resulting deflection is referred to as the first deflection. When the galvanometer returns to rest, the current is interrupted and the deflection observed is referred to as the "off" deflection. The primary field is again turned on, in the same direction, and the resulting deflection is referred to as the second deflection. This terminology is applicable for ΔH parallel or antiparallel to H_a. After a series of such measurements, H_a is changed to a new and larger value and the sequence is repeated.

Alternating current susceptibility measurements were performed by incorporating the mutual inductance coil system, described above, into a Hartshorn-type bridge.[12] The bridge was balanced with the metal in the superconducting state. The unbalanced emf of the bridge as a function of magnetic field was observed at various

[11] N. M. Wolcott and R. A. Hein, Phil. Mag. 3, 591 (1958).
[12] D. de Klerk, *Encyclopedia of Physics* (Springer-Verlag, Berlin, Germany, 1956), pp. 71–76.

fixed temperatures. This signal was filtered, amplified, rectified, and displayed on one axis of an X-Y recorder. The longitudinal magnetic field (H_a) was continuously and smoothly varied. That is, the time rate of change in H_a was approximately constant in any given field sweep. This was accomplished by means of a motor which drove the control of a variable voltage power supply. The value of the magnetic field was displayed on the other axis of the recorder. In this manner a continuous record of the unbalance as a function of magnetic field was obtained. Alternating current mutual inductance data were also obtained by interrupting the sweep of the field H_a and recording the steady-state unbalanced emf. We refer to this method as the point-by-point method. The amplitude of the ac signal was, unless otherwise stated, about 1.8 gauss (3.6 gauss peak to peak). The frequency used in obtaining all data presented here was 30 cps.

The specimens used in this work were machined spheres, both of nominal 1.3-cm diam. The tin sphere was annealed for two days in an oil bath at 200°C. The tantalum was not annealed, as we wanted this sample to display the characteristics of a "hard" superconductor.

RESULTS

Moment Measurements

The results obtained with the tin sphere at a temperature of 3.17°K are shown in Fig. 1(a). Galvanometer deflections, observed with a series resistance of 2000 ohms, have been plotted as a function of the external magnetic field H_a. Results obtained with the tantalum sphere, at a temperature of 4.2° and 2.93°K, are shown in Figs. 2(a) and 3(a), respectively. In order to keep the galvanometer deflections on scale, for the larger moment values, it was necessary to increase the value of the series resistance. Therefore, the ordinates in Figs. 2(a) and 3(a) are the observed deflections normalized to a series resistance of 2000 ohms. Data are shown for both increasing and decreasing values of H_a.

Direct Current Susceptibility

The data obtained for tin at 3.17°K is presented in Fig. 1(b) while that for tantalum at 4.2° and 2.93°K is presented in Figs. 2(b) and 3(b), respectively. Figure 1(b) contains data obtained with a 6.6-sec period and a 20-sec period galvanometer. The left-hand ordinate yields the actual deflections observed with the longer period galvanometer. The shorter period galvanometer deflections have been scaled in such a manner that the superconducting and normal deflections of both galvanometers coincide. The right-hand ordinate in Figs. 1(b), 2(b), and 3(b) has been obtained by setting the normal state deflection equal to zero and setting the superconducting deflections equal to minus unity. We have plotted the first and second deflections (see experimental details) obtained by the application of the incremental field ΔH parallel to the external field H_a. These data are for increasing values of H_a.

