ENVIRONMENTAL TEST PROGRAM

FOR

SUPERCONDUCTING MATERIALS AND DEVICES

Final Report

to

National Aeronautics and Space Administration
Langley Research Center
Hampton, VA 23665-5225

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Summary

This final report details work that has been carried out on a 18-month program involving the environmental testing of superconducting conducting links similar to those which may be used in the NASA-sponsored SAFIRE program. It covers the period from May, 1990 to June, 1991. The work was performed in the Ceramic Engineering Department of Clemson University and at the facilities of the Westinghouse Savannah River Company under NASA contract No. NAG-1-1127. As far as it is known, this study represents the first systematic approach to obtaining real time, long term aging and performance data on the high Tc superconducting $YBa_2Cu_3O_{7-x}$ materials.

The work described in this report was carried out under the overall direction of Clemson University with tasks being performed at both Clemson and Westinghouse (Aiken, SC). Clemson prepared the tapecast superconducting 123 material and fabricated it into substrate-supported, environmentally-protected conducting links. Following this, all of the elements were individually tested for resistance vs. temperature and Tc; and then a portion of them were kept at Clemson for further testing while a randomly selected group was delivered to Westinghouse for specialized testing and evaluation in their low temperature/high vacuum and radiation facilities. In addition, a number of control samples (12 ea.) were put on the shelf at Clemson for further reference at the end of the testing period.

Specific tests conducted at Clemson were:

all	- resistance vs. temperature, Tc
5 ea.	- thermal shock/thermal cycling
8 ea.	- long term LN immersion
5 ea.	- water immersion
10 ea.	- humidity
12 ea.	- drop test
all	- visual test

Specific tests conducted at Westinghouse/SRC were:

*8 ea.	- long term hi-vac at LN temperature
8 ea.	- radiation
*8 ea.	- outgassing
4 ea.	- vibration
8 ea.	- magnetic field
*8 ea.	- resistance vs. temperature, Tc (with and without current)
all	- visual

* indicate tests run on the same elements

A summary of the results are as follows:

1. Overall yields from the tapecast stage to the final elements is approximately 7[illegible]% - most of the fall out is due to warping during firing the tapecast strips.

2. Yields after firing are greater than 95%.

3. Mechanical failures during thermal cycling required a re-design of the element which significantly improved its performance.

4. Long term LN immersion tests are very positive - no failures.

5. Water immersion tests show that the elements are vulnerable to direct contact with water over an extended period of time at room temperature, but the encapsulant is sufficiently good to protect the element for at least three months.

6. High humidity (90% at 38 C) has had the most detrimental effect on the elements, however, the encapsulant will protect the element for at least 45 days. A heat treatment of the encapsulant has been the most significant factor in extending the protection from a few days to the present 45 days. At liquid nitrogen temperatures, humidity is not a factor of any consequence.

7. Long term hi-vacuum at LN temperatures has not had any measurable degradation effect on the elements structurally or in regard to its superconducting properties.

8. Gamma radiation did not have any effect on the properties of the elements.

9. There was no detectable difference between the samples which were subjected to 10 ma current during the long term high-vac test at LN temperature and those which had no current applied.

10. Magnetic fields (1000 Gauss) were noted to have a deleterious effect on the superconducting properties of some of the elements.

11. Vibration did not change the physical or electrical properties of the elements.

12. Outgassing of the parts over an extended period of time was very low and not considered to be a problem.

An overall summary of the results show that the elements performed very well. Indications are that this type of design would probably meet qualification specifications.

I. Introduction

The discovery of superconductivity in the high Tc (>90K) ceramic perovskite materials in 1987 has subsequently led to a large body of research which has primarily focused either in the direction of developing still higher Tc materials or in gaining a better understanding of the mechanisms responsible for superconductivity and has almost totally ignored the obvious concerns involving the application of these materials in the real world of harsh environments and extended longevity. Understandably, these concerns will become of paramount importance when devices are designed, fabricated and put into service. Since little is known about the long term stability of these materials, especially in the unique environment of outer space where large temperature fluctuations occur in a high vacuum ambient setting while being continually exposed to high energy electromagnetic radiation, it is critical to their successful application to obtain real time test data as soon as possible.

At present, the most widely researched and thoroughly characterized of the high Tc oxide materials is the composition Y Ba Cu O (designated as 123 material). Previous investigations have amply demonstrated that this material, in bulk form, is readily amenable to preparation by a variety of powder processing methods (mixed oxides, coprecipitation, sol-gel) and can be fabricated into a number of different form factors via techniques such as dry pressing, tapecasting, extrusion and injection molding; however, this material is also known to be relatively weak, brittle and sensitive to both humidity and oxygen stoichiometry. Thus, when incorporated into superconducting devices, it requires encapsulation for environmental protection as well as physical support for mechanical integrity.

The high Tc ceramic superconductor effort at Clemson University has centered on a specific application for the NASA-sponsored SAFIRE program; i.e., a low-noise, low thermal conductivity, superconducting grounding strap for a highly sensitive, far infrared, atmospheric detector. The device utilizes a pre-formed, sintered and tested material that is bonded to a rigid substrate such as in a hybrid circuit. This concept has the advantages of (1) pre-testing of the superconducting material separate from the substrate, (2) optimization of the superconducting properties of the material without limitations imposed by the substrate, (3) wider selection of substrate materials since the high temperature processing step precedes mounting onto the printed circuit board, (4) freedom from firing shrinkage and other numerous material compatibility problems and (5) high anticipated reliability because of its rigid design and encapsulation from the environment.

The effort reported here outlines a collaborative and interactive testing program between personnel at Clemson University (Clemson, SC) and Westinghouse Savannah River Company (Aiken, SC) which is directed toward obtaining first-time field test data on the superconducting grounding strap described above.

II. Objectives

This report describes work which complements and builds on the efforts previously carried out at Clemson University. It was designed to provide preliminary real time data on the suitability of using the 123 superconducting material in a space environment.

The tests of primary concern were specifically chosen to critically evaluate the various materials (e.g., 123 ceramic, epoxy encapsulants, substrates and connectors) and devices made from them in an environment which simulates, as close as possible, the actual conditions in space. Accordingly, these include (1) long term stability in a high vacuum, (2) radiation damage due to high energy gamma rays, (3) degradation of properties as a result of thermal cycling and thermal shock, (4) mechanical stability due to vibration, (5) moisture sensitivity and (6) loss of superconductivity under to exposure to magnetic fields.

III. Scope of Work

The work described in this report was carried out under the overall direction of Clemson University with tasks being performed at both Clemson and Westinghouse (Aiken, SC). Clemson prepared the tapecast superconducting 123 material and fabricated it into substrate-supported, environmentally-protected conducting links. Following this, all of the elements were individually tested for resistance vs. temperature and Tc; and then a portion of them were kept at Clemson for further testing while a randomly selected group was delivered to Westinghouse for specialized testing and evaluation in their low temperature/high vacuum and radiation facilities. In addition, a number of control samples (12 ea.) were put on the shelf at Clemson for further reference at the end of the testing period.

The following tests and testing procedures were determined from the specifications set forth for the space orbital platform (POP) and also from other conditions anticipated for the devices during service. These include:

1. Resistance vs. Temperature
2. Radiation
3. Magnetic Field
4. Long Term High Vacuum at LN Temperatures
5. Outgassing
6. Humidity
7. Vibration
8. Drop

The specific series of tests and the sequence of the testing procedure are attached to this report.

The report is divided into two parts; i.e., the first dealing with work involved with Clemson University and the second with the results from Westinghouse Savannah River Company.

