G. J. Kahan
R. B. DeLano, Jr.
A. E. Brennemann
R. T. C. Tsui*

# Superconducting Tin Films of Low Residual Resistivity†

**Abstract: Evaporated tin films of low residual resistivity have been produced by using very high deposition rates in a conventional vacuum system. The substrates were cooled with liquid nitrogen. After the film edges are removed by mechanical trimming or chemical etching, these films show sharp magnetic and temperature transitions from the superconducting to the normal state, a critical field - temperature characteristic which is close to a modified version of the London theory, a transition temperature very close to the value of bulk tin, and a reversible resistance - critical current characteristic. These characteristics are compared with those of films deposited on substrates at room temperature using low deposition rates. Evidence is presented to indicate that the edge effect in the temperature transition of films is caused by a concentration of impurities in the edges. The low-temperature mean free path, rather than the resistivity ratio, is suggested as a figure of merit for estimating film purity because the size effect limits the resistivity ratio for thin films.**

Investigation into the operation of thin-film cryogenic devices is complicated by the problems of making thin films which have reproducible characteristics. The major characteristics of interest are the critical temperature, the critical field as a function of temperature and the sharpness of the magnetic transition from the superconducting to the normal state.

Very small amounts of absorbed gas can have an appreciable effect on the superconducting properties of bulk materials,[1] and one would expect that the superconducting properties of thin films would also be affected. Conventional evaporation procedures call for a vacuum in the range of $10^{-5}$ to $10^{-6}$ mm Hg, with an evaporation rate less than 1000 A/sec. Under these conditions, an appreciable percentage of the molecules striking the substrate during the film deposition are residual gas and, since many of the gas molecules will remain on the clean metal surface presented by the evaporated film, one expects these films to have a high percentage of impurities. The gas concentration can be reduced by improving the vacuum, by increasing the deposition rate, or both.

This paper discusses the effects on film purity and superconductive characteristics of increasing the deposition rate to several thousand angstroms per second. Special techniques will be described for preventing globules of the tin charge from flying out of the crucible. The accentuation of the edge effect by the evaporation techniques used to secure high deposition rates will also be discussed.

The resistance ratio of room temperature to liquid-helium temperature is generally used as a figure of merit in discussing purity of metals. Because the size effect limits this ratio in thin films, some other figure of merit is needed. Although the mean free path cannot be accurately determined at low temperatures, it is shown to be a better figure of merit than the resistivity ratio.

This paper covers work which has been in progress over the last two years.

## Experimental techniques

The films were evaporated in a conventional, bell-jar system evacuated by an oil-diffusion pump trapped with liquid nitrogen. The system pressure before evaporation was below $10^{-6}$ mm Hg. The tin was evaporated from a

* Now at Cornell University, Department of Engineering Physics, on leave of absence from IBM.
† This work was supported in part by the Department of Defense.

cylindrical tube furnace made of spectrographic grade graphite and heated by passing current through the tube. The tube was horizontal, and the charge was evaporated through a slot in the top of the tube.

During the course of the work the deposition rate has been increased from a few hundred to over 40,000 angstroms per second. These high rates have been achieved successfully by: (1) providing large amounts of power for the source, (2) using a source-to-substrate distance of less than two inches, (3) adding tantalum to the tin charge to prevent tin globules from flying out.

Power up to 6 kw was available for the source. This power will heat the graphite tube to a temperature of 1700° C as measured with an optical pyrometer. Radiation from the source was reduced by enclosing the graphite tube in a copper shield, which was water cooled. A water-cooled shield was also used between the source and the substrate during the outgassing procedure. The arrangement is shown in Fig. 1.

The addition of tantalum to the tin charge prevented globules from flying out of the source. Uneven deposition apparently had been caused by the formation of an oxide skin over the molten tin. The skin would burst when the internal pressure built up, and large molten particles would fly out. When the tantalum was used, the tin remaining after an evaporation was bright and shining; otherwise, it had a dull, dark coating. A chemical reaction probably took place between the tin oxide and the tantalum. One of the products of such a reaction would be tantalum oxide, which has a high vapor pressure and would evaporate.

The use of tantalum in the tin charge or a tantalum boat has found wide acceptance in this laboratory. Because tantalum boats deteriorate after a few evaporations when operating at the higher deposition rates, the use of a graphite crucible is indicated. The tantalum should be outgassed by heating in a vacuum if the evaporation is to be done at pressures much less than $10^{-6}$ mm Hg.[2]

The tin charge had a purity of 99.995% or better. The substrates were soda-lime glass microscope slides having contact areas of silver paint[3] along the side which come in contact with the evaporated film. The slides were cleaned by wiping with alcohol and firing at 600° C immediately before placing them in the evaporator.

The slides were supported in the evaporator on a copper plate on which a beryllium-copper mask was mounted. The mask-to-substrate distance was a few thousandths of an inch and was determined by the irregularities produced in welding the mask to the plate. The pattern of the mask was in the shape of a conventional four-terminal network having a distance between voltage leads of 0.17 inch and a width of 0.004 to 0.006 inch. The copper plate was attached to a chamber which was filled with liquid nitrogen during the evaporation. The substrate temperature was not measured because of the experimental difficulties associated with methods that would also account for the temperature rise caused by radiation.

Film deposition was carried out after the chamber pressure had dropped below $10^{-6}$ mm Hg. For films having low residual resistivity, a flow of liquid nitrogen was established through the substrate cooling box, and a good portion of the tin was evaporated from the source before the shutter was opened. This latter step was necessary to insure adequate outgassing of the source.