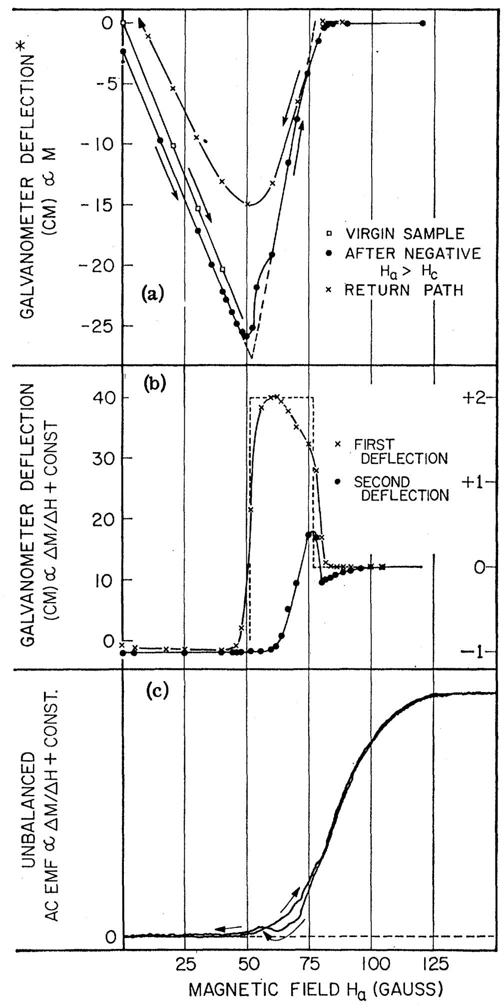

FIG. 2. Magnetic field dependence of (a) the magnetic moment (b) the dc susceptibility, and (c) the ac susceptibility of the tantalum sphere at 4.2°K. The deflections obtained in the moment measurements are corrected to a series resistance of 2000 ohms.

Alternating Current Susceptibility

The data obtained with tin at 3.17°K are presented in Fig. 1(c), while Figs. 2(c) and 3(c) show the data obtained with tantalum at 4.2° and 2.93°K, respectively. This data consists of a recorder trace of the unbalanced voltage across the bridge as a function of H_a. The external field H_a was increased to its maximum value and then decreased to zero in a relatively slow and continuous manner. Figure 3(c) also includes the results obtained when H_a was increased and decreased in a step-wise manner, the unbalanced voltage being measured at various fixed values of H_a. Figure 4 shows the results obtained for tantalum at various fixed temperatures between 4.2° and 1.57°K.

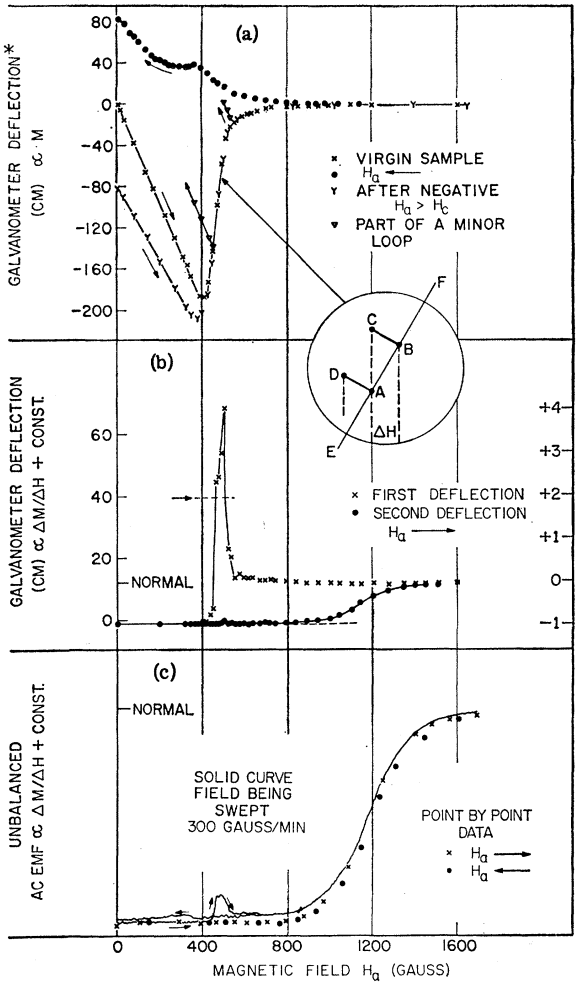

FIG. 3. Magnetic field dependence of (a) the magnetic moment (b) the dc susceptibility, and (c) the ac susceptibility of the tantalum sphere at 2.93°K. The deflections obtained in the moment measurements are corrected to a series resistance of 2000 ohms.

DISCUSSION OF RESULTS

Occurrence of DPE

Direct Current Susceptibility

We refer to the DPE as reproducible when the first and second deflections are equal in magnitude and both deflections indicate that $\Delta M/\Delta H$ is large and positive. We take the over-all behavior observed for tin, Fig. 1(b), as a practical example of a reproducible DPE. Ta, on the other hand, exhibited a nonreproducible DPE, Figs. 2(b) and 3(b). The deviations from reproducibility observed for tin in the early stages of the intermediate state are discussed later.