IV. PART I

CLEMSON UNIVERSITY

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Abstract

Low noise, low thermal conductivity superconducting grounding links used in the NASA-sponsored SAFIRE (Spectroscopy of the Atmosphere using Far Infra-Red Emission) project were prepared from $YBa_2Cu_3O_{7-x}$ superconducting tape, individually mounted on a printed circuit board substrate and encapsulated with epoxy resin. The link's original configuration was re-designed according to preliminary results from the liquid nitrogen immersion test. The re-designed links were made via a mold process which allowed for better coverage of the superconducting strip and the solder pads. The improved elements were then evaluated in the performance test program. This program proceeded for 18 months from May, 1990, to October, 1991. The temperature vs. resistance curves(T_c) of the samples were used as to evaluate the condition of the links. The links maintained their structural integrity and electrical properties after thermal cycling, liquid nitrogen immersion, radiation, and 3 foot drop test. Consistent results were also obtained from the control specimens maintained at ambient conditions since May, 1990. High humidity was the most significant factor in the degradation of the grounding links. In humidity conditions of R. H. >90%, the elements preserved their structural integrity for at least 90 days when the environmental temperature was lower than 32°C but this was reduced to 50 days at 38°C.

I. Introduction.

Since $YBa_2Cu_3O_{7-x}$ was reported as a high T_c superconductor material in 1987, many investigators have worked on the application of this material. Its brittle behavior and moisture sensitivity, however, needed to be improved before any commercial application could be inplemented. De Gurie et. al.[1] used epoxy as a protective coating for $YBa_2Cu_3O_{7-x}$ superconductor; however, their published work was of a more basic nature and no actual $YBa_2Cu_3O_{7-x}$ superconductor devices protected by the epoxy were reported.

A low noise, low thermal conductivity superconductor grounding link for a remote infrared detector was developed at Clemson University[2-4]. This link uses a PC board substrate and an epoxy encapsulant as a rigid support and protective coating in order to maintain structural and electrical integrity of the superconductor. As far as we know, the grounding link is the first component which has been made by this technique for commercial application.

A performance test program, sponsored by NASA-Langley Research Center under contract No NAG-1-1127, was used to evaluate the grounding links. The samples used in this project were prepared at Clemson University. After the samples were prepared, temperature vs. resistance curves of the links were measured. The elements, then, were tested at Clemson University and Westinghouse / Savannah River Co. in Aiken, SC. Among the various tests, thermal cycling, liquid nitrogen immersion, water immersion, humidity, and drop tests were measured at Clemson University. The properties of the links after radiation exposure at Westinghouse were also characterized. This report records the sample preparation procedure, configuration of the sample design, and results obtained since May 1, 1990, at Clemson University.

II. Experimental Procedure.

Sample design, preparation process, devices and conditions used in property testing are described in this section.

II.1 Sample preparation.

Figure 1 shows the preparation process of the grounding links. Raw materials consisting of $BaCO_3$, CuO, and Y_2O_3 were mixed with distilled water in

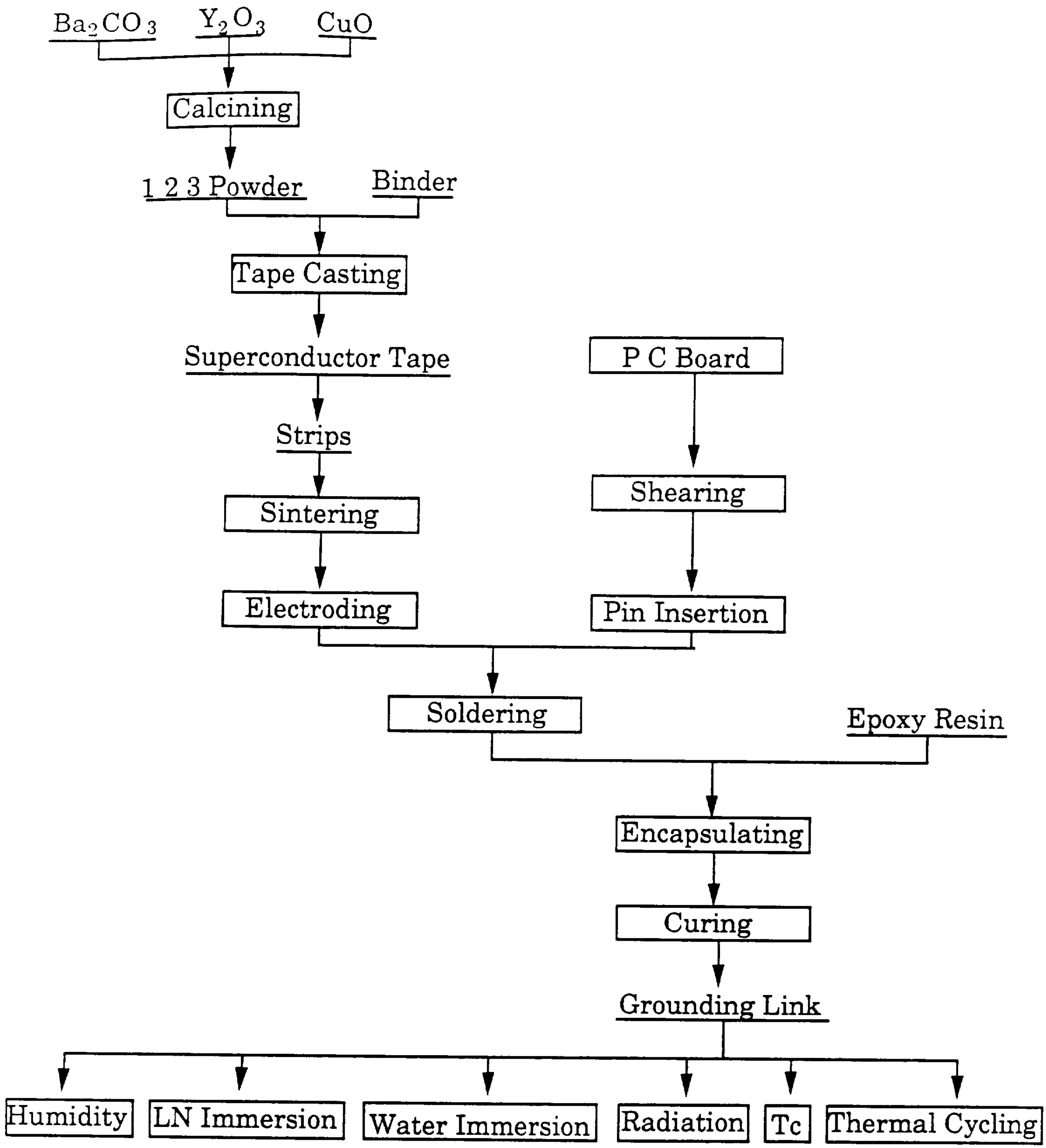

Figure 1: Fabrication process of the grounding links

a ball mill for 1 hour. The mixed powder was calcined at 900°C for 5 hours and annealed at 450°C for 12 hours in air. This calcination procedure was repeated three times. After final calcination, a tape casting slurry was prepared by mixing the calcined powder and binder (Metoramic Sciences Inc., B73305) in the ratio of 150 grams powder to 80 grams binder. A $YBa_2Cu_3O_{7-x}$ superconductor tape made by the tape casting method, as shown in Figure 2, was cut into strips 0.135 inch wide x 4.0 inch long x 0.025 inch thick. The strips were sintered at 910°C for 12 hours and annealed at 450°C for another 12 hours before they were cooled to room temperature. An electrode firing process(5) was used to apply a high density silver electrode (Heraeus Cermalloy 8710) onto both end of the strips, as shown in Figure 3. The best electroding conditions found from the previous project (Contract No. NAG-1-820); i.e., firing the electrodes at 900°C for 12 minutes and annealing at 450°C for 12 hours, were used to fire the electrodes. After electroding, the superconductor strips were soldered to silver tabs or to gold plated pins inserted into the PC boards.

A 0.05 inch thick uncoated PC board (Westinghouse) was cut (sheared) to a size of 0.225 in x 4.6 in. Silver foil and gold-plated pins (Aim Pin, 40-9856) were used as end connections. The soldered strips were temporarily mounted on a support stage and encapsulated with epoxy resin (Envirotex thermosetting epoxy), as shown in Figure 4. When the epoxy became semi-rigid, the samples were cured at different temperatures and times. After curing, the grounding links were marked with a serial number; C-batch #-firing #-thickness-width-part #. An S was added after the serial number if Ag tabs were used as the end electrodes, as shown in Figure 5.

II.2 Property testing.

