# Irreversibility in the Superconducting Transition of Lead*

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The nature and origins of the hysteresis in the magnetic transition of pure superconducting lead have been studied in some detail. The effect can be introduced in nonhysteretic specimens by plastic deformation at liquid helium temperatures. The hysteresis becomes apparent somewhat below $T_c$ and its width increases monotonically with decreasing temperature. Similar effects can be caused by dilute additions of Ca to Pb. Strain induced hysteresis anneals out near 300°K but temperatures approaching the melting point appear necessary to remove impurity induced effects. Isothermal resistive measurements show a small fraction of the superconducting phase persisting to fields several hundred gauss above $H_c$. The residual superconductivity at high fields is increased by plastic deformation, and in general seems closely related to the hysteresis effect. The observations suggest the existence of a connected network which pervades the entire specimen volume and consists of very small filaments having a critical field exceeding the reversible critical field of bulk lead. The filaments are believed to be associated with defects in the crystalline lattice.

## I. INTRODUCTION

THE recent measurements of the critical field of lead isotopes by Decker *et al.*[1] were complicated by the occurrence of a distinctive hysteresis in the superconducting transition of lead and a preliminary account of this phenomenon was given. The present paper is a continuation of the study of the hysteresis and an attempt to relate this behavior to the frequently observed anomalous behavior in the resistive transition of lead.[2–4] Both ballistic induction (magnetic) and resistive measurements are reported. These are dealt with separately in the experimental and results sections and the close connection between them pointed out in the discussion. The principle means of varying the properties of the specimens has been through low-temperature plastic strain.

## II. EXPERIMENTAL

### A. Apparatus

*Ballistic Induction Measurements*

Precision solenoids provided the very homogeneous fields used in these measurements. The samples (usually the sample under observation and a "reference" sample) were placed in coils which could be connected, one at a time, in series opposition with an empty, but otherwise identical, coil. The signal, developed across the pair of coils when the field was changed by small steps, was measured by a ballistic galvanometer. Details of this technique have been discussed in earlier papers.[5,6]

In order to strain a sample while in its coil and at low temperature, the apparatus in Fig. 1(a) was built. It consists of two concentric thin-walled tubes of Cupronickel[7] which extended from the top of the cryostat into a central coil. Each end of the sample to be strained was connected to one of these tubes by means of a brass socket and Wood's metal solder.[8] Like many superconducting alloys, the magnetic transition of this $W$-58 solder is nearly complete at rather low fields, but it shows zero resistance to very high fields. This suited the present purposes admirably, since the distortion of magnetic field by the solder was small, but it provided a zero resistance path for the resistive measurements.

The sample stress and strain were measured at the top of the cryostat, stress by means of a calibrated spring and strain by the relative displacement of the two tubes. The annealing measurements were also made with this apparatus which could be raised most of the way out of the cryostat without breaking the vacuum seal. Thus, by proper positioning, any temperature between liquid helium and room temperatures could be reached and maintained quite readily to $\pm 0.5$°K. This temperature was read with a copper-constantan thermocouple silver soldered into the upper sample socket. The interpolation of the thermocouple calibration between 73°K and 4.2°K may be in error by 5°K.

All measurements were made at constant temperature maintained by controlling the pumping speed over the helium bath and the power input to a heater in the

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1 D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. **112**, 1888 (1958).
2 J. G. Daunt, Phil. Mag. **28**, 24 (1939).
3 D. K. C. MacDonald and K. Mendelssohn, Proc. Roy. Soc. (London) **A 200**, 66 (1949).
4 H. Preston-Thomas, Can. J. Phys. **30**, 626 (1952).
5 J. F. Cochran, D. E. Mapother, and R. E. Mould, Phys. Rev. **103**, 1657 (1956).
6 R. R. Hake and D. E. Mapother, J. Phys. Chem. Solids **1**, 199 (1956).
7 This Cupronickel tubing was found to be sufficiently nonmagnetic that it would not interfere with the ballistic measurements.
8 This solder [in percent, bismuth (49), lead (18), tin (12), indium (21), melting point (58°C)] is only one of many termed Wood's metal and so will be referred to as $W$-58 solder.

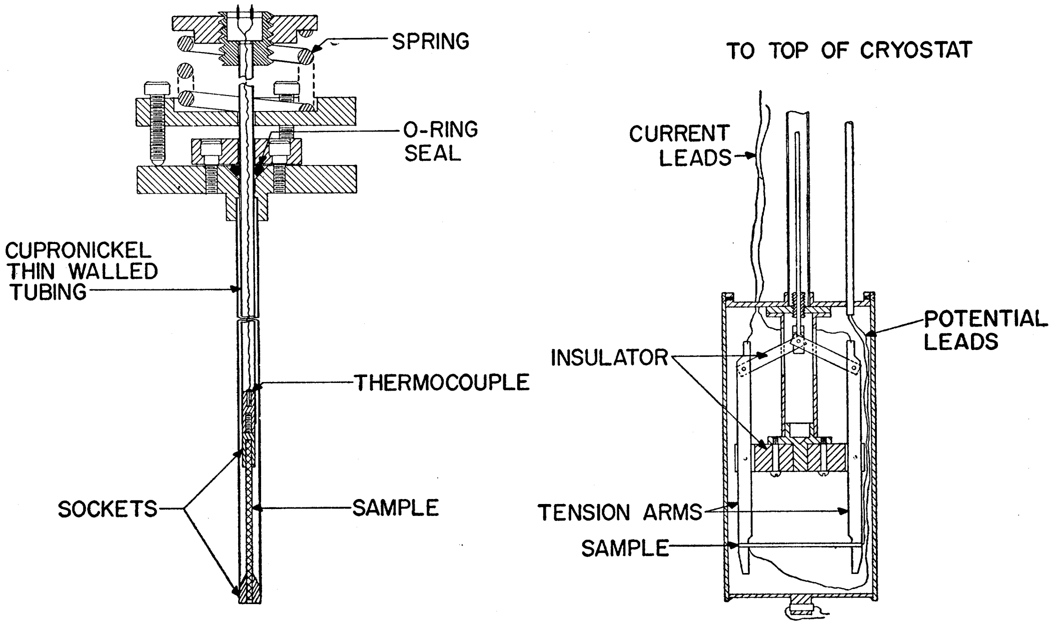


FIG. 1. Apparatus used to apply tension to samples while at low temperature for (a) ballistic induction measurements and (b) resistive measurements.

bath. A carbon resistor was used as secondary thermometer and heater control in a manner which has been outlined previously.[5] The resulting variation in temperature over the period of a measurement (20 minutes) was approximately $\pm 0.002°K$ in the present apparatus, resulting in an uncertainty in the critical field values of the order of 0.2 gauss.

