TABLE I. Summary of results.

Resonance condition	$(h-G^2)/\sqrt{k_0}$	$(\sqrt{k_0})\mu_R$	$(\sqrt{k_0})\mu_2$	$(\sqrt{k_0})\mu_1$
μ_R max	−0.57771	6.31239	3.13269	−0.54473
μ_2 max	−0.55490	6.30266	3.13958	−0.42136
$\mu_1=0$	−0.49809	6.19846	3.09923	0

somewhat when the earlier expressions for the roots are substituted, better simplification occurs when

$$\mu=(2i)^{-1}[\sqrt{\mu_R}+i\sqrt{|\mu_L|}]^2$$
$$=(4\pi\sigma/i\omega)[Z^{(2)}(0)]^2$$

is calculated instead. We find

$$\mu\cong(ik_0)^{-1}\frac{t_1t_3[t_1+2(t_1t_3)^{\frac{1}{2}}+t_3]}{[t_1+(t_1t_3)^{\frac{1}{2}}+t_3]^2}.$$

On substituting the roots and neglecting k_0 compared to $\sqrt{k_0}$, this expression becomes

$$\mu\cong\frac{(h-G^2)+2(ik_0)^{\frac{1}{2}}}{[(h-G^2)+(ik_0)^{\frac{1}{2}}]^2}.$$

This is the AAR result for zero phenomenological damping expressed in terms of the present notation. The quantity k_0 equals $2\epsilon^2$ in the AR notation.

Finally, using the above expression we may investigate the various resonance conditions. Ament and Rado have already given the condition which makes $\mu_1=0$; in addition, the conditions for μ_R and μ_2 to reach their maximum values are of interest, together with the actual values of μ_R, μ_2, and μ_1 in the three cases. All these quantities may be expressed in terms of $\sqrt{k_0}$, and the desired results are summarized in Table I. In applying these results, it must be remembered that they are valid only when the AR approximations are well satisfied. Since one of these approximations requires that $\sqrt{k_0}\ll1$, the results in Table I may only be used when μ_R max and μ_2 max are of the order of 10^2 or greater.

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Trapped Flux in Impure Superconductive Tin*†

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We have measured the percentage of trapped flux in cylindrical tin samples containing antimony, bismuth, or indium, with particular regard to the effect of annealing. The flux was trapped by the application and removal of a large transverse magnetic field. Our results do not confirm Pippard's conclusion that a marked change in flux trapping behavior occurs at a critical concentration of impurity. Instead we find that all samples, whether of high- or of low-impurity concentration, follow the same behavior, namely, that the percentage of trapped flux rises steeply near the transition temperature, and that this rise decreases monotonically with annealing time. In all cases in which this rise is discernible its temperature dependence is linear with the function $(1-t^4)^{-\frac{1}{2}}$ up to $t\gtrsim0.98$, where $t=T/T_c$. We believe that the binary specimens used by us as well as those used by Pippard have a substructure of filaments of different concentration, which trap flux when the sample is insufficiently annealed. In support of this view we cite extensive metallurgical evidence for the existence of such a substructure, and a crude measurement on two of our annealed specimens which showed that the magnetic field needed to restore resistance was much higher than the threshold field of the bulk material, and that this transition was quite broad.

I. INTRODUCTION

WHEN a superconductive substance passes from the normal to the superconducting state in the presence of an external magnetic field, it becomes ideally a perfect diamagnetic, excluding the applied field entirely except in a thin surface layer. In practice, however, during the course of transition multiply-connected parts within the specimen may develop which have the general form of closed superconducting regions surrounding cores of normal metal. Such cores will have magnetic flux running through them. The perfect conductivity of the enclosing superconducting regions now makes it impossible for this flux to change. Thus the specimen retains a small magnetic moment proportional to the amount of flux trapped in this fashion even after the external field has been reduced to zero.

Although the phenomenon of flux trapping has been known since the first discovery of the diamagnetic nature of superconductors, the few studies of this effect

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† The measurements with annealing times up to about 30 days formed part of a dissertation submitted by one of us (J.I.B.) to the Graduate Faculty of Rutgers University in partial fulfillment of the requirements for the Ph.D. degree.

