# Hysteresis in Superconductors. III. Effect of Surface Energies on the Shielding and Field-Retaining Properties of Hollow Cylinders of Type-I Superconductors*

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The diamagnetic and field-retaining properties of thin-walled type-I hollow cylinders can be changed by more than an order of magnitude through the introduction of surface strains. High-purity hollow cylinders of Pb and Sn in which the surface strains are minimal shield external fields of only a few percent of $H_c$ and do not retain appreciable fields in the void when an external field exceeding $H_c$ is removed isothermally. The shielding and field-retaining properties are influenced by localized phenomena. The introduction of local surface strains increases the local shielding properties during the application of an external field and leads to the retention of large axial field gradients in the void after the applied field is removed. Fields of both senses can be retained in the void simultaneously when cycles are performed involving both senses of the applied field. Some experiments are summarized showing spontaneous field enhancement when type-I superconductors are cooled in applied fields. A number of unexpected reversibility relations are associated with these phenomena. The effects can be accounted for by including surface and interface energy terms in the thermodynamic state function of the superconductor. An example of how hysteresis arises from equilibrium changes is described.

## I. INTRODUCTION

THE purpose of this paper is to describe new properties exhibited by solids, hollow cylinders, and various geometries of solids in hollow cylinders of Pb, Sn, and In and ultimately to show that these properties are related to effects generally associated with hysteresis in type-II superconductors.[1,2] Studies were made on how the shielding and field-retaining properties of type-I superconductors are affected by surface strains, radial and axial dimensions, oxidation, chemical purity, grain size, temperature, field-sweep speed, cooling rates, different straining techniques, and annealing procedures. The effects of these parameters on the diamagnetic properties were studied under isothermal conditions where the applied fields were varied and under conditions where the temperature was varied when the applied fields were kept constant. The roles of the various factors will be described in detail in separate papers. In this paper, we summarize some of the gross features and offer a general explanation of the effects which will be used as a framework in which the details will be compared. The properties of hollow cylinders will be considered first.

The predicted properties of hollow rings and cylinders of type-I superconductors have been discussed by a number of authors.[3–5] The thermodynamic and electrodynamic treatment by London[3] requires that the equilibrium state of a simply connected type-I superconductor satisfies the conditions $B=0$ and $\dot{B}=0$, where $B$ is

the magnetic induction. For the multiply connected superconducting ring, the London conditions[3a] are $d\phi c/dt=0$ or $\phi c=$const, where the fluxoid $\phi c$ becomes the magnetic flux when the wall thickness is greater than the penetration depth. This treatment and the treatment by Shoenberg[4] predict that the systems will shield to that value of the external field which drives some portion of the sample into the intermediate state. The field retained in the void after an external field exceeding $H_c$ is removed is approximately equal to the shielding field. The discussion given by Livingston and Shadler[5] for ideal hollow cylinders (ignoring end effects) predicts that the cylinder will shield to $H_c$ when it abruptly goes normal. When the field is decreased to below $H_c$ the hole retains $H_c$, which remains trapped as the external field goes to zero. Measurements of the flux trapped in hollow lead cylinders have been reported previously.[6] It was observed that, contrary to the predictions for an ideal, infinitely long cylinder, the external field started to penetrate for $H_{ext}<H_c$ and that a field less than $H_c$ (between 0.5 and $0.9H_c$) was trapped in the hole when $H_{ext}$ was removed. This deviation from ideal behavior was attributed to end effects. However, the present work demonstrates that the field inside the cylinder can exhibit maxima or minima along the long axis and is a fairly arbitrary function of $H_{ext}$, depending strongly on the state of the surface in the immediate vicinity of the probe. In addition, it is shown here that the retained fields can be more than an order of magnitude less than the measured critical fields when surface strains are removed. In none of the earlier discussions cited is there any indication of how strongly the properties depend upon intrinsic surface energies nor are there any estimates of the magnitude of the deviations that can exist in ideal (long-high purity-annealed)

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[2] D. G. Schweitzer and M. Garber, Phys. Rev. 160, 348 (1967).

[3] F. London, *Superfluids* (Dover Publications, Inc., New York, 1960), Vol. I, (a) pp. 11, 47–51, (b) pp. 125–130.

[4] D. Schoenberg, *Superconductivity* (Cambridge University Press, New York, 1952), p. 27–34.

[5] J. D. Livingston and H. W. Schadler, Progr. Mater. Sci. 12, 209 (1964).

[6] D. L. Coffey, W. F. Gauster, and H. E. Rorschach, Jr., Appl. Phys. Letters 3, 75 (1963).

specimens. One aspect of this work is to show that long high-purity annealed samples in which the surface strains are minimal show marked deviations from this behavior. The same samples can be made to approach the predicted behavior when both surfaces are heavily strained. In experiments where circumferential strains are produced at the cylinder ends, the multiply connected strained regions act in a similar manner to end rings.[6] The strains tend to minimize or eliminate end effects. Predictions of the properties expected when type-I hollow cylinders are cooled in constant applied fields also have been discussed.[5] It was concluded in Ref. 5 that upon reaching its critical temperature, the specimen will expel flux from its own volume but not from its hole. When it reaches the test temperature the field within the hole will still equal the external field.

The properties exhibited after these measurements show large systematic deviations from the predicted properties, which include spontaneous enhancement of the field in the void and a number of unexpected reversibility relations. These new properties appear to be intrinsic properties of the systems. In this work, the gross features are qualitatively explained by including the surface and interface energy terms in the thermodynamic state function of the superconductor.

## II. EQUIPMENT AND TECHNIQUES

Only the equipment and techniques used in these studies are described here. The gross properties summarized here occur in polycrystalline samples of 99.999% Pb and Sn, with average grains sizes from $\sim 10^3$–$10^4$ $\mu$. The annealing and etching techniques used differ from Pb and Sn. For convenience only the techniques applied to Pb are described here. Strains were produced by machining, mechanical twisting, specimen elongation, sanding with silicon carbide cloth, and impingement of 50-$\mu$ aluminum oxide particles carried in pressurized air streams (sandblasting). Through a systematic study of straining and annealing it was found that surface strains are not removed after heat treatments that produce annealing and grain growth in the bulk. Samples in which the bulk consists of grains of $\sim 10^3$ $\mu$ show no visible changes in the surface grain size after several hours of heating in boiling glycerol ($\sim 270$–290°C). After the surface layer is removed by etching (in either 20% peroxide in glacial acetic acid or 5% HNO$_3$ in methyl alcohol) an increase in bulk grain size to about $5 \times 10^3$–$10^4$ $\mu$ due to the heat treatment was observed. The introduction of surface strains by sanding or twisting in large grain samples can lead to a visible reduction of the grain size in the surface. Prolonged ($\sim 3$ months) annealing at room temperature or heating at $\sim 270$°C for several hours does not change properties associated with the surface strains. The surface strains can be removed by etching with or without previous annealing. The majority of bulk strains in high-purity

Pb anneal rapidly at room temperature. The shielding and field-retaining properties of surface-strained thin-walled (5–50 mils or 0.0125–0.125 cm) cylinders show large decreases with etching. In machined thick-walled (100–500 mils or 0.25–1.25 cm) polycrystalline samples the changes with etching are greatly reduced.