*Resistive Measurements*

In each run on the resistive transition, two lead wire samples were measured: one a test sample which could be strained, the other a comparison sample. Both were suspended horizontally in the usual double dewar system, the whole being mounted in the gap of a Varian magnet. The magnet was mounted on a turntable allowing the field to be applied parallel or perpendicular to the specimen axes. The sample to be strained was mounted between two brass arms which served as current leads and also as tension arms through a scissors arrangement [see Fig. 1(b)]. The scissors communicated with the outside via a thin-walled tube by which the sample strain could be controlled and measured. No attempt was made to measure stress on the sample in this phase of the experiment.

The leads used to read the voltage developed across the sample were imbedded in the *W*-58 solder which attached the sample to the arms. The reference sample was also soldered to its current and voltage leads by means of this solder. The voltages were measured with a limit of resolution of approximately $10^{-8}$ volt.

## B. Specimens

*Ballistic Induction Measurements*

The specimens for the ballistic induction measurements were prepared from a common sample of 99.999% pure lead obtained from the American Smelting and Refining Company. These specimens were cast and then remelted and crystallized into nearly single crystals in carbon coated glass tubes which had been previously baked at 400°C. The whole process was carried out in a vacuum of approximately $10^{-5}$ mm Hg. Five small sections were cut from the ends of some of these specimens and were analyzed spectrographically by Detroit Testing Laboratory. Impurities found, in percent, were Ag (0.0008), Cu (0.0004), Ni (0.0002), and Sn (0.0006) so that, in growing the crystals, the purity was reduced to 99.998%. This does not include gaseous impurities which have been found to be fairly important in the mechanical properties of lead.[9] Gaseous impurity of 0.01% appears possible.

Just prior to mounting in the cryostat, the samples were annealed 8 hours in vacuum at 260°C to reduce the hysteresis effect to a minimum.[1] Mounting the specimens to be strained involved heating them in air momentarily for soldering into their sockets. The samples which were not to be strained were usually put into woven glass bags prior to annealing to lessen the possibility of damage to the sample in later handling. Such a sample was used as reference in almost all runs.

In order to observe the effect of impurity, two samples of 0.03% calcium in lead were prepared. Calcium was

[9] R. C. Grifkin, Acta Met. 6, 132 (1958).

chosen as the impurity because the low calcium end of this alloy system has been studied by Schumacher and Bouton.[10] They found that calcium in very low concentrations precipitates in lead and it was felt that the effect of precipitation might be of interest. The samples were prepared by rapid cooling of the final 0.03% melt from 500°C to keep the separation of $Pb_3Ca$ to a minimum. To prepare a sample in the unprecipitated state, it was heated to 300°C for 30 minutes and then quenched in liquid nitrogen where it was stored until use.

### *Resistive Measurements*

The lead for the resistive measurements was in the form of 0.006-inch diameter wire fabricated by the Indium Corporation of America from 99.999% pure lead. The resulting wire purity was reported to be 99.99+%. The resistivity ratio between room temperature and 4.2°K in the normal state was found to be approximately 6000. Prior to mounting in the cryostat, the wire was annealed for eight hours at 260°C in vacuum. Mounting involved handling and therefore some cold work of the fine wire.

## III. RESULTS

### A. Ballistic Induction Measurements

The results of these measurements are presented in terms of the effective permeability, $\mu_e=[\varphi(H_a)/\Delta\varphi]_{av}$, where $\varphi(H_a)$ is the magnetic flux penetrating the specimen at an applied field $H_a$ and $\Delta\varphi$ is the integrated flux change in the specimen in the course of the complete transition. The subscript, av, denotes the fact that the measuring method is responsive only to flux changes averaged over the entire specimen volume. The procedures used in obtaining $\mu_e$ from the observed data have previously been given in detail.[5]

### *The Hysteresis*

The deviations among the critical fields of various isotope samples reported by Hake *et al.*[11] were found by Decker *et al.*[1] to be connected with the presence of a hysteresis in the magnetic transition. This hysteresis also occurs in pure lead samples and is made up of an *S-N* and an *N-S* transition of approximately equal widths (in field) separated from each other by a significant field interval, the *S-N* transition occurring at the higher field. Thus the complete *S-N-S* cycle, when plotted as $\mu_e$ versus $H$, has the appearance of a hysteresis loop such as is shown in Fig. 2 (solid curve). For a hysteretic sample, a decrease of field after reaching some intermediate value of $\mu_e$ in the *S-N* transition results in no flux change in the sample until the full *N-S* transition curve is intersected. Upon increasing the field again no flux enters the sample until the *S-N* transition curve is reached. This behavior is shown in the dash-dot curve in Fig. 2.

This figure also shows the transition for the nearly ideal sample 4*F* which lies roughly in the center of the hysteresis loop of sample 2*J*. In particular, the critical field (defined as the extrapolation of the linear portion of the transition to $\mu_e=1$) for the 4*F* sample is very nearly midway between those for the hysteresis loop. This observation suggests a means of determining the reversible critical field for samples which show hysteresis: The hysteresis is measured and $H_c$ taken to be the field midway between $H_c(S\text{-}N)$ and $H_c(N\text{-}S)$. This method is now standard practice in this laboratory and is valid to within 10% or less of the hysteresis width as long as a linear portion of the transition can still be delineated to permit an extrapolation to $\mu_e=1$.

No sample has yet been prepared which did not show some hysteresis at the lowest temperatures. However, for the best specimens, the hysteresis after annealing was so small that it could be completely masked by the supercooling in the *N-S* transition at all temperatures. Thus, in Fig. 3, if the *S-N* transition is carried to completion ($\mu_e=1$) then upon lowering the field again the typical supercooling effect shown by the solid line will occur. Cycling the field in the intermediate state revealed such hysteresis as remained. The thermodynamic critical field was again taken to be the midpoint of the values $H_c(S\text{-}N)$ and $H_c(N\text{-}S)$ found from the two sides of the loop. From this figure it is apparent that supercooling and hysteresis are distinct phenomena. We shall reserve the term hysteresis for those permeability loops in which both transitions have a width in field comparable to that expected on the basis of sample geometry.

The main characteristics of the hysteresis are as follows:

1. Both transitions are fairly sharp, such broadening and rounding as they show increasing as the hysteresis width increases.