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have until recently been either fairly qualitative[1] or incidental to other magnetic studies.[2] The first to embark on a systematic and exclusive study of this phenomenon has been Pippard,[3] who measured the amount of flux trapped in monocrystalline Sn-In cylinders, to which a large transverse magnetic field had been applied and then removed, so that the specimens passed through the intermediate state in making the phase transition. As Pippard's aim was to determine the variation of trapped flux with indium concentration in as nearly homogeneous superconductors as possible, he studied the effect of annealing in several of his samples and found a general decrease of trapped flux with increasing annealing time. In one specimen there was an appreciable change even after 110 days of annealing, but on the whole Pippard believed that 20–30 days of annealing would produce a sufficiently uniform sample. He annealed most of his specimens for that length of time.

Pippard's detailed study of this series of tin-rich alloys established a certain regularity in their behavior. The amount of flux trapped increased with greater indium concentration, due, in all probability, to the inevitable decrease in the crystallographic perfection of the samples. Superimposed on this Pippard's results indicate a second effect, which he attributed to the nature of superconductivity. He found that for most specimens containing less than about 2.5% of indium by weight, the percentage of flux trapped (i.e., 100 times the actual magnetic moment of the sample after removal of the magnetic field divided by the maximum diamagnetic moment the sample can have at a given temperature), tended to zero at the transition temperature, T_c, whereas for greater indium concentrations this percentage rose rapidly near T_c, approaching a value of 30–50%. The critical concentration of indium at which this change of behavior seemed to occur corresponded to a ratio of the resistances

$$R_{\text{residual}}/R_{\text{ideal } 0°\text{C}} \simeq 0.145,$$

which in turn corresponds to a definite value of the electronic mean free path.

Pippard explained this effect on the basis of his concept of a range of coherence of the superconducting electrons.[4] He assumed that flux can be trapped only if the neighboring superconducting regions in the intermediate state coalesce at a few points to form multiply connected regions. Such coalescing is always possible near crystallographic flaws, so that one would expect a general increase in trapped flux with increasing indium concentration and hence decreasing crystal perfection. Pippard proposed that in addition to this, coalescence throughout the specimen occurs freely when the mean free path of the electrons becomes smaller than the penetration depth. According to this view there should be a critical concentration beyond which even flawless single crystals could trap a large amount of flux, particularly near the transition temperature.

The foregoing model of flux trapping differs in principle from the earlier explanations.[1,5] These attributed the trapping to the presence of small inhomogeneous regions in alloys having different superconductive properties than the bulk of the material.

A preliminary account of Pippard's work[6] led us to measure the amount of trapped flux in tin containing antimony and bismuth as well as indium, as part of a general investigation of the effect of impurities on the superconductive properties of tin. For if the apparent change in flux trapping behavior found by Pippard is indeed a mean free path effect, then a similar change in the percentage of trapped flux should occur in any tin-rich solid solution for which the resistance ratio exceeds the critical value of approximately 0.145. In addition we decided to investigate with somewhat greater care the effect of annealing on the amount of trapped flux. In particular, we extended the annealing time.

Our investigation has shown that the rise in the percentage of trapped flux near the transition temperature always appears initially, but then decreases with increasing annealing time in *all* samples, irrespective of their resistance ratio. In one specimen with a resistance ratio considerably larger than 0.145, the rise practically disappears after about 100 days of annealing. Since, in addition, the rise in trapped flux has the same temperature dependence for all samples, we conclude that within the range of concentrations studied there is no sudden change in flux trapping behavior, and hence no evidence for the appearance of free coalescence.