The relative behavior of the first and second deflections is determined by the degree to which the magnetization curve is reversible. To show this, the results of a series of measurements are discussed with the aid of the insert in Fig. 3. The line EF represents a segment of the magnetization curve. When the externally applied magnetic field H_a was increased to, and held constant at, a value corresponding to point A on the magnetization curve, the observed deflections are interpreted as follows: With the tin specimen the first application of the measuring field ΔH parallel to H_a produced a deflection which indicated $\Delta M/\Delta H$ was positive. Therefore the moment changed along a path with termini A and B. From measurements such as these we can only deduce the termini of the path and not the actual path itself. However, for the sake of brevity we shall speak of the path AB. When ΔH was removed the resultant deflection, referred to as the "off" deflection, not included in the graphs, indicated that path AB was retraced. The second and all subsequent applications of ΔH indicated that the moment always changed along the path AB. The application of ΔH antiparallel to H_a produced equal, but opposite, deflections as did ΔH parallel. This type of behavior, observed with tin, gives rise to the reproducible DPE.

With Ta, Fig. 3, the situation is quite different. Here, the first application of ΔH parallel to H_a indicated that $\Delta M/\Delta H$ was positive and therefore the moment changed along the path AB. When ΔH was removed the resulting deflection indicated that $\Delta M/\Delta H$ was negative and equal to the superconducting value. This means the moment changed along a path similar to BC with an effective slope equal to that of the superconducting state. For the same value of H_a a second application of ΔH parallel to H_a produced a deflection, second deflections in the graphs, which also indicated the superconducting value for $\Delta M/\Delta H$. Path CB must have been retraced. If ΔH were initially applied anti-parallel to H_a, the deflections not included in the graphs indicated that $\Delta M/\Delta H$ was negative and equal to the superconducting value. Paths like AD must have been taken on both the first and second deflections. Upon increasing

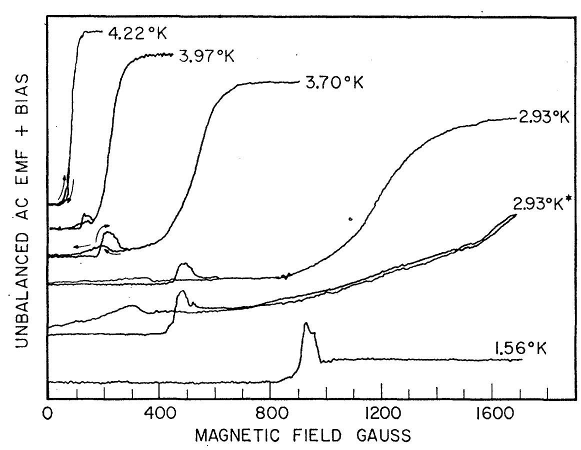

FIG. 4. Magnetic field dependence of the ac susceptibility of tantalum for several different temperatures. For curves marked with an asterisk, the data were obtained with an ac primary field equal to $\frac{1}{10}$ of that normally employed.

H_a to a new value greater than $H_a+\Delta H$, similar behavior was noted.

The Ta data obtained at 4.2°K, Fig. 2, show a DPE for both first and second deflections. This is not considered a reproducible DPE as the second deflections were consistently smaller than the first. Also, the range of H_a for which the effect shows up in the second deflections is smaller than the corresponding range for the first deflections. With the exception of the virgin data, the magnetization curves in Figs. 2(a) and 3(a), obtained after subjecting the sample to magnetic fields greater than the critical magnetic field H_c, are referred to as the major magnetization curves. Realizable paths such as BC and AD, in the insert of Fig. 3, are denoted as minor hysteresis paths. Therefore in order for the nonreproducible DPE to show up in the second deflections two requirements must be met. First, the major magnetization curve, for decreasing values of H_a, must possess a region of positive slope. Second, this region of positive slope must lie within ΔH of the major magnetization curve obtained for increasing values of H_a. If these two conditions are met, then the minor hysteresis path can intersect the major magnetization curve in such a manner that the resulting $\Delta M/\Delta H$ is positive. Figures 2(a) and 2(b) indicate that these conditions are met with Ta at 4.2°K for H_a in the vicinity of 75 gauss and with ΔH equal to 1.8 gauss. The fact that the second deflections are slightly diamagnetic for $H_a > 80$ gauss is due to hysteresis in the magnetization curves observed near H_c. This is not evident in Fig. 2(a) because of its reduced scale.

Figure 3(b) indicates that there is a range of H_a for which the first deflections indicate normal values for $\Delta M/\Delta H$, while the second deflections indicate the superconducting values. This means that although the specimen is behaving as a normal metal for increasing magnetic flux, it can still trap in all the flux due to ΔH when ΔH is removed. Therefore, when ΔH is removed the minor hysteresis path must still depart from the major magnetization curve with a slope equal to that for the superconducting state. The second deflections depart from the superconducting value at that value of H_a for which the minor hysteresis path starts to intersect or is influenced by the nearness of the return major magnetization curve. Comparison of Figs. 3(a) and 3(b) shows this to occur at approximately 900 gauss for Ta at 2.93°K.

