

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

A STUDY OF THE SUPERCONDUCTIVITY OF METALS CONDENSED AT k-JK

### Permalink

<https://escholarship.org/uc/item/0h48k2pt>

### Author

Roberts, James Adams

### Publication Date

1970-06-01

c.2

**RECEIVED  
LAWRENCE  
RADIATION LABORATORY**

**JUL 21 1970**

**LIBRARY AND  
DOCUMENTS SECTION**

**A STUDY OF THE SUPERCONDUCTIVITY OF  
METALS CONDENSED AT 4°K**

James Adams Roberts, Jr.  
(M. S. Thesis)

June 1970

AEC Contract No. W-7405-eng-48

**TWO-WEEK LOAN COPY**

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 5545*

**LAWRENCE RADIATION LABORATORY**  
**UNIVERSITY of CALIFORNIA BERKELEY**

UCRL-19624

*cy J*

*g5*

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

## TABLE OF CONTENTS

ABSTRACT	
I. INTRODUCTION-----	1
II. EXPERIMENTAL-----	3
A. Review of Previous Results-----	3
B. Apparatus-----	7
C. Experimental Procedure-----	14
D. Results-----	17
III. CONCLUSIONS-----	23
ACKNOWLEDGEMENTS-----	24
REFERENCES-----	25
FIGURE CAPTIONS-----	27
FIGURES-----	29

A STUDY OF THE SUPERCONDUCTIVITY OF  
METALS CONDENSED AT 4°K

James Adams Roberts, Jr.

Inorganic Materials Research Division, Lawrence Radiation Laboratory  
Department of Materials Science and Engineering, College of Engineering  
University of California, Berkeley, California

ABSTRACT

The superconducting transition temperatures  $T_c$ , of electron beam evaporated metals (Al, Sn and Pb) condensed on liquid helium cooled substrates have been measured. The  $T_c$ 's of Al and Sn were increased above the bulk values to 3.1°K and 5.09°K respectively. The  $T_c$  of Pb remained unchanged. The metals were also co-condensed with xenon resulting in further increases for the  $T_c$ 's of Al(3.7°K) and Sn(6.22°K) and a decrease for Pb. The effects of annealing on  $T_c$  and normal state resistance were also measured.

## I. INTRODUCTION

In 1968 McMillan<sup>1</sup> published an expression for the superconducting transition temperatures,  $T_c$ , of strong coupled superconductors. This expression showed  $T_c$  to be inversely proportional to the average phonon frequency squared  $\langle \omega^2 \rangle$ . McMillan also pointed out that if  $\langle \omega^2 \rangle$  could be lowered without disturbing the other parameters  $T_c$  could be increased. The McMillan theory was later generalized to give more realistic numerical results by Garland and Allen.<sup>2</sup>

Garland et al.<sup>3</sup> pointed out that the vibrational modes at the surface of a crystal are lower than in the interior. Thus one way to lower the average phonon frequency is to increase the surface to volume ratio. This can be accomplished by making an extremely thin film, or by making an extremely fine grained material. Dickey<sup>4</sup> has actually carried out a molecular dynamics calculation on the decrease in  $\langle \omega^2 \rangle$  of small particles.  $\langle \omega^2 \rangle$  can also be reduced if a crystalline material is transformed into an amorphous structure where the atoms occupy positions of reduced symmetry.<sup>3</sup> Vapor depositing an element, or a combination of elements, onto a cold substrate is one way to form extremely small grains which are internally disordered.

There have been many investigations of the superconducting properties of the soft metals such as Al, Sn and In when deposited onto liquid helium cooled substrates. However, before the present investigation, there had been few, if any, reports of the superconducting properties of the transition metals deposited in a similar manner. This was not hard to understand. The soft metals are easy to vaporize and their superconducting

properties are not readily degraded by the incorporation of impurity gases such as  $O_2$  and  $N_2$  during deposition. Transition metals on the other hand are difficult to vaporize and are easily contaminated by small amounts of impurities.

The original aim of this investigation was to build an apparatus capable of vapor depositing high purity films of transition metals onto a liquid helium cooled substrate. High purity was attained by combining a moderate vacuum and high deposition rates. Critical temperature measurements were made in situ so the films could be evaluated before warming to room temperature. This also avoided contamination from the atmosphere. While the apparatus was under construction it was suggested that it might be possible to introduce additional disorder into the films by co-depositing the metal with an inert gas such as xenon.<sup>5</sup> An inert gas was selected because it was thought that this type of impurity would cause the least change in the electronic structure of the metal. Xenon was selected because it is a large atom and because it is more readily condensed than the other non-radioactive inert gases.

In order to test the equipment and the idea of co-deposition with xenon it was decided to first run a series of experiments on some soft metals for which there were some data available for comparison. This report describes the equipment and experimental procedure and gives the results, including a brief summary of previous work, of depositing some soft metals both in vacuum and with xenon gas onto a liquid helium cooled substrate. A report of the work on transition metals using the apparatus described here, is contained in reference 6.

## II. EXPERIMENTAL

### A. Review of Previous Results

Shalnikov was perhaps the first to report an increase above the bulk  $T_c$  value for a cold deposited film when, in 1938, he reported an increase in the  $T_c$  of a Sn film.<sup>7</sup> The first comprehensive study of films deposited on liquid helium cooled substrates was made by Buckel and Hilsch in the early 1950's.<sup>8</sup> They deposited Sn, Al, Zn, In, Tl, Pb, and Hg on crystalline quartz substrates held near 4°K and found an increase in  $T_c$  for all of these metals, except Pb which remained practically unchanged, and Hg which decreased. On annealing to room temperature the resistance of all samples decreased irreversibly and their  $T_c$ 's were found to have changed so as to approach the bulk values. Sn films were also cold codeposited with up to 10% Cu.<sup>9</sup> This produced an amorphous structure with a very high  $T_c$  for Sn, 7°K or 1.9 times the bulk  $T_c$  of pure Sn.

Since this early work there have been many experimental attempts to increase the  $T_c$ 's of films and also to demonstrate the enhancement mechanism. A summary of the general techniques used is given below. Various combinations of these techniques have also been tried.

#### 1. Variation of Substrate Material.

This has been found to have little effect at temperatures below room temperature (the only temperatures considered in this report.)

#### 2. Variation of Substrate Temperature

Generally for non-transition metals the lower the deposition temperature the greater the enhancement (exceptions are Pb and Hg).

#### 3. Deposition Rate

The effect of rate is difficult to assess since many experimental



variables such as background pressure and cooling capacity of the substrate play a part. However within reasonable limits the rate itself does not seem to be an important variable.

#### 4. Film Thickness

For films thicker than  $\sim 100\text{\AA}$ , (the exact thickness depending on the material), thickness does not seem to affect  $T_c$ . As the thickness is decreased below  $100\text{\AA}$ ,  $T_c$  has been shown to increase for several elements, while for Pb,  $T_c$  is said to decrease.<sup>10</sup>

#### 5. Layered Films

Alternate layers of a superconductor and an insulator, a superconductor and a normal metal, and two different superconductors have been deposited.<sup>11-12</sup> In several systems increases in  $T_c$  were observed. These increases were later attributed to the properties of the individual superconducting layers and not to the layered structure as such.

#### 6. Co-Deposition

Elements have been both deposited in the presence of a high background pressure of a gas and also co-evaporated with another material. An initial increase in  $T_c$  was usually observed, which either leveled off or decreased if too much of the second component was added.

In Table I, due partially to Gamble and Shimshick,<sup>13</sup> the maximum  $T_c$ 's attained by several methods are listed. It should be remembered when reading the table that in this type of work there is experimental scatter from film to film and the values listed are the maximum values reported by various authors.

TABLE I. Summary of Critical Temperatures Reported in the Literature

Column#	2	3	4	5	6	7
Element	$T_c$ (bulk)	$T_c$ (LTD) <sup>a</sup>	$T_c$ (O <sub>2</sub> )	$T_c$ (layers)	$T_c$ (LTCD) <sup>b</sup>	$T_c$ (GM) <sup>c</sup>
Al	1.196	2.70	2.3	5.7	5.84	10
Zn	0.875	1.40	---	1.8	----	3
Sn	3.722	4.84	4.1	6.0	7.0	8
In	3.403	4.08	3.7	4.4	4.6	5
Pb	7.193	7.19	7.2	7	---	7.2
Hg	4.154	3.88	---	---	---	4.2

a) LTD = Low temperature deposition

b) LTCD = Low temperature codeposition

c) GM = Generalized McMillan

All the films referred to in Table I, unless otherwise noted were thick films. A thick film here is any film of sufficient thickness such that its  $T_c$  is not a function of thickness. Using this definition a film thicker than  $100\text{\AA}$  can be considered thick for most materials. The  $T_c$  measurements for all films deposited on cold substrates were made in situ before the films were allowed to anneal, (see Table I).

A description of some of the particular experiments and references for the various entries are given below:

Column 2. These are the critical temperatures of the elements in bulk form as given by Roberts.<sup>14</sup>

Column 3. Buckel and Hilsch obtained these results on thick films deposited on a crystalline quartz plate held at  $4^\circ\text{K}$ .<sup>8</sup> Other authors<sup>15</sup> have reported slightly higher values for cold deposited films of Al and Zn.