II. EXPERIMENTAL DETAILS

A. Preparation of Specimens

All metals used were obtained from Johnson-Matthey, Ltd. The tin was very pure (99.998%), while the bismuth, antimony, and indium were of somewhat lesser but adequate purity (99.99%). The metals were first melted in a vacuum, and kept molten for 24 hours before cooling. A portion of the alloy prepared in this way and the Pyrex specimen tubes were then placed in a large Pyrex tube which was evacuated. The metal was again melted, and the system was vibrated for half a day to remove any trapped gas bubbles. Helium gas was then used to force the melt into the specimen tubes, after which the samples were grown in an oven which produced a sharp temperature gradient over the length of the specimen. The temperature of the oven, initially slightly above the melting point of tin, was

[1] K. Mendelssohn, Proc. Roy. Soc. (London) **A152**, 36 (1935).
[2] J. W. Stout and L. Guttman, Phys. Rev. **88**, 703 (1952).
[3] A. B. Pippard, Trans. Roy. Soc. (London) **A248**, 97 (1955).
[4] A. B. Pippard, Physica **19**, 765 (1953).
[5] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), pp. 44 ff.
[6] A. B. Pippard, *Third International Conference on Low Temperature Physics and Chemistry* (Rice Institute, Houston, 1953).

then lowered slowly until the sample solidified. All the specimens used for the trapped flux measurements were approximately 4 mm in diameter and 9 cm long. Upon cooling, the Pyrex tubes were gently cracked from the specimens, after which the sample ends were cut carefully with a sharp blade and rounded off. The samples used had very bright surfaces, and consisted of a few large crystallites.

Before and between runs all samples were annealed *in vacuo* in an oven at about 185–190°C. The mixes were made from a temper alloy of known high concentration to which were added accurately weighed amounts of tin. In this fashion all quantities involved were large and could be weighed accurately, so that the concentrations were known with good precision. From each melt we cast both the large cylinder used for the flux trapping measurements, and several small cylinders, about 2 mm in diameter and 4 cm long, whose resistance ratio was measured. This ratio in all cases increased linearly with the calculated concentration, and, in the case of indium, agreed with Pippard's results. Moreover, we determined the resistance ratio of a few of the large cylindrical specimens, and found them to agree within experimental error with our measurements on the smaller specimens.

TABLE I. Characteristics of the specimens.

Sample	Impurity	Concent. (at. %)	$R_{\text{resid.}}{}^{a}/R_{\text{id. }0°\text{C}}$	Anneal. time (days)	Slope (arb. units)
1	Bi	1.55	0.130	6	16.5
				28	1.18
				106	0.64
2	In	2.14	0.120	0	23.6
				29	1.73
				163	0.45
3	Sb	1.85	0.120	0	32.2
				6	23.3
				31	17.2
				132	3.36
4	Bi	2.18	0.185	26	3.87
				37	3.06
				108	0.20
5	In	3.11	0.185	35	9.1
				119	3.75
6	Sb	2.89	0.185	0	17.8
				35	8.1
				107	5.4
7	Bi	0.87	0.068	0	28.7
				130	0.29
8	Sb	0.97	0.066	0	10
				25	3.1
9	Sb	3.80	0.245	33	10.5
				109	6

[a] These resistance ratios were in each case calculated from measurements taken after maximum annealing time.

B. Apparatus and Procedure

The principal parts of the apparatus used to measure the trapped flux are shown in Fig. 1. The sample A is glued to a small brass holder C which in turn is secured in the center shaft D by a set screw. This shaft is a stainless steel tube which passes through the cryostat cap by means of a double O-ring seal F–F. The handle L is used to rotate the sample manually, stops K limiting this to 180°. The rectangular pickup coils B, shorter than the specimens to avoid end effects, are placed with their planes perpendicular to the applied field direction, and are attached to the fixed outer tube. Leads from these coils are passed continuously through the cap to avoid extraneous thermal emf's. Sealing wax in the narrow tube H provides the vacuum seal.