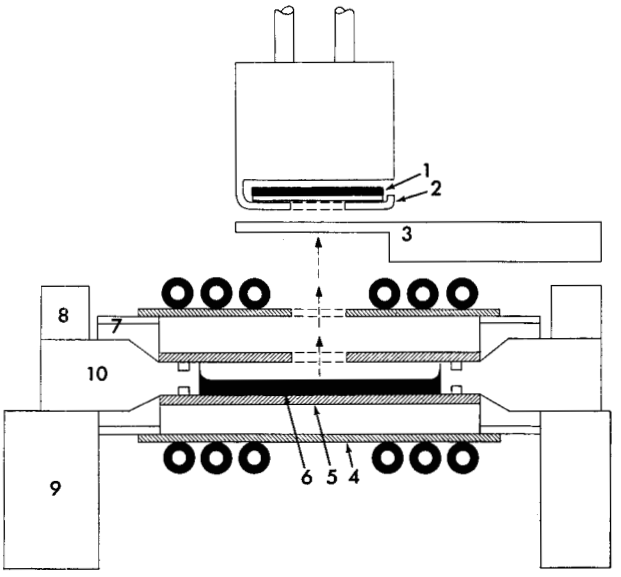



*Figure 1* **Arrangement of source and substrate for high deposition rates.**
*(1) liquid-nitrogen-cooled substrate; (2) mask and support; (3) water-cooled shutter; (4) water-cooled shield; (5) graphite crucible cylinder; (6) tin; (7) quartz insulator ring; (8) cooling block; (9) water-cooled electrode; (10) graphite crucible end.*

Films of high residual resistivity could be produced in the same equipment by reducing the deposition rate. Omitting the liquid-nitrogen cooling also gave high-residual-resistivity films, but the mechanism is not understood clearly.

After evaporation, the films were warmed to room temperature and removed from the evaporator. The room temperature resistance was measured, and the films were then immersed in liquid helium contained in a conventional double dewar for the low temperature measurements.

The temperature was varied by changing the pressure inside the liquid-helium dewar. Measurements were made as the temperature was decreased because of the long time required for the helium bath to come to equilibrium temperature after the pressure had been increased. The temperature was determined by using tabulated values of temperature as a function of vapor pressure. These measurements may be in error by 0.015 degree because of manometer errors; however, these inaccuracies do not affect the conclusions which have been drawn.

Thickness was determined for the first films by both optical interferometric means and geometric calculations

based on the room temperature resistance. The agreement between the two methods was fairly good, the worst error being less than 25% for a number of films. Good agreement was not expected, because the same resistivity was used for films having orders of magnitude difference in residual resistivity. Changes in structure may have also contributed to the error. The resistance method was used in later work because it was much easier and the films were frequently scratched by the optical flat. The resistivity used in these calculations was $11.8\times10^{-6}$ ohm-cm at 20° C.

The field coil was a two-layer solenoid with an additional layer at the end for compensation. The coil was placed over the helium dewar and immersed in the liquid nitrogen. A small coil having a known area and number of turns was used with a galvanometer to determine the field. This calibration had an accuracy of 2%. The sample was rotated in the field coil to insure alignment with the field.

Measurements of the temperature and field transition were made by passing a current through the outer terminals of the sample and measuring the voltage drop appearing across the center pair of terminals. The voltage was measured with a potentiometer (Leeds and Northrup, Type K3) using a breaker-type dc amplifier (Liston-Becker Model 14) as null indicator. Magnetic transition data were taken on an $x$ - $y$ recorder using another dc amplifier (L and N, Type 9835).

## Experimental results and discussion

- *Reversibility of current transition and film purity*

The critical current characteristic of a tin film produced in a conventional evaporator is shown in Figs. 2a and 2b. The curve in Fig. 2a shows the detail of the onset of resistance as the current is increased while the curve in Fig. 2b shows the over-all characteristic. The sensitivity of the voltage measurements for the curve in 2a was 1000 times that of 2b.

The curve in Fig. 2b shows the rapid increase of resistance and the hysteresis characteristic of films having a large residual resistivity. Both of these effects result from the joule heating. As the current was increased past the critical point, there was a slow increase in resistivity, as shown in the curve of Fig. 2a. This increased until a portion of the film became warm. This heating caused the normal area to spread rapidly,[4] and the increase in resistance was nearly discontinuous until the normal value of the film was reached. As the current was decreased, the heating kept the film normal until the current was below the critical value, when a sudden drop to zero resistance occurred. This phenomenon of hysteresis in current we have called *heat latching*.

The ratio of room-temperature resistance to liquid-helium temperature resistance for this film was 46. While such a ratio is frequently used to indicate the purity of bulk materials, it is not a good criterion for films because the maximum ratio is limited by the size effect. The resistivity of a film is composed of three components:

$$\rho_{\text{total}}=\rho_{\text{thermal}}+\rho_{\text{residual}}+\rho_{\text{thickness}} \quad (1)$$

where

$\rho_{\text{thermal}}$ = resistivity due to thermal lattice vibrations,
$\rho_{\text{residual}}$ = resistivity due to impurity and defect scattering,

and

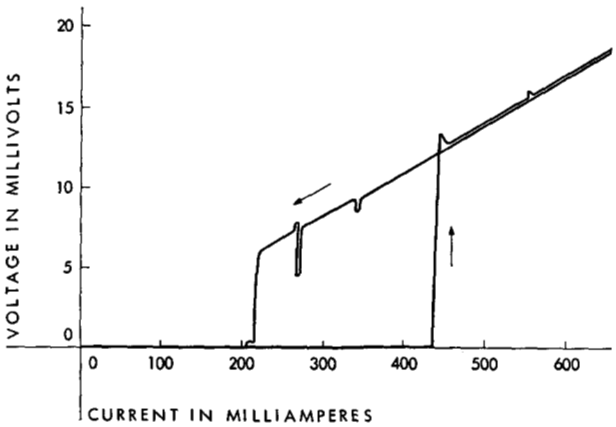
$\rho_{\text{thickness}}$ = resistivity due to electron scattering at the film surfaces.

At low temperatures the thermal resistivity becomes very small and, for thin films, the last term becomes much larger than the residual term. Consequently, the resistivity ratio is not a good figure of merit to be used in describing the purity of thin films.

The electron mean free path of the equivalent bulk material appears to be a better figure of merit for use with thin films having a small residual resistivity. Since this term is a bulk figure, it is independent of film thick-

*Figure 2a* **Hysteresis in critical current characteristics of film with high residual resistivity.**
*Film No. 12-16-58, width 0.030 in., thickness 2800 A, $R_{293}/R_{4.2}=46$, $T_c=3.82°K$. Bath temperature 3.605°K.*


*Figure 2b* **Experiment repeated at 1/1000 voltage sensitivity.**



ness. The formula which relates resistivity ratio and bulk electron mean free path is:

$$\frac{R^f_{293}}{R^f_{4.2}} = \frac{0.75t(\ln l^b_{4.2} - \ln t)}{l^b_{293}} \text{ for } l^b_{4.2} \gg t, \qquad (2)$$

where:

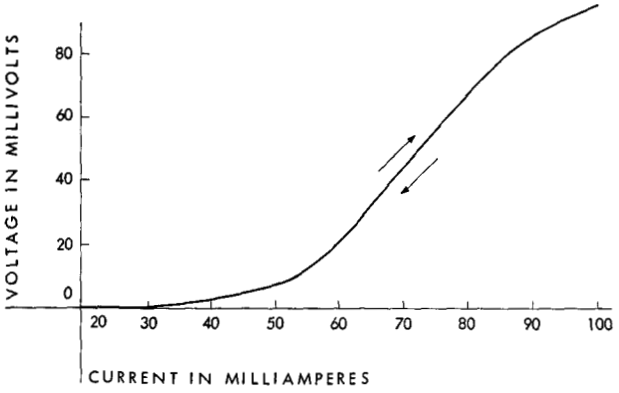
$R^f_{293}$ = resistance of film at 293°K,
$R^f_{4.2}$ = resistance of film at 4.2°K,
$t$ = film thickness in cm,
$l^b_{293}$ = bulk mean free path at 293°K $\approx 170 \times 10^{-8}$ cm, and
$l^b_{4.2}$ = bulk mean free path at 4.2°K.

This formula is based on Fuchs' formula[5] and is valid only where the bulk mean free path is much larger than the thickness, which is the case for the films considered in this paper. The formula is derived in Appendix A. The main disadvantage of the figure of merit is its sensitivity to film thickness. An error of 20% in a 5000-A film having a resistance ratio of 190 will change the computed mean free path by an order of magnitude. This sensitivity to thickness is to be expected because the main component of resistivity is that due to electron scattering at the film surfaces.

Since variations in residual resistivity can change the mean free path by more than four orders of magnitude, and since inaccuracies in film thickness should be less than 20%, the mean free path can be computed with sufficient accuracy to be used as a figure of merit. Further work is necessary before the computed values of mean free path can be considered as representative of the actual mean free path of the electrons.

The critical current characteristic of a film having low residual resistivity does not have hysteresis, as may be seen in Fig. 3. This film was deposited at a rate of over 3000 A/sec on a substrate which had been cooled to liquid-nitrogen temperature. The resistivity ratio for this film was 444, and the mean free path figure of merit was 1 cm, indicating that the film had very few imperfections. The mean free path figure of merit for the high-residual-resistivity film whose characteristics were shown in Fig. 2 was $1.1 \times 10^{-3}$ cm.

*Figure 3* **Critical current characteristics of film with low residual resistivity.**
*Film No. 49, width 0.0045 in., thickness 10,900 A, $L^b_{4.2} \sim 1$ cm. Bath temperature 3.60°K.*




### *Magnetic transitions and the edge effect*

The sloping edges[6] existing in the penumbra cause a broadening of the magnetic transition and an increase in the critical field of films made by evaporating through a mask. Since the critical field increases as the film thickness decreases, the center portion of the film becomes normal first and the measuring current is forced into the edges. No resistance is measured until the field is sufficient to drive the edges normal and the width of the transition is determined by the characteristics of the edges.

The low-residual-resistivity films had extremely wide transitions and high critical fields. A field of 600 oersteds was seldom sufficient to complete the transition when operating at 3.6°K. Removing the edges reduced the critical field by more than an order of magnitude, and produced sharp magnetic transitions.

After the edges were trimmed, the parallel critical field for films of both high and low resistivity varied with temperature in the expected manner. The variation of critical field is plotted in Fig. 4 as a function of the square of the reduced temperature for a low- and a high-residual-resistivity film. The characteristics of these films are discussed in more detail in the next section. The solid curves are obtained by applying corrections to the bulk values appearing in Shoenberg.[7] Derived by the use of London's theory, these corrections are discussed in Appendix B.

Films that were made with a large substrate-to-source distance do not have as wide a penumbra as those made with the short distance used in obtaining high deposition rates. Consequently, the reduction in critical field obtained by removing the edges is not as large for the former group. Critical field data for such a film before trimming are also shown in Fig. 4.

The removal of edges has been shown to be so important in considering the characteristics of evaporated films that it is a standard technique in this laboratory. A later section reports on the use of etching, as well as mechanical trimming, to remove edges.

Two techniques have been found for depositing films which are free from the edge effect. One is to deposit the film in a baked system at a vacuum of $10^{-9}$ mm Hg.[8] The other method is to use a heated substrate in a more conventional system.[9] In both cases the edges of the film are composed of particles which are not electrically continuous. The transitions of films having this type of edge are as sharp as films whose edges have been removed.

A hysteresis effect has been noted in the magnetic transitions of good tin films which do not have the edge effect. Since films which have hysteresis have been produced by several techniques, the actual method of production is not critical. The width of the hysteresis can be a large fraction of the critical field; moreover, the hys-

teresis is reproducible and the points on the side of the loop are stable. Hysteresis effects have been observed before, and have been explained on the basis of supercooling.[10] In those cases, however, the intermediate supercooled state was not stable, whereas the intermediate state was stable for these films.

- *Temperature transitions and the edge effect*

The critical temperature transition for a film of low residual resistivity was very broad, as shown in Fig. 5a. In addition, the transition shifted toward lower temperatures as the current was increased.