The fields in the void of the hollow cylinders were measured with various Hall probes (Seimens Hall-generator) with sensitivities ranging from 40–100 Oe/mV, depending upon the probe and the probe currents (30–300 mA) used. When the field distributions along the lengths of the cylinders were measured by moving the probe, reproducibility of about $\pm 0.1$ Oe could be obtained. The reproducibility obtained when the samples were removed from the helium bath and then remeasured with different probes which were maintained in fixed positions was of the order of $\pm 5$ Oe. Most of the error in the latter procedures appeared to be associated with the accumulation of errors due to the different calibration curves for each probe and the errors associated with the thermal contraction estimates from 300 to 4.2°K necessary to determine the precise position of the probe. These differences only affected the measurements where large field gradients were produced in the void. The external fields were produced by a copper solenoid immersed in liquid nitrogen. The solenoid was 35 cm long with an inside diameter of 3.8 cm in which the helium Dewar was inserted. The useable inside diameter of the helium Dewar was 2.5 cm. Probe measurements of the axial variation of the field produced by the solenoid showed that this variation was less than 3% in the region in which the superconducting samples were placed. No radial variation was detected. When hollow cylinders were cooled from above $T_c$ to below $T_c$ in constant applied fields, the measurements were performed over a range of cooling rates from $\sim 1$°K in 10 sec to 1°K in $5 \times 10^3$ sec. No effect of cooling rate was observed in this range. In these experiments the Sn and In cylinders were cooled and heated with and without heating coils. The slower cooling rates were obtained by pumping on the helium bath with varying pumping speeds. Warming was accomplished by intrinsic heat leaks in the system or by bubbling room-temperature helium gas through the liquid helium at different flow rates. Rapid cooling and warming was accomplished by winding 60-cycle ac resistance heaters around the outside of the cylinder and also by placing ac heating coils in the voids of the hollow cylinders. In the former case, during the application of current through the windings, the liquid helium boiled off at the outside surface first. In this case, when the samples were cooled below $T_c$ by reducing the heater currents the inner surfaces cooled first. The values of the spontaneous enhancements were not affected by these differences in procedures. Rapid oxidation of etched Pb samples in a 200°C flowing air stream produces a blue-brown oxide in $\sim 15$ min. The formation of this type of

oxide surface on samples which retained fields as low as $0.03H_c$ produced no detectable changes in the shielding or field-retaining properties. Prolonged oxidation in moist air produces surfaces which include oxides, hydroxides, and carbonates, with occasional localized pitting. This type of surface results in a gradual increase in shielding and field-retaining properties with oxidation time. To avoid this oxidation, prolonged annealing at room temperature was performed by covering the samples with anhydrous glycerol.

Absolute values of $H_c$ were measured to determine if the critical fields varied along the length of the cylinders because of the surface treatments. The measurements defining $H_c$ were made by comparing the probe readings in increasing and decreasing applied fields to the calibration curves of the probes. The calibration curves of the probes were obtained by determining the voltage produced by a change in applied field in the absence of a superconducting sample. The critical field corresponding to a particular position in the etched and strained cylinders was taken as that value of the applied field where the probe reading was the same as the calibration curve. The value of the applied field for which the probe reading corresponded to the calibration curve was found to be independent of position and was the same in both increasing and decreasing fields. The absolute values obtained were the same as the known bulk critical fields of Pb and Sn. The results showed that the surface treatments did not produce increases or decreases in $H_c$ that were detectable in these measurements. In contrast to the properties of Sn, the increases in the critical field of Pb that might have been expected with surface changes[7] do not appear to create currents that are sufficiently



FIG. 2. Retained field distributions in sample shown in Fig. 1 for: curve 6, two asymmetrically spaced locally sanded regions; curve 7, changes in distribution shown by curve 6 after 30-sec etch in 20% peroxide in acetic acid.

large to appreciably change either the gross shielding or the gross field-retaining properties of cylinders with the dimensions studied. Thus it is convenient to plot all fields as a fraction of the critical field.

## III. RESULTS

The field distribution along the length of a sandblasted cylinder of Pb with a wall thickness of 0.037 cm and an i.d. of 0.37 cm is shown in curve 1 of Fig. 1. The distribution was obtained after a field exceeding $H_c$ was applied and removed at 4.2°K. The field in the void is uniform along the length to within 0.15 cm from each end with an absolute magnitude of $0.96H_c\pm2\%$. The field measurements along the length were reproducible to $\pm0.1\%$. The falloff in the outer 0.15 cm at each end amounts to 5 or 6%. Curve 2 was obtained after five 30-sec etches in $4HA_c-1H_2O_2$. After each etch the sampled was rinsed in either water, alcohol, or glycerol and dried before measuring. Measurements between etches showed a systematic monotonic reduction in retained field with etching. After curve 2 was obtained the center 0.3-cm section of the inside surface was lightly sanded as shown schematically in the upper part of Fig. 1. The field distribution resulting after this procedure is shown by curve 3. Curve 4 was produced after sanding the 0.3-cm section on both surfaces. Curve 5 was obtained by applying more pressure during sanding. A second section of both surfaces was sanded asymmetrically as shown in the upper part of Fig. 2, with the resulting distribution given by curve 6. Probe measurements showed that the falloff of $\sim150$ Oe at the point denoted by 7.5 cm occurs in a region of width between 0.015 and 0.007 cm. Curve 7 was obtained after a 30-sec etch. Further etching reduces the field trapping to curve 2 or slightly lower values, depending upon whether the wall thickness is reduced. Samples which exhibit gradients in the void between $10^3$ and $10^4$
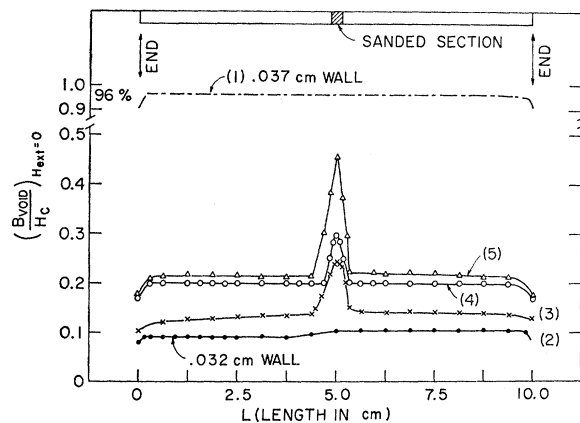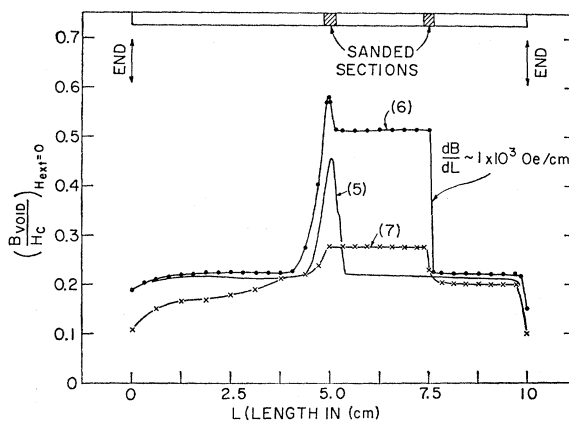


FIG. 1. Retained field distributions in Pb cylinder with 0.037-cm wall and i.d. of 0.37 cm after applied field exceeding $H_c$ is removed at 4.2°K. ($H\|1$ in all cases.) Curve 1, both surfaces uniformly sandblasted; curve 2, distribution after five 30-sec etches; curve 3, distribution after center 0.3-cm section was sanded on inside surface completely around the circumference; curve 4, distribution after center 0.3-cm section was sanded on both surfaces; curve 5, distribution after heavier sanding.