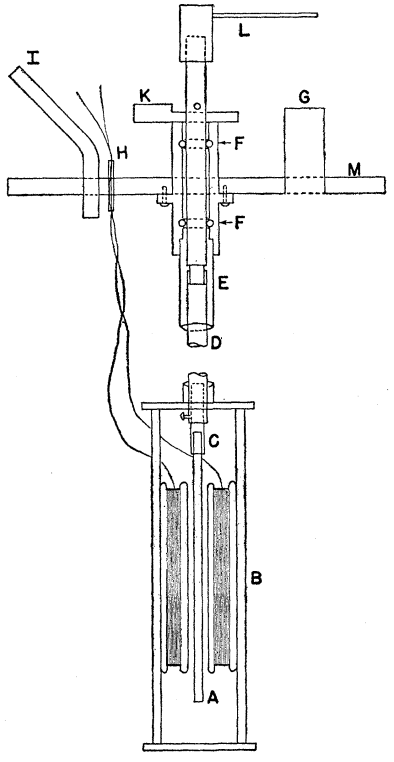

FIG. 1. Schematic diagram of the apparatus used to measure the trapped flux.

The magnetic moment of the sample after a high magnetic field has been applied and again removed is a measure of the trapped flux. It was obtained by observing with a ballistic galvanometer the emf generated in the coil B when the sample was rotated through 180°. The field was supplied by a pair of Helmholtz coils capable of producing a magnetic field up to about 275 oersted.

The Meissner effect in a superconducting lead cylinder was used to provide an absolute calibration of the apparatus. A cylinder of lead of very nearly the same diameter as the samples under investigation was withdrawn from the detecting coils in the presence of a known magnetic field considerably less than the threshold field of lead. This was repeated for various fields. From the known magnetic moment of the lead and the observed galvanometer deflection we calculated our sensitivity. In most of our early runs this was about 1.2×10^{-2} emu/cm^3 per mm of deflection; later we rewound B with more turns and achieved a sensitivity about ten times greater. The sensitivity of the galva-

nometer was checked from run to run by connecting it to the secondary of a fixed mutual inductance, passing known currents through the primary, and observing the resulting deflections.

To obtain the fraction of flux trapped, one must divide the measured magnetic moment per unit volume by $H_c(T)/4\pi$, the maximum moment the sample can have at any temperature T. For temperatures between T_c and $0.9T_c$, the critical field $H_c(T)$ can with a high degree of accuracy be considered to vary linearly with (T_c-T). Data obtained in an independent investigation at this laboratory[7] show that the slope of this variation is essentially the same for both pure and impure tin, and has a value of 147 oersteds/°K. For temperatures below $0.9T_c$, the value of $H_c(T)$ was calculated by using an analytical expression for $h(t)=H_c(t)/H_c(0)$,[8] where $t=T/T_c$; $H_c(0)$ was taken to be 306 oersteds for all samples. Again this was justified by the results of the independent investigation just mentioned. In both temperature ranges the accuracy of the critical field values of course depends primarily on the precision with which the transition temperature of the sample was determined. In all cases in which this was important, T_c was determined by switching on a small current through a few turns of wire wound over the coils B, and observing the resulting galvanometer deflection. The mutual inductance between these turns and the coils B changes when the sample between the coils becomes superconducting, i.e., diamagnetic, so that the deflection changes. The value of T_c obtained in this fashion agreed well with the temperature at which the extrapolated magnetic moment of the sample vanished.

III. RESULTS

We measured the trapped flux in a large number of samples of tin containing varying amounts of antimony, bismuth, or indium in solid solutions. Their characteristics are listed in Table I. Figure 2 shows the effect of annealing on the percentage of trapped flux in samples

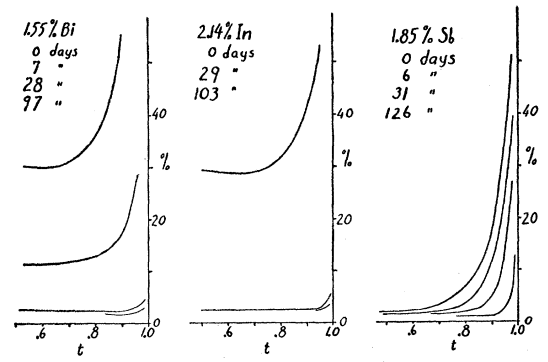

FIG. 2. Plots of the percentage of trapped flux as a function of $t=T/T_c$ for three samples after different annealing times. In each case, the ordinates decrease with increasing annealing time.