The grounding links made in this project were evaluated by the following testing procedure:

1. resistance vs. temperature- T_c,
2. liquid nitrogen immersion,
3. water immersion,
4. humidity test,
5. thermal cycling test,

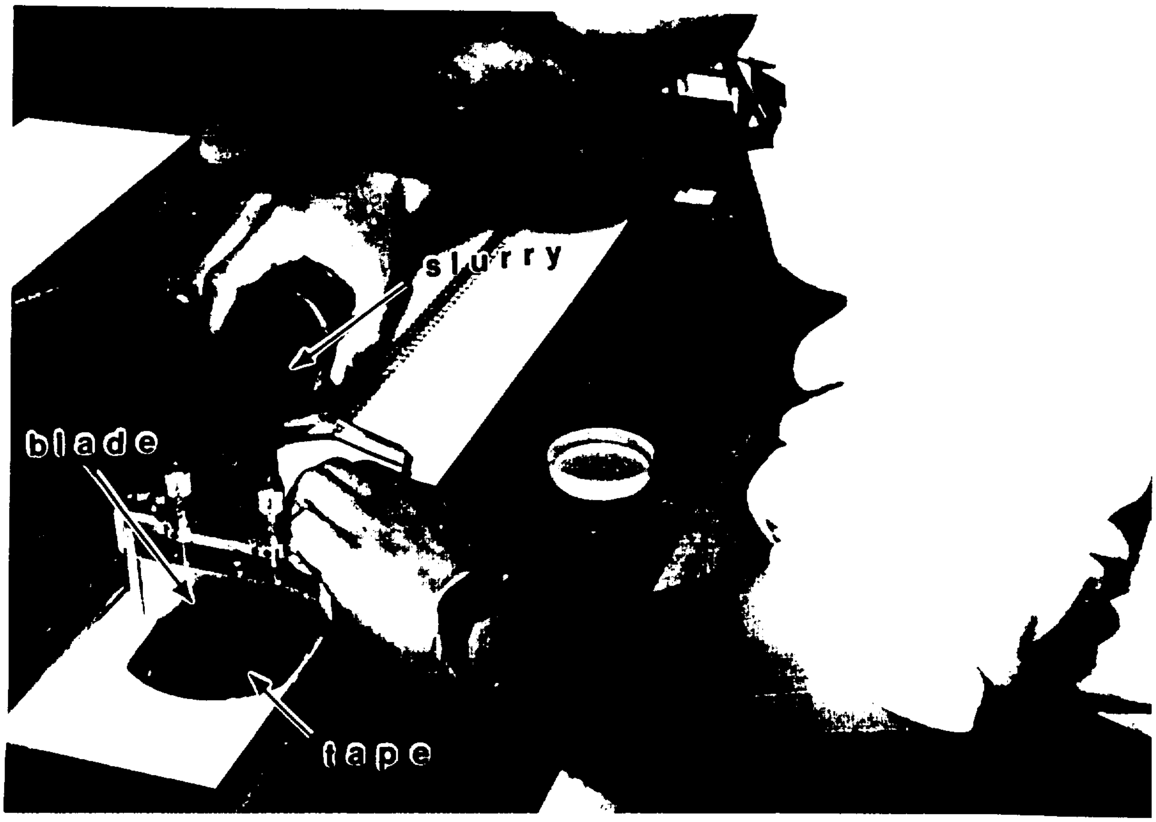

Figure 2: Tape casting of $YBa_2Cu_3O_{7-x}$ superconductor.

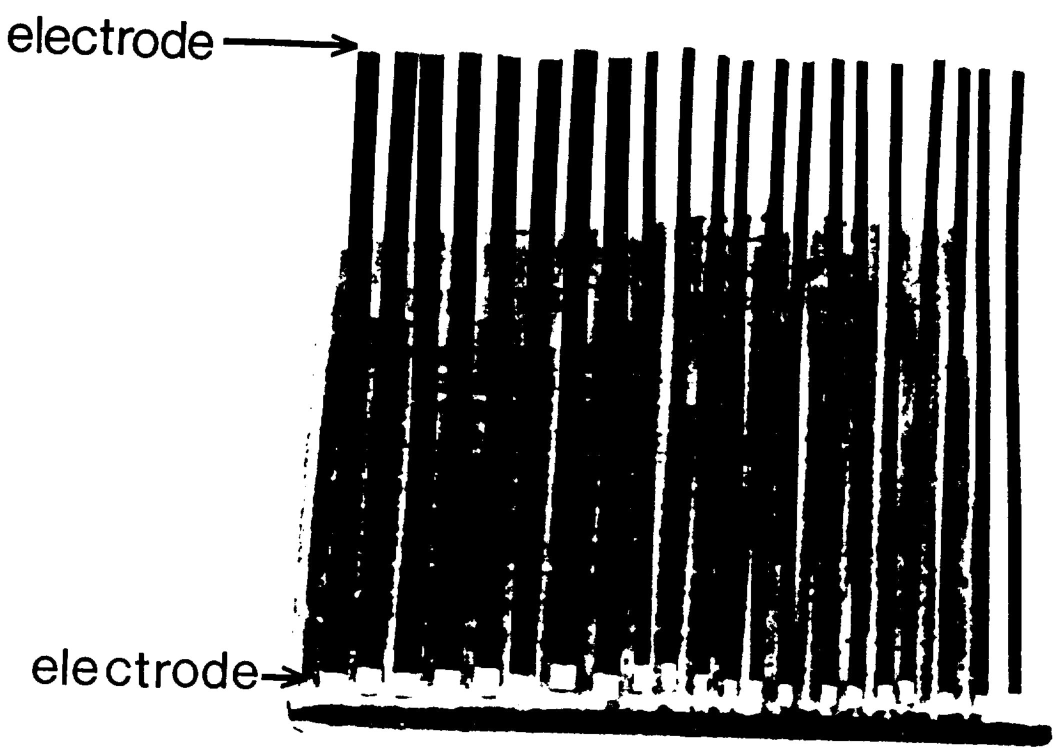

Figure 3: Electroding process for $YBa_2Cu_3O_{7-x}$ superconductor strips.

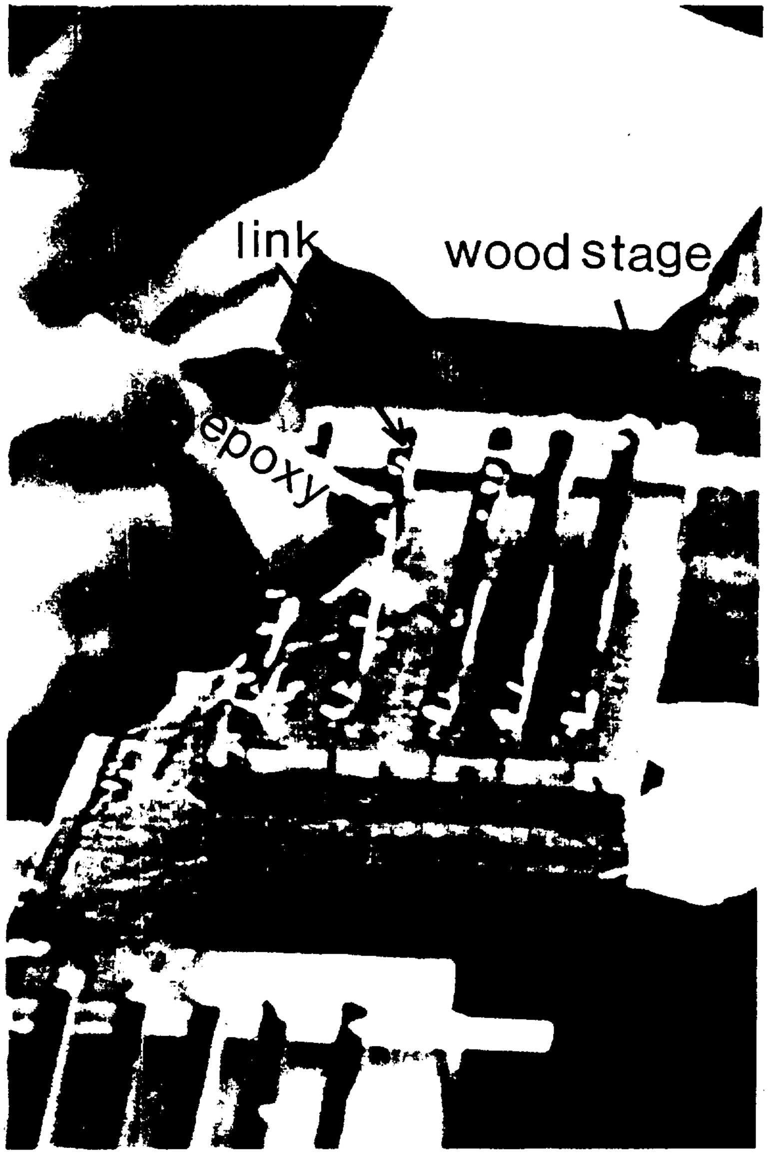

Figure 4: Encapsulating of the superconductor links.