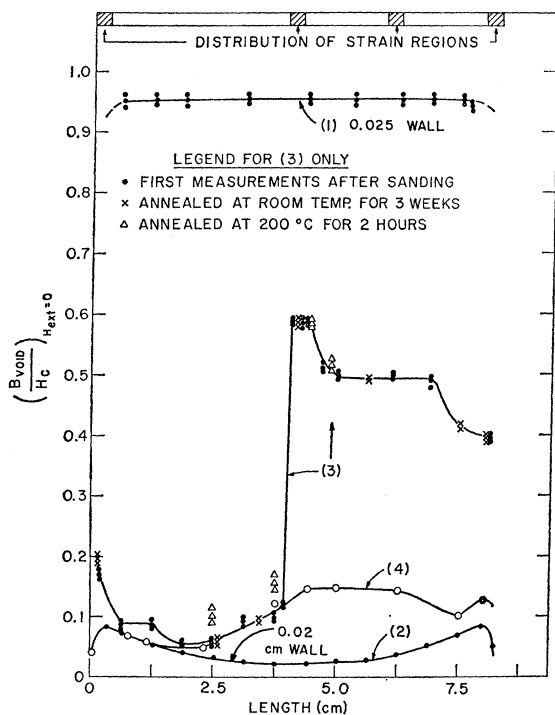[7] W. F. Druyvesteyn, Philips Res. Rept. Suppl. 2 (1966).

Fig. 3. Retained field distribution in a 0.025-cm-wall Pb cylinder with i.d. of 0.37 cm. Curve 1, distribution after sandblasting; curve 2, distribution after a series of etches; curve 3, distribution with four locally sanded regions before and after a number of heating procedures; curve 4, changes in curve 3 after a 30-sec etch.

Oe/cm were also cycled between 4.2 and 300°K 30 times, annealed at room temperature for 3 weeks, and measured with different probes under conditions where the probes were stationary. Curve 1 in Fig. 3 shows the field-trapping distribution in the sandblasted condition
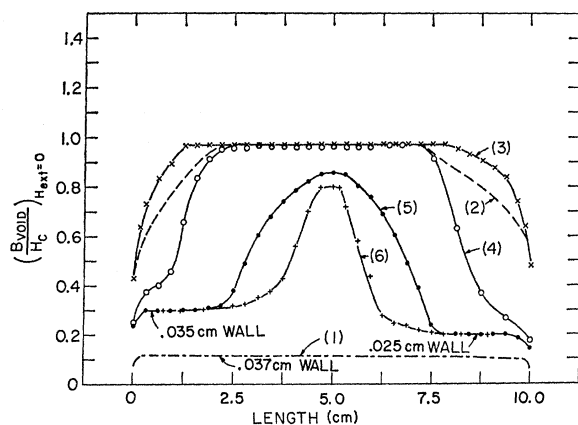


Fig. 4. Retained field distributions in 0.03 7-cm-wall Pb cylinder with an i.d. of 0.75 cm after removing an applied field greater than $H_c$ at 4.2°K. Curve 1, distribution after etching; curve 2, distribution after first sandblasting; curve 3, distribution after second sandblasting of ends only; curve 4, distribution after 1.25-cm lengths at each end were etched; curve 5, distribution after 2.5-cm lengths at each end were etched; curve 6, distribution after 3.8-cm lengths at each end were etched.

along the length of a Pb cylinder with a 0.025-cm wall and an inside diameter of 0.37 cm. Curve 2 shows the distribution obtained after a series of etches which removed the surface strains. After curve 2 was obtained a number of local strains were produced in both surfaces by sanding with silicon carbide cloth. Curve 3 shows the distribution after four 0.3-cm sections were sanded in the positions shown in the schematic of the cylinder in the upper portion of the figure. The section at the end denoted by 0 differed from the others in that it was lightly sanded. The different types of data points denote measurements made with different probes after various procedures and annealing treatments. (This sample was cycled between 4.2°K and room temperature 30 times, annealed at room temperature under glycerol for 3 weeks, and then annealed at 200°C for 2 h. No appreciable changes resulted, indicating no appreciable
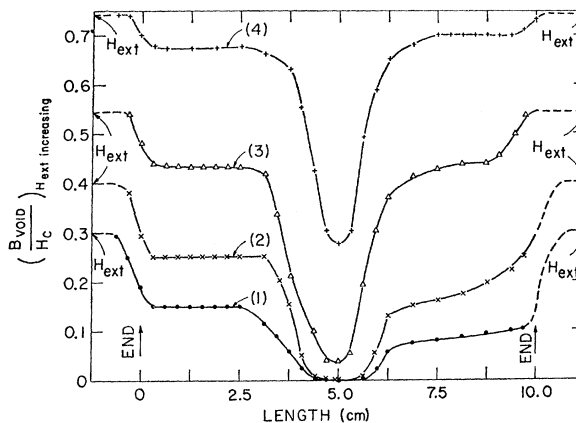


Fig. 5. Distributions of field in the void for various values of increasing applied fields for sample used to obtain curve 6 in Fig. 4.

annealing of the localized surface strains. The maximum spread after any given procedure due to temperature cycling and changing probes was about ±5 Oe.) Curve 4 shows the changes in the distribution given by curve 3 after a 30-sec etch.

The field distributions just described were obtained by local surface straining of a sample in which the surface strains were minimal initially. The reverse procedure of removing strains is shown in Fig. 4. The original Pb sample was 10 cm long with a 0.037-cm wall and an i.d. of 0.75 cm. After the sample was machined to these dimensions it was etched until curve 1 was obtained. The sample was then sandblasted, resulting in curve 2. A second sandblasting of the ends only resulted in curve 3. Curve 4 was obtained by etching the inside and outside end surfaces over a length of 1.25 cm. Curve 5 resulted after etching 2.5-cm lengths at each end. Curve 6 resulted from etching 3.8-cm lengths leaving the center 1-in. section sandblasted. After these procedures the wall thickness varied at the ends as denoted in Fig. 4.