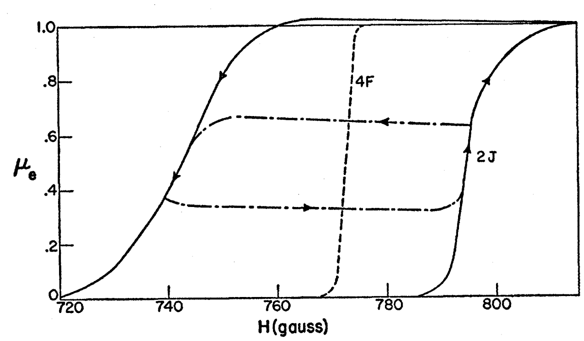


FIG. 2. Example of a magnetic transition in pure Pb specimen 2*J*, showing a large hysteresis effect. The nearly vertical dashed line near the center of the loop shows the transition at the same temperature (1.40°K) for specimen 4*F* which showed little hysteresis.

[10] E. E. Schumacher and G. M. Bouton, Metals & Alloys 1, 405 (1930).

[11] R. R. Hake, D. E. Mapother, and D. L. Decker, Phys. Rev. **112**, 1522 (1958).

2. The $N$-$S$ transition of the hysteresis is readily distinguished from a supercooled transition by the more gradual change of $\mu_e$ with field.

3. A hysteresis loop may be traced by cycling the field while the sample is in the intermediate state.

4. The $S$-$N$ and $N$-$S$ transitions are approximately equidistant above and below the reversible transition of a good lead sample at the same temperature.

### *Effect of Impurity*

The first method which succeeded in creating hysteresis was the addition of 0.03% calcium to a pure lead sample. This small amount of calcium in conjunction with rapid cooling from the melt had a strong effect on the superconducting properties. The transitions were very broad (the approximately linear portion covered 15 gauss at 2.1°K) and bumpy, indicating large scale inhomogeneities in the superconducting properties within the specimen. The hysteresis, centered about a slightly lower field than the true critical field of lead at the same temperature, had a total width of about 20 gauss at 4.2°K and 45 gauss at 2.1°K.

In this concentration (0.03%) calcium precipitates in lead and the effect of precipitation on the hysteresis has been observed. This was done by measuring hysteresis on the same sample, first as quenched from 300°C and then after a five day anneal at room temperature. Hardness data of Schumacher and Bouton indicate that precipitation is well advanced by this time.[10] The hysteresis at 4.2°K was increased by about a factor of two by precipitation (from 8.3 gauss to 17.8 gauss) while that at 2°K was unchanged (to within the greater experimental error caused by the very broad transitions at low temperatures).

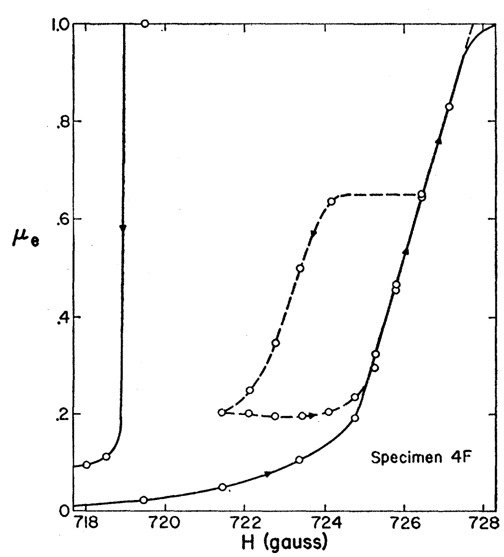


FIG. 3. Small hysteresis loop for a nearly ideal Pb specimen which also showed supercooling when taken completely normal. Temperature of measurement was 2.34°K.

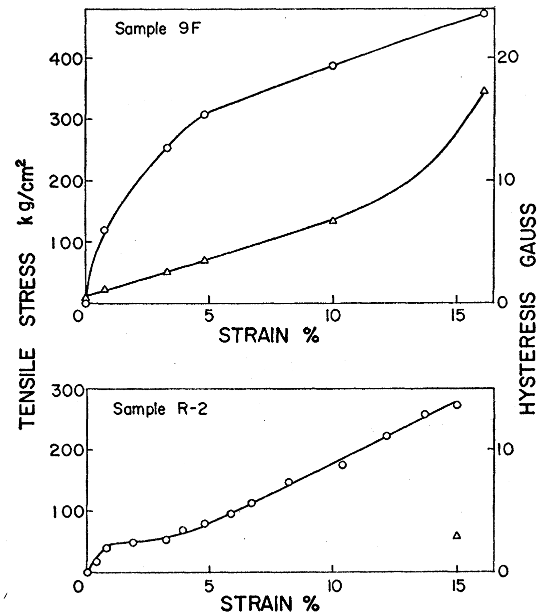


FIG. 4. Relation of sample strain to tensile stress (circles) and hysteresis (triangles) for polycrystalline sample $9F$ and nearly single crystalline sample $R$-2.

After the discovery that hysteresis could be produced by low-temperature strain, the impurity study was abandoned in favor of the greater convenience and control available in mechanical deformation. However, the hysteretic behavior which occasionally appears in unstrained pure lead samples is thought to result from the impurities present. As stated in reference 9, failure to clean lead with hydrogen gas to remove gaseous impurities (which was not done in the present research) can lower the purity by as much as 0.01%. In view of the results on 0.03% calcium in lead, this could cause the observed zero strain hysteresis if the gaseous impurities have effects similar to calcium.

Several attempts were made early in this research to check the extent to which the sample surface was involved in the hysteresis. Prolonged heating in air, suspension in water, and the heavy etching of a sample showing hysteresis all gave no effect, indicating that a surface condition is not responsible for hysteresis.

### *Effect of Strain*

Some of the early attempts to create hysteresis involved room-temperature strain. The sample was placed in a flexible, woven glass bag and its hysteresis measured while hanging freely in its coil. Between measurements the sample was pulled out of the cryostat and severely strained. The measurements were made at the normal boiling point of liquid helium (4.2°K) immediately (1 or 2 minutes) after straining. No increase in hysteresis as a result of room-temperature strain was found although some increase (perhaps as much as 2 gauss at 4.2°K) may have been masked by the super-

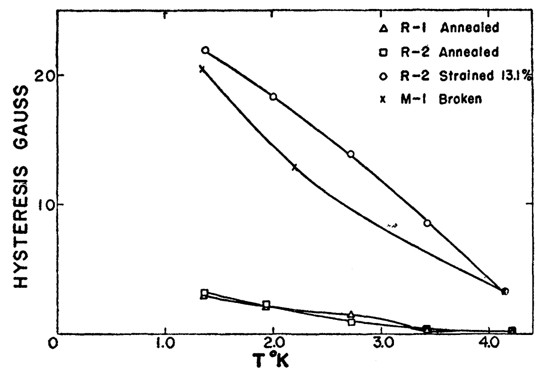


FIG. 5. Temperature dependence of the hysteresis in several pure lead specimens in the liquid helium range.

cooling. The amount of supercooling was definitely decreased by this strain.