Column 4. The films here were deposited on room temperature<sup>16</sup> quartz substrates in the presences of a high background pressure of  $\text{O}_2$ . The grain size of the Al films, as measured by electron microscopy, was as small as  $45\text{\AA}$ . Varying the thickness of the Al film from 300 to  $3000\text{\AA}$  did not change  $T_c$ . An additional increase in  $T_c$  from  $2.3^\circ\text{K}$  to  $3.0^\circ\text{K}$  was achieved for Al by using the same procedure as above but holding the substrate at  $100^\circ\text{K}$  during deposition.

Column 5. The films here were made of repeated layers,<sup>11</sup> approximately  $50\text{\AA}$  thick, of metals and insulators. Various insulators ( $\text{SiO}$ ,  $\text{LiF}$ , metal oxides and anthracene) were tried with  $\text{SiO}$  generally giving the highest  $T_c$ . Layers of Al and Al deposited in a high background pressure of argon gave an ultimate  $T_c$  of  $2.9^\circ\text{K}$  after several layers. All these results were later attributed<sup>10</sup> to the thinness of individual superconducting layers and not to the layer effect.

Column 6. This column is for films made by the co-condensation at 4°K of a superconductor and another substance. It is difficult to decide what to include in this column since after a certain amount and type of a second material has been added one really has a completely new material which should not be compared with the other entries in the table. The systems selected to be listed in the table were: Al+6% Cu,<sup>17</sup> Sn+10% Cu<sup>9</sup> and In<sup>18</sup> co-deposited with anthraquinene. Some higher  $T_c$ 's have been found for Al, Sn and In by codepositing them with 10% of a semimetal or semiconductor such as Sb, Bi, Ge, As and Si.<sup>15</sup> The  $T_c$  of Zn was also increased in this way.

Another system which should be mentioned for comparison with the present work is the Al tetracyanoquinodimethan (TCNQ) system. The  $T_c$  of Al increased asymptotically to 5.2°K as the amount of TCNQ relative to the amount of Al directed to the substrate was increased.<sup>19</sup>

Column 7. The values here are the maximum possible  $T_c$ 's for the disordered metals as predicted by Garland and Allen using their generalized McMillan equation.<sup>2</sup>

## B. Apparatus

### 1. Vacuum Chamber

The vacuum chamber (see Fig. 1) was a three foot diameter by 3 foot long water cooled stainless steel horizontal cylinder with a 10 inch diameter hole in the top through which the cryostat holding the substrate was hung. To outgas the chamber during pump down water at ~100°C could be circulated through its cooling coils. Pumping was done by a liquid nitrogen baffled 12" oil diffusion pump backed by a Kinney (KD-130) mechanical pump. Near the rear of the chamber there was a 3 foot diameter

by 1/16 inch thick stainless steel wall which could be cooled to near liquid nitrogen temperature by circulating liquid nitrogen through stainless steel tubing heliarced to it. A reactive surface was maintained on the wall by evaporating titanium onto it. The diffusion pump together with the titanium gettering on the cold wall achieved an ultimate pressure, as read by a Veeco RGLL-6 ion gauge, in the mid  $10^{-8}$  torr range.

## 2. Evaporation Sources

Materials to be evaporated were held in water cooled copper crucibles and electron beam heated by Temescal 180° magnetic deflection electron beam guns operated at 8 kV. One of the chamber's three evaporation sources was mounted below the cryostat leaving 4 inches between the evaporating material and the substrate. This source had a rotatable crucible with six separate holes so more than one material could be evaporated during a single run.

To prevent contamination of one material by another during evaporation, a copper shield covered 5 of the holes during evaporation from the sixth. A one inch high vertical water cooled copper wall surrounded the edges of the copper shield. This provided a relatively cool area behind which the gas source or a small evaporation source could be mounted.

Only one of the other two electron beam heated sources, both of which had fixed crucibles, was used during a run. This source was mounted near the rear of the chamber and was used to evaporate titanium onto the liquid nitrogen cooled wall.

The rate of evaporation was monitored and controlled by an Allen-Jones Mark I ion gauge type rate monitor. The rate control was done through a feedback loop which modulated both the electron beam gun filament

current and the amplitude of variation, about some mean value, of the current in the deflection magnet windings of the electron beam gun. The former modulation influenced the total power applied to the evaporating material while the latter influenced the power concentration by changing the area of the evaporating material on which the electron beam impinged. The magnetic beam sweeping type rate control had a much shorter response time than did the emission regulation type rate control and thus was needed to reduce short time variations in rate.

To convert the reading of a rate monitor from arbitrary units to a more useful value, such as  $\text{A}/\text{sec}$ , the monitor had to be calibrated for each geometry and element used.

### 3. Gas Source

The gas source was made of copper and sat on the water cooled copper plate on the rotary source (Fig. 2). Seven  $1/8$ " diameter holes in the top of the source directed the gas to the substrate. Two copper tubes were soldered to the bottom of the source. One of these led out of the vacuum chamber to the gas inlet system while the other led to an Allen-Jones rate monitor. Thus the gas let into the system was divided in some unknown but presumably unchanging proportion between that directed at the substrate from the holes in the top of the source and that directed to the rate monitor.

The flow rate of the gas was controlled by a precision needle valve and read on the rate monitor. The rate monitor readings here were not calibrated. However as a check of the repeatability of the rate monitor set up from run to run there was a sapphire float type flow meter located near the needle valve. To trap any residual water, the gas was passed through a copper coil cooled by a dry ice and acetone mixture.

#### 4. Cryostat

The cryostat (Figs. 1 and 2) used the conventional principle of an outer liquid nitrogen cooled radiation shield, "77°K shield," made of copper surrounding an inner liquid helium container. The liquid helium container was made of stainless steel except for its 4"x2"x1/8" thick bottom plate, "4°K plate," made of OFHC copper. The sapphire substrate (1"x1/2"x 1/16") was held in an aluminum mask (Fig.3) and clamped directly against the 4°K plate. This provided a maximum of cooling since most of the top surface of the 4°K plate was in direct contact with liquid helium. Pressure was maintained between the substrate and 4°K plate by spring loading the stiff stainless (TRIP) steel forked device that supported the mask. To further enhance thermal contact between the substrate and the 4°K plate a soft thick layer of gold was deposited on the back surface of the substrate. The entire cryostat was separated from the sources by a water cooled copper shield.

As can be seen in Fig. 3 the aluminum mask had five separate sample positions. Using a system of three shutters moved by mechanical drives from outside the vacuum chamber it was possible to independently deposit on each of the sample positions without breaking the vacuum. The 4°K shutter was a 1/8" thick strip of copper that slid in slots in the aluminum mask. The shutter had a single opening just slightly larger than one of the openings in the mask. This opening was positioned directly under the sample position selected to receive the evaporant. The 77°K shutter, which ran in slots on the liquid nitrogen cooled radiation shield, was basically the same design as the 4°K shutter only with a slightly larger opening. It was positioned, in line with the 4°K shutter, directly

beneath the sample position to be deposited on. These two shutters minimized the heat input to the substrate and aluminum mask since an area only slightly larger than the actual sample was exposed to the high temperature of the source. Both the  $4^{\circ}\text{K}$  and  $77^{\circ}\text{K}$  shutters were thermally connected to their respective temperatures by copper braid. The  $\text{H}_2\text{O}$  cooled shutter was a  $1\text{-}1/2'' \times 1'' \times 1/16''$  piece of tungsten which ran in slots on the  $\text{H}_2\text{O}$  cooled shield. The shutter could be moved to either cover or uncover a hole of sufficient size in the  $\text{H}_2\text{O}$  cooled shield to expose all the sample positions to the sources. Since it did not have to be carefully positioned and could be moved rapidly, this shutter was used to control the duration of deposition while the  $77^{\circ}\text{K}$  and  $4^{\circ}\text{K}$  shutters were used to select the sample position to receive the evaporant. All the shutters could be completely closed to protect against radiation during  $T_c$  or resistance measurements.

The cryostat was equipped with two heaters. The low power or resistance heater was a twenty foot length of manganin wire through which a current could be passed wound around a protrusion in the  $4^{\circ}\text{K}$  plate. The high power or electron bombardment heater consisted of a tungsten filament mounted on the liquid nitrogen cooled shielding directly beneath the  $4^{\circ}\text{K}$  plate to the side of the aluminum mask. The filament could be biased to -2500 volts and resistance heated until electrons were emitted from it and accelerated to the  $4^{\circ}\text{K}$  plate held at ground potential.

##### 5. Temperature Measurement

Temperature measurements were made with a factory calibrated ( $1.5^{\circ}\text{K}$ - $40^{\circ}\text{K}$ ) Texas Instruments two lead germanium resistance thermometer and a



gold - .07% iron vs chromel thermocouple. The germanium thermometer was thermally anchored to the edge of the 4°K plate by placing its two leads through two holes in the 4°K plate and soldering one lead into one hole with a low melting point (170°F) solder (Cerobend 170) and potting the other lead into the other hole with General Electric 7031 electrically insulating varnish. To protect against radiation the thermometer was completely surrounded by a copper box which was itself fastened, through an indium gasket, to the 4°K plate. To prevent heat leaks the copper wire leads to the thermometer were wound several times around the thermometers protective copper box and secured there with General Electric 7031 varnish. Also several inches of a low thermal conducting wire, No. 36 manganin were included in the otherwise copper leads.

The gold-iron vs chromel thermocouple junction covered by an indium foil was clamped to the 4°K plate. To prevent accidental breakage and to provide a heat sink and radiation shield the thermocouple was enclosed in a copper tube that was clamped to the 77°K shielding. The thermocouple passed out of the vacuum chamber through a standard thermocouple feed-through then into a 77°K reference bath where copper leads were connected. The thermocouples output voltage was read on a Hewlet Packard dc differential volt meter (Model 3420A).