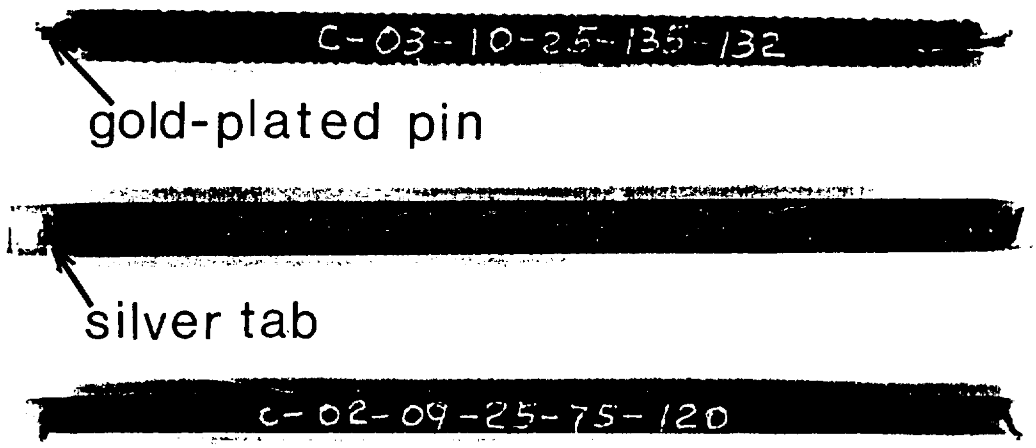

Figure 5: Serial number of grounding links.

6. drop test, and
7. radiation test.

Table 1 lists the device and/or conditions used in this testing.

Table 1: Devices and conditions used in the property measurements.

Property	Device	Conditions
Critical temperature	Keithley micro-ohmeter Model No.580	0.1 A current for R_{77} Measurement
LN immersion	LN dewar	LN temperature
Water immersion	Water pan	Room temperature
Humidity test	Blue M Model No. VP-100RAT-1	38°C, 90% R.H.
Thermal cycling	Hand	3 minutes in LN 10 minutes in the air
Dropping test	Hand	3, 6, 12, 24 foot dropping height
Radiation test*		Cs_{137} Gamma radiation

*: The radiation exposure was made at Westinghouse / Savannah River Co. in Aiken, SC.

II.3 Configurations of the sample design.

The sample design was improved according to the preliminary results from the liquid nitrogen immersion test.

a. Step 1

Originally, the links were made by pouring the epoxy onto the superconductor strips and the PC board, and allowing the surface tension of the liquid to form a coating over and under the part. This process was named the "no-mold" process. In this process, there were three kinds of defects, i.e., Type I, II and III defects, as listed in Table 2. These occurred individually or in combination with one another after liquid nitrogen immersion. In the no-mold process, the epoxy was prepared at low viscosity to insure coverage of the superconductor, however, this usually resulted in poor coverage of the solder area by the epoxy. Thus, Type I defect formed around the solder areas of the links during liquid nitrogen immersion, as shown in Figure 6. Differential thermal expansion and interface mismatching between the solder and the epoxy accounted for this kind of defect.

Table 2: Occurrence and mechanism of different types of defects in the grounding links after the liquid nitrogen immersion test.

Type	Occurrence	Mechanism
I	Crack formed around the solders	Mismatching between the epoxy and the solders,when the solder was not completely covered by the epoxy
II	Cracks along the edge of the superconductor	High stress concentration along the edge of the superconductor, when the edge of the superconductor was only covered by a thin layer of epoxy
III	Bubbles formed at the interface between the epoxy and the superconductor	Deformation of the links during the immersion test caused the delamination between the epoxy and the superconductor
IV	Bubbles formed at the interface between the electrodes and the superconductor	Deformation of the links during the immersion test caused the delamination between the electrode and the superconductor
V	Delamination between the epoxy and the substrate	High stress concentration located at the edge of the epoxy and the substrate interface

Type II defects were specified as those due to high stress concentration along the top edges of the $YBa_2Cu_3O_{7-x}$ superconductor strips where less epoxy was present. When the epoxy was not thick enough to resist the thermal stress,

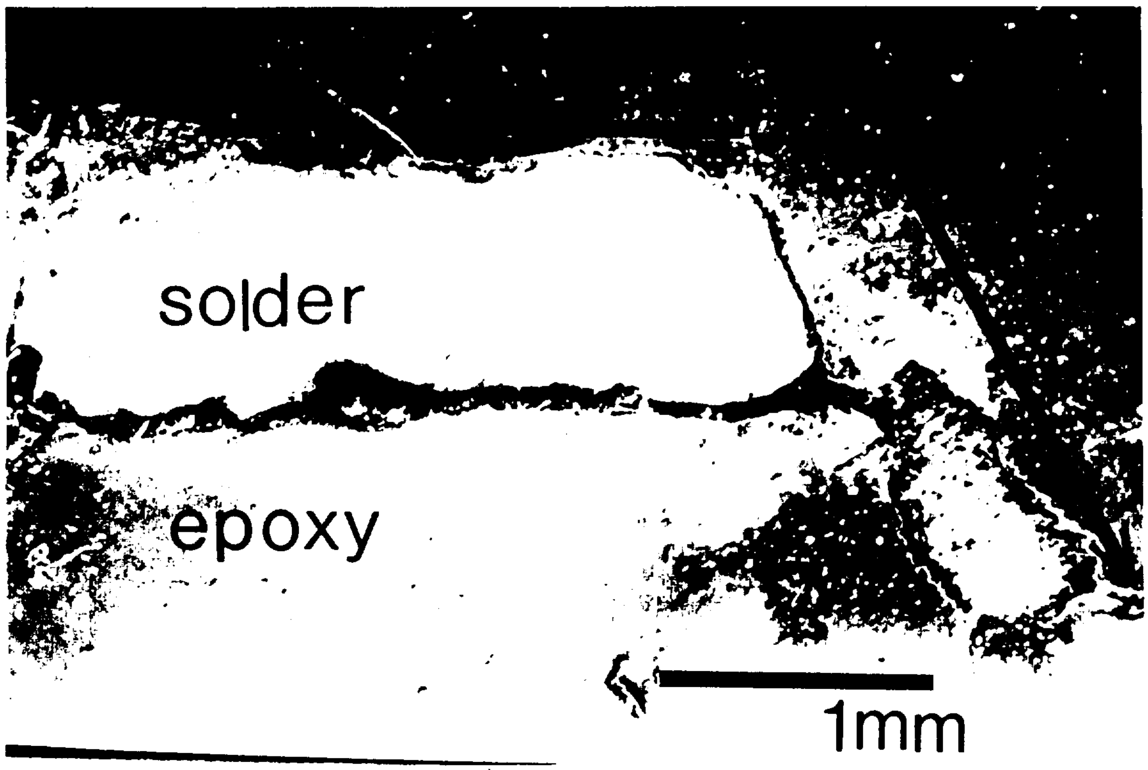

Figure 6: The cracks formed around the electrode area after the LN immersion test.

cracks were generated along this edge. Once this kind of defect was formed, it progressed along the edge of the $YBa_2Cu_3O_{7-x}$ superconductor and penetrated into the interior of the link along the interface between the epoxy and the $YBa_2Cu_3O_{7-x}$ superconductor.