[7] Lynton, Serin, and Zucker (to be published).
[8] Serin, Reynolds, and Lohman, Phys. Rev. **86**, 162 (1952).

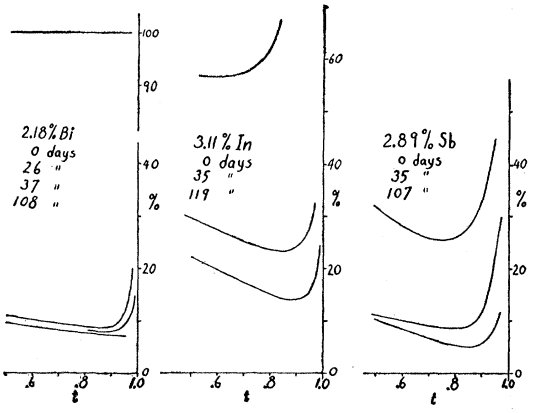

FIG. 3. Plots of the percentage of trapped flux as a function of $t=T/T_c$ for three samples after different annealing times. In each case the ordinates decrease with increasing annealing time. For the unannealed 2.18% Bi specimen, the percentage of trapped flux was taken to be 100 as the amount determined on the basis of the calculated threshold field was greater than this. This indicates a higher threshold field for the unannealed, highly inhomogeneous sample. After 26 days of annealing, the threshold field became essentially equal to that calculated.

1, 2, and 3, all of which have a resistance ratio well below, and hence an electronic mean free path much larger than that predicted by Pippard as critical. Figure 3 shows the percentage of trapped flux after different annealing times for samples 4, 5, and 6, all of which have a larger resistance ratio and therefore smaller electronic mean free path than the predicted critical value. For all these samples the annealing appears to have two results. At temperatures well below the transition temperature the initially very high percentage of trapped flux is reduced markedly after about 30 days of annealing, by which time it has in most cases reached a fairly stable behavior, little affected by further annealing. In all cases, the percentage of flux has a minimum value between $t=0.8$ and $t=0.9$, where $t=T/T_c$, and rises by a factor 1.2–1.4 as t decreases to 0.5. For samples 1, 2, and 3 this minimum value is about 1–3%; for samples of higher impurity concentration it is 6–14%.

The second effect of annealing is to reduce the rise in the percentage of trapped flux near the transition temperature. While this is most marked in the 1.85% Sb sample, the same effect occurs with all specimens: the longer one anneals, the smaller and less pronounced becomes the rise. In the case of the 2.18% Bi, the rise has virtually disappeared after 108 days of annealing. Since with all other samples the decrease of the rise is monotonic with annealing time, it appears that one can assume that it will vanish in all cases if only one anneals long enough.

Although this change near T_c shows up fairly clearly in the plots of the percentage of trapped flux *versus* reduced temperature, as shown in Figs. 2 and 3, we searched for a function against which the rise would appear linear, as this would simplify the evaluation of

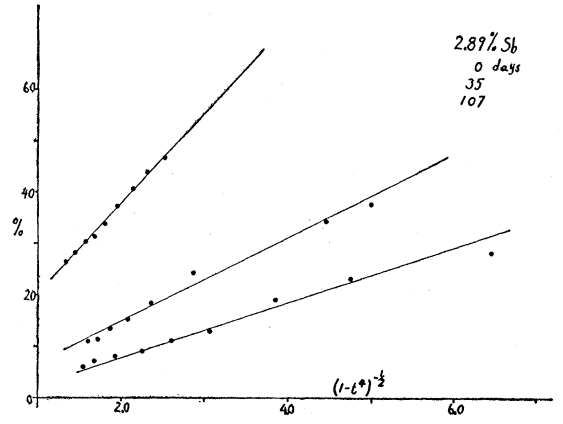

FIG. 4. Plots of the percentage of trapped flux as a function of $(1-t^4)^{-\frac{1}{2}}$ for the 2.89% Sb sample. The slopes of the lines decrease with increasing annealing time.