#### 6. Substrate

The substrates were 1"x1/2"x1/16" sapphires supplied by the Union Carbide Co. The material and crystallographic orientation were chosen to make use of the high thermal conductivity of sapphire at low temperatures. The sapphires were cleaned by first placing them in an ultrasonic cleaner containing a Teepol soap solution for five minutes then into a boiling 50%

$H_2O$  - 50%  $H_2O_2$  solution for 30 minutes and finally into boiling distilled water for another 30 minutes. After cleaning, five sets of gold contacts were evaporated, in a vacuum of  $10^{-6}$  torr, onto the front surface and sides of the sapphire. A thick film of gold was also evaporated onto the sapphires back surface to improve the thermal contact between it and the cryostat. During the gold evaporation the sapphire was maintained at a temperature of  $\sim 300^\circ C$ .

#### 7. Electrical Measurements

A schematic of the circuits used to measure the germanium thermometer and sample resistances is shown in Fig. 4. Contact was made with each of the gold contacts on the substrate with a platinum tipped spring loaded phosphor bronze wire. The phosphor bronze wires were held in position by insulating boron nitride strips which were in turn fitted into slots in the aluminum substrate holder. Manganin (No. 36 wire) current and voltage leads were attached to the ends of the phosphor bronze wires providing pseudo four point contacts. Between the phosphor bronze wires and the plug on the  $77^\circ K$  shielding the leads were thermally anchored to the  $4^\circ K$  bottom plate.

The rest of the circuit in which copper wiring was used is adequately described by the schematic. The sample measuring current was  $0.5\mu$  amp dc. The current direction could be manually reversed to eliminate the effects of any spurious emfs. The sample voltage was measured with an Astrodata (Model 121 RZ) nanovoltmeter whose output was displayed on the Y axis of an Electro Instruments X-Y Recorder (Model 520).

The thermometer measuring current was  $1\mu$  amp dc. The thermometer voltage was displayed directly on the X axis of the X-Y recorder. This

axis was calibrated in terms of resistance by displaying the voltage across standard resistors in series with the thermometer and the constant dc measuring current supply.

### C. Experimental Procedure

Before making a run the rate monitor for the metal source had to be calibrated. This was accomplished by simply placing a substrate in the normal position, depositing the metal to be studied at an indicated rate for a known time, and then measuring the thickness of the deposit. The thickness measurements were made by overcoating the entire substrate with a shiny film of aluminum then measuring the height of the step caused in the aluminum film by the sample metal with a multiple beam interferometer (Varian Å scope). It was then a simple matter to convert the rate monitor readings to Å/sec.

Obviously the above procedure could not be used to calibrate the monitor for the Xe gas. Thus all the results having to do with Xe were reported in arbitrary units and give only an indication of the effect of increasing or decreasing the Xe flow rate to the substrate. How much Xe actually remained in the various samples is not known and probably varied for any particular Xe flow rate depending on the metal being simultaneously deposited due to changes in Xe sticking coefficient. Thus a comparison based on any absolute Xe content between different metals should not be made when reviewing the data presented below. A test made on a niobium film codeposited with xenon indicated that ~1% xenon was retained after warming to room temperature.<sup>6</sup>

As a preliminary check of the equipment, a thick Pb film was deposited on the substrate held at room temperature. The critical temperature of

the film was then measured in the apparatus and this result compared with the bulk  $T_c$  of Pb. Agreement to well within  $\pm 0.1^\circ\text{K}$  was found. Pb was used for this test because it has been reported by many investigators that the  $T_c$  of Pb films is unchanged from its bulk value except under the most extreme conditions.<sup>16</sup> The above test of the temperature measurement accuracy when repeated using Sn or In films gave the same good results as with Pb.

The above procedures had only to be repeated as periodic checks or as new metals were investigated. The following is a list of the general experimental procedures that were followed with only minor variations during each run.

(1) The cleaned substrate with the five sets of gold contacts evaporated onto it was placed in the aluminum holder and positioned so that the platinum tips of the phosphor bronze wires were in contact with the gold contacts. The aluminum holder was then clamped in place beneath the  $4^\circ\text{K}$  plate.

(2) The vacuum chamber was closed and evacuated. Hot water ( $\sim 100^\circ\text{C}$ ) was circulated through the tanks cooling coils.

(3) After 8 to 12 hours of baking and pumping the system pressure reached  $\sim 1 \times 10^{-6}$  torr. At this point the hot water was turned off and the cooling water started. The liquid nitrogen jacket on the liquid nitrogen cooled shielding was filled. It then took about three hours for the lower portions of the liquid nitrogen shielding to cool by conduction. By the time the liquid nitrogen shielding had reached its lowest temperature (100 to  $110^\circ\text{K}$ ), the tank pressure was  $\sim 4 \times 10^{-7}$  torr.

(4) The back wall was cooled with liquid nitrogen and titanium evaporated onto it. The substrate, which had cooled somewhat by radiation, was heated to  $\sim 50^{\circ}\text{C}$  in an attempt to remove any contaminants condensed on it. The metal to be studied was then melted.

(5) While the titanium continued to be evaporated, the center liquid helium container holding the substrate was first pre-cooled with liquid nitrogen before being filled with liquid helium. The substrate temperature was then  $\sim 4.25^{\circ}\text{K}$  and the pressure in the vacuum chamber was between  $4 \cdot 10^{-8}$  and  $8 \cdot 10^{-8}$  torr. (These procedures were rearranged if it was desired to make the deposition at some higher temperature, such  $77^{\circ}\text{K}$  or  $300^{\circ}\text{K}$ ).

(6) The  $4^{\circ}\text{K}$  shutter and the  $77^{\circ}\text{K}$  shutter were positioned under the sample position to receive the evaporant.

(7) The metal source and, if desired, the Xe gas source were turned on and their respective rates brought to the desired levels. The titanium was turned off during the deposition of a sample to prevent any possible contamination of the sample.

(8) When the rates had stabilized, the desired exposure time was achieved by opening and closing the water cooled shutter.

(9) The sources were turned off, the  $77^{\circ}\text{K}$  and  $4^{\circ}\text{K}$  shutters closed and the resistance of the sample measured.

(10) To measure the  $T_c$  of the sample the substrate was either cooled below  $4.25^{\circ}\text{K}$  by pumping on the liquid helium (minimum temperature  $\sim 1.7^{\circ}\text{K}$ ) or warmed above  $4.25^{\circ}\text{K}$  by allowing all the liquid helium to boil away. As the temperature was changed both the temperature (germanium thermometer resistance) and sample resistance were continuously plotted on the X-Y recorder.  $T_c$  was then determined from this plot.

(11) The resistance behavior of the sample as it was warmed towards room temperature could then be monitored. Above  $\sim 20^{\circ}\text{K}$  the temperature measurement was shifted from the germanium thermometer to the gold-iron vs chromel thermocouple. At any point the sample could be re-cooled to see what effect the annealing had on its  $T_c$ . This could be repeated as often as desired.

(12) After the apparatus had warmed to room temperature the substrate was removed and the sample could be observed by other desired techniques.

The above is a description of the making of only one sample. However as stated earlier five samples could be made during a single run. Thus, to save time, normally a group of samples was made and measured together rather than going through the above procedure for each sample separately.

#### D. Results

All films were deposited with liquid helium in the cryostat so that the temperature of the substrate before deposition was  $\sim 4.2$  to  $4.7^{\circ}\text{K}$ . During deposition the germanium thermometer indicated a temperature rise of  $< 0.2^{\circ}\text{K}$ . However this was probably not indicative of the situation at the surface of the substrate where there was a direct heat load due to: radiation from the source, the high temperature of the incident evaporant and the heat of condensation released as the evaporant condensed. A test of the surface heating due to radiation from the source was made by exposing a superconducting film with a  $T_c$  of  $7.2^{\circ}\text{K}$  to a tungsten source heated to the point of vaporization. The film remained superconducting indicating a temperature rise of  $< 3^{\circ}\text{K}$ .

The vacuum pressures reported during deposition of a metal plus Xe sample are not indicative of the Xe flux to the substrate since the Xe source was aimed directly at the substrate and pumping of the entire

system was continued during the deposition. All resistance measurements for which a specific temperature of measurement is not specified were made at a temperature just above the temperature at which the sample started to go superconducting. The critical temperature ( $T_c$ ) reported is the temperature at which the sample resistance reached 1/2 its normal state value. In the figures the error bars denote the values where the resistance was 10% its normal state value and 90% its normal state value. Unless otherwise noted all films were deposited for 20 seconds at a metal deposition rate of  $50\text{\AA}/\text{sec}$ .

#### Aluminum

Films at various Xe/Al ratios (See Fig. 5) including (Xe/Al) = 0 were deposited in a vacuum at a pressure which increased from  $\sim 1 \times 10^{-7}$  torr during the deposition of pure Al (Film No. 1) to  $\sim 3 \times 10^{-6}$  torr during the deposition of the highest Xe rate sample (Film No. 5). Film No. 3 was made at an Al rate 1/3 that of the other samples for  $\sim 3$  times the time.