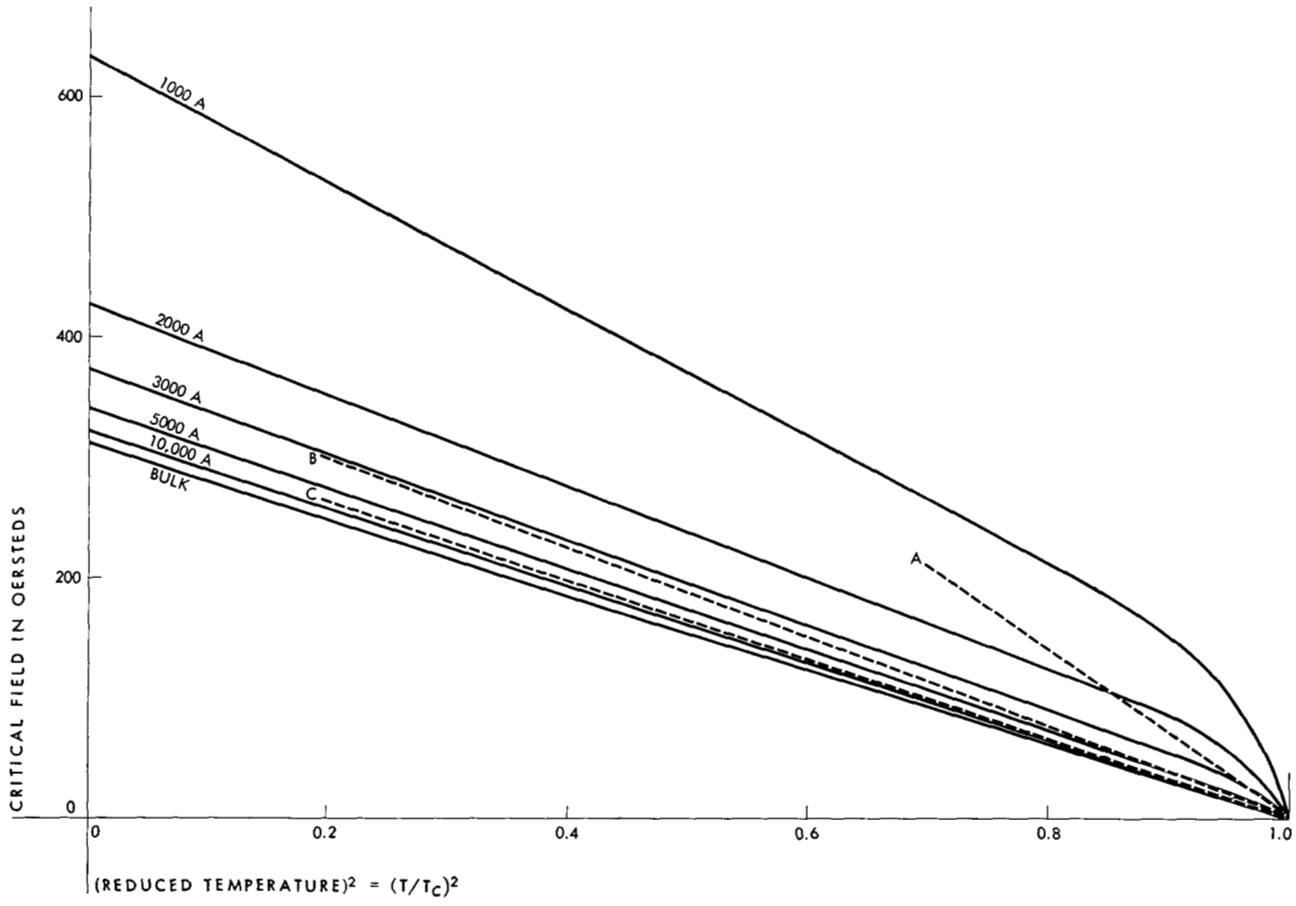
If a portion of the edges was removed mechanically, part of the temperature transition was much narrower. With both edges removed for the whole length, the transitions became quite narrow, as shown in Fig. 5b. The shift with measuring current also became much less, and the transitions for the smaller values of current occurred at a lower temperature.

The lowering of the small current-transition temperature as the edge was removed indicated that the current originally flowed mostly in the edges. This is to be expected if the edges have a higher critical temperature and become normal last. The change in transition temperature indicated that the edges contained a large number of imperfections, since changes in thickness do not affect the transition temperature although they do affect the critical field. This will be discussed more fully in later sections.

The width of the transition, after trimming, compares favorably with transition widths obtained by other workers for bulk materials. The width of the 100-$\mu$a transition from 10 to 90% resistance is 13 millidegrees. For nearly single-crystal tin, Aziz and Baird report a transition width of 3 millidegrees, and for tin having a grain size of 10 mm, they report a width of 18 millidegrees.[11]

A small edge effect was also found in the temperature transitions of tin films produced by more conventional techniques. Figure 6 shows the transitions, before and after trimming, for a film produced by the usual techniques. A reduction in the transition temperature upon trimming has been found with all films.

*Figure 4* **Critical field data.**
*Solid lines, theoretical values for various film thicknesses and for bulk material. Broken lines, experimental data. (A) Film No. 10-7-58 before removal of edges (thickness 3800 A). (B) Film No. 10-7-58 after removal of edges. (C) Film No. 52 after removal of edges (thickness 9570 A.)*



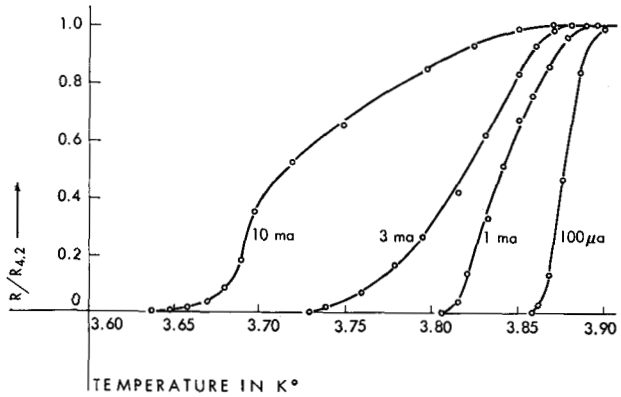



*Figure 5a* **Temperature transitions for a film of low residual resistivity with varying measuring currents.**
*Film No. 52, width 0.0045 in., thickness 9570 A, $R_{293}/R_{4.2}=382$, $L^{B}_{4.2}\sim 0.09$ cm.*

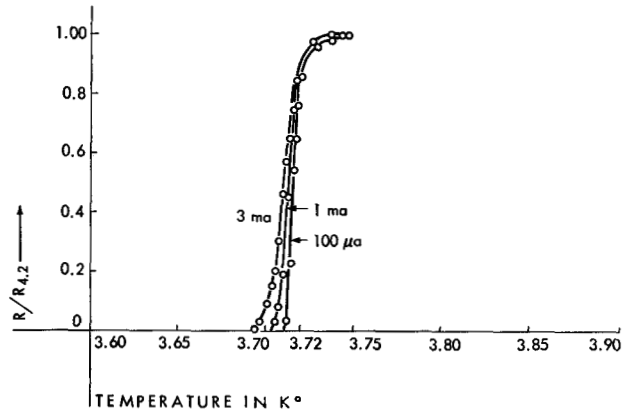



*Figure 5b* **Temperature transitions of Film No. 52 after edges were removed.**

The mean free path figure of merit for this film was $3.7\times10^{-4}$ cm and the resistivity ratio was 38. The transition width was 4.5 millidegrees. Comparing this width to that obtained for the previous film showed that the transition width was not a function of film purity. Annealing and etching evidence presented later shows that width is a function of homogeneity.