These considerations can be applied to the work below 1°K mentioned above. Direct current mutual inductance data in this temperature region are usually obtained in the following manner: The specimen is cooled to as low a temperature (T) as is feasible and then the external field H_a is applied. Measurements of $(\Delta M/\Delta H)_{H_a}$ are made as the system warms up due to the natural heat leak into it. For those superconductors which possess a reversible magnetization curve (ideal Meissner-type superconductors) the DPE is always observed. For specimens which do not display a reversible magnetization curve, the DPE may or may not be observed. If ΔH is applied antiparallel to H_a, the DPE is not observed in the warmup curves. If, however, ΔH is applied parallel to H_a, and H_a and T are such to place the specimen in the "intermediate state" the first application of ΔH produces a positive $\Delta M/\Delta H$. The "off" deflection, however, indicates the superconducting value for $\Delta M/\Delta H$. This measurement leaves the specimen with a magnetic moment less than that corresponding to the major magnetization curve appropriate for the values of H_a and T, see Fig. 3.

The behavior of subsequent deflections depends upon the increase of the temperature (ΔT) which occurs between successive measurements. An increase in T has the effect of displacing the major magnetization curve to lower absolute values of the moment. Therefore if ΔT is sufficient to displace the major magnetization curve so as to anneal out the effects of the previous measurement, $\Delta M/\Delta H$ again is positive. However, if the increase in T is quite small so that the saturation magnetization curve is only slightly shifted, with respect to ΔH, subsequent measurements correspond closely to the second deflections of isothermal measurements. This behavior should persist throughout the superconducting-to-normal transition. To sum up, the absence of a DPE in the warmup curves obtained for Ti,[8,9] U,[10] and Zr,[9] is the result of (1) a poor Meissner effect, and (2) either the incremental field is directed oppositely to the applied field H_a, or if ΔH is parallel to H_a, the temperature increase between successive measurements is too small to produce a positive $\Delta M/\Delta H$.

Alternating Current Susceptibility

In general, one would expect ac data to be related to the second deflections of the dc data as both have to do with the reversibility of the magnetization curve. Therefore, if a sample shows a reproducible DPE, the effect should show up in ac measurements as well. This is the case with tin, Fig. 1.

Let us now consider the behavior of a hard superconductor. Since the bridge was balanced when the sample was in the superconducting state, no unbalanced emf is induced as long as the specimen allows no flux to penetrate. If H_a is increased to some constant value such that the sample is in the intermediate state (point A in the insert of Fig. 3) and then the ac primary field is turned on, the following behavior should occur: The first time the primary field increases in a direction parallel to H_a the accompanying magnetic flux penetrates the sample (path AB). When the primary field decreases and then increases in the opposite sense, no change in flux through the sample occurs. All further oscillations of the primary ac field leave the flux through the sample unchanged.

Since the emf induced in the secondary coils by the initial increase in flux, in most cases, passes unnoticed, the data indicates superconducting behavior; i.e., no unbalanced emf. This condition persists until H_a reaches the value at which the sample can no longer trap in all the flux change due to ΔH. Hence the ac transition commences at this value of H_a. We call this field the ac penetration field $(H_p)_{ac}$. A qualitative similarity between the ac transition and the behavior of the second deflections is evident in Fig. 3. However, the ac data at 4.2°K, Fig. 2(c), do not show the DPE observed in the second deflections of the dc data, Fig. 2(b).

However, if H_a is not held constant at the various values, but rather is increased in a steady and continuous manner, the situation is somewhat different. In the time required for the primary ac field to go through one cycle (1/30 sec) the field H_a has increased somewhat. Therefore, each time the primary field increases in the parallel direction, a small amount of additional flux penetrates into the specimen where it is held. Thus the unbalanced emf will consist of small unidirectional pulses of 30 cps. The 30-cps component of this passes through the filter and is recorded. Over the range of H_a, where the moment curve exhibits a large positive slope, these pulses give rise to the "bump" or transient unbalance on the emf trace. This is tantamount to saying that the signal is partially composed of first deflections. The tail region of the moment curve [H_a greater than 600 gauss in Fig. 3(a)] in this manner produces a small and virtually constant unbalanced emf until the field $(H_p)_{ac}$ is reached. This then explains the difference between the point-by-point ac measurements and the continuous or dynamic ac measurements.