$T_c$  of the as deposited films increased from  $\sim 3.1^\circ\text{K}$  for pure Al to  $\sim 3.7^\circ\text{K}$  for the highest Xe/Al ratio film (Fig. 5a Curve 1). The resistance vs Xe/Al ratio behavior for the samples as deposited is shown in Fig. 5b Curve 1, and shows no consistent trend. The resistances of all films (except No. 3) were observed to decrease while the temperature remained constant at  $\sim 4.6^\circ\text{K}$ . The resistance values reached after any noticeable change in resistance had stopped are given in Fig. 5b curve 2. Some of the difference in resistance between curves 1 and 2 may be attributed to a slight heating of the previously deposited samples that may occur during the deposition of new samples, or to annealing when the substrate temperature was inadvertently allowed to rise to  $15^\circ\text{K}$ . However much of the change was

directly observed before the deposition of any new samples and while the substrate was held at a constant  $4.6^{\circ}\text{K}$ . "As deposited" resistance values (Fig. 5b curve 1) may be lower than the values actually were immediately after deposition since it took up to a minute from the time of deposition until the resistance was measured. During this time annealing may have taken place. The above remarks should also be kept in mind when examining the "as deposited"  $T_c$  (Fig. 5a curve 1). After the resistance had stopped decreasing  $T_c$  was measured again and as shown in Fig. 5a curve 2 there were shifts in  $T_c$  ranging from an increase of  $\sim .2^{\circ}\text{K}$  for film No. 1 to a decrease of  $\sim .1^{\circ}\text{K}$  for film No. 5.

#### Annealing

The samples were heated at  $\sim 1^{\circ}\text{K}/\text{min}$  to  $100^{\circ}\text{K}$ . The resistance vs temperature values are shown in Fig. 6. The only resistance values claimed here are those explicitly marked on the curves. Intermediate values of resistance were measured during heating. However, it was found that the heater interfered with the resistance measurements. The points marked on the curves were taken with the heater off and are valid. Curves for films No. 3 and 5 are not shown since at  $\sim 80^{\circ}\text{K}$  both exhibited a drastic increase in resistance indicating either cracking or peeling of the film. The samples were re-cooled to liquid He temperature. The  $T_c$  of all samples was found to have decreased somewhat (Fig. 5a curve 3), however all remained superconducting well above the bulk value of  $\sim 1.2^{\circ}\text{K}$ . The normal state resistances (Fig. 5b curve 3) showed no change that can be correlated with the Xe/Al ratio.

The samples were next heated rapidly to  $270^{\circ}\text{K}$  then re-cooled immediately to  $4.6^{\circ}\text{K}$ . All the normal state resistances were found to have decreased and showed a slight increase with increasing Xe/Al ratio. On



attempting to measure  $T_c$  it was found that none of the samples had become superconducting above  $2.85^\circ\text{K}$ , which was the lowest attainable temperature during that particular run.

When the samples were removed from the vacuum chamber and examined under the optical microscope, all showed cracking or peeling except film No. 1. It is uncertain at what point this cracking and peeling occurred.

### Tin

Ten Sn and Sn+Xe samples were deposited at the usual rate and time while one sample (run 12, film No. 5) was deposited for four times the regular time to make a  $4000\text{\AA}$  thick film (see Fig. 7). Since there were only five sample positions per substrate the samples were deposited during three separate runs (5 samples each during runs 6 and 12, and 1 sample during run 5). The total pressure in the vacuum chamber rose from a minimum of  $4 \times 10^{-8}$  torr during the deposition of the pure Sn sample (run 12, film No. 1) to a maximum of  $9 \times 10^{-5}$  torr during the deposition of the highest Xe/Sn ratio sample (Film No. 11).

The critical temperatures (Fig. 7a curve 1) increased with increasing Xe/Sn ratio until a maximum was reached at the Xe/Sn ratios corresponding to films No. 5, 6 and 7.  $T_c$  then decreased as the Xe/Sn ratio was further increased. The  $T_c$  of the pure Sn sample (run 12, film No. 1) was  $5.09^\circ\text{K}$  or an increase of 1.37 times the bulk value of  $3.72^\circ\text{K}$ . The maximum  $T_c$  attained,  $6.22^\circ\text{K}$  for film No. 5 is 1.67 times the bulk value.

The normal state resistances just above the transition temperature are given in Fig. 7b curve 1. Several samples, films No. 7 and 11 in particular, showed some residual resistance in the superconducting state. This was assumed to be contact resistance and has been subtracted from

the measured values of the normal state resistance to give the normal state values quoted in Fig. 7b curve 1. As the Xe/Sn ratio was increased the normal state resistance increased to a maximum for the samples with the maximum  $T_c$ . As the Xe/Sn ratio was further increased the normal resistance and  $T_c$  both decreased until the normal resistance passed through a minimum and then rose rapidly.  $T_c$  continued to decrease.

### Annealing

The samples made during run 12 (films No. 1, 5, 6, 9 and 10) were heated to  $\sim 150^\circ\text{K}$  at a heating rate of  $\sim 1.3^\circ\text{K}/\text{min}$ . and then heated to  $250^\circ\text{K}$  at a heating rate of  $\sim 7^\circ\text{K}/\text{min}$ . The resistance vs. temperature curves are given in Fig. 8 for films No. 1, 6 and 10. Curves for films No. 5 and 9 are not given since they showed erratic annealing behavior, indicating either cracking or faulty contacts.

The pure Sn sample (film No. 1) showed a rather flat R vs T behavior whereas films No. 6 and 10 showed obvious sharp decreases. The resistance of film No. 6, and a high resistance high  $T_c$  sample, started decreasing immediately on heating, while the resistance of film No. 10, a lower resistance lower  $T_c$  sample, remained approximately constant up to  $\sim 60^\circ\text{K}$ . At  $60^\circ\text{K}$  film No. 6 had decreased in resistance to a value approximately equal to that of film No. 10. As the temperature was further increased both film No. 6 and No. 10 decreased in resistance until at  $\sim 100^\circ\text{K}$  film No. 6 leveled off at a value of  $\sim 5$  ohms and at  $\sim 120^\circ\text{K}$  film No. 10 leveled off at  $\sim 4$  ohms. On recooling to liquid helium temperature the resistance decreased in the normal fashion to give nearly equal resistances when measured just above  $T_c$  (curve 3 Fig. 7b). The  $T_c$ 's had also decreased

with the decrease being the greatest for the Sn+Xe samples ( $\sim 1$  to  $1.8^\circ\text{K}$ ) and the least for the pure Sn sample ( $\sim .2^\circ\text{K}$ ). The width of the transition of the pure Sn had increased from  $\sim .06^\circ\text{K}$  to  $\sim .40^\circ\text{K}$  while the widths of the transitions of the Sn+Xe samples had decreased (curve 2 Fig. 7a). The  $T_c$ 's of films No. 3 and 5 were not remeasured after annealing. No annealing data were taken for runs 6 or 5.

### Lead

One sample of pure Pb and three samples of Pb plus Xe were made in a vacuum of between  $1 \times 10^{-7}$  and  $7 \times 10^{-7}$  torr (see Fig. 9). As the Xe/Pb ratio was increased,  $T_c$  decreased from  $\sim 7.1^\circ\text{K}$  for the pure Pb sample to  $5.5^\circ\text{K}$  for the highest Xe/Pb ratio sample (Fig. 9a). The normal state resistances increased with increasing Xe/Pb ratio (Fig. 9b).

No annealing data were taken although the  $T_c$  of a sample (not shown in Fig. 9) which had the same Xe/Pb ratio as film No. 4 was measured after it had been warmed to room temperature and exposed to air.  $T_c$  was found to be below the bulk value of  $7.19^\circ\text{K}$  by less than  $0.1^\circ\text{K}$ .

### III. CONCLUSIONS

It was concluded that the increases in  $T_c$  which were observed for Al and Sn were a result of lattice disorder. The higher  $T_c$ 's obtained by cold co-depositing with Xe as opposed to cold deposition without Xe were taken as an indication that the Xe somehow increased the lattice disorder resulting from cold deposition. How this effect occurred is not certain. The Xe may have actually remained in the film or may have merely influenced the growth of the film while not remaining trapped in the film.

The annealing data support the above conclusions in that as the films were annealed they underwent irreversible decreases in resistance which was interpreted as indicative of a decrease in the disorder of the films. This decrease in the disorder of the films was in turn reflected in a decrease in  $T_c$ , which was observed when  $T_c$  was remeasured after annealing.

The decrease in  $T_c$  of Pb when co-deposited with Xe is not surprising when it is examined in light of the McMillan theory. The McMillan theory as applied by Garland and Allen (See Table I) predicts no increase in  $T_c$  for disordered Pb. Thus all that can be expected when the structure of Pb is disturbed is that  $T_c$  either will remain unchanged from its bulk value or, if the structure is sufficiently disrupted, that  $T_c$  will decrease. This latter argument can also be used to account for the observed decrease in the  $T_c$  of Sn at high Xe/Sn ratios.

Finally it can be said that the results reported here are in general agreement with the experimental results reported by the other authors and with the theoretical predictions of the McMillan Theory (See Table I).

#### ACKNOWLEDGMENTS

Professors Earl Parker, Victor Zackay and Leo Brewer provided overall supervision of the project and also offered many helpful suggestions on specific problems. For day to day operation, I owe my thanks to Dr. Milton Pickus who helped with equipment design and administrative details, Larry Hartsough who contributed his experience in electron beam evaporation, Dick Loop who helped with some of the experimental details, and Don Whitaker who built and frequently repaired the apparatus. Mike Collver worked with me throughout this project providing the technical help needed to operate the equipment and the entertainment needed to keep one's perspective.