Some bubbles were formed between the epoxy and the superconductor after 48 hours liquid nitrogen immersion. This kind of crack was indicated as Type III defect. Because the thermal expansion of the epoxy was larger than that of the PC board and the superconductor(2), bending deformation occurred in the links during liquid nitrogen immersion. This kind of deformation and the mismatching between the epoxy and the $YBa_2Cu_3O_{7-x}$ superconductor were considered to be the mechanisms responsible for Type III defects.

Figure 7 illustrates the location of different types of defects on the links. Figure 8 shows examples of the links with different types of defects. Type I, II and III defects were found in the samples made by the no-mold process. In order to eliminate these defects, increased coverage of the epoxy over the solder area, increased epoxy thickness along the superconductor strips and decreased bending deformation of the links during liquid nitrogen immersion were necessary and needed to be incorporated into the fabrication process.

b. Step 2

An inverted, half-round mold the size of a soda straw, as shown in Figure 9, was used to cover the top of the link during encapsulation as a means of retaining the epoxy on the solder surfaces and keeping the solder areas and the strips completely covered by the epoxy. This technique was named the "mold" process. Figure 10 shows different links' side views between the mold and no-mold process. Type I and II defects did not occur in links made via the mold process. The delamination between the epoxy and the superconductor strip, however, was still observed. Instead of forming the bubbles between the epoxy and the superconductor interface, the defect formed at the interface between the epoxy and the electrodes and propagated to the superconductor and the epoxy interface. This type of defect was designated as Type IV. Decreasing the deformation strain seemed to be one of the best methods of avoiding Type IV defects. After decreasing the epoxy thickness on the top of the link, the link's deformations decreased during liquid nitrogen immersion. Type IV defect has not occurred after this modification.

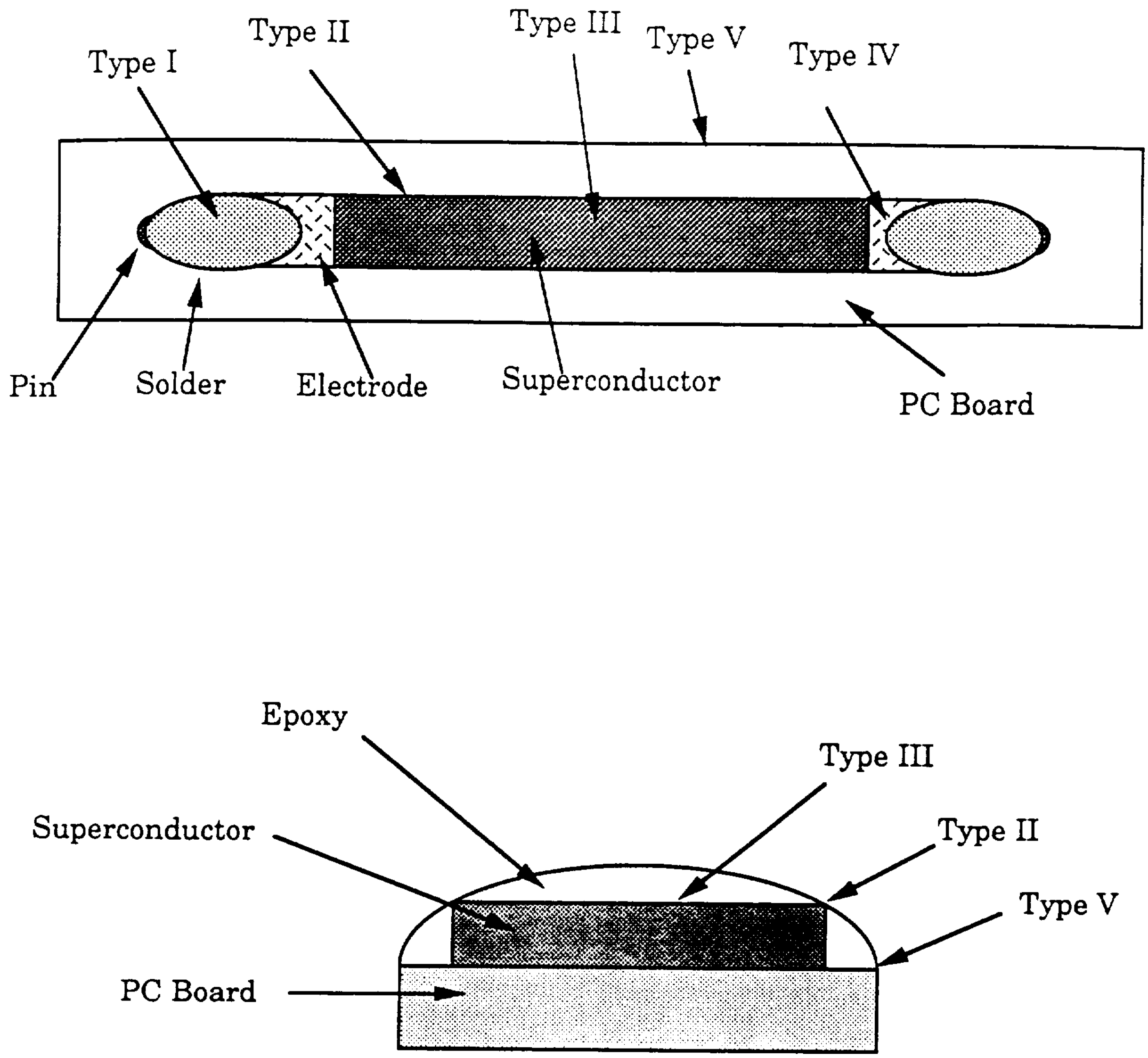

Figure 7: The location of different types of the defects on the links.

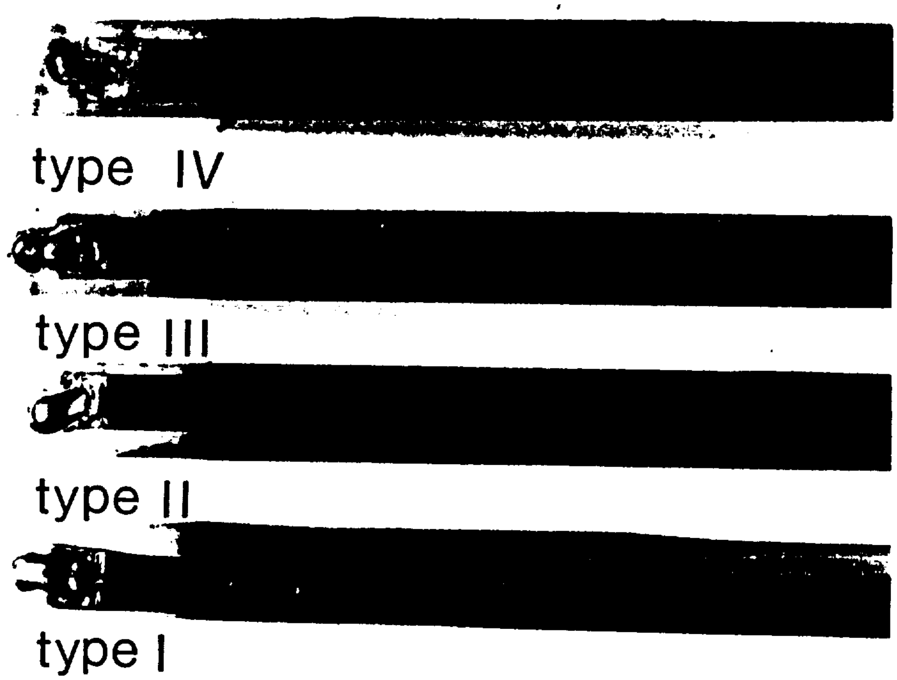

Figure 8: Examples of the type I, II, III and IV defects.