The curves shown in Figs. 5 and 6 are representative of the type of distributions of the field in the void that can be obtained in increasing and decreasing external fields. The data were obtained from the sample which produced curve 6 in Fig. 4. The sample was removed from the helium bath driven normal and cooled again in the absence of an applied field. The distribution shown by curve 1 in Fig. 5 was obtained when the external field was increased from zero to $0.3H_c$. After the measurements were completed, the external field was increased further to a value of $0.4H_c$, resulting in curve 2. Further increases produced the distributions shown by curves 3 and 4. After obtaining curve 4, the external field ($0.74H_c$) was then reduced. The field distributions for various values of the decreasing field are shown by curves 5–9 in Fig. 6. Slight oxidation due to exposure to air for a few days produces only small changes in samples which retain uniform fields along the length. The same procedures applied to samples exhibiting large gradients also produce only small changes. After 3 days in air the sample from which the data in Figs. 5 and 6 were obtained was remeasured. Only minor differences were observed. The effects of subjecting the sample to field cycles involving both senses of the applied fields were then measured. A field exceeding $H_c$ was applied and removed from the sample. The polarity of the dc current in the external solenoid was then reversed. An applied field of $0.15H_c$ of negative sense relative to the original field was then applied and removed. The distribution of retained field along the length of the cylinder (in the absence of an external field) is shown by curve 1 in Fig. 7. A negative field of magnitude equal to $0.3H_c$ was then applied and removed with the resulting distribution in zero external field given by curve 2. After these measurements, the negative field applied before removal was $0.45H_c$. The results are given by curve 3. Curves 4–8 apply for similar procedures where the respective maximum
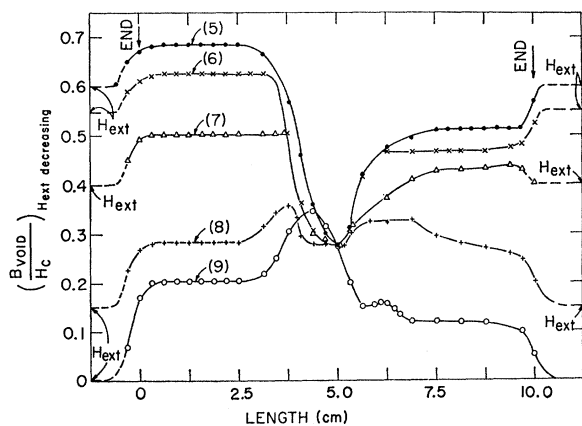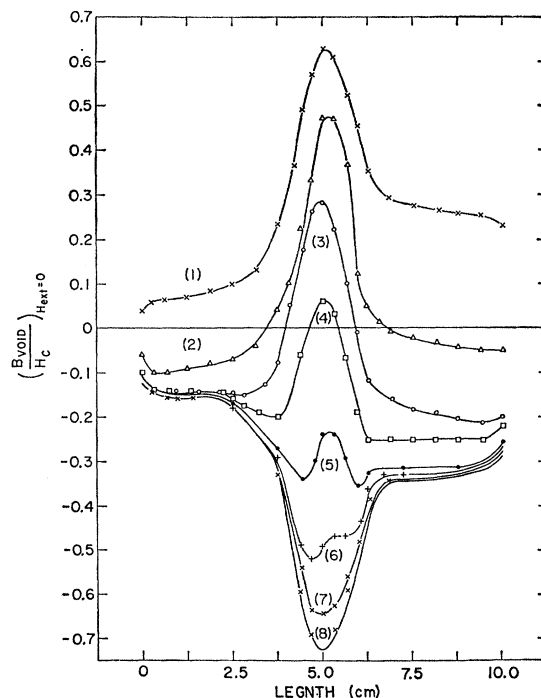


FIG. 7. Distribution of field in the void for $H_{ext}=0$ when sample used to obtain curve 6 in Fig. 4 was subjected to field cycles using both senses of the applied field.

applied negative fields correspond to 0.6, 0.75, 0.85, 0.9, and $2.0H_c$. Curves 2–4 show that the cylinders retain fields of both senses simultaneously.

## A. Relative Roles of Inner and Outer Surfaces and Interactions between Localized Strains

Studies in which one surface was etched and one was uniformly sandblasted show that the outer surfaces are slightly more effective in increasing field retention. When more than one local strain is introduced, the axial gradients between the strains are reduced and cause a relatively uniform increase of the field in the void between the strains. The increase of field in the void over the strain-free regions results from interactions of the field gradients in the void. This conclusion is based on measurements in which the strained regions were cut from the cylinders. Subsequent measurements of the sections that were originally strain-free showed that the shielding and field-retaining properties were about the same as they were before the local strains were produced. A typical example of the relative effects of localized strains produced on the outer surface and then on both surfaces is shown in Fig. 8 for a 10-cm-long Pb cylinder with a 0.05-cm wall and an i.d. of 0.37 cm. Curve 1 shows the field distribution after etching the originally machined sample. Two 0.3-cm sections were then sanded, circumscribing only the outer surfaces in the positions



FIG. 6. Distribution of field in the void for various values of decreasing external fields for sample used to obtain curve 6 in Fig. 4.
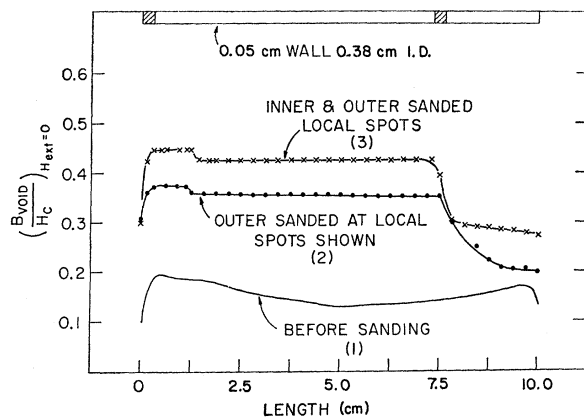
FIG. 8. Effect of inside and outside surfaces on the distributions resulting from localized strains. Curve 1, distribution after arbitrary etching; curve 2, distribution after localized sanding on outer surface; curve 3, distribution after localized sanding on both surfaces.



FIG. 10. Distribution of retained field when ends of sample used in Fig. 9 were sanded on both surfaces.

shown schematically in the figure. The resulting distribution of the field in the void after applying and removing a field exceeding $H_c$ is shown in curve 2. Curve 3 shows the distribution when both surfaces were sanded in the same positions. The effects of introducing local strains and then cutting off the strained sections are shown by the data in Figs. 9–13. Curve 1 in Fig. 9 shows the distribution along the length of an etched sample with an original wall thickness of 0.037 cm and an i.d. of ∼2.2 cm. Curve 2 is the distribution obtained after a 1-min sandblasting of both surfaces. Curve 3 was obtained by sandblasting only the ends a second time. After this procedure the wall thickness at the end denoted by 10 cm was reduced more than the remaining portion of the cylinder. Curve 4 was obtained after subsequent etching which left the wall ∼0.03 cm thick with the thin end ∼0.025 cm. After

this treatment, 1.25-cm lengths at each end were sanded on the inner and outer surfaces. The distribution of field in the void after an external field greater than $H_c$ was applied and removed and was then measured. The resulting data are given by curve 1 in Fig. 10, which is compared to the etched condition before local sanding (curve 4 of Fig. 9) and to the distribution obtained after complete sandblasting (curve 2 of Fig. 9). It is seen that local strains on the ends of cylinders are highly effective in increasing the overall field-retaining properties. After these measurements the strained sections were cut off with a razor. In one case (where the wall was 0.025 cm thick) 1.25 cm were removed and in the other case 2.5 cm were removed. The remaining section was ∼6 cm. The field distribution obtained after cutting is shown in Fig. 11 for the 6-cm section. The field distributions of the end pieces are shown in Figs. 12 and 13, where they are
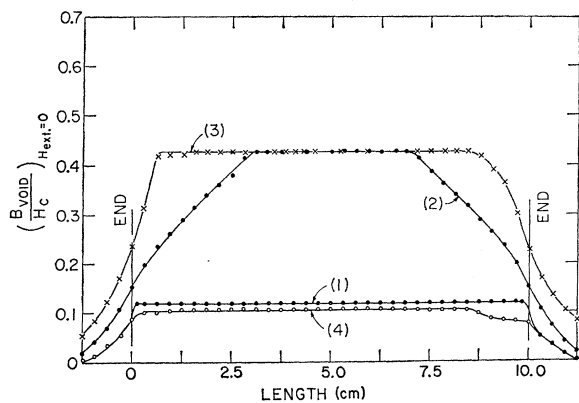