This project could not have been undertaken without the direction of Dr. Robert Hammond who proposed the project, designed the equipment, and developed much of the experimental procedure. To Dr. Hammond I express my thanks not only for his scientific advice but more importantly for his friendliness and patience in working with a novice experimenter.

This work was done under the auspices of the U. S. Atomic Energy Commission.

REFERENCES

1. W. L. McMillan, Phys. Rev. 167, 331 (1968).
2. J. W. Garland and P. B. Allen, International Conference on the Science of Superconductivity (Stanford University) (1969) to be published.
3. J. W. Garland, K. H. Bennemann, and F. M. Mueller, Phys. Rev. Letters, 21, 1315 (1968).
4. J. M. Dickey, Phys. Rev. Letters 21, 1441 (1968).
5. Leo Brewer, private communication.
6. M. M. Collver, Superconducting Transition Temperature of Disordered Transition Metal Films, M.S. Thesis, U.C. Berkeley, UCRL-19186.
7. A. Shalnikov, Nature 142, 74 (1938).
8. W. Buckel and R. Hilsch, Z. Physik, Bd. 138 S.109 (1954), Z. Physik, Bd 132, S420 (1950).
9. R. B. Hilsch, Non-crystalline Solids, ed. V. S. Frenchette (John Wiley and Sons, Inc., N.Y., 1958) p. 348.
10. M. Strongin and O. F. Krammer, JAP 39, 2509, (1968).
11. M. Strongin and O. F. Krammer, Phys. Rev. Letters 19, 121 (1967).
12. M. Strongin and O. F. Krammer, Phys Rev. Letters 21, 1320, (1968).
13. F. R. Gamble, and E. J. Shimshick, Phys. Letters 28A, 25 (1968).
14. B. W. Roberts, Superconductive Materials and Some of Their Properties NBS Technical Note 482, (1969).
15. F. Meunier, J. J. Hauser, J. P. Burger, E. Guyon and M. Hesse, Physics Letters 28A, 37, (1968).
16. B. Abeles, R. W. Cohen, and G. W. Cullen, Phys. Rev. Letters 17 632 (1966).
17. G. V. Minnigerode and J. Rothemberg, Z. Physik, 213, 397 (1968).

18. F. Meunier, J. P. Burger, G. Deutscher, and E. Guyon, Phys. Letters 26A, 309 (1968).
19. F. R. Gamble and H. M. McConnell, Phys. Letters 26A, 162 (1968).

FIGURE CAPTIONS

- Fig. 1. Photograph of the cryostat with the side of the 77°K shield and the Xe rate monitor removed. The liquid nitrogen cooled wall is seen in the background.
- Fig. 2. Schematic diagram of the cryostat and sources. Also shown are the rate monitors for both the Xe (rate monitor No. 3) and the metal (rate monitor No. 2).
- Fig. 3. Photograph of the substrate and substrate holder. From right to left are shown: the sapphire substrate with five sets of gold contacts and three sample films evaporated onto it; the aluminum mask which held the substrate; and the stainless steel spring which held the aluminum mask and sapphire against the cryostat.
- Fig. 4. (a) Schematic of the circuit used to measure the resistance of the samples.  
(b) Schematic of the circuit used to measure the resistance of the germanium thermometer.
- Fig. 5. (a) Critical temperatures of Al and Al + Xe films in the as deposited and annealed conditions.  $T_c$  values are not shown for the films after annealing to 280°K since on attempting to measure  $T_c$  it was found that no films had become superconducting down to 2.8°K which was the lowest attainable temperature during that particular run.  
(b) Electrical resistance of the Al and Al + Xe films in the as deposited and annealed conditions. Measurements were made just above  $T_c$ .



Fig. 6. Annealing data for three of the Al and Al + Xe films. The numbers on the curves indicate the chronology of the resistance vs temperature path: (1) as deposited resistance, (2) isothermal resistance drop, (3)  $T_c$  measurement, (4) isothermal resistance drop, (5)  $T_c$  measurement, (6) heat to 100°K, (7) re-cool and measured  $T_c$ , (8) heat to 280°K, (9) re-cool and measure  $T_c$ . Resistance measurements were made at the indicated temperatures.

Fig. 7. (a) Critical temperatures of Sn and Sn + Xe films in the as deposited condition (Curve 1) and after annealing to 250°K (curve 2). (b) Electrical resistance of Sn and Sn + Xe films in the as deposited condition (Curve 1) and after annealing to 250°K (curve 2). The value plotted for run 12 film 5 is four times its as deposited resistance. This multiplication was performed to account for the film being four times the thickness of the other films. Measurements were made just above  $T_c$ .

Fig. 8. (a) Annealing data for three Sn and Sn + Xe films. The numbers on the curves indicate the chronology of the resistance vs temperature path (1) as deposited resistance and  $T_c$  measurement, (2) heat to 250°K, (3) cool to 7°K, (4) measure  $T_c$ . Resistance measurements were made at the indicated temperatures.

Fig. 9. (a) Critical temperatures of Pb and Pb and Xe films in the as deposited condition. (b) Electrical resistance of Pb and Pb + Xe films in the as deposited condition. Measurements were made just above  $T_c$ .

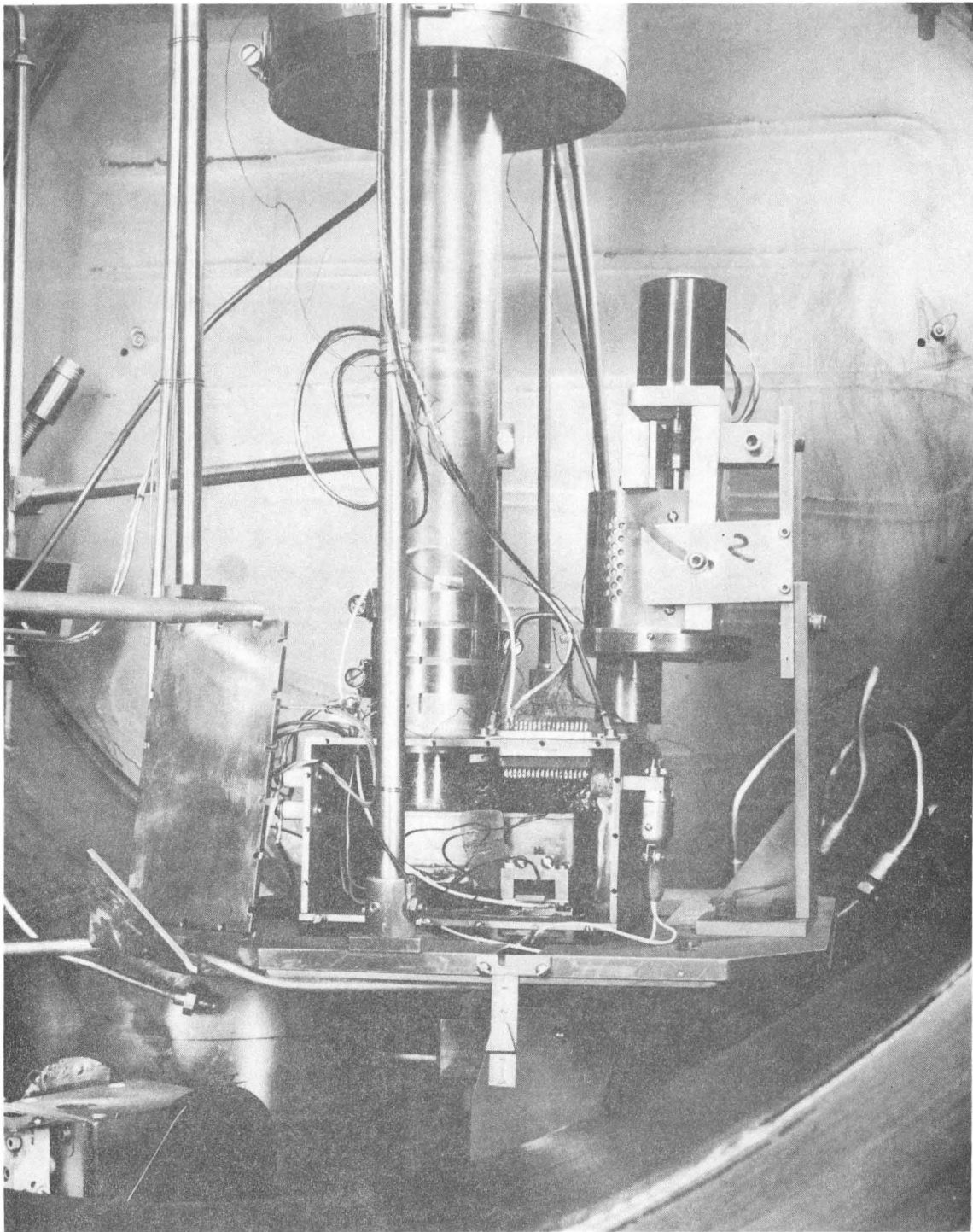
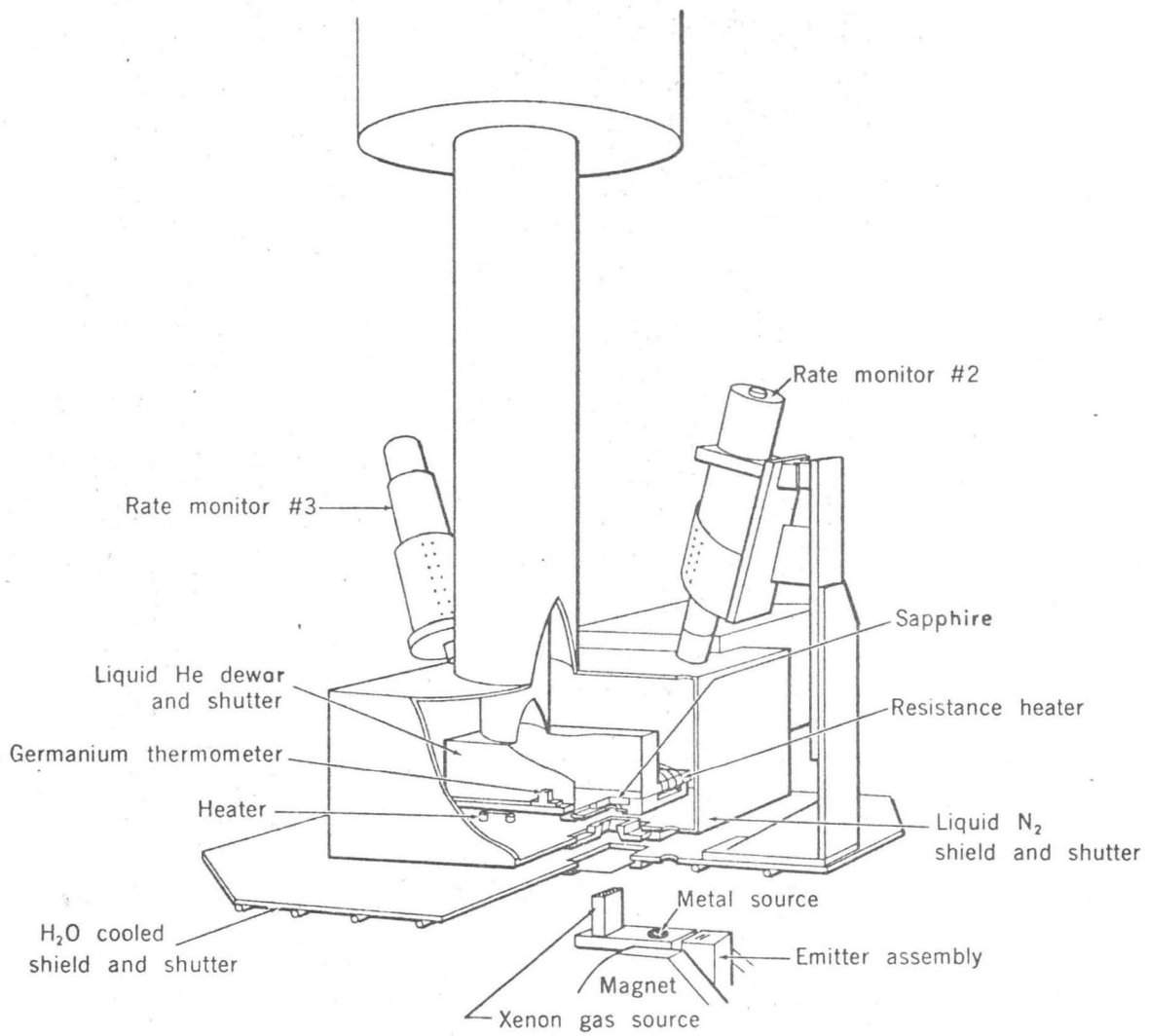