Tensile strain applied at liquid helium temperatures always resulted in hysteresis and this technique proved to be the most useful tool for introducing hysteresis and controlling its size. The relation between hysteresis width, stress, and strain is illustrated in Fig. 4. Figure 4(a) shows the results for sample 9*F*, one of the first samples cast in the present series of experiments. It had seen considerable handling and so was certainly not a single crystal. In view of this, the stress-strain curve is not too significant. The hysteresis-strain curve for this same sample shows a linear rise throughout most of the region of strain. The transition at the largest strain was considerably broadened.

The stress-strain curve for sample *R*-2 is shown in Fig. 4(b), although the hysteresis was measured only for the largest strain. This sample had not been used previously and so was more nearly single crystalline than 9*F*. The hysteresis measured after strain is much lower than that for 9*F* at the same strain but agrees fairly well with the 9*F* hysteresis at the same stress. However, hysteresis is not found to be a very reproducible function of stress or strain among various samples.

### *Temperature Dependence*

Figure 5 shows the hysteresis width measured in the liquid helium range for several samples. Sample *R*-2, to be strained, was soldered into sockets at either end with *W*-58 solder after being annealed. Sample *R*-1 was annealed and then placed directly into its coil in the cryostat. The close agreement of these two samples before *R*-2 was strained indicates that neither the soldering process nor the presence of the superconducting solder at the sample ends appreciably changed the observed hysteresis. After low-temperature plastic strain the hysteresis width for *R*-2 fell on the top curve in Fig. 5 increasing approximately linearly as the temperature was lowered. Three points are also shown for sample *M*-1 which had been strained past the breaking point. Comparison of these curves serves to indicate the extent of reproducibility of the hysteresis width temperature dependence between various samples. Although the data do not extend above 4.2°K, these curves all show a marked tendency toward zero hysteresis at temperatures well below $T_c$ as is to be expected from earlier measurements at higher temperatures.[11]

### *Annealing Characteristics*

No increase in hysteresis had been observed as a result of room-temperature strain so that the annealing rate of the defects responsible was thought to be rapid at this temperature. In order to observe the annealing rate below room temperature, the following procedure was adopted: The sample was severely strained at low temperature and the hysteresis measured. The sample was then pulled out of the liquid helium and maintained at a temperature $T_1$ for a specified length of time after which it was returned to the helium bath and the hysteresis remeasured. The sample was next warmed to a higher annealing temperature, $T_2$, and so forth. A time of 20 minutes was chosen for the anneals, being long compared to the warm up time (approximately 2 minutes) but of a workable length. Temperature intervals of 20°K were used in the region in which significant annealing was found to occur.

The result of these measurements is shown in Fig. 6. The important features of this annealing are (a) the slow but continuous drop throughout the low-temperature range and (b) the sharp drop occurring just below 300°K. This behavior is substantially that shown by another specimen for which, however, there was some difficulty due to the transition width. It should be pointed out here that this annealing is characteristic

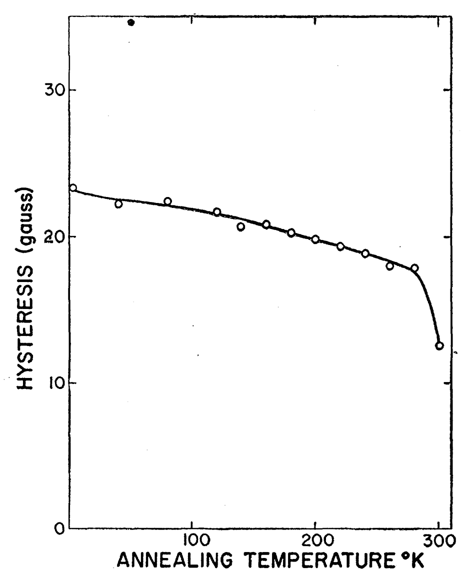


FIG. 6. Annealing of the hysteresis brought about by low-temperature plastic strain. The annealing time for each point was 20 minutes. The hysteresis was measured at 3.0°K after each anneal.

only of the low-temperature strain induced hysteresis. Hysteresis caused by impurity usually anneals nearer the melting point, if at all.

### *Experiments on Other Superconductors*

Samples of pure tin and indium were also strained at low temperature and the superconducting transitions measured. The tin sample showed a hysteresis of 0.2 gauss when cycled in the intermediate state at a critical field of 195 gauss. This hysteresis and critical field value were not significantly influenced (±0.2 guass) right up to the breaking point. The positive effects of strain were (a) a decrease in the original supercooling (12.8 gauss) to zero and (b) a small shift in critical field while the stress was applied which is in reasonable agreement with the value expected from $(\partial H_c/\partial P)_T$. Some superheating (a sharp rise from $\mu_e=0$ in the $S$-$N$ transition at slightly higher fields than normal) was observed here, probably as a result of the $W$-58 solder cap over each end of the sample. Due to the lower critical field of the tin (relative to lead) the solder was relatively more effective in altering the local field and therefore the transition shape.

The indium sample had an initial hysteresis of 0.15 gauss at a critical field of 166 gauss which remained constant over most of the range of stress applied. Near the breaking point the hysteresis rose sharply to 0.5 gauss, a small but real effect. No supercooling was observed in the indium but the small superheating due to the $W$-58 solder and the stress induced shift were present.

Measurements at 1.3°K after the samples had broken indicated that no hysteresis effect had occurred at the lower temperature which might have gone unobserved at 2.1°K. Also, no significant change in the hysteresis midpoint as a result of plastic strain was observed for either metal. Thus no effect which might correspond to that found by Chotkevich and Golik near $T_c$ was seen in the magnetic transition at lower temperatures.[12] It seems likely that resistive measurements on the present strained tin and indium samples would have shown broadened transitions but none were undertaken.