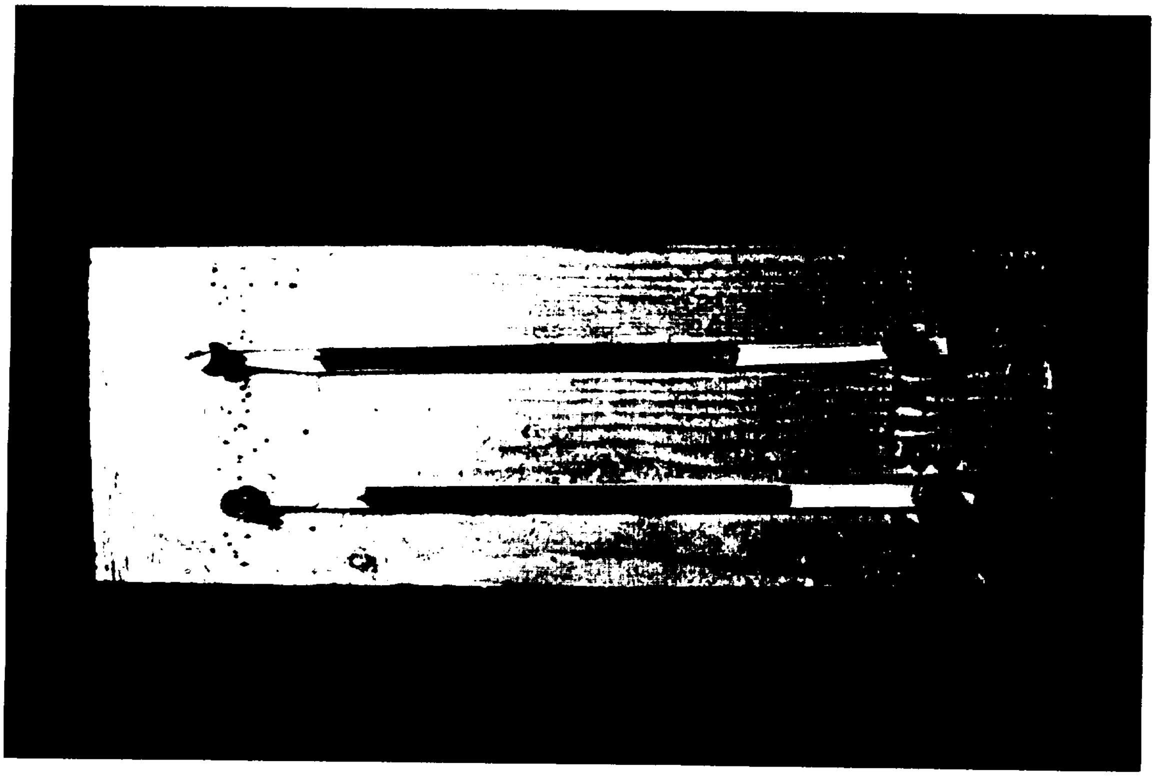

Figure 9: The encapsulation step of the mold process.

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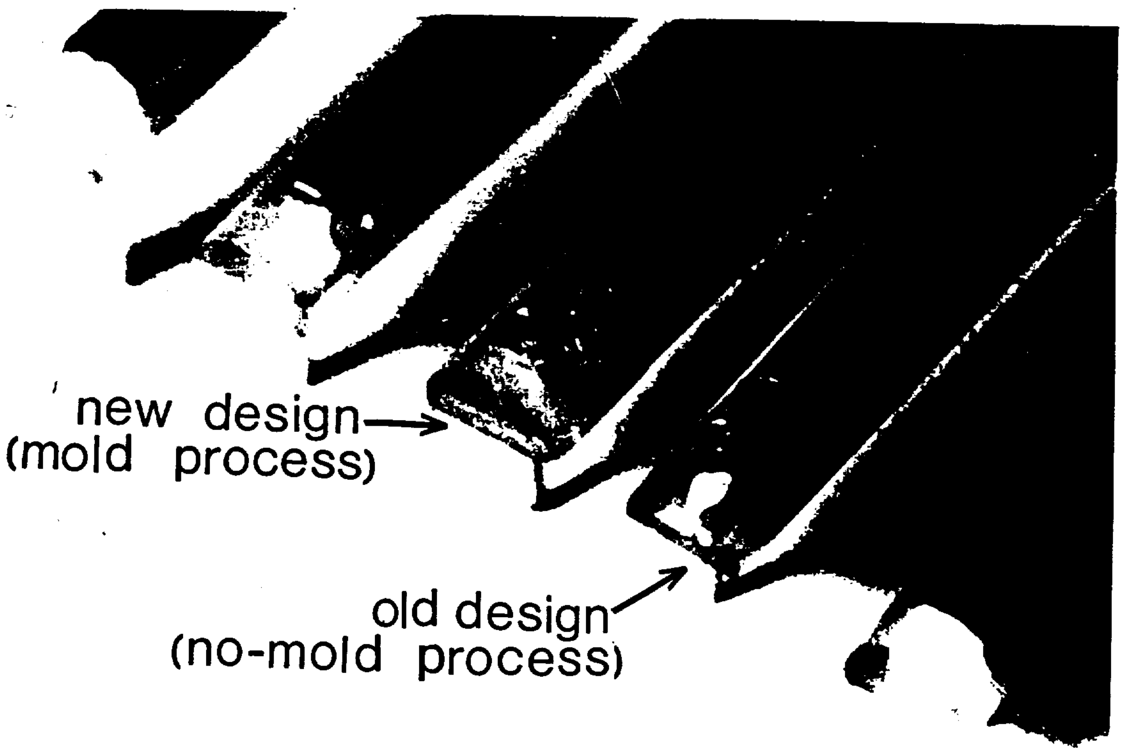


Figure 10: Side view of the links made by the mold and no-mold process.

c. Step 3

Another type of defect, which was observed after the preceeding modifications had been implemented, was noticed to occur at the edge of the epoxy and the PC board interface. This defect was determined to be a delamination between the epoxy and the PC board. The defect was caused by a high stress concentration along the edge of the interface. Changing the cross section of the PC board from rectangular to trapezoidal changed the stress distribution. In this configuration, the epoxy essentially covered three sides of the PC board, as shown in Figure 11, and the stress concentration at the interface edge decreased. Thus, the deformation of the links in the liquid nitrogen immersion test decreased.

From the performance results, as will be discussed in the next section, the re-designed links made by a modified process which included all of improvements showed good reliability and excellent structural integrity after the liquid nitrogen immersion test.

III. Results and Discussion.

III.1 Resistance variation in the fabrication process.

Table 3 lists the resistance change of the $YBa_2Cu_3O_{7-x}$ superconductors, at room temperature, after the electroding, soldering, encapsulating and curing steps. The resistances, by necessity, were measured by the two-point method. At room temperature, the pin, electrodes and solder had a lower combined resistance (~ 3-10 mΩ) than the $YBa_2Cu_3O_{7-x}$ superconductors. Hence, the major contribution to the resistances of the links were from the $YBa_2Cu_3O_{7-x}$ superconductors, themselves. It can be seen from Table 3 that the resistances of the $YBa_2Cu_3O_{7-x}$ superconductors started to increase after the encapsulating step. Only a few parts were found to increase at this step, however, there was a 10.8% average resistance increase after heat treatment. The heat treating conditions consisted of curing the encapsulated samples at 110^{o}C for 1 hour. The links which were not heat treated had a similar 10.8% resistance increase, as shown in Appendix I, after three months aging in air. The heat treated samples still had 2.1% increase in resistance after this aging. Therefore, the $YBa_2Cu_3O_{7-x}$ superconductor had about 13% room temperature resistance increase before the epoxy became stable.