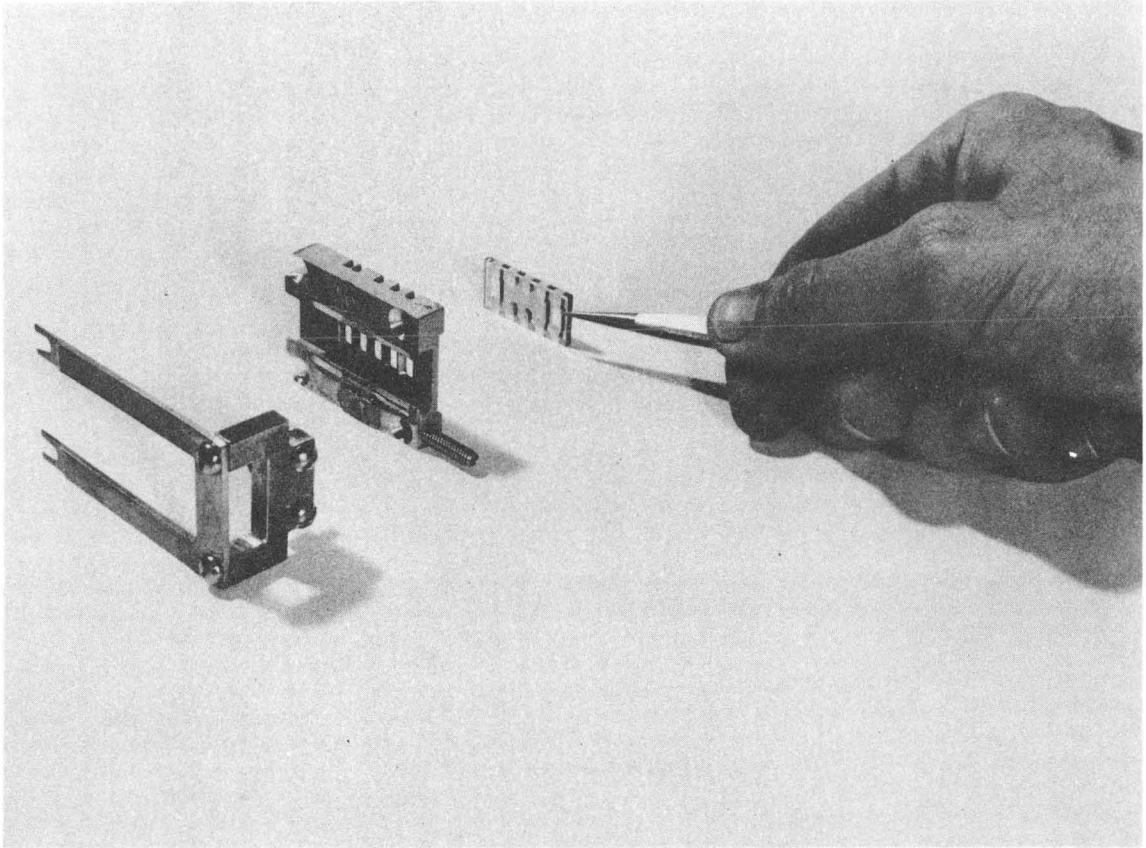
Figure 1

CBB6912-7884



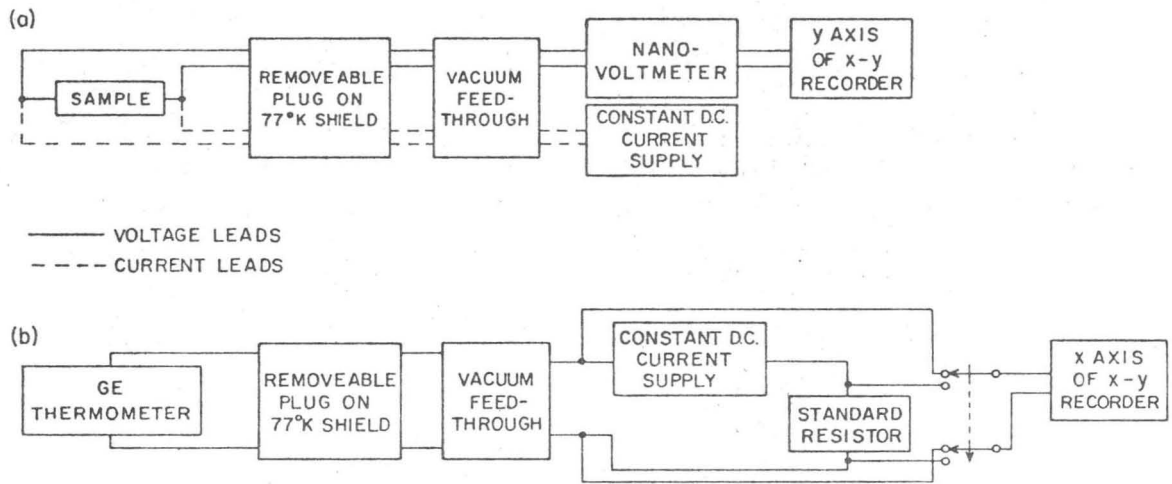
XBL698 - 3448

Figure 2



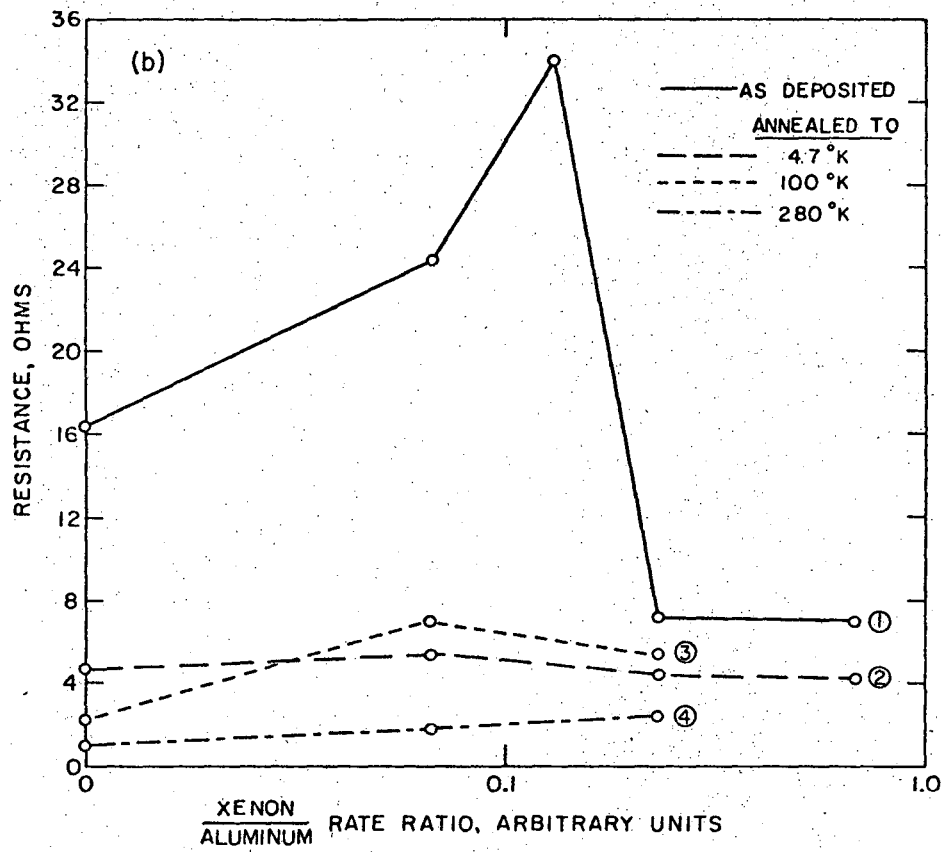
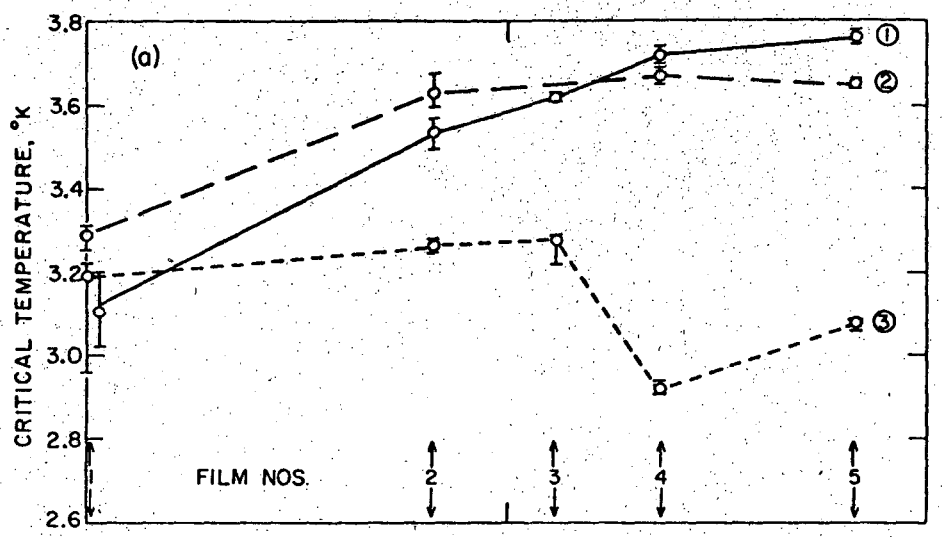
CBB6912-7886