## B. Resistive Measurements

These measurements were made in the gap of a Varian magnet in order to have higher fields available. The hysteresis of the magnet yoke and the inhomogeneity in field when used with a large gap lowered the accuracy of these results relative to the ballistic induction measurements by about an order of magnitude. Fortunately, the effects to be observed are an order of magnitude larger. Typical resistive transitions for a 64-cm long lead wire sample are shown in Fig. 7. These were taken at 2.51°K and the indicated measuring currents. For a current of 1 ampere the transition shows a rather sharp step at $H_c$, but as the current is lowered, the step disappears and the transition moves to higher field in agreement with earlier work of Preston-Thomas.[4] In order to achieve the 64 cm length of this sample, the wire was strung between two Teflon arms several times and had about 4% of its length perpendicular to the applied field. This transverse part of the wire entered the intermediate state at fields well below $H_c$ and accounts for the nonzero resistance in this range. The uncertainty in the lowest current measurements was approximately 10% of the normal resistance so that some resistance at lower fields may have gone unobserved.

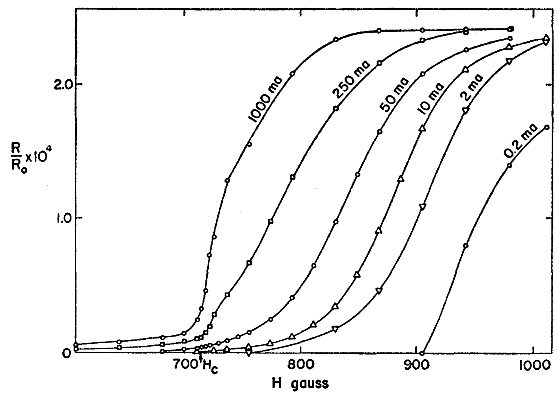


FIG. 7. Resistive transitions at 2.51°K and various measuring currents for a 64-cm long lead wire sample.

### *Nature of $H_{\rm I}$*

The field $H_{\rm I}$ is defined as the extrapolation of the linear portion of the resistive transition to zero resistance. This is done to eliminate the effect of the transverse part of the wire and is indicative of the highest field at which the longitudinal wire can carry the measuring current with zero resistance. As is obvious from Fig. 7, $H_{\rm I}$ depends upon the measuring current. It also depends upon the temperature and sample strain. Note that $H_{\rm I}$ is by no means the highest field at which traces of superconductivity can be observed (as evidenced by a resistance ratio less than the normal state value).[13]

### *Current and Temperature Dependence of $H_{\rm I}$*

The behavior of $H_{\rm I}$ when the current is varied is shown for four temperatures in Fig. 8. These data were all taken on the 64-cm sample in an unstrained state with current and field parallel. The curve for 2.51°K

[12] V. I. Chotkevich and V. R. Golik, J. Exptl. Theoret. Phys. U.S.S.R. **20**, 427 (1950). These authors compressed wire samples of tin and indium (and several other metals) and measured $T_c$ resistively. They observed a rise in $T_c$ as the load was increased and a further rise after removal of the load.

[13] It is of interest to note that the magnetoresistance of Pb in the normal state is large enough to complicate the determination of the normal resistivity, particularly for transverse field. The field at which superconductivity ceases completely and magnetoresistance is dominant is difficult to determine precisely.

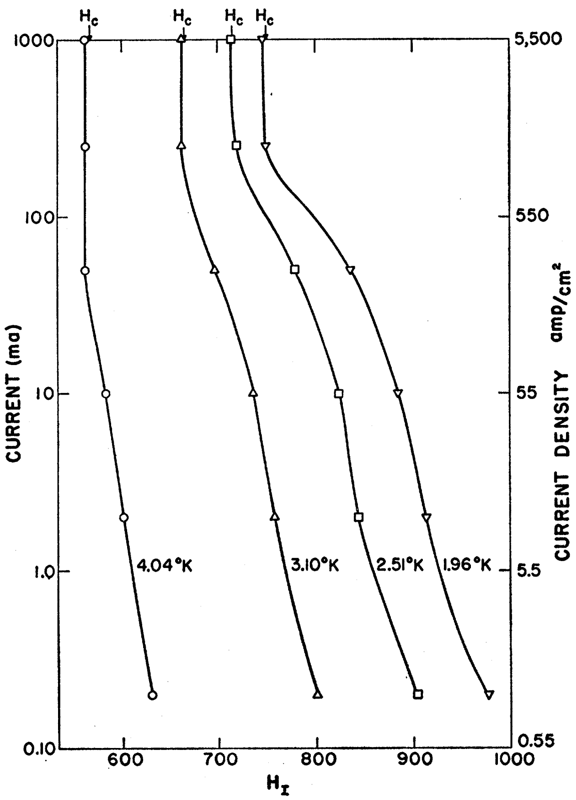


FIG. 8. Variation of $H_I$ with measuring current at several temperatures for the 64-cm lead wire sample.

comes directly from Fig. 7 by extrapolation of the transitions to zero resistance and the other curves come from similar plots at other temperatures. Because of the wide range of currents used (1000 to 0.2 ma), the current $I$ has been plotted logarithmically. The corresponding average current density has been plotted on the right-hand margin of the figure.

At large current, all of the curves show a vertical section where $H_I$ does not vary with $I$. In this range, $H_I$ is slightly below $H_c$ for that temperature, a result of the field generated by the current (26 gauss or less to be added vectorially to the applied field), the extrapolation procedure used, and possibly a small misalignment of the field and sample. As the measuring current is lowered, however, $H_I$ deviates to fields well above $H_c$. This deviation is more marked and begins at higher currents as the temperature is lowered. The transition for an ideal superconductor should be sharp and should occur at $H_c$ for all currents (except for the small shift to lower fields due to the field generated by the current itself). Thus here, as with the magnetic transition, there are deviations from ideal behavior which become more pronounced as the temperature is lowered.

### *Strain Dependence of $H_I$*

The length of the samples to be strained was limited by the apparatus to approximately 4.5 cm and for such samples, measurements were not made at currents lower than 10 ma. The dependence on measuring current is readily visible, however, as is shown in Fig. 9(a), for a sample strained 1.5%. These data are as good as any taken in this series, but the scarcity of points on the low current curves results in an uncertainty in $H_I$ determined from these curves of $\pm 10$ gauss.

A cylindrical sample in a magnetic field transverse to its axis has a demagnetizing factor of $\frac{1}{2}$ and so enters the intermediate state at $\frac{1}{2}H_c$.[14] Typical resistive transitions for the 4.5-cm wire sample in transverse field are shown in Fig. 9(b). There is a strong current dependence which ideally should cease at $H_c$. The low current curves for this geometry and sample do not reach normal resistance until the applied field is well above $H_c$, but do show a sizable resistance at $H_c$. $H_I$, defined as the extrapolation to zero resistance of these curves, is not expected to have any fundamental significance. On the other hand, it is a quantity which is indicative of the field at which the transition occurs and, as such, will be used for these transitions.

Figure 10 gives $H_I$ vs $I$ for four states of strain in the same sample in longitudinal and transverse field.