The appearance of the transient reveals features about the magnetization curve that the point-by-point ac measurements do not. The transient indicates the range of field, tentatively identified as the intermediate state, over which the moment is undergoing a rapid decrease. The magnitude of the transient is a function of how fast the external field H_a is swept with respect to the frequency and amplitude of the primary ac field.

Alternating current mutual inductance measurements have been employed to determine critical magnetic fields below 1°K.[13,14] In these investigations the entire superconducting-to-normal transition in the presence of a magnetic field was not observed. Therefore, one cannot say anything about the DPE. In these particular investigations, critical magnetic fields were deduced from observations of the ac penetration fields.

Magnitude and Shape of the DPE

Direct Current Susceptibility

For vanishingly small measuring fields, ΔH, an ideally behaved spherical sample, would produce a DPE of twice the magnitude of the observed diamagnetism. Such behavior is depicted by the dashed curve in Figs. 1(b) and 2(b). With ΔH finite, but small compared to nH_c where n is the demagnetization factor of the specimen and H_c its critical magnetic field, the sharp rise at $(1-n)H_c$ and subsequent decrease at H_c should be spread over a range of H_a equal to ΔH. If, however, ΔH is larger than nH_c, the deflections will always be smaller than the ideal maximum. This follows because the application of ΔH, when $(1-n)H_c=H_a$, will carry the specimen completely through the intermediate state. Hence $\Delta M/\Delta H$ will always be less than the slope of the intermediate state magnetization curve. In this case the magnitude of the DPE should be temperature dependent. It should increase with decrease in temperature due to the temperature dependence of the ratio $\Delta H/nH_c$. In the present work this ratio was always less than 1/14 and no temperature dependence of the reproducible DPE was observed. Ideal behavior also manifests itself in that the area under the $\Delta M/\Delta H$ curve, referred to the right-hand coordinate scale, is zero.

The DPE exhibited by the tin specimen fell considerably short of ideal behavior since the area under the curve, Fig. 1(b), is considerably less than ideal, the net area being negative. Also for values of H_a, which just place the specimen in the intermediate state, the first and second deflections were not reproducible. Although the main purpose of this paper is to emphasize the utility and importance of the DPE in superconductivity studies, we want to comment briefly upon the lack of ideality in the DPE observed for the tin specimen.

Extrapolations of the linear portions of the magnetization curve, Fig. 1(a), produce values for H_c and $(1-n)H_c$ consistent with the spherical shape of the specimen where $n=\frac{1}{3}$. However, moment measurements, obtained with increasing H_a, indicate that the superconducting state persists above $\frac{2}{3}H_c$. We believe this is a time effect and not superheating. The first measurements at 54 gauss, Fig. 1(a), 30 sec after adjusting H_a, yielded a value for the moment which was 10% higher than the value indicated by the linear extrapolation of the intermediate state portion. A second measurement, two minutes later, yielded a value only 5% too high. This behavior is depicted in Fig. 1(a) by data points with the same value for the abscissa. Shoenberg[15] observed similar time effects and estimated that the equilibrium times were of the order of 5 sec. Our measurements indicate considerably longer equilibrium times.

Time effects were also evident in the dc susceptibility measurements, Fig. 1(b). They first appeared when H_a was approximately equal to $\frac{2}{3}H_c$ and manifested themselves in the following manner. The application of ΔH, parallel to H_a, produced a deflection which was less diamagnetic than the superconducting value, or actually paramagnetic if in the DPE region. The subsequent return swing of the galvanometer to its zero position required a time considerably longer than that required when the specimen was in either the superconducting or

[13] B. B. Goodman and E. Mendoza, Phil. Mag. **42**, 594 (1951).
[14] J. K. Hulm and B. B. Goodman, Phys. Rev. **106**, 659 (1957).
[15] D. Shoenberg, Proc. Roy. Soc. (London) **A155**, 712 (1936).

the normal state. The time required by the galvanometer to return to its approximate zero was greatest at $\frac{2}{3}H_c$ and decreased as H_a was increased. For H_a greater than $\frac{3}{4}H_c$ the return swing appeared to behave in the ordinary manner. Behavior such as this, taken in conjunction with the fact that the deflections were less than ideal, leads to the following picture. Upon the application of the measuring field ΔH, magnetic flux starts to penetrate the specimen. The rate of penetration, which is initially large, decreases to zero as the magnetic moment of the specimen approaches its equilibrium value appropriate for the field $H_a+\Delta H$. The sluggish return swing of the galvanometer indicates that the emf pulse induced in the secondary coils due to this flux penetration is of long duration with respect to the period of the galvanometer. Faber[16] has pointed out that eddy currents could be especially effective in retarding phase propagation in the intermediate state. This results from the presence of superconducting domains which provide the eddy-currents paths of low resistance.