FIG. 9. Distribution of retained field in a 0.037-cm-wall Pb cylinder with an i.d. of 2.25 cm. Curve 1, distribution after etching; curve 2, distribution after 1-min sandblasting of both surfaces; curve 3, distribution after ends were sandblasted again; curve 4, distribution after subsequent etching.
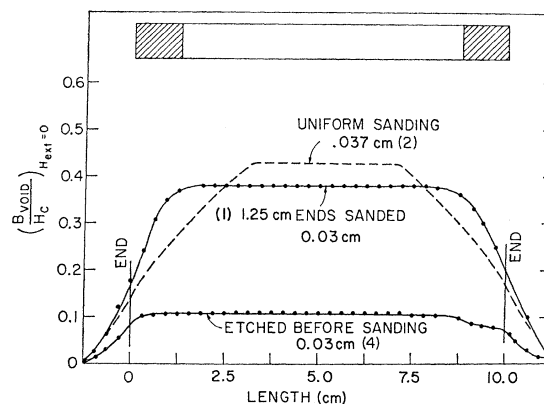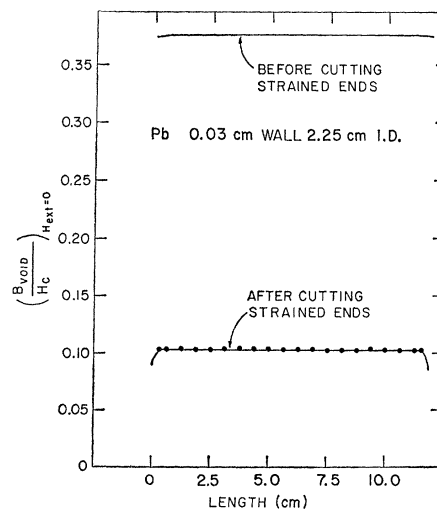


FIG. 11. Distribution for strain-free portion of sample used in Fig. 10 after sanded ends were cut off.

compared to subsequent distributions obtained after 1-min etches.

## B. Spontaneous Enhancement of Field in the Void and Associated Reversibility Relations

Hollow cylinders of type-I superconductors in which the wall material is reversible in the slit cylinder configuration retain fields in the wall and exhibit spontaneous enhancement of the field in the void when the continuous cylinders are cooled below $T_c$ in external fields. The latter effect was first noted by Smith and Rorschach[8] and described empirically by Gayley and Young.[9] In addition to the observation that the magnitude of the effect depends upon the radial dimensions of the cylinder, it was found here that after cooling from above $T_c$ in applied fields the changes are reversible with temperature in applied fields and when the applied field is removed. When the external field is removed after cooling below the superconducting transition temperature, the wall also retains field. Subsequent decreases and increases between the transition temperature and lower temperatures show that the fields in the wall and in the void exchange reversibly both in the presence and absence of an external field. The source of the field lines pumped into the void is determined by the field present in the wall at the normal→ superconducting transition. The temperature region over which the enhancement occurs consequently depends upon the wall thickness, hole size, applied field, etc. For a cylinder of given o.d. and i.d. the field in the void begins exceeding the value of the applied field at the temperature corresponding to the critical temperature for the applied field. As the temperature is lowered progressively, the field in the void increases with the same temperature dependence as that of the
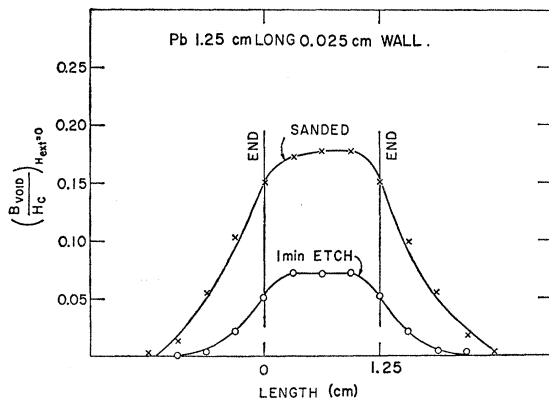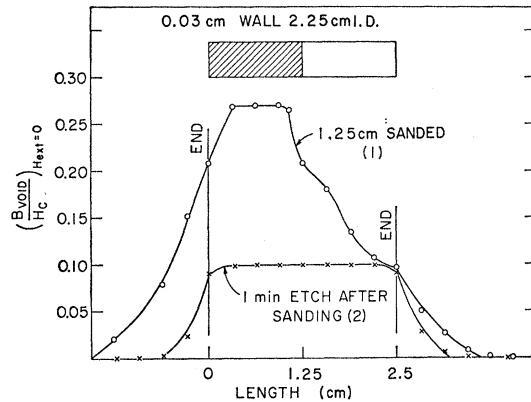


FIG. 13. Distribution for 2.5-cm end (cut from sample used for Fig. 10) before and after etching.

critical field, although in thin-walled etched cylinders the magnitude can be less than $H_c$. At some temperature determined by the radial dimensions of the cylinder, the enhancement ceases. Upon further cooling the field in the void remains constant. The changes occurring when the temperature is subsequently increased follow the same curves obtained during cooling.

When the external field is removed at a temperature below the transition temperature for the applied field, enhancement also occurs. The effect shows that the field lines pumped into the void come from a field retained by the wall in the superconducting state. Moreover, subsequent temperature cycling between the temperature at which the external field was removed and lower temperatures shows reversible increases and decreases of the field in the void in the absence of an external field. Representative data are shown for a machined Pb sample in an applied field in Fig. 14(a). In Fig. 14(b), the data shown were obtained from 10 cycles of heating and cooling a Sn cylinder between 2 and 1.0°K in the absence of an applied field after initially cooling from above $T_c$ to 2°K in an external field of 200 Oe. The same reversible effect was observed in In cylinders which were cycled between 2.0 and 1°K for 15 cycles. The In cyclinders were cooled from 4.2°K in a field of 160 Oe. At 2°K ($H_c \sim 175$ Oe) the external field was removed. Subsequent cooling and heating between 2 and 1°K showed spontaneous reversible increases and decreases of the field in the void. The effect of etching and other surface treatments result in only small changes in the thick-walled samples The data will be described in a detailed paper on the enhancement properties.

## IV. DISCUSSION

As a first approximation, the surface and interface energy terms $(A\sigma)$ associated with polycrystalline metals are expected to be the same in both the normal and superconducting states. The terms will cancel



FIG. 12. Distribution for 1.25-cm sanded end (cut from sample used for Fig. 10) before and after etching.