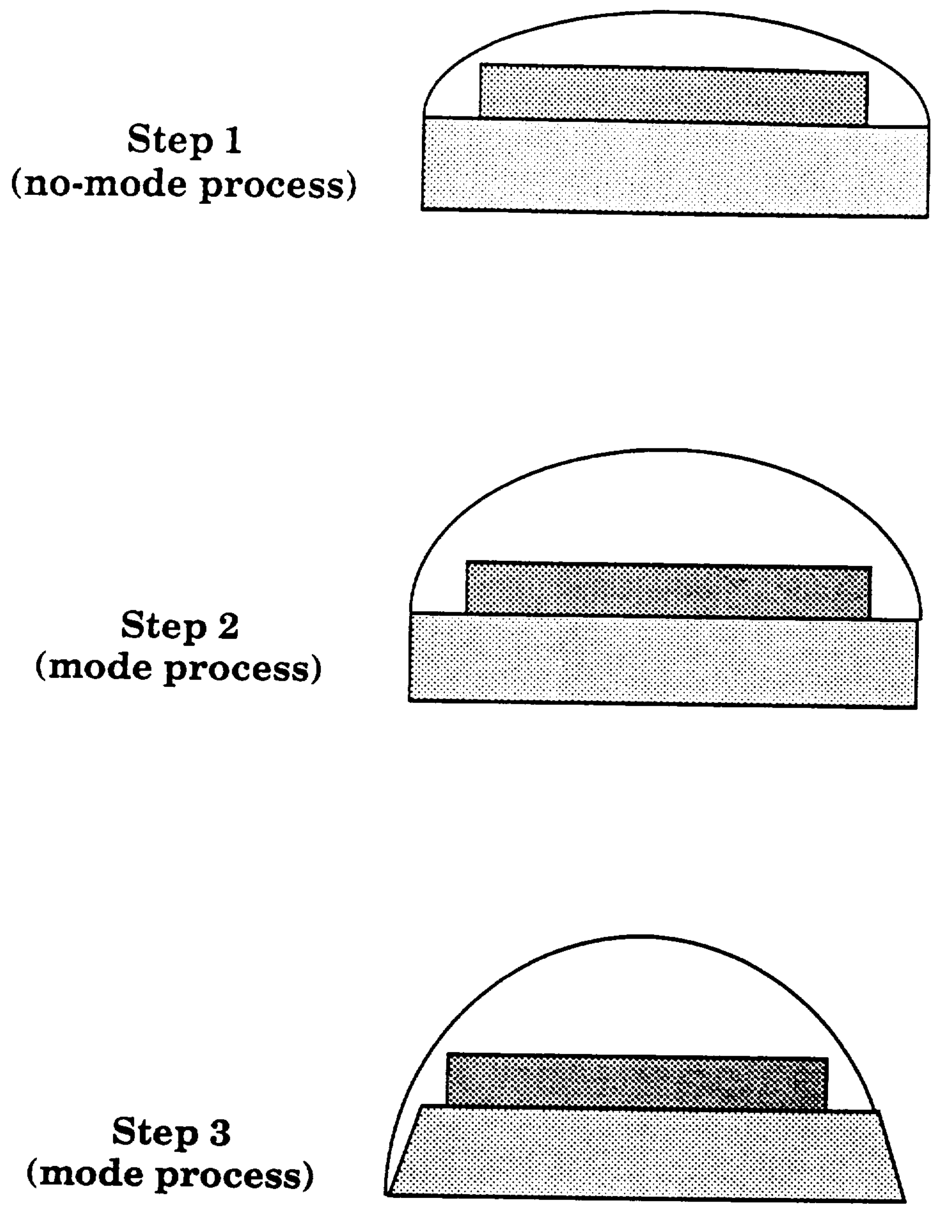


Figure 11: Cross section of the links at each step.

Table 3: The variation of the $YBa_2Cu_3O_{7-x}$ resistance at each step of the fabrication process.

unit: Ω

link No	Electroding	Soldering	Encapsulating	Heat Treatment
341	1.19	1.21	1.23	1.36
342	1.05	1.04	1.06	1.18
343	0.95	0.95	0.97	1.08
344	0.95	0.95	0.97	1.08
345	0.89	0.90	0.93	1.02
346	0.90	0.90	0.93	1.02
347	0.94	0.95	0.97	1.08
348	0.95	0.96	0.98	1.08
349	0.96	0.96	0.98	1.09
350	0.99	1.00	1.03	1.14

III.2 Temperature vs. resistance- T_c.

The temperature vs. resistance (T_c) curve of each link was measured before it was used in performance testing. Since only two electrodes were applied to each part, a two-point method was used in this measurement.

The resistance of the links at room temperature were in the range between 1.0 to 2.5 Ω. Some selected results of the links' resistances at room temperature are listed in Table A-2, in Appendix II. Because the $YBa_2Cu_3O_{7-x}$ superconductor's resistance at room temperature dominated the resistance of the links, the links with silver tabs or gold-plated connectors had the same resistance range at this temperature. The variation in the resistances of the links might be caused by variability in the sample dimensions or by a non-uniform firing temperature due to location within the furnace, since 30 superconductor strips were fired at the same time.

Figure 12 shows typical results of temperature vs. resistance (T_c) measurements of the links with gold-plated or silver tab connectors. Both curves showed a temperature-resistance relationship which was similar to the curve obtained from the superconductor tape as shown in Figure 13 (bottom figure). The transition temperatures of the links were around 85~90 K, as listed in Table A-2. Because the links were mounted on the sample holder in the direction perpendicular to the liquid nitrogen surface (vertical direction) during T_c

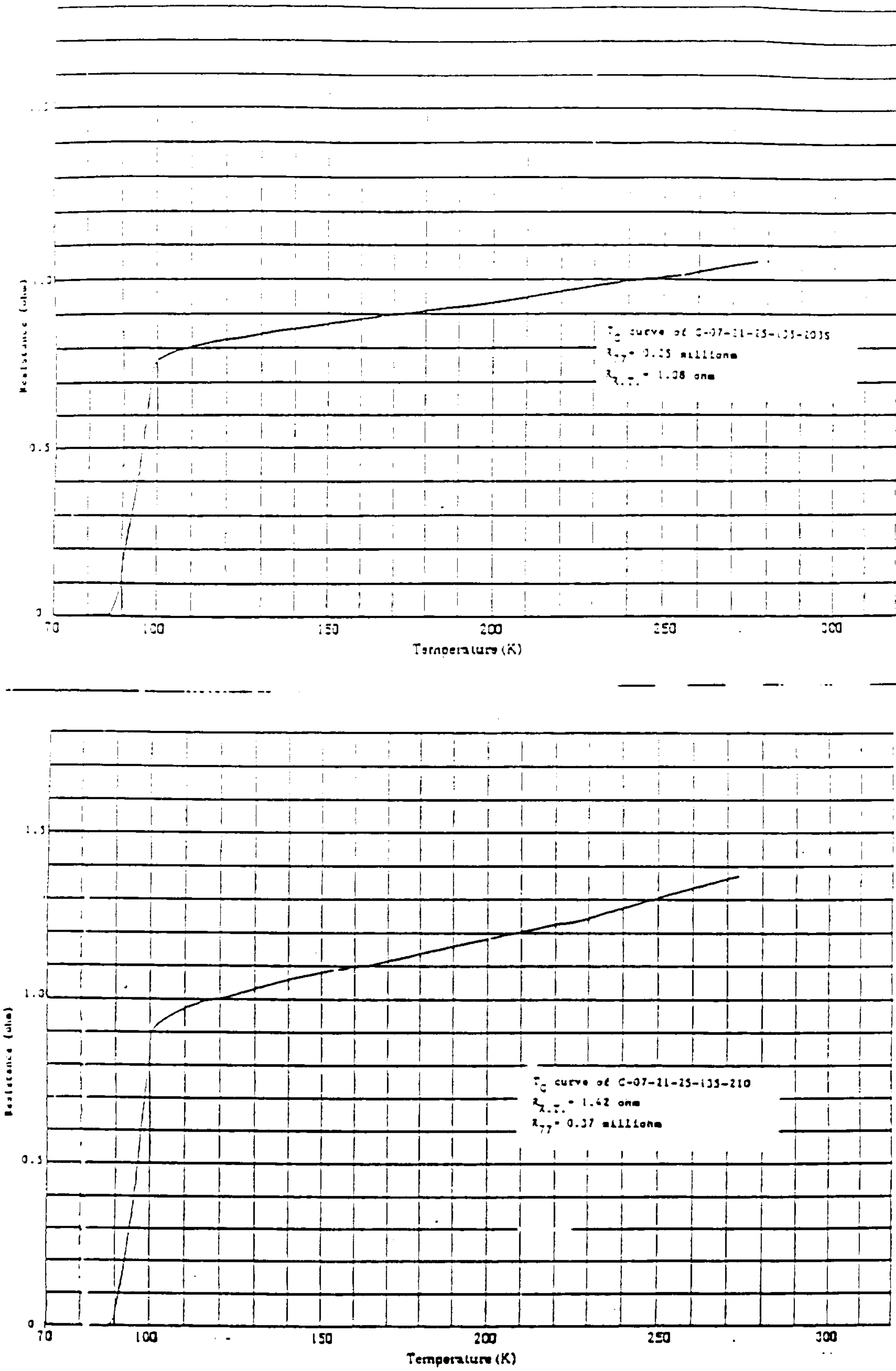
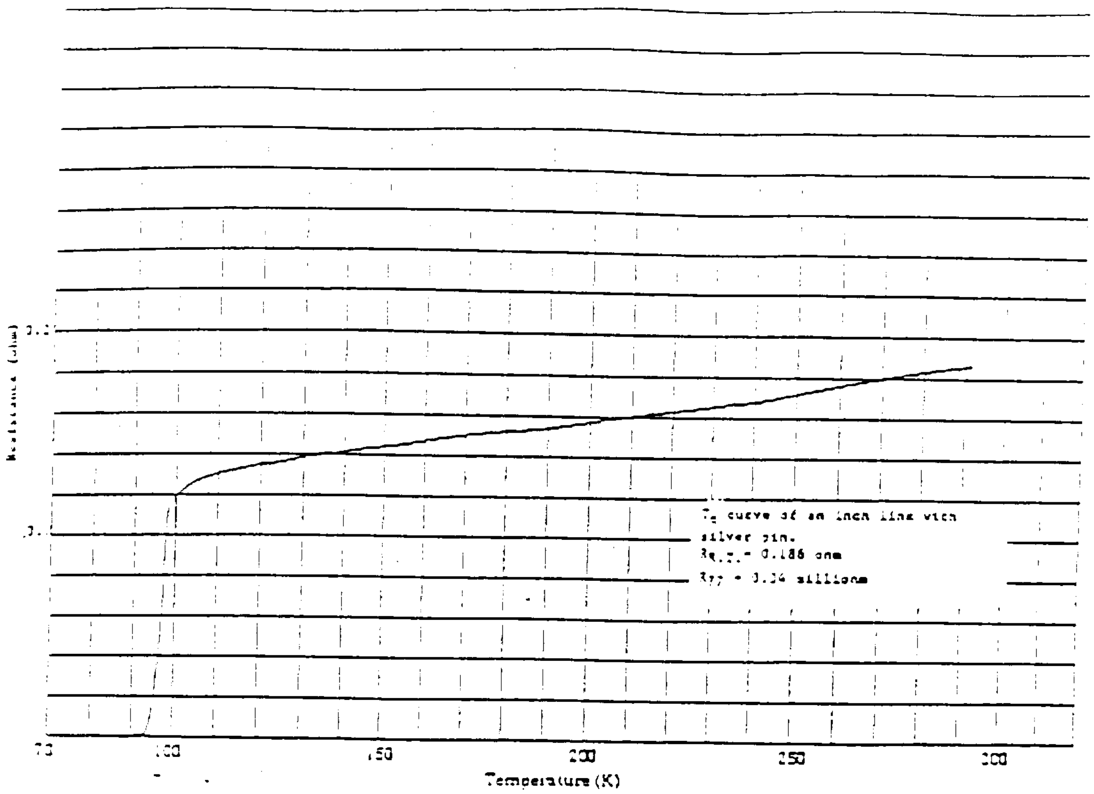


Figure 12: T_c curves of the links with silver tabs (top) and gold-plated pins (bottom).



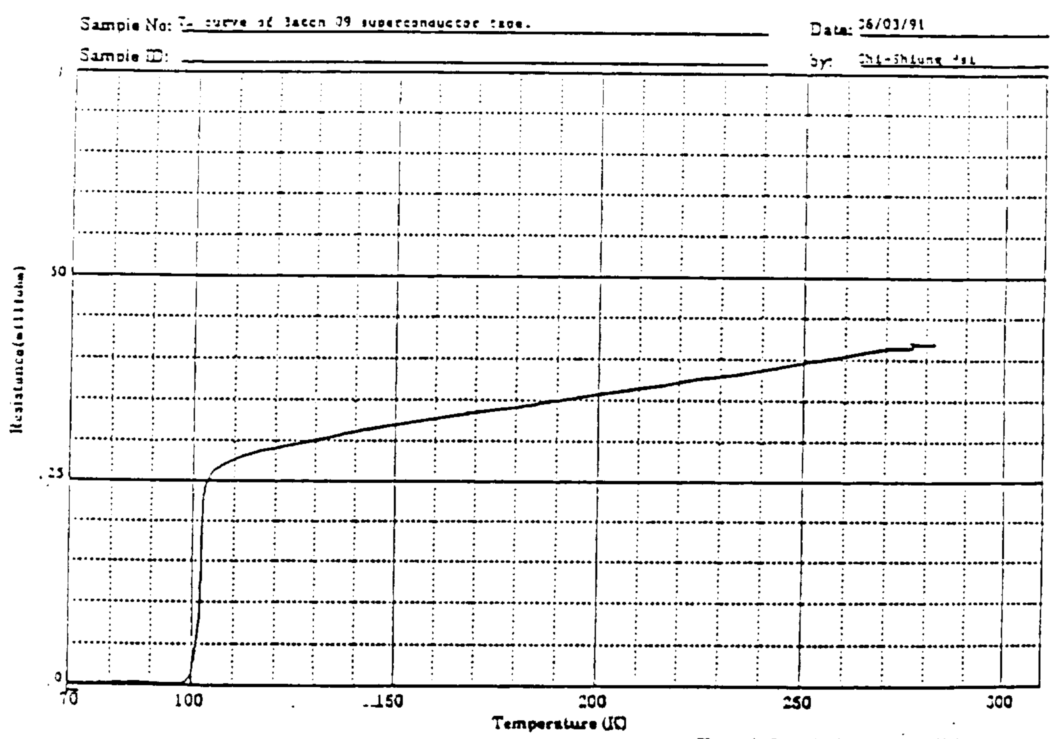


Figure 13: T_c curves of a one inch link (top) and a superconductor tape (bottom).

measurement, the temperatures were measured at the center of the links. The links, therefore, had a more broadened transition temperature range (ΔT) than that of a superconductor tape or a one-inch link, as shown in Figure 13. The type of pins used did not have much influence on the transition temperature; i. e., gold plated or silver tab, as shown in Appendix II. Some temperature vs. resistance results are included in Appendix III. All of them show a similar shape of the T_c curve.

The resistances of the links at 77K were not influenced by the resistance of the links at room temperature. Below the transition temperature, the links with gold-plated pins had resistances from 1.0 to 2.5 milliohms, whereas the links with silver tabs exhibited resistances between 0.23 and 0.5 milliohms. Thus, there was a one milliohm difference in the resistance between the links made with gold-plated pins and the links made with silver tabs at 77K. The one-inch link made with silver tabs, as shown in Figure 13, also had a resistance in the same range as the links made in the regular length. Therefore, when the materials were in the superconducting state, the resistances of the links were dominated by the resistances of the pins, solder and electrodes.

III.3 Thermal cycling test.

Five samples were used in thermal shock testing. The links were immersed in liquid nitrogen for two minutes and exposed in air at room

Table 4: The resistances of the links during thermal cycling test. The resistances were measured at room temperature.

unit: Ω

	No . of cycles						
Link No.	0	1	3	5	7	9	10
181	1.61	1.61	1.61	1.62	1.59	1.60	1.60
182	1.72	1.72	1.72	1.71	1.70	1.70	1.70
183	1.54	1.55	1.55	1.54	1.54	1.54	1.54
184	1.56	1.58	1.57	1.58	1.56	1.56	1.56
185	1.65	1.66	1.66	1.65	1.64	1.65	1.65

temperature for five minutes. The links were tested for 10 times. Table 4 lists the resistances of the links after each testing period. Consistent results were obtained from the samples at the beginning and after thermal cycling 10 times. The links also retained their mechanical integrity after the test; i.e., they did not have any defects, cracks, delaminations, etc.

III.4 Long term liquid nitrogen immersion.