The behavior of the return swing of the galvanometer suggests that for H_a greater than $\frac{3}{4}H_c$ the time of duration of the emf pulse is of such a length that the return swing is not discernibly affected. However, the nonideal magnitude of the deflections for H_a greater than $\frac{3}{4}H_c$ implies that the pulse is still too long for the galvanometer to integrate it properly.

Ta at 4.2°K, Fig. 2(b), while failing to show a reproducible DPE, yields first deflections that are more nearly ideal than are those of the tin specimen. This statement is based upon the observation that the area under the first deflection curve, referred to the right-hand ordinate scale, is zero. Time effects were not noted in the return swing of the galvanometer and it is apparent that the $\Delta M/\Delta H$ measurements, which result in the first deflections, are good approximations to the slope of the magnetization curve, Fig. 2(a).

This agreement is perhaps fortuitous in that the slope of the "intermediate state" magnetization curve, which results from the type of moment measurements employed here, can be quite nebulous. That is, the moment of the tantalum sample was observed to be quite sensitive to mechanical "jarring."[17] Jarring of the sample was accomplished by causing the sample to strike the stops, provided in the coil system, with some authority. In the vicinity of the maximum moment, jarring (for increasing values of H_a) produced a 25% decrease in the magnitude of the moment. Moment measurements were initiated approximately 20 sec after adjusting the field H_a. In Figs. 2(a) and 3(a) we have plotted the results of the first displacement, for a given H_a. The results of these first displacements are felt to be more suitable for comparison with susceptibility data [Figs. 2(b), 2(c), 3(b), and 3(c)] than are the results of the subsequent displacements. With susceptibility measurements, the magnitude of the galvanometer deflections is governed by the rapid change in the magnetic moment accompanying the application of ΔH. Hence, it is felt that the susceptibility data should correlate best with the slope of the magnetization curve which results from the unjarred, first displacement values of the moment.

Lower temperature data, Fig. 3(b), show that the first "on" deflections attained a maximum value twice that expected for a spherically shaped specimen. These data are in accord with the magnetization curve, Fig. 3(a). Here we see that the slope of the linear portion of the intermediate state curve is approximately twice the superconducting slope. The area under the first deflection curve, in Fig. 3(b), is not zero. Curiously, the diamagnetic (negative) area is very nearly twice the paramagnetic (positive) area.

The slope of the superconducting portion of the virgin magnetization curve, Figs. 2(a) and 3(a), is temperature independent and is consistent with the spherical shape of the specimen. The intermediate state slope, in general, was steeper than that of an ideally behaved superconducting sphere and was observed to increase with decreasing temperature (fourfold between 4.2° and 1.56°K). Such behavior of the intermediate state slope is not characteristic of a Meissner-type superconductor.

Alternating Current Susceptibility

This subject has been dealt with in considerable detail by Shoenberg.[4] He investigated the ac susceptibility of both lead and tin spheres by means of a self inductance technique. The results are discussed in terms of a complex permeability. Both the imaginary and real parts were found to pass through a maximum as the external magnetic field was increased from zero. The point we wish to discuss here is the effect of the ac field amplitude on the magnitude of the maxima. Shoenberg noted that as the amplitude of the ac field was reduced (normally he used a 0.7-gauss ac field) the maximum became less and less pronounced. He concluded that this was not the result of his measuring technique but rather a property of the intermediate state. To explain this effect he invoked the idea that the electrical conductivity of the sample increased with decrease in ac amplitude.

The interpretation which we have placed on our measurements indicates that such an effect should be observed for all but the truly "ideal" superconductors. The amplitude effect we envision is merely due to the relative size of the ac measuring field $(\Delta H)_{ac}$ compared to the width of the hysteresis loop. For the sake of discussion let us set the width of this loop at 0.2 gauss. For a $(\Delta H)_{ac}$ of, say, 1.0 gauss, a DPE should be observed, the magnitude of which is, of course, less than ideal. That this is so can be seen by taking the specimen through such a path in the insert of Fig. 3. Now as the size of $(\Delta H)_{ac}$ is reduced, a larger percentage of the over-all path is confined within the hysteresis loop, hence the magnitude of the DPE decreases. When the

[16] T. E. Faber, Proc. Roy. Soc. (London) **A219**, 75 (1953).
[17] W. F. Love, E. Callen, and F. C. Nix, Phys. Rev. **87**, 844 (1952).

entire path is confined within the loop, $(\Delta H)_{ac}\sim 0.1$ gauss in our case, no DPE is observed. All this merely emphasizes the fact that if ac measurements confine the region of observation to within the hysteresis loop, the sample must exhibit features characteristic of "hard" superconductors.