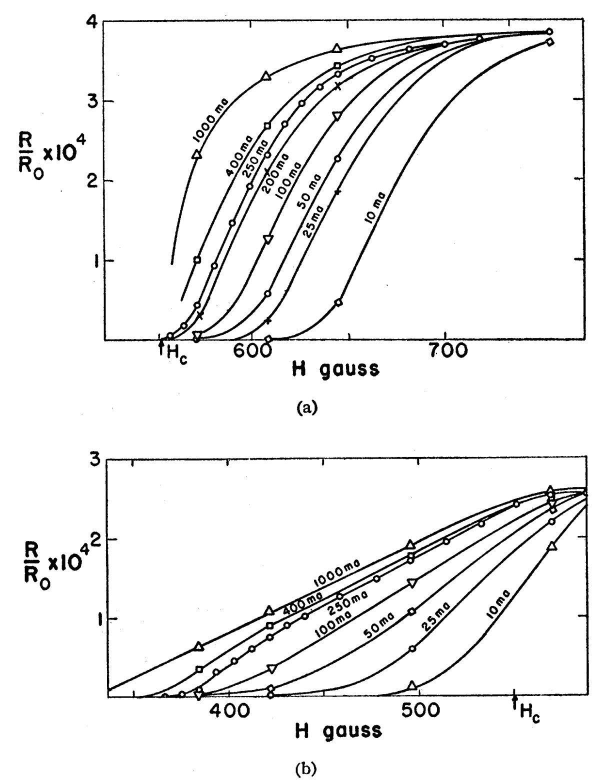


FIG. 9. Resistive transitions for 4.5 cm long lead wire sample at 4.21°K. (a) Sample strained 1.5% and measured in longitudinal field. (b) Sample unstrained and measured in transverse magnetic field.

[14] See, for example, D. Shoenburg, *Superconductivity* (Cambridge University Press, New York 1952), p. 24.

A current of 1 ampere is sufficient to bring the curves at various strains together to within the experimental error, but the deviations at lower currents become more pronounced the higher the strain. The curves taken in longitudinal field converge at $H_c$, those taken in transverse field, at 0.60 $H_c$. The difference between this value and 0.5 expected for a bulk sample is probably due to the small size of the wire and the energy required to form a superconducting-normal boundary in the metal. The magnitude of the effect measured here agrees well with the data of Andrew on tin wire.[15] The measurements for Fig. 10 were all taken at the normal boiling point of helium (4.21°K). On the basis of the measured temperature dependence it is safe to conclude that the deviations to fields above $H_c$ and 0.6 $H_c$ would commence at higher currents and become more pronounced at lower temperatures.

### IV. DISCUSSION

All of the results of measurements on lead described above are evidence that traces of superconducting material persist to fields well above $H_c$, a fact which has been generally appreciated for many years. The resistive transitions in longitudinal field [Fig. 7 and Fig. 9(a)] do not reach the normal resistance ratio until the applied field has been raised as high as three or four hundred gauss above the critical field in some cases. This is a result of small superconducting regions remaining in this range of field which lower the apparent resistance. Several properties of these superconducting regions can be inferred fairly directly from the data.

The regions which are superconducting above $H_c$ occupy only a small fraction of the total specimen volume. The effective permeability, $\mu_e$, is approximately the fraction of the sample volume which is normal. Thus, if $\mu_e$ has reached 0.95 at 10 gauss above the transition (which it does in almost all cases) only 5% of the sample still remains in the superconducting state. The regions which persist at hundreds of gauss above $H_c$ occupy less than 0.1% of the total volume.

The substantial measuring current dependence of the resistive transitions also indicates a small volume for the superconducting regions. A semiquantitative estimate is possible from the data of Fig. 7 where it is seen that changing the measuring current from 2 to 0.2 milliamps causes an increase in $H_I$ of the order of 50 gauss. Assuming (rather naively) that the residual superconducting phase exists as uniform filaments of radius, $r$, carrying currents, $i_f$, and that the displacement of $H_I$ results from the reduction of local field at the surface of the filaments (i.e., the Silsbee effect[16]), it is easily shown that $r=0.2\Delta i_f/\Delta H_I$ (with $r$ in cm, $i_f$ in amp, and $H_I$ in gauss). The value for $\Delta i_f$ depends upon the number of filaments present in the wire but it cannot exceed the total measuring current through the wire. Upon substitution this indicates an upper limit on $r$ of the order of $10^{-5}$ cm.

This estimate cannot be considered as more than a qualitative guidepost. It is evident that a larger upper limit on $r$ will result from data for larger measuring currents since the ratio $\Delta i_f/\Delta H_I$ becomes larger. Variation in both size and density of filaments with measuring current is also likely, but this cannot be discussed without a clearer idea of the nature of the filaments.

In addition to the small volume of the regions of abnormally high $H_c$, the ballistic measurements of hysteretic transitions clearly show that large fractions of the specimen volume can be sustained in a "metastable" normal state at field values less than $H_c$. This behavior can be attributed to the presence and distribution of the high critical field phase within the specimen as originally explained by the Mendelssohn "sponge" model.[17] If the abnormal phase is distributed as a continuously connected filamentary network, it can carry persistent currents which will shield the bulk of the specimen from changes in the externally applied field. The fact that $\mu_e$, at any point on a hysteresis loop, is metastable and very reproducible is clear evidence that the shielding current is undamped, i.e., a supercurrent. The requirement of continuity of the filaments seems essential to explain the hysteresis since a disjointed distribution of high critical field phase could not

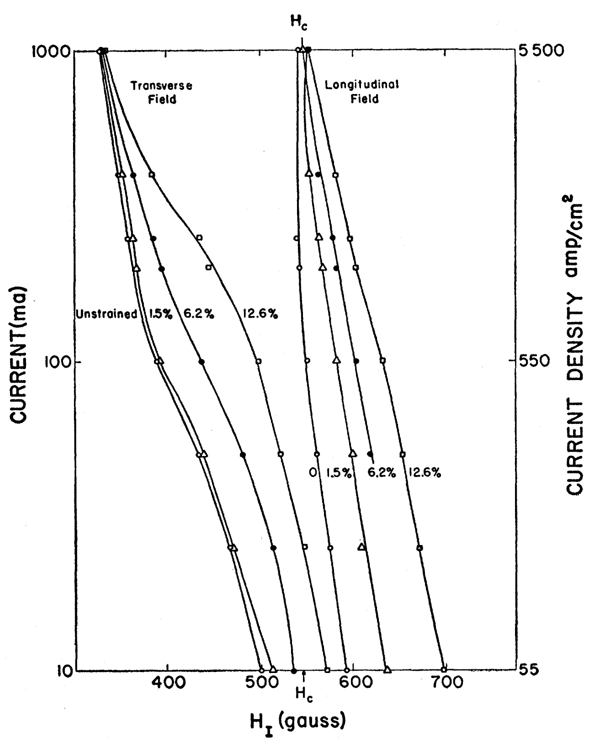


FIG. 10. Variation of $H_I$ with current in 4.5-cm long lead wire sample at 4.21°K and various strains (in percent elongation).