Figure 3



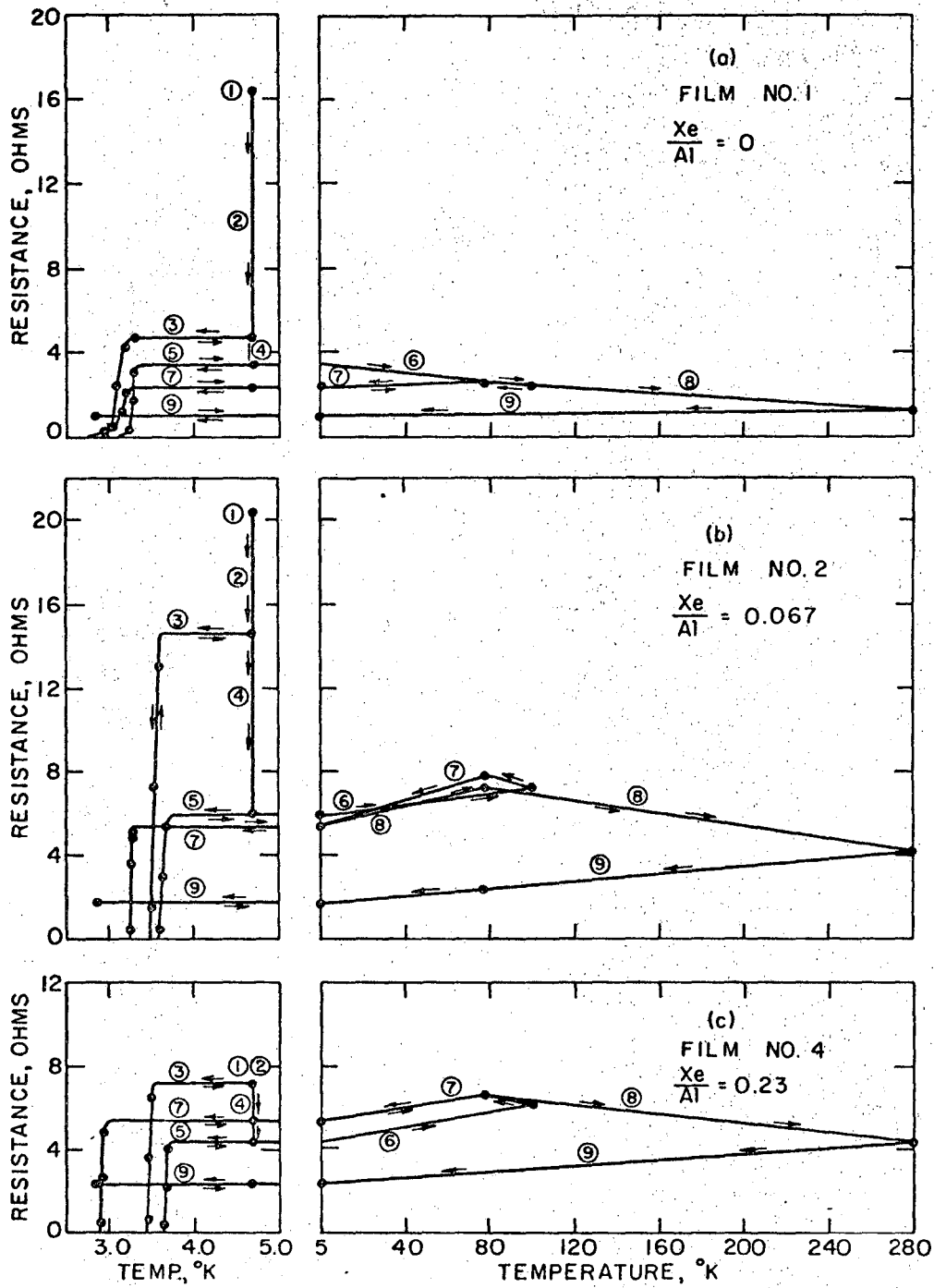
XBL 705 991

Figure 4



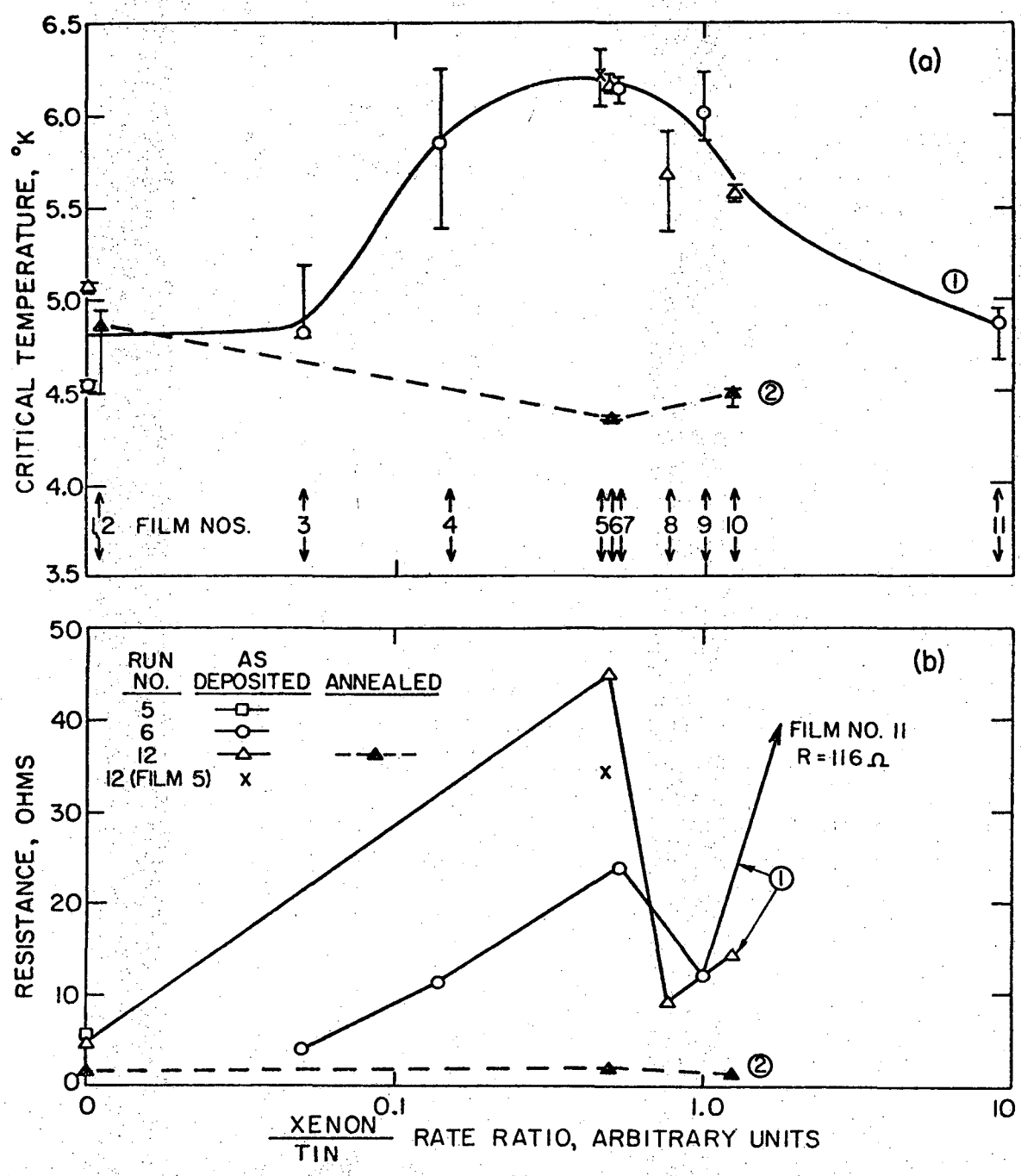
XBL 705-990

Figure 5



XBL 705-987

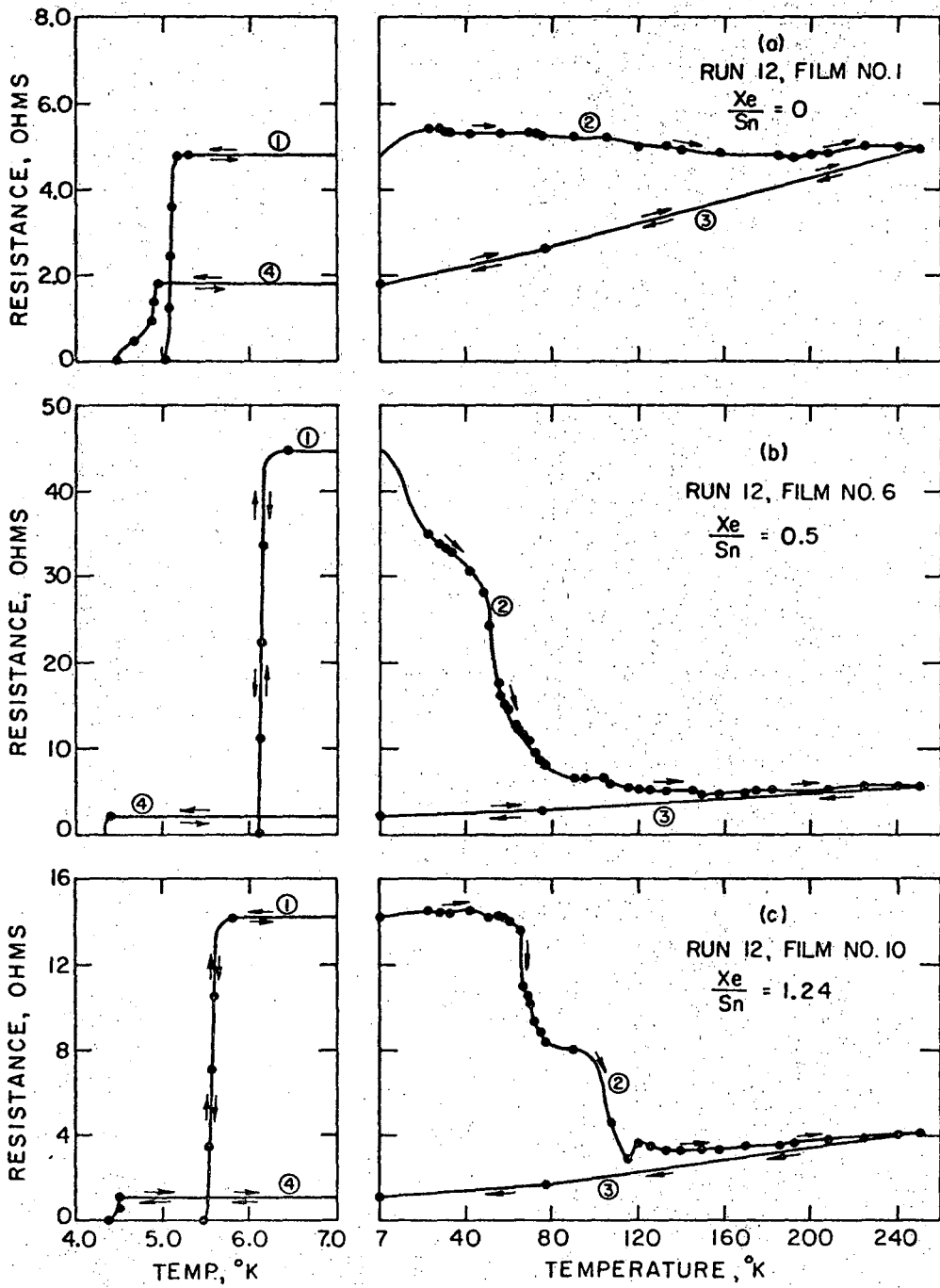
Figure 6



XBL 705-986

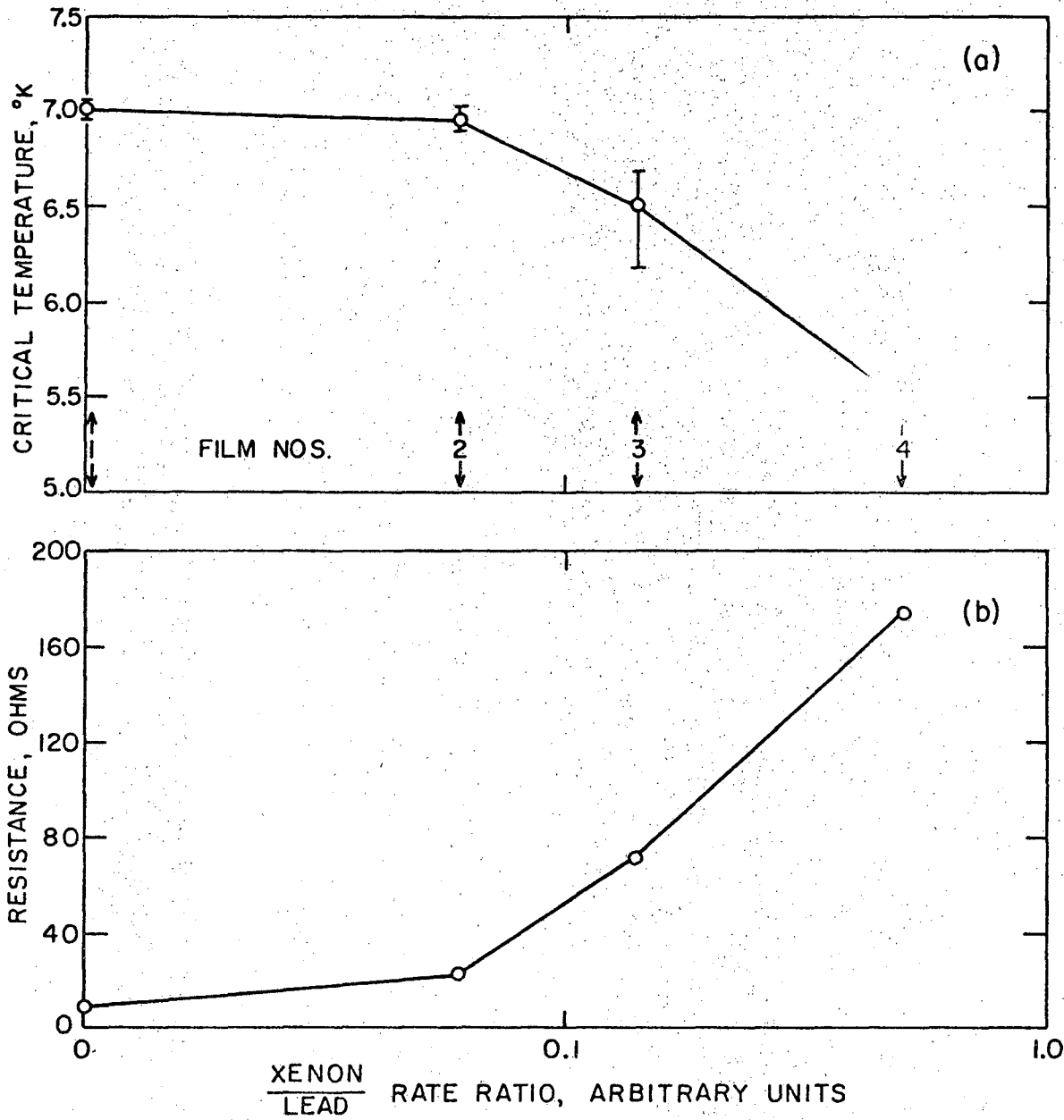
Figure 7





XBL 705-988

Figure 8



XBL 705-989

Figure 9

## LEGAL NOTICE

*This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:*

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or*
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.*

*As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.*

TECHNICAL INFORMATION DIVISION  
LAWRENCE RADIATION LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720