100 Percent Superconductivity and Critical Magnetic Fields

Direct Current Susceptibility

The appearance of a reproducible DPE allows one to state safely that the specimen is showing a good Meissner effect. Therefore, in order to establish that the observed diamagnetism is due to superconductivity of the specimen as a whole, it is necessary to (1) observe the correct volume diamagnetic susceptibility—this establishes the perfect shielding property of the sample; and (2) observe a reproducible DPE—this establishes the inability of the sample to trap magnetic flux. If (1) and (2) are satisfied, the diamagnetism cannot be due to a network of superconducting filaments. These two facts taken together allow one to say safely that the observed diamagnetism is truly a property of the bulk of the specimen.

When the reproducible DPE is not observed, what is the significance of the "characteristic fields" as determined by mutual inductance measurements? The critical magnetic fields and temperatures reported in the literature for Ti,[8] U,[9] Zr,[10] Ru,[18] and Os [18] are the completion values deduced from dc mutual inductance measurements. That is, they are the values of H_a and T at which $\Delta M/\Delta H$ first returns to the normal state value. As mentioned earlier, the absence of the DPE in these measurements indicates that the observed deflections correspond to the second deflections of the isothermal data and that the samples showed a poor Meissner effect. For specimens which do not show a good Meissner effect, the relationship between the field or temperature at which the second deflections return to the normal state value and the superconducting bulk properties is rather nebulous.

A poor or incomplete Meissner effect can be attributed to the existence of a network of superconducting filaments within the specimen.[19] In keeping with this filament concept, the dc critical magnetic fields reported for the above "hard" superconductors would correspond to the highest critical magnetic field of the filaments. We take the critical magnetic field of a filament to be that value of H_a above which the filament loses its property of zero electrical resistance.

The value of the external magnetic field H_a for which the moment attains its maximum negative value is closely related to that value of H_a at which the first deflections start to deviate from the full superconducting value. We call this field the dc penetration field and denote it as $(H_p)_m$. This field is characteristic of the breaking down of the perfect shielding property of the sample. That is, at this value of H_a the sample can no longer keep out all the magnetic flux due to H_a. Therefore, the field is either the highest magnetic field which the filaments can exactly compensate or it denotes the actual entry into the intermediate state of the bulk of the material.[20] In this latter case, $(H_p)_m=(1-n)H_c$. The behavior of the first and second deflections indicates that in tantalum $(H_p)_m$ is related more closely to the behavior of the filaments than to what might be called bulk properties.

Alternating Current Susceptibility

The penetration field deduced from point-by-point ac measurements is denoted as $(H_p)_{ac}$. As discussed earlier $(H_p)_{ac}$ is that value of the external field H_a at which the filaments first lose their ability to trap in all the increase in flux due to ΔH. This feature also determines the value of H_a at which the second deflections of the dc inductance measurements start to deviate from the superconducting value. This means that the minor hysteresis path due to ΔH no longer has an effective slope $\Delta M/\Delta H$ equal to that of the superconducting state. Hence, the minor hysteresis path due to ΔH either intersects the return major magnetization curve, or is influenced by its nearness. Therefore it follows that if smaller measuring fields are employed, both the penetration field and the completion field should occur at higher values of H_a. In Fig. 4 we have included data obtained at 2.93°K, for which the amplitude of the ac primary field was equal to $\frac{1}{10}$ of that normally employed. Normally a peak-to-peak ac primary field of 3.8 gauss was used. Although the entire transition could not be obtained due to the limitation of H_a, it is obvious that the completion field has been displaced to higher values of H_a. The effect of the smaller primary field on the magnitude of the penetration field is somewhat in doubt. It appears to have been shifted to a smaller value of H_a. This, however, could be the result of a net increase in sensitivity.