Most films deposited in a conventional system do not have transitions as sharp as the one shown in Fig. 5. This film was chosen to demonstrate that a narrow transition does not indicate that the film has a low residual resistivity.

Most films evaporated in a conventional evaporator on glass substrates have a critical temperature considerably above that for bulk tin. This was shown by Lock to be caused by the difference in thermal expansion bebetween the film and the substrate.[12] Further work must be done to determine why the films deposited at high rates have a critical temperature so close to the value for bulk tin.

The critical current appeared to be a linear function of temperature, after the films were trimmed, over the limited temperature range covered by the measurements. The current required to restore a given percentage of the normal resistance before and after removing the edges is shown in Fig. 7. Critical-current transitions are given by lines parallel to the ordinate, and critical-temperature transitions are the intercepts on horizontal lines.

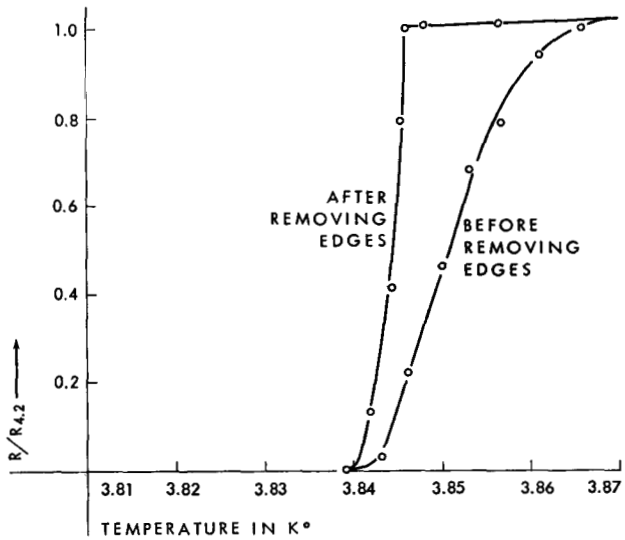
The width of the critical-current transition increased as the temperature was lowered. If heat latching does occur in these films, it must be at a much lower temperature than 3.2°K since the transition width is still increasing at this temperature.

• *Annealing studies*

Before the edge effect was understood, the results of annealing films were difficult to interpret. The residual resistance would decrease by as much as a factor of five, but the transitions did not improve. Sometimes they became worse. The reduction in residual resistance showed that there was a decrease in impurities or defects in the film, while the broadening of the transition indicated that the film was becoming less homogeneous.

When the transition for a film was studied in greater detail, the critical temperature, measured with a large current, increased as a result of annealing, while the small-current value of critical temperature decreased. This is shown in Fig. 8a for a film having a large value of residual resistivity. Since the transitions at small measuring current are characteristic of the film edges, the

*Figure 6* **Temperature transitions of film with high residual resistivity before and after removal of edges.**
*Film No. 10-7-58, thickness 3800 A, $R_{293}/R_{4.2}=38$, $T_c=3.844$ $L^{b}_{4.2}\sim 3.7\times10^{-4}$ cm, $I_m=100\mu a$.*



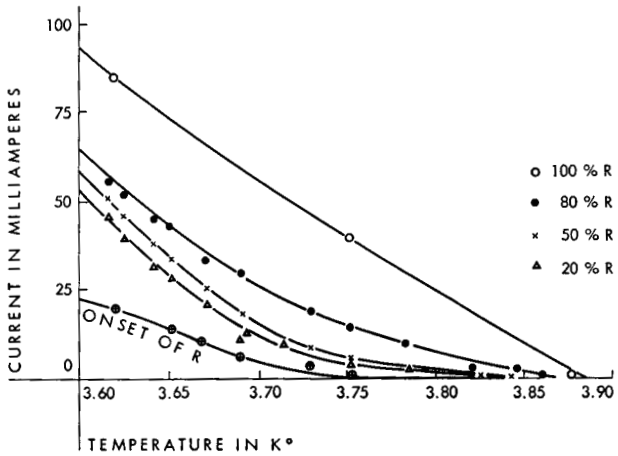



*Figure 7a* **Critical current vs temperature for film with few imperfections before removal of edges.**
*(Film No. 52.)*

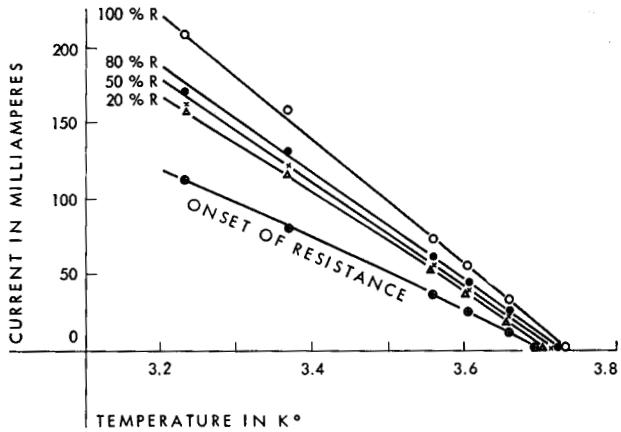



*Figure 7b* **Critical current vs temperature for film with few imperfections after removal of edges.**
*(Film No. 52.)*