the sharpness of the rise, and perhaps give a clue as to the origin of the flux trapping. We found that for all samples the percentage of trapped flux varies linearly with the function $(1-t^4)^{-\frac{1}{2}}$ in the region between the start of the rise and $t \geqslant 0.98$. This result is illustrated for the 2.89% Sb sample in Fig. 4, in which the trapped flux is plotted as a function of $(1-t^4)^{-\frac{1}{2}}$ for different annealing times. It is evident from this figure that the slopes of the linear portions decrease monotonically with annealing time. This conclusion is supported by the slopes listed in Table I for the measurements on all of our remaining specimens. We also measured the slopes for those two of Pippard's specimens for which the trapped flux was displayed on a graph large enough to allow us to read off the values of percentage as a function of reduced temperature. For these samples also the trapped flux seemed to vary linearly with $(1-t^4)^{-\frac{1}{2}}$.

IV. DISCUSSION

In our opinion the fact mentioned in the preceding two sentences and the results contained in Table I indicate clearly that the rise in the percentage of trapped flux near T_c is due to the same causes for all specimens, regardless of their concentration of impurity. Thus, it appears that this rise in samples of both high and low electronic mean free path could be made to vanish in all cases after sufficient annealing, although this might take a very long time.

The flux trapping must, therefore, be mainly attributed to some persistent inhomogeneity in the specimens. There is much metallurgical evidence for the existence of inhomogeneities of concentration in binary alloys. It is well known that when a solution of two liquid metals is cooled at a finite rate, the resulting binary solid is in general inhomogeneous.[9] This comes about because for most systems there is a separation of the solidus and the liquidus, which means that at any given temperature the solid and the liquid phases do not have the same equilibrium concentration. A finite cooling rate then in general does not allow sufficient time for the solid and liquid phases to come into equilibrium as the temperature passes through the region of the phase diagram between the liquidus and the solidus. Most pertinent to our work are the recent studies of Rutter and Chalmers[10] and of Tiller and Rutter[11] on the detailed effects of growth conditions upon the solidification of dilute binary alloys of several metals, including tin. These authors found that when crystals of impure metals are grown under a wide variety of conditions, they tend to form a substructure. This structure develops essentially because of the lack of time for equilibrium to be established. It takes the form of fairly regular cells of bulk material (in some cases resembling a honeycomb) surrounded by *thin layers of material having a different impurity concentration* than the metal inside. The initial width of these layers is of the order of 10^{-4} cm. The substructures were observed by examining the growing surface of the solid, and even a cursory glance at the photographs obtained by these investigators reveals that we have here just the sort of inhomogeneous structure which can trap appreciable amounts of flux as a result of the layers becoming superconductive in fields higher than the critical field of the bulk.

Annealing in our specimens can only have the effect of making them more uniform, because the solubility of the solute metal is in all cases greater at the annealing temperature than at the solidification point. Furthermore, in the Sn-Bi system the eutectic temperature is lower than the annealing temperature. This view is supported by the direct observations of Rutter and Chalmers[10] of the homogenization by annealing of a lead crystal containing radioactive antimony. (The phase diagram of the Pb-Sb system is similar to those of the Sn-Bi and the Sn-Sb systems.)

In this connection we must also mention some relatively crude measurements we made to determine the magnetic fields necessary to restore the resistance of two of our specimens when they were superconducting. The specimens tested were No. 4 and No. 9, 2.18% Bi and 3.80% Sb, respectively, both of which had been annealed for more than 100 days. The magnetic field was applied longitudinally to the specimen axis, and the resistance along the axis was determined with a measuring current of 10 ma. In both cases the first trace of resistance did not appear until the applied field was about 1.5 times the calculated threshold value, and the full resistance was restored only after the field reached about $1.8H_c$. Earlier magnetic measurements on the 3.80% Sb specimen had indicated that the threshold field of the bulk

[9] See, e.g., G. E. Doan and E. M. Mahla, *Principles of Physical Metallurgy* (McGraw-Hill Book Company, Inc., New York, 1941), pp. 162–165.