The dynamic ac measurements yield an additional penetration field. That is, the initial rise of the transient unbalance tells us the field value at which the specimen can no longer keep out all the flux due to $H_a+\Delta H$. This field should be the same as $(H_p)_m$ as deduced from dc susceptibility and moment measurements. Figures 2 and 3 support this point of view. The field sweep carried out with tantalum at 1.56°K, Fig. 4, shows that $(H_p)_{ac}$ exceeds $(H_p)_m$ by over a factor of 2. While this transition is not complete, we can say that $(H_p)_{ac}$ must be in excess of 1900 gauss.

[18] J. A. Carruthers and A. Connoly, *Low Temperature Physics and Chemistry* (University of Wisconsin Press, Madison, Wisconsin, 1958), pp. 276–279.

[19] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, England, 1952), p. 45.

[20] This statement applies only to the virgin magnetization data. It is evident, Fig. 3(a), that the slope of the major magnetization curve indicates the lack of "perfect" shielding when H_a is applied oppositely to the direction of the frozen-in field.

CONCLUSIONS

We use the results of the dc mutual inductance method to classify the DPE as reproducible or nonreproducible. The reproducible DPE (see the section dealing with the occurrence of the DPE) is characteristic of an ideal Meissner-type superconductor. As pointed out in the text, measurements of $(\Delta M/\Delta H)_{H_a}$ performed with slowly increasing temperatures do not show any DPE unless the sample exhibits a good Meissner effect. Therefore the attributing of the observed DPE in the warmup curves obtained for Al and Zn to the presence of multiply-connected superconducting regions[2] is not in keeping with the ideas expressed in the present paper. The nonreproducible DPE in which the second deflections always correspond to negative values of $\Delta M/\Delta H$ is displayed by superconductors in which the infinite conductivity behavior predominates over the Meissner effect. It is interesting to note that of the seven elemental superconductors with zero-field transition temperatures below 1°K, only Cd and Zn show a reproducible DPE.

In using either ac or dc mutual inductance methods to investigate the magnetic properties of superconductors it is preferable to have the external magnetic field H_a coaxial with the coil system. With this arrangement the reproducible DPE is always observed, provided the sample is exhibiting a good Meissner effect. The nonreproducible DPE does not show up in the point-by-point type ac measurements. It does, however, give rise to a transient unbalance in the dynamic ac method employed in the present work. Dc measurements always show the nonreproducible DPE, provided the measuring field is parallel to H_a. This follows because the magnetization curve, for increasing H_a, always possesses a region of positive slope.

The appearance of the nonreproducible DPE in dc measurements reveals details about the magnetization curve, and hence the characteristic fields, that the point-by-point ac method does not. However, the dynamic ac method employed in this work reveals all of the details that the dc measurements do, except in the region near the zero-field transition temperature.

The occurrence of a reproducible DPE is also of practical importance in critical magnetic field measurements. In the absence of the DPE, the superconducting-to-normal transition is characterized by a change in susceptibility from $-\frac{1}{4}\pi(1-n)$ in the superconducting state to essentially zero in the normal state. However, with the DPE the change in susceptibility at H_c is from $+\frac{1}{4}\pi n$ to zero. Therefore we see that the ratio of the change observed with the DPE to that observed without the DPE is given by $-(1-n)/n$ or $1-1/n$. From this it is seen that as n becomes small, the magnitude of this ratio becomes quite large. Therefore, one can look upon the DPE as a built-in amplifier, the gain of which is given by the above quoted ratio. Since this change in susceptibility occurs over a narrow range of magnetic field, it marks the entry into the normal state in a rather dramatic fashion. The signal enhancement due to the DPE allows the transition to be detected clearly even when the diamagnetism of the superconducting state is too small to be readily detectable. This was of great aid in the study of Th.[11]

Comparing the characteristic fields as deduced from the various methods employed here shows that the point-by-point ac method is the least favorable one. Furthermore, this data emphasizes that setting the ac penetration field $(H_p)_{ac}$ equal to $(1-n)H_c$ in order to deduce H_c may lead to erroneously large values of H_c.[13] This latter technique is justified only if one knows *a priori* that he is dealing with a superconductor whose magnetization curve is that of an ideal Meissner-type material, or if he observes at least one complete transition which exhibits a DPE.

Thermodynamic calculations based on ac or dc differential induction measurements, in which the reproducible DPE is not observed, are certainly questionable. The observation and reporting of the DPE is of importance for it yields information about the Meissner effect and hence the volume participation of the sample. In the absence of a reproducible DPE, the determination of the bulk critical magnetic field by ac or dc mutual inductance methods is somewhat nebulous. In fact, if the reproducible DPE is not observed, one cannot be certain that the bulk of the sample becomes superconducting.