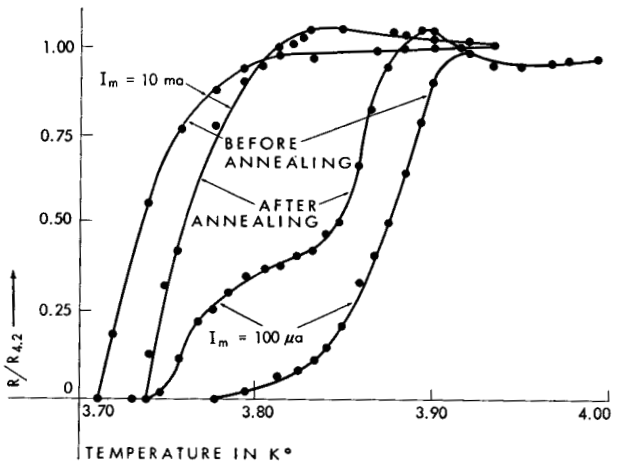
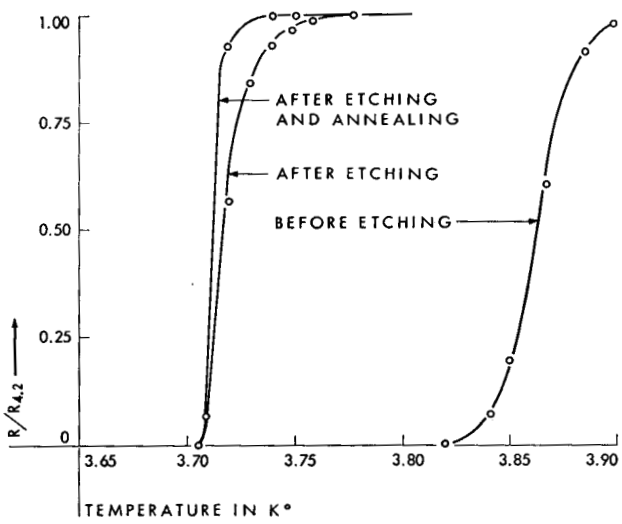
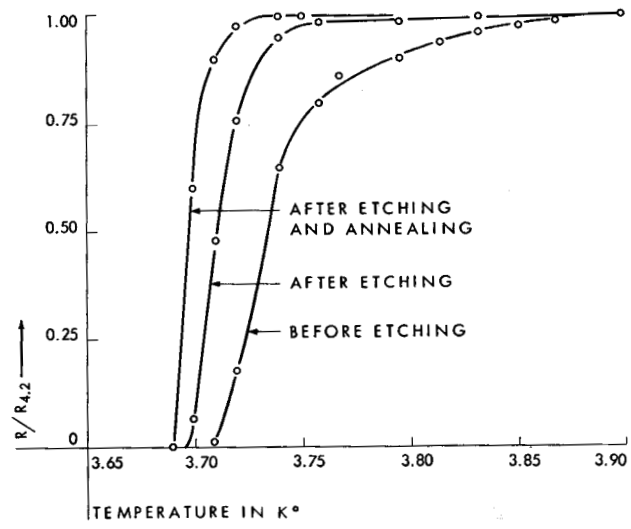



*Figure 8a* **Effect of annealing on temperature transitions when edges are not removed.**
*Film No. 320, thickness 28,000 A, $R_{293}/R_{4.2}=38$ before anneal, $R_{293}/R_{4.2}=163$ after anneal, annealed 3 hours at 400°F. in $H_2$.*

*Figure 8b* **Effect of etching and annealing on temperature transitions.**
*Film No. 342, thickness 85,000 A before etch, thickness 79,000 A after etch, $R_{293}/R_{4.2}=350$ before anneal, $R_{293}/R_{4.2}=390$ after anneal, annealed 4 hours at 205°C in $H_2$, measuring current 100μa etched in 0.1% hydrofluoric, 0.1% nitric acid in glycerin.*

*Figure 8c* **Temperature transitions at higher measuring currents.**
*Film No. 342, measuring current at 10 ma.*



lowering of the transition temperature seen at small measuring current indicated that annealing removed some of the impurities in the edges.

The transition for a large measuring current occurred at a higher temperature after annealing. The superconductive current-carrying capacity of the edges had been decreased during the annealing, as shown by the lowering of the critical temperature when measured with a small current. Consequently, the effect of the edges on the large current transition would have been to lower this transition. The fact that this transition occurred at a higher temperature indicated that perhaps the imperfections which were driven out of the edges diffused into the bulk of the film.

This conclusion was tested further by annealing a film after the edges had been removed by etching. Temperature transitions were taken for two values of measuring current with the film in each state, before etching, after etching, and after annealing in hydrogen. The results are shown in Figs. 8b and 8c.

The etching sharpened the transitions in a manner similar to a mechanical removal of the edge. The critical temperature of the transition, as measured with a small current, was lowered much more after etching than when measured with a large current. This is in accordance with the premises that (1) the concentration of imperfections is greatest in the edges; (2) etching proceeds faster in material having the largest number of imperfections; and (3) the transitions obtained with a small measuring current are characteristic of the edges of the film.

The most important fact gleaned from this investigation was that the transition temperature measured with a large current did not increase when the etched film was annealed, as it did when the film having edges was annealed. Similar results have been obtained with other films. The edges obviously had an effect on the rest of the film during the anneal, and it seems probable that this effect was caused by the diffusion of imperfections from the edges into the bulk of the film.

*Figure 9* **Etch pattern showing grain size and uniformity of film having a sharp transition. Magnification 250 ×.**

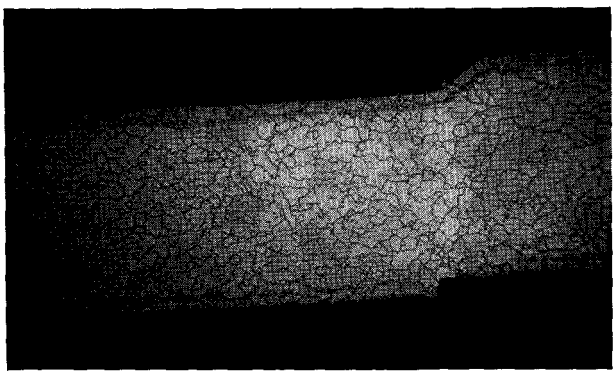


*Figure 10* **Etch pattern showing inhomogeneities in the structure of film having broad transition. Magnification 400 ×.**

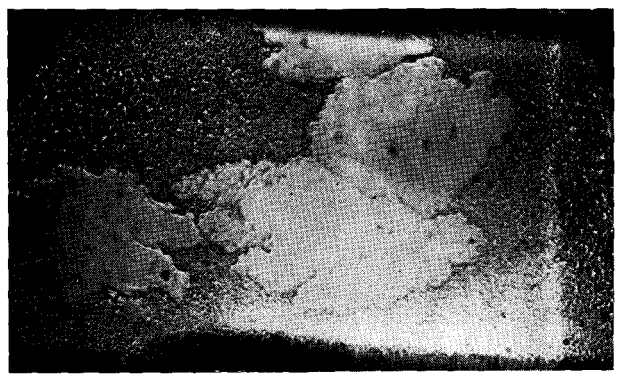


*Figure 11* **Etch pattern showing the fine grain structure of a film with high residual resistivity. Magnification 400 ×.**