[15] E. R. Andrew, Proc. Roy. Soc. (London) **A194**, 80 (1948).

[16] F. B. Silsbee, J. Wash. Acad. Sci. **6**, 597 (1916).

[17] K. Mendelssohn, Proc. Roy. Soc. (London) **A 152**, 34 (1935).

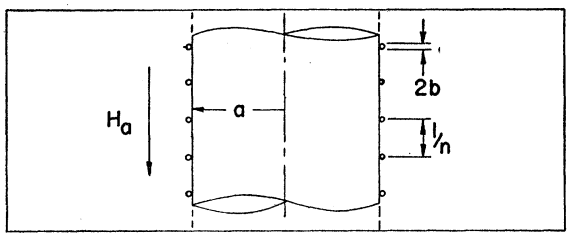


FIG. 11. The model used in deducing the hysteresis from a filamentary structure.

sustain the necessary supercurrents. The observable effect of this phase, if disconnected, would be limited to the Meissner effect in its own volume. Thus we shall take the continuous filament model as a hypothesis and inquire (a) to what extent it explains the various observed features, and (b) what physical origin can explain the existence of such a network.

### A. Elementary Filament Model

An exact treatment of the magnetic properties of a superconducting filamentary network running throughout a material which is itself a superconductor is very difficult. However, a much simplified model is of value in pointing out the considerations which must enter the real case and in acting as a starting point in a qualitative discussion of that case.[18]

The model (shown in Fig. 11) consists of an infinitely long cylinder, radius $a$, of superconducting material with uniform critical field $H_c$ (corresponding to the bulk material in the real case). On this cylinder are loops of superconducting wire of cross-sectional radius $b$ and critical field $H_f$ greater than $H_c$ (corresponding to the filaments in the real case). The loops are regularly spaced, $n$ per centimeter. The applied field, $H_a$, is parallel to the axis of the cylinder (and therefore perpendicular to the wire axis). To retain simplicity at this stage, we include the effects of both size and shape of the wires in the assumption that the loop transitions begin sharply at $H_f$. We further assume that $a \gg b$ and that the loops are far apart relative to $b(nb \ll 1)$, but are closely spaced relative to $a(na \gg 1)$. In view of these assumptions, the field at the surface of a loop generated by the current in the loop is approximately that of a long straight wire, $H=2i/b$, and the field within the cylinder generated by a current $i$ in all the loops is the long solenoid field, $H=4\pi ni$.

A field $H_a$ is now applied parallel to the cylinder axis. For a certain range of applied field, persistent current in the loops will shield out the entire field. However, when the total field at the wire surface reaches $H_f$, the current will thenceforth be limited by the condition that that field not exceed $H_f$:

$$H_f = H_a + 2i/b. \quad (4)$$

[18] This discussion has several features in common with the case of the magnetic moment of an isolated superconducting ring in externally applied field. See reference 14, p. 27 ff.

This current decreases as $H_a$ is further increased. In this range of field the cylinder itself will feel and have to exclude the field not excluded by the loops:

$$H = H_a - 4\pi ni = \mathrm{H}_a - 2\pi nb(H_f - H_a). \quad (5)$$

When $H_a$ has been raised far enough that the cylinder experiences its critical field, $H_c$, the transition will take place. Setting $H$ equal to $\mathrm{H}_c$ in (5) leads to

$$H_a - H_c = [2\pi nb/(1+2\pi nb)](H_f - H_c), \quad (S\text{-}N \text{ transition}). \quad (6)$$

Under the assumption that $nb \ll 1$ this equation becomes

$$H_a - H_c \cong 2\pi nb(H_f - H_c), \quad (S\text{-}N \text{ transition}). \quad (7)$$

Thus the transition occurs at an applied field greater than the cylinder critical field by $2\pi nb(H_f - H_c)$.

When this condition obtains, the loops are already carrying the maximum persistent current possible for that applied field. Therefore, when the cylinder begins to allow flux to enter, the loops can carry no additional persistent current and the transition goes essentially to completion at constant field. The sharpness of this transition is a consequence of the infinite length of the cylinder in the model. For a specimen of finite demagnetizing factor, the penetration of flux past the shielding loops will lower the local field at the outer edge of the loops and allow a restoration of shielding current. The resulting transition would have a width determined by the demagnetizing factor of the bulk specimen, but displaced from $H_c$ by the action of the loops as in the case of the infinite cylinder.

The $N$-$S$ transition is treated in much the same way, the initial field now being greater than $H_f$. As it is lowered below $H_f$, the loops become superconducting and act to trap in the field. The maximum current which the loops can carry is that which maintains the field at the inner loop surface at $H_f$:

$$i = (b/2)(H_f - H_a). \quad (8)$$

The field inside the loops then decreases as

$$H = H_a + 4\pi ni = H_a + 2\pi nb(H_f - H_a). \quad (9)$$

When this field reaches $H_c$ the $N$-$S$ transition will occur. Setting $H = H_c$ in (9) yields

$$H_c - H_a = [2\pi nb/(1-2\pi nb)](H_f - H_c), \quad (N\text{-}S \text{ transition}). \quad (10)$$

Since $nb \ll 1$ this becomes

$$H_c - H_a \cong 2\pi nb(H_f - H_c), \quad (N\text{-}S \text{ transition}). \quad (11)$$

Thus the $N$-$S$ transition occurs at an applied field below $H_c$ by the amount $2\pi nb(H_f - H_c)$. As before, this transition is sharp.

Comparing (7) and (11) shows that the $S$-$N$ and $N$-$S$ transitions occur above and below $H_c$ by the same field interval, $2\pi nb(H_f - H_c)$. Thus the hysteresis shown by the model is symmetric about $H_c$ and the individual transitions have geometrical sharpness, the essential features of the observed behavior. The loops and nearby material will, of course, add small effects at other fields.