[8] T. I. Smith and H. E. Rohrschach, Jr., Rev. Mod. Phys. **36**, 277 (1964).
[9] R. I. Gayley and E. F. Young, Phys. Letters **20**, 104 (1966).

when properties determined by the free-energy differ-ence between the normal and superconducting states are considered. However, if the magnetic induction in the superconducting state changes these energies relative to the normal state, then the thermodynamic state function for the superconducting state contains a term in $A\sigma$ not common to the normal state:

$$G^s = U - TS - HM + [A_s\sigma_s + \sum_i A_i\sigma_i]. \quad (1)$$

The terms $\sigma_s$ and $\sigma_i$ denote the changes in surface free energies due to the magnetic induction in the geo-metric surface ($\sigma_s$) and interface surface ($\sigma_i$) energies. These changes can be larger or smaller than the ori-ginal normal-state surface energies. The areas $A_s$ and $A_i$ are only those surface and interface areas associated with the surface energies that change due to the mag-netic induction in the superconducting state. When included in the thermodynamic-state function the $A\sigma$ terms are normalized and have units of energy per unit volume. In conventional systems where the mag-nitude of free-energy changes is typically $10^2$ cal/gm, the surface contributions to the total free-energy changes can be neglected. In the superconducting case where the stabilizing free energy relative to the normal state is the order of $10^{-3}$–$10^{-4}$ cal/gm the surface terms play a greater role. The surface and interface energies can be treated as independent variables since they can be changed by varying the geometry and poly-crystalline nature of the sample. These terms then become the magnetic analog of the chemical potential term $\mu N$ which defines the thermodynamic-state function of a conventional two-component system. In the superconductor the magnetic induction $B$ corre-sponds to the second component concentration $N$. Define the volume average $\sigma_0$ of the changes in surface and interface energies due to the induction $B$ by

$$A_0\sigma_0(B) = A_s\sigma_s(B) + \sum_i A_i\sigma_i(B); \quad (2)$$

then

$$d(A_0\sigma_0)(B)_{H,T} = [\partial(A_s\sigma_s)/\partial B]_{H,T}dB$$

$$+ \sum[\partial(A_i\sigma_i)/dB]_{H,T}dB \quad (3)$$

and from (1)

$$(dG/dB)_{H,T} = [d(A_0\sigma_0)/dB]_{H,T} \quad (4)$$

or $(dG)_{H,T} = \mu_B dB$ where the magnetic potential

$$\mu_B = [d(A_0\sigma_0)/dB]_{H,T} = (dG/dB)_{H,T}$$

is defined analogously to the chemical potential $\mu_N = (dG/dN)_{P,T}$. The independent variable $A_0\sigma_0$ can be replaced by the magnetic induction since $A_0\sigma_0 = f(B)$. The thermodynamic definition of an independent variable $A_0\sigma_0$ with respect to the other independent

variables $H$ and $T$ is

$$[d(A_0\sigma_0)/dH]_T = 0 = [d(A_0\sigma_0)/dT]_H. \quad (5)$$

For functional dependences such as $A_0\sigma_0 = aB^n + c$, (5) reduces to

$$(dB/dH)_T = 0 = (dB/dT)_H \quad (6)$$

for both $B = 0$ and $B \neq 0$. The experimental properties of the hysteretic superconductors considered here satisfy this condition.[10]

## A. Unique and Nonunique States of Thermodynamic Equilibrium

At a given temperature and pressure a two-compo-nent phase has a unique equilibrium state only when a solubility limit exists. The unique state is defined when one component is in excess, or when two con-densed phases are present. Completely miscible solu-tions and undersaturated solutions do not have unique equilibrium configurations. They can exist in many states, all of which are time-stable and can exist in thermal or constrained equilibria. Constrained equi-librium is defined as the condition where the final state is not prevented from undergoing a spontaneous change by an activation energy or thermal barrier. There is no driving force to lower the Gibbs free energy. These states differ from the unique state in that their free energy must be lowered by a change in an independent concentration variable. In contrast to unique equi-librium states, the final configuration of a constrained equilibrium can be dependent upon the geometry and time involved in its formation process. The final con-centration of an undersaturated solution formed by flowing liquid over a salt bed is determined by the
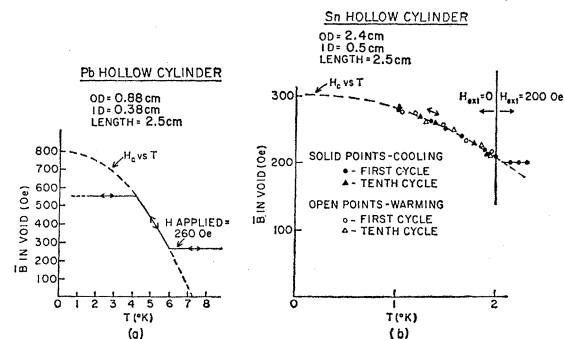


FIG. 14. (a) Reversible changes with temperature of field in the void of a Pb hollow cylinder in a constant applied field. (b) Reversible changes with temperature of field in the void and the wall of a Sn hollow cylinder in the absence of an external field. Initial state was formed by cooling from above $T_c$ to 2°K in an external field of 200 Oe. The external field was removed when the sample first reached 2°K.

[10] D. G. Schweitzer, Phys. Letters **24A**, 718 (1967).

flow rate, the length and width of the bed, the particle size of the salt, etc. Nevertheless, the final state, once formed, is stable. Similarly the heat and work associated with the formation of the state is a variable since the heat of solution is composition-dependent.

### B. Relations between Surfaces and Phases

The equilibrium condition for the coexistence of two phases of one component is that the Gibbs free energies of both phases are equal. When two components are present the free energies can differ at equilibrium. The equilibrium restriction is that the rate of change of free energy with a composition variable is the same for each component common to both phases. The generation of a new independent variable in thermodynamic systems formally permits the formation of a new phase. In a solid reversible type-I superconductor where the magnetic induction is not considered to be an independent variable the phase rule is given by $F = C - P + n$. At the phase boundary where the normal and superconducting phases are in equilibrium with the external field, the two magnetic components $(C)$ are the metal and the magnetic field. The three phases $(P)$ are the condensed normal and superconducting phases and the external or analogous pressure phase, the field. For the two independent variables $H$ and $T$, $n = 2$ when pressure-volume and electric field charge changes are neglected. Only one degree of freedom $(F)$ is permissible so that a unique curve exists in the critical-field–temperature plane. When surface energies are ignored, the London[3b] treatment for the thermodynamically stable superconducting state formed from the normal state in a field requires that the Meissner effect will not occur. In order to provide for a Meissner effect, an independent assumption must be made,[3b] that a positive surface energy exists between diamagnetic superconducting regions and regions in which field exists. In polycrystalline samples where the magnetic induction changes the intrinsic surface and interface energy terms in the superconducting state, the proposed positive surface energy between field-free regions and regions retaining field can be varied by different degrees in localized regions of varying grain size or varying surface energies. The new surface-energy terms represent an additional variable in the superconducting thermodynamic-state function and $n \rightarrow 3$. If no new phase is formed $F \rightarrow 2$ and the $H_c$-$T$ curve is no longer uniquely determined. The observation that the $H_c$-$T$ curve is the same in systems where the Meissner effect is incomplete, implies the existence of a new phase. Under this condition $P \rightarrow 4$ when $n \rightarrow 3$ and $F$ remains unity. When $H_c$ is not changed, the new two-component solution phase is considered to be in equilibrium with the original one-component diamagnetic phase which determines $H_c$.

For two superconducting condensed phases to coexist, there can be two distinguishable external field phases. Hollow cylinders or polycrystalline solids in which grains are surrounded by grain boundaries where the width of the grain boundary is larger than the coherence length of the superconducting solution phase provided appropriate geometries. The fields in the void represent the external phase with which the solution phase is in equilibrium. The diamagnetic phase is in equilibrium with the applied field. Solutions of different compositions have different equilibrium vapor pressures. In solids where differences in surface energies are localized and are the mechanism for solution formation, the variation of surface energies with position in the solids requires corresponding variations in the external field phase with position. Interactions between isolated regions of different surface energies can occur when the regions are in contact with a continuous external phase just as different solutions which are isolated in the condensed phase interact when they are enclosed in a single vapor phase. In the magnetic case the energy associated with the field is determined by both the square of its magnitude and, for a linear gradient in one dimension, by the square of the gradient with dimension. This allows a single total thermodynamic energy value to be associated with a multiplicity of distributions and field magnitudes. Alternatively such a field distribution is associated with a nonuniform distribution of electric currents. The appropriate thermodynamic energy is then not simply the kinetic-energy density of the current but will include possible entropy terms due to the nonuniform distribution. In the vacuum the field energy is the thermodynamic energy or activity just as in conventional systems the vapor pressure is the activity or fugacity. In the condensed phase the magnitude of the field-energy change is not reflected with a 1:1 correspondence in the Gibbs free-energy change. The distributions are associated with different internal energies and entropies required by phase concepts. Two-component solutions in which one component is common to both the condensed and vapor phase exhibit specialized reversibility relations when cycled with temperature. The component in the vapor exchanges reversibly between the condensed and vapor phase in a similar manner to which the field in the void and in the wall of a hollow cylinder exchanges reversibly when cycled with temperature. In a conventional system the vapor phase has mass and is required to satisfy a second equilibrium by establishing a pressure gradient in a gravitational field. In an open system, this second equilibrium along with Brownian motion are driving forces which cause the vapor component to leak out. In the superconductor where the magnetic field is the external phase there is no second equilibrium associated with the property of mass nor is there Brownian motion which is associated with mass which serve as driving forces to cause the field to leak out of an open hollow cylinder.

The absence of unique equilibrium states in poly-crystalline metals in which the solubility of materials such as carbon or nitrogen is changed by surface energies has been discussed by Swalin.[11] In such systems there is no unique solubility limit. Macroscopic samples have no predetermined unique equilibrium state but represent the summation of total properties determined by the localized equilibria conditions for the individual grains. A multiplicity of thermodynamically equivalent equilibrium states allows for a dependence on treatment prehistory. There also is a correspondence between surfaces and phases in liquids. In solutions the surface energy is changed by the addition of solute. The equilibrium condition obtained from the Gibbs equation for solutions is one in which the solute concentration in the surface region differs from the uniform bulk concentration. The difference is restricted by the requirement that the chemical potential is a constant throughout. In the surface region where a concentration gradient exists and $N$ varies the equilibrium condition is $\mu = $const and $d\mu \mid dN = 0$ or $dG/dN = $const and $d^2G/dN^2 = 0$. These same conditions are required for a phase separation.[12] The region in which gradients exist under equilibrium conditions can be considered a region of coexistence of two-dimensional phases where the fiducial energies and free energies can differ but where the rate of change of free energy with composition $(\mu_N)$ is constant. In the superconductor, the maximum permissible gradient in $B$ also corresponds to a circulating current which determines $J_c$ even under equilibrium conditions. In conventional two-component phase equilibria the differential form of the thermodynamic function at equilibrium leads to the reversibility relations $\sum N d\mu \neq 0$ and $\sum \mu dN = 0$. The latter condition results from the requirement that no change in total mass results when a component transfers from one phase to another. In the superconductor the analogous terms are $\sum A d\sigma$ and $\sum \sigma dA$. If the area terms were the actual physical areas associated with a particular sample the $\sum \sigma dA$ would vanish under appropriate conditions. However, the area terms apply to the areas where the induction changes the surface energies and the $\sum \sigma dA$ need not vanish. This difference leads to formal differences in the reversibility relations between the two types of systems. In some cases, localized equilibrium conditions are reflected in different macroscopic changes that are reversible and in some cases the macroscopic changes are hysteretic. In the experiments shown in Fig. 14, temperature changes cause a reversible redistribution of field between the wall and the void. The localized reversibility condition for the wall is $dB/dT \neq 0$ and for the void is $dB/dT \neq 0$. Magnetization measure-

ments for the total system (wall+void) show that the reversibility condition is $dB/dT = 0$. Hysteretic behavior results from a coupling of the $\sigma$ and $A$ terms on a local scale, which results in a coupling of $H$ and $B$ on a macroscopic scale. In conventional systems, the parameters $\sigma$ and $A$ are independent. In the explanation given here, the two terms are coupled. The pertinent are terms for the thermodynamic state function are only those areas in which the magnetic induction changes the surface energies. Both the $A$ and $\sigma$ terms depend on $B$. The regions in which the $A\sigma$ terms vary with $B$ are in equilibrium with the diamagnetic phase. A change in applied field changes the free energy of the diamagnetic phase. The diamagnetic phase is in equilibrium with the solution phase. The free-energy change in the diamagnetic phase due to a change in $H$ requires a corresponding change in free energy of the solution phase. This change can be reflected experimentally through a change in magnitude of $B$, through a change in distribution of $B$, or through a change in both. When the free-energy change due to a change in $H$ can be satisfied by a change in distribution of $B$, the average measured value of $B$ remains constant and the induction behaves like an independent variable, i.e., the changes are reversible with $H$. When the free-energy change due to a change in $H$ requires a change in magnitude of $B$, $B$ is coupled to $H$ and varies so as to keep the solution phase on the phase boundary with the diamagnetic phase. This coupling can lead to hysteretic behavior. To illustrate, consider an experimental artifact in which the coupling of the two variables $T$ and $P$ leads to analogous hysteretic behavior in a conventional equilibrium process. Figure 15 represents a plane in which the ordinate is the total volume for a mass of water in equilibrium with ice. The abscissa is a coordinate $X$, in which the pressure is coupled to the temperature in the following manner. In the temperature interval where ice and water can coexist under different external pressures, the temperatures of the ice-water equilibria are converted to voltages through
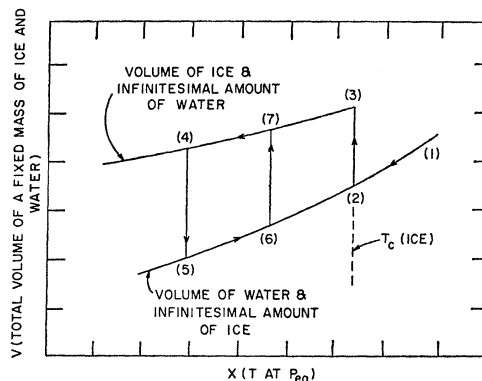


FIG. 15. Hysteretic behavior exhibited by equilibrium changes in the water-ice system when the equilibrium pressure is coupled to the independent temperature variable.

[11] R. A. Swalin, *Thermodynamics of Solids* (John Wiley & Sons, Inc., New York, 1962), p. 143–148.
[12] G. S. Rushbrooke, *Introduction to Statistical Mechanics* (Oxford University Press, New York, 1951), p. 327–329.

a thermocouple. Each voltage reading is programmed through a transducer to correspond to a specific pressure applied by a piston. The pressure at each temperature is exactly the pressure required to maintain ice and water at equilibrium. The broken line in Fig. 15 is the critical temperature of ice. Ice cannot exist above $T_c$ under any value of applied pressure. A temperature variation below $T_c$ is associated with a simultaneous predetermined pressure change. The coordinate $X$ is single-valued with respect to both $T$ and $P$. The cooling path from point (1) to (2) occurs in a temperature region where only water can exist. At point (2) ice and water can coexist. Any attempt to cool the system by removing heat leads to an isothermal phase transition along the path $(2)\rightarrow(3)$. Further cooling to point (4) now occurs with simultaneous pressure changes. At point (4) the temperature process is reversed and heat is put into the system. Because the temperature is coupled to the equilibrium pressure the system is on the phase boundary and the phase transition is reversed. The heat introduced in the system first causes the ice to melt isothermally along path $(4)\rightarrow(5)$. As soon as all the ice has melted the first incremental increase in the temperature of the water causes the pressure to change to the appropriate equilibrium pressure for the new temperature. The system remains on the phase boundary to point (6). Subsequent reversal of the temperature changing process at point (6) leads to the isothermal transition from (6) to (7) and so on. Every point on each path in Fig. 15 is an equilibrium configuration. The system is hysteretic with respect to changes in the variable $X$. The hysteresis results from the condition that the independent variable $T$ is coupled to a second thermodynamic variable $P$. The boundary curves associated with the hysteretic cycles are the limiting phase-boundary curves for the variable volumes associated with a single equilibrium.

In this explanation, hysteresis is a phenomenon associated with the coexistence of different phases. It occurs when a thermodynamic variable is coupled to a second independent variable. In the superconductor, the second solution phase is field-induced and does not exist when the metal is cooled from above $T_c$ in the absence of a field. The free energy of the temperature-induced diamagnetic phase is changed in an applied field. The free energy of the solution phase is determined by the induction through localized mechanisms originating from surface and interface energy changes. When the two phases are in the equilibrium, the change in free energy in the diamagnetic phase due to an applied field change requires a corresponding change in free energy of the solution phase so that $B$ is coupled to $H$. A change in $H$ causes a change in $M$, the magnetic analog of the volume. This change is not reversible with $H$ when $B$ is coupled to $H$. The changes nevertheless correspond to different equilibrium configurations in the $M$-$H$ plane.

## V. PHYSICAL CONSIDERATIONS

The discussion pertinent to Fig. 15 is a specific example of how hysteresis originates from equilibrium properties in a conventional system. Thermodynamics has been applied to hysteretic superconductors in which the magnetic induction need not be uniformly distributed. This treatment assumes the surface and interface energies are changed by the magnetic induction. The nonuniform spatial distribution of a parameter that changes surface and interface energies is qualitatively, a general result arising from the *a priori* assumption of equilibrium in systems where surface and interface free-energy changes lower the free energy. In practice, normal metals will not be in thermodynamic equilibrium at very low temperatures. The state which corresponds to a minimum in the Gibbs free energy is one in which there is finite equilibrium concentration of defects. In a single crystal, the Gibbs free energy is lowered by the existence of defects due to the generation of distributional entropy. At finite temperatures, the lowest free-energy state is one in which the temperature entropy term due to defects produces the largest difference from the increase in internal energy due to the work necessary to form a specific concentration of the defects. The defects all have migration energies. When the normal metal is cooled, a temperature range is reached where the rate of movement of the defects becomes negligible. The excess concentration cannot anneal out. At the low temperatures associated with superconductivity, the immobile excess defects leave the normal state with a free energy above the minimum. In polycrystalline samples, the difference between the actual free energy and the hypothetical minimum free energy is even greater, because of the presence of excess interface energies. In a single-component system, the only method of lowering the free energy is through removal of the excess defects and interfaces. In a two-component system, there is an alternative. The formation of a solution results in a net lowering of the Gibbs free energy of the solution relative to the solute and matrix. If the matrix was originally metastable, the final solution need not be. The stability of the polycrystalline solution can be achieved by having the solute distribute itself in a nonuniform manner so that the excess defect and interface energies are cancelled by solute concentration differences. The distribution will depend upon the number of crystallites, their relative surface-to-volume ratios, and, since different crystallographic planes have different surfaces energies, the nature of the crystallographic orientation.

The Gibbs surface-equilibrium equation requires that the surface concentration of solute differs from the bulk concentration when the surface energy is altered by the solute. The conventional derivation of this equation treats the surface region as a plane where the

thickness is negligible. The thickness of the region over which the concentration gradient changes from the surface to bulk value is not obtained from simple macroscopic free-energy arguments. Independent assumptions must be made. In conventional systems where the bulk free energy of solution formation generally is about six orders of magnitude greater than the surface free-energy changes, the observable physical properties due to surfaces may be small. In the superconductor where the surface energy changes are closer in magnitude to the bulk free energy of formation of the superconducting state (condensation energy), the surface region over which the induction exhibits a gradient may be an appreciable fraction of the total volume. Any parameter which changes a surface or interface energy in principal permits the formation of a new phase. The thermodynamic properties identifying the surface-induced phases cover the regions in which the gradients exist. In contrast to conventional systems where the surface thermodynamic energies are determined solely by gradients in solute mass, a fixed value of the thermodynamic energy resulting from surface-energy changes due to the magnetic induction can be associated with different induction distributions. Using the information observed in the hollow-cylinder measurements, the gradients generated by surface strains are minimized or eliminated between the strains and only manifest themselves at the outer regions. This interaction implies that the local gradients which might be expected at the interfaces of the individual grains can be smeared without changing the total free energy. The internal induction distribution can be near uniform, with the resultant gradients manifesting themselves near the sample surfaces.

In analogy with conventional phase equilibria, the relative volumes of the bulk and surface-induced phases will depend upon the direction from which the two-phase equilibrium is approached. In a solid–liquid–phase equilibrium, the first equilibrium configuration will be solid with a small volume of liquid when the temperature of the pure solid phase is raised. In approaching the superconducting state from the normal state in a field, the first two-superconducting–phase equilibrium will correspond to the largest value of the induction relative to other configurations with the same Gibbs free energy. The relative volumes of two phases in equilibrium can be altered while maintaining the Gibbs free-energy constant by changing other thermodynamic parameters through latent heat and work terms. In a polycrystalline superconductor, the identification of these terms and the appropriate normalization of surface-to-volume energy changes depend upon a knowledge of the crystallite size distribution and interface-energy topography. Since such information generally is not available, the approach taken here is qualitative. In a superconductor, the magnetic induction also corresponds to a persistent current. It is possible to alternatively attribute the surface-energy changes to a surface persistent current. The two-superconducting–phase equilibrium can then be treated through direct free-energy arguments rather than through chemical potential concepts. Such an approach yields additional information about observable properties of the paths between the two superconducting phases and provides an alternative view of the irreversibility arising from equilibrium conditions. This treatment will be described in another paper.

## ACKNOWLEDGMENTS