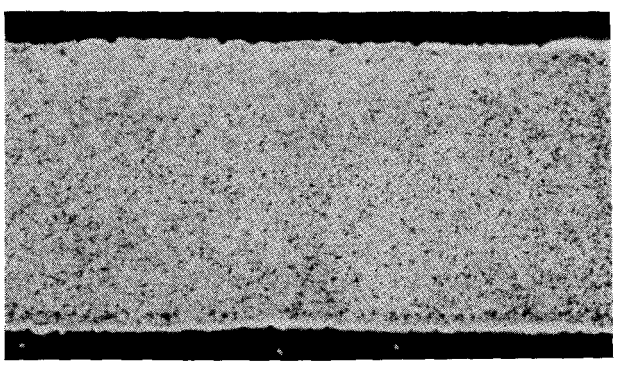
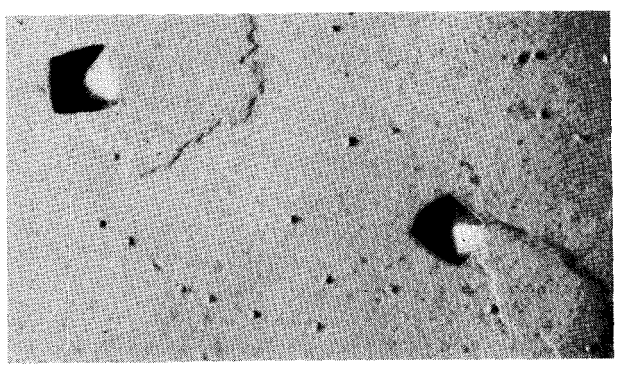


*Figure 12* **Etch pits in tin film with low residual resistivity. Magnification 1400 ×.**



• *Etching studies*

Examination of films after etching with a glycerin solution of nitric and hydrofluoric acids showed metallurgical characteristics which could be correlated with the superconductive behavior.

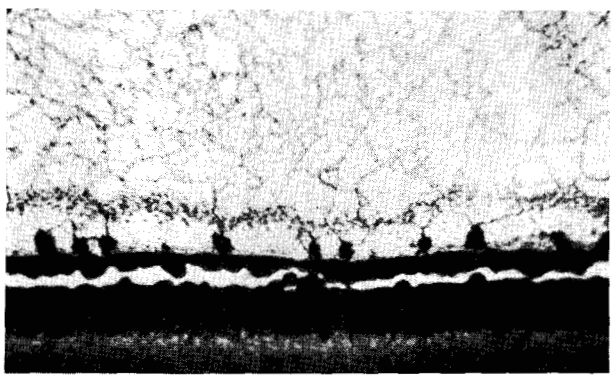
The difference in the grain structure of films having sharp transitions and those having broad transitions is shown respectively in Figs. 9 and 10. The structure of a film having high residual resistivity is shown in Fig. 11.

The low-residual-resistivity films showed a definite coarse grain structure and an average grain diameter somewhere between 5 and 25 microns. Upon etching with sulfuric acid in glycerin, etch pits were observed that had the shapes of octahedrons, as shown in Fig. 12. The concentration of the etch pits was less than $2\times10^7$ per square centimeter, providing further indication that the films were pure. All the etch pits have the same orientation within one grain with the (001) face approximately parallel to the glass substrate but with different grains having random rotation about this axis.

The films which had broad transitions lacked homogeneity, as shown in Fig. 10. This film had a transition width (10-90%) after etching of 80 millidegrees as compared to 26 millidegrees for the film of Fig. 9 and other low-residual-resistivity films. The films of high residual resistivity had a grain structure which was so fine as to be near the limit of optical resolution.

The manner in which the etching proceeded in the edges, as shown in Figs. 9 and 11, provided further proof that the edges had a greater concentration of imperfections than the rest of the film. As more of the edge was etched away, a ribbon of material was left, as shown in Fig. 13. No explanation has been found for the existence of this ribbon. Optical determinations of edge thickness showed a smooth variation with distance. The existence of the ribbon did prove that the preferential etching of the edges was caused by a difference in the film properties rather than in thickness.

*Figure 13* **Etch pattern of an edge showing ribbon left after most of edge has been removed. Magnification 500 ×.**



The large grain size and the orientation within the grains indicated that the atoms had a high degree of mobility after striking the substrate. Films deposited on cool substrates would be expected to have very small grain size. The films deposited at high deposition rates had a large grain size, and therefore the face of the substrate must have been quite warm to allow recrystallization. The techniques described in this paper for consistently producing films having low residual resistivity gave high-residual-resistivity films when single-crystal sapphire was used as the substrate. This material has a higher thermal conductivity, which prevents the surface from warming up. These factors point to the possibility that the concentration of impurities in the edge was caused by precipitation from a molten area.

## Conclusions

Films of tin having low residual resistivity can be deposited on glass substrates in vacuum systems having a pressure in the range of $10^{-7}$ to $10^{-6}$ mm Hg by cooling the substrates with liquid nitrogen and using high deposition rates. These films do not have sharper magnetic or temperature transitions than films produced in conventional systems, since the width of these transitions is a function of homogeneity rather than film purity. They do lack hysteresis in the critical current characteristic, and this may be useful in devices. Because of their high purity, they will also be useful in basic studies.

If films having sharp transitions and small values of critical field are desired, special techniques are necessary to eliminate the effects of the edges. These techniques can be applied as a part of the evaporation process, or the edges may be removed by trimming or etching after the films have been made. Precautions must be taken during the annealing of films to be used in superconducting work to be sure that the annealing makes the films more homogeneous.

This work shows that, in addition to the broadening of the magnetic transition caused by the sloping edges, imperfections can concentrate in the edges during the evaporation process and cause a broadening of the temperature transition. The concentration of imperfections in the edges is very pronounced when the deposition rate is high and the substrates are in contact with a surface cooled by liquid nitrogen.

## Appendix A: A figure of merit for evaluating film quality

The ratio of the room-temperature resistance to the liquid-helium temperature resistance is frequently used as a figure of merit for evaluating the purity of bulk materials. The room-temperature resistance is associated with scattering by lattice vibrations and the low-temperature resistance is determined by impurities and defects. If this ratio is to be used to evaluate purity alone, careful annealing is required to remove the defects.