### B. The Real Case

The experimental procedures (plastic deformation and impurity addition) which cause the hysteresis make it seem quite certain that the filaments are distributed throughout the specimen rather than being confined to the surface as strict analogy to the model would require. Moreover, several experiments designed to test for an abnormal surface layer gave negative results. Thus the real filamentary system seems to be a three-dimensional connected mesh which permeates the entire specimen volume. A considerable extension of the model is therefore required in discussing this system.

As the resistive transitions indicate, the filamentary mesh retains some degree of superconductivity at fields well above $H_c$ for the bulk lead. Thus, in the course of the $S$-$N$ magnetic transition of bulk lead, the advancing interphase boundary will leave the superconducting mesh exposed in a matrix of normal lead. This situation departs from the assumptions of the simple model and raises the question of the influence of the "exposed" filaments on the shape of the magnetic transition. If the "exposed" filaments were able to carry persistent currents to oppose flux penetration into the superconducting phase, the effect would be to broaden the magnetic transitions substantially. A similar argument can be advanced for the $N$-$S$ transition.

The experimental data indicate that the "exposed" filaments have little effect except in the most extreme cases of hysteresis.[19] In most observations the width of the magnetic transition increases only slightly over that to be expected on the basis of the demagnetizing factor of the specimen. From this fact we infer that the "exposed" filaments, while still partially superconducting, are no longer able to support significant persistent currents when exposed to the full applied field, and that the filaments active in the magnetic shielding process must lie in or near the interphase boundary region. This explanation is supported by the observation that the resistive transitions in transverse field show appreciable resistance well below $H_c$ for bulk lead, even for small measuring currents [see Fig. 9(b)]. Such behavior is expected due to the demagnetizing effect of filaments in transverse field, and it is the transverse filaments which contribute to the hysteresis in the ballistic induction measurements.

Another interesting facet of the hysteresis is the temperature variation of its magnitude. As shown in Fig. 5, the principal features are a monotonic increase in hysteresis with decreasing $T$ and the fact that it generally vanishes well below $T_c$. The resistive transitions indicate that the current carrying capacity of the filaments also increases as the temperature is lowered (see Fig. 8). These two effects are certainly closely connected. Decrease in the magnetic penetration depth as temperature is decreased may also make the filaments more impervious to penetrationn of flux.

### C. Lattice Defects and Filaments

It seems clear from the present observations that the hysteretic effects arise from some strain configuration in the metallic lattice. Other experiments, particularly those of Faber on nucleation, have been interpreted as evidence for the role of dislocations in promoting the survival of microscopic traces of superconductivity.[20] This seems like the most probable explanation in the present case.

Since dislocation strain fields vary inversely with some power of the radial distance from the center, the filament is, in fact, the manifestation of a microscopically inhomogeneous strain field. Thus it seems quite certain that it can have neither a well-defined radius nor a definite critical field as was assumed in the simple model. At least two effects come to mind as a means of explaining the larger-than-average critical field of a filament.

In the first place it is well known that strain itself can displace the critical field, and very localized strains of great magnitude (both compressive and tensile) occur near dislocations. This is a "bulk" effect in the sense that the critical field curves of large specimens can be displaced under conditions of uniform strain (e.g., the pressure effect). However, the magnitude of this shift at the stress characteristic of a reasonable size of filament ($4\times10^{-6}$ cm) is only 1.7 gauss and so the usual bulk effect appears incapable of explaining the present observations. There is, of course, some question regarding the validity of applying the bulk pressure coefficient to a region of such highly localized strain as occurs near a dislocation.

The second consideration concerns the microscopic character of the boundary region between the superconducting and normal phases. Within this region gradients exist in the magnetic field (characterized by the penetration depth, $\lambda$) and the order parameter (characterized by the range of coherence, $\xi$) where $\xi$ is of the order of ten times $\lambda$. This question has been discussed in detail by Pippard and Faber who show that a surface free-energy contribution, $\Delta$, arises in consequence of this difference.[20] The interphase free energy, while normally positive, can become negative in a situation which causes a sufficient reduction in $\xi$. Inhomogeneous strain and impurity atoms are believed to have this effect. The negative surface energy contri-

[19] The alloyed specimens generally show a larger hysteresis and more broadening of the magnetic transitions than the strained specimens.

[20] T. E. Faber and A. B. Pippard, *Progress in Low-Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1955), Vol. I, p. 142.

bution comes into play as the interphase surface contracts about a region of local strain and makes possible the survival of the small enclosed superconducting region to fields greater than the bulk critical field. Experimental support of these ideas rests on somewhat indirect measurements and, while agreement with theory is satisfactory, it cannot be said that the detailed situation at the interphase surface (especially in a region of inhomogeneous strain) is well understood.

### *Filaments in the Absence of Strain*

In the unstrained cases the negative surface energy could result from the concentration of impurities near dislocations. Doidge has shown that, for impurity concentrations above a certain value, superconducting inclusions occur which have higher critical fields than the bulk.[21] The stress field of a dislocation creates a region of lower energy impurity atoms which do not fit well into the parent lattice. It is thought that for this reason a dislocation may collect a cloud of impurity atoms during anneal at moderate temperatures.[22] (For lead, this could be room temperature.) This would account for the observed behavior both of some nominally pure lead samples, in which hysteresis increased during room-temperature storage, and the calcium-lead sample, in which aging increased the hysteresis (at 4°K). We therefore suggest the impurity cloud near dislocations as the basis of the superconducting filaments in the absence of low-temperature strain.

### *Strain Induced Filaments*

There are many defects present in a cold worked lattice which might give rise to an increased critical field. In a face-centered cubic crystal such as lead, dislocation pile-ups are thought to occur during plastic deformation.[23] They are probably in the form of loops which may sometimes touch one another at the line common to their glide planes. The dislocation pile-up is thought to have the proper geometry and also sufficient extent and strain field to explain the present results. The annealing of the hysteresis in the low-temperature range (see Fig. 6) indicates a small decrease in filament strength such as might be expected if a few dislocations left the pile-ups in this range. The sharp drop at 300°K is probably related to recrystallization[24] and results from the pile-ups breaking up.

The absence of significant strain induced hysteresis in tin and indium may be the result of the complex crystal structure of these metals. The mechanism of work hardening is dependent on crystal structure[23] so that it may be that pileups or connected regions of extreme local strain do not occur in tin and indium during cold work. In this regard measurements on aluminum (also fcc but with a much lower $T_c$ than lead) will be of interest.

## V. ACKNOWLEDGMENTS

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[22] A. H. Cottrell, *Dislocations and Plastic Flow in Crystals* (Clarendon Press, Oxford, 1953), pp. 134–136.
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[24] G. F. Bolling and W. C. Winegard, Acta Met. **6**, 281 (1958).