[10] J. W. Rutter and B. Chalmers, Can. J. Phys. **31**, 15 (1953).

[11] W. A. Tiller and J. W. Rutter, Can. J. Phys. **34**, 96 (1956).

of the specimen was very close to the calculated value. Moreover, the ratio of the field necessary to restore completely the resistance of the 2.18% Bi sample to the bulk critical field showed a clear rise near the transition temperature, and the field values had roughly the same temperature dependence as the percentage of trapped flux. The 3.80% Sb sample showed indications of similar behavior.

In the interpretation of these observations (which are in general agreement with the more extensive results of Doidge[12] published after completion of our work), two features must be kept separate. The general increase of the field restoring resistance over the threshold field for the magnetic transition shows that the samples contain threads which remain superconducting in fields much larger than the critical value of the bulk material. The spread between the field value at which the resistance begins to appear, and that at which the resistance is fully restored, indicates that different threads have different critical fields, and that thus the specimen is still inhomogeneous even after prolonged annealing. We note, however, that although this is true for both specimens tested, only one of them (3.80% Sb) still showed a pronounced rise in the trapped flux near T_c. Thus it appears that whereas prolonged annealing still permits the appearance of superconducting threads in high fields, it does decrease and ultimately destroy the mechanism whereby these regions can retain flux. This change in behavior with annealing may come about because the migration or leakage of flux[3,13] out of the specimen becomes increasingly effective.

We must mention that even in our purest specimen we never observed the percentage of trapped flux to approach zero as T_c was approached. At best, it tended to a constant value. We believe that this is the result of our specimens being less perfect (in the sense that they contained a few crystallites and may have been slightly strained in handling) than those of Pippard's samples which contained very little impurity.

To summarize, it seems to us that the rise of the percentage of flux trapped near T_c is due to the existence of a substructure of inhomogeneities in the metal. Our measurements indicate that when diffusion during annealing broadens out this network and diminishes concentration gradients, the structure can still become superconductive at fields higher than the critical field of the bulk metal, but that near T_c it loses its ability to resist the leakage of any flux initially trapped. We offer no explanation of the mechanism involved when the flux is trapped, but we must note that the similarity of the temperature variation of the percentage of trapped flux to that of the surface energy parameter,[13] Δ, suggests that the latter may determine the resistance to flux leakage. Regardless of the details of the mechanism, however, we conclude that in sufficiently annealed samples there will be no rise in the percentage of trapped flux near T_c. Hence there is no direct evidence for the spontaneous coalescence of neighboring superconductive regions predicted by Pippard[3] for specimens of sufficiently low electronic mean free path. If such spontaneous coalescence does occur, its effect on flux trapping is rendered unobservable by the subsequent escape of the flux from the specimen when the external field is reduced.

It is clear that our interpretation of these experiments corresponds in many of its qualitative aspects to Mendelssohn's "sponge" model[1] of flux trapping in alloys. However, we are fairly convinced that the detailed mechanism whereby flux is trapped and its change with annealing can be understood only in terms of the ideas developed by Faber[13] and Pippard[3] concerning the role which surface energy plays in the phase transition, and the effect of impurities on this energy.

V. ACKNOWLEDGMENTS

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We are very grateful to Dr. A. B. Pippard for several discussions which helped greatly to clarify our understanding of the results. Two of us (E.A.L. and B.S.) are greatly indebted to Dr. A. L. Schawlow, Dr. H. W. Lewis, and Dr. B. T. Matthias for a most illuminating conversation.

One of us (J.I.B.) acknowledges most gratefully the award of a Socony-Mobil Graduate Fellowship for 1954–1955.

[12] P. R. Doidge, Trans. Roy. Soc. (London) **A248**, 553 (1956).
[13] T. E. Faber, Proc. Roy. Soc. (London) **A223**, 174 (1954).