As discussed in this paper, the resistivity ratio is not a good figure of merit for thin films because the low-

temperature resistance is largely determined by the resistivity due to electron scattering at the film surfaces. The resistivity ratio is plotted in Fig. 14 as a function of film thickness using the values of mean free path and resistivity obtained by Kunzler and Renton and the values obtained for a typical film deposited in a conventional evaporator.[13] These values were obtained using Sondheimer's tables[14] to obtain size-effect corrections for both the low-temperature and the room-temperature resistance. A resistance ratio of 25 could mean a relatively pure film that is 450 A thick or a rather impure film that is 3000 A thick, or appropriate values of purity and thickness in between.

The mean free path figure of merit will now be derived. The free electron gas theory gives the product of resistivity and mean free path as

$$\rho^b l^b = \frac{mv}{ne^2}, \tag{A1}$$

where

$n$=number of conduction electrons per cm$^3$,
$e$=electron charge,
$m$=electron mass,
$\rho^b$=bulk resistivity,
$l^b$=electron mean free path of bulk material, and
$v$=electron velocity.

From quantum mechanics, $v$ is a constant given by

$$\frac{1}{2}mv^2 = \frac{h^2}{2m}\left[\frac{3n}{8\pi}\right]^{2/3}. \tag{A2}$$

Substitution of this value for $v$ in Eq. (A1) gives

$$\rho^b l^b = \frac{h}{n^{2/3}e^2}\left(\frac{3}{8\pi}\right)^{1/3}. \tag{A3}$$

This equation shows that the product $\rho^b l^b$ is a constant independent of temperature, assuming that the number of conduction electrons remains the same. It has been determined to be $2.0\times10^{-11}$ for 99.996 tin and the ratio

$$\frac{\rho^b{}_{293}}{\rho^b{}_{4.2}} = 15.6\times10^3$$

has also been determined for the same tin.[15] If the value $11.8\times10^{-6}$ ohm-cm is used as the room temperature resistivity, then $l^b{}_{293}=170$ A, and $l^b{}_{4.2}=0.95\times10^{-2}$ cm. Fuchs' formula for determining the size effect with diffuse scattering at the surface is[16]

$$\frac{\rho^b{}_T}{\rho^f{}_T} = \frac{3t(\ln l^b - \ln t)}{4l^b} \qquad \text{for } l^b \gg t.$$

Now, for moderately thick films, we may place $\rho^b{}_{293}$ equal to $\rho^f{}_{293}$. Since the room-temperature mean free path is small, the resistance ratio then becomes

$$\frac{R_{293}}{R_{4.2}} = \frac{\rho^f{}_{293}}{\rho^f{}_{4.2}} = \frac{\rho^b{}_{293}/\rho^b{}_{4.2}}{\rho^f{}_{4.2}/\rho^b{}_{4.2}} = \frac{l^b{}_{4.2}/l^b{}_{293}}{(4/3)l^b{}_{4.2}/t[\ln l^b{}_{4.2} - \ln t]}$$

$$= \frac{3}{4}\frac{t[\ln l^b{}_{4.2} - \ln t]}{l^b{}_{293}}, \tag{A4}$$

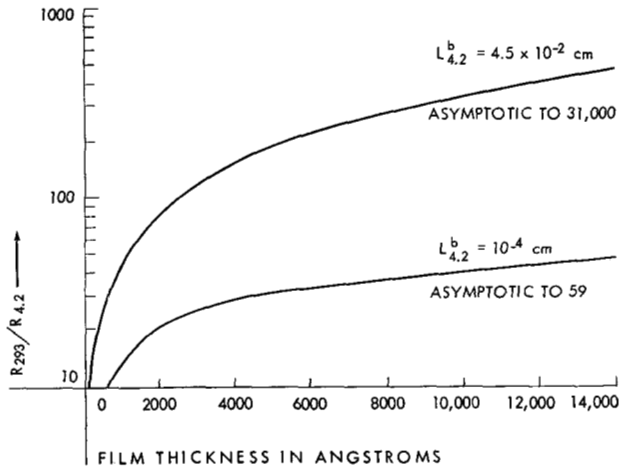



*Figure 14* **Theoretical changes in resistivity ratio as a function of thickness for two films of different purity.**

and values of the mean free path can be computed. For the case $t \gg l^b$, the value of $\rho^f/\rho^b = l + (3/8)l^b/t$ must be used to obtain the mean free path. For in between values the table in Sondheimer may be used. For films having a thickness comparable to the room-temperature mean free path (170 A) the size-effect correction must also be applied to the room-temperature resistance.

The use of the free electron gas model for tin has given reasonable values of the electron mean free path in Andrew's experiments and appears justified under these conditions for our purpose. It must be emphasized however, that the use of this model presumes conditions such as a constant number of electrons available for conduction from 4.2° to 293°K, which may not necessarily be fulfilled for tin.

## Appendix B: Critical field for thin tin films

The ratio of the critical field for a film to that for the bulk material may be computed from:[17]

$$\frac{h_f}{h_b} = \sqrt{\frac{1+(\alpha_n-\alpha_s)16\pi/dh^2{}_b}{1-(2/\beta d)\tanh(\beta d/2)}}, \tag{B1}$$

where

$\beta=1\lambda$,
$\lambda$=penetration depth,
$d$=film thickness,
$\alpha_n$, $\alpha_s$=normal and superconducting surface energy,
$h_f$=film critical field, and
$h_b$=bulk critical field.

Neglecting the difference in surface energy, this equation reduces to

$$\frac{h_f}{h_b} = \frac{1}{\sqrt{1-(2/\beta d)\tanh\beta d/2}}. \tag{B2}$$

The value $\beta$ may be obtained from the usual temperature relationship

$$\frac{\lambda}{\lambda_o} = \frac{1}{\sqrt{1-(T/T_c)^4}}, \tag{B3}$$

where $\lambda_o$=penetration depth at absolute zero.

A more recent relationship has been derived by Lewis using an energy gap model.[18] The ratio of the new values of $\lambda$ to those determined by Eq. (B3) are given in Fig. 4 of the Lewis paper. Equation (B2), together with the usual parabolic relationship for the bulk critical field of tin, was used to compute the critical field values shown in Fig. 4. The bulk critical field at absolute zero was taken to be 305 oersteds.


## Acknowledgments

We gratefully acknowledge the assistance given to us by other members of the Cryogenic Research Department in IBM Research, in particular the assistance given by Dr. D. R. Young through helpful discussions and suggestions, and the help of E. S. Spinaci and F. S. deCormier in film preparation.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*Received December 4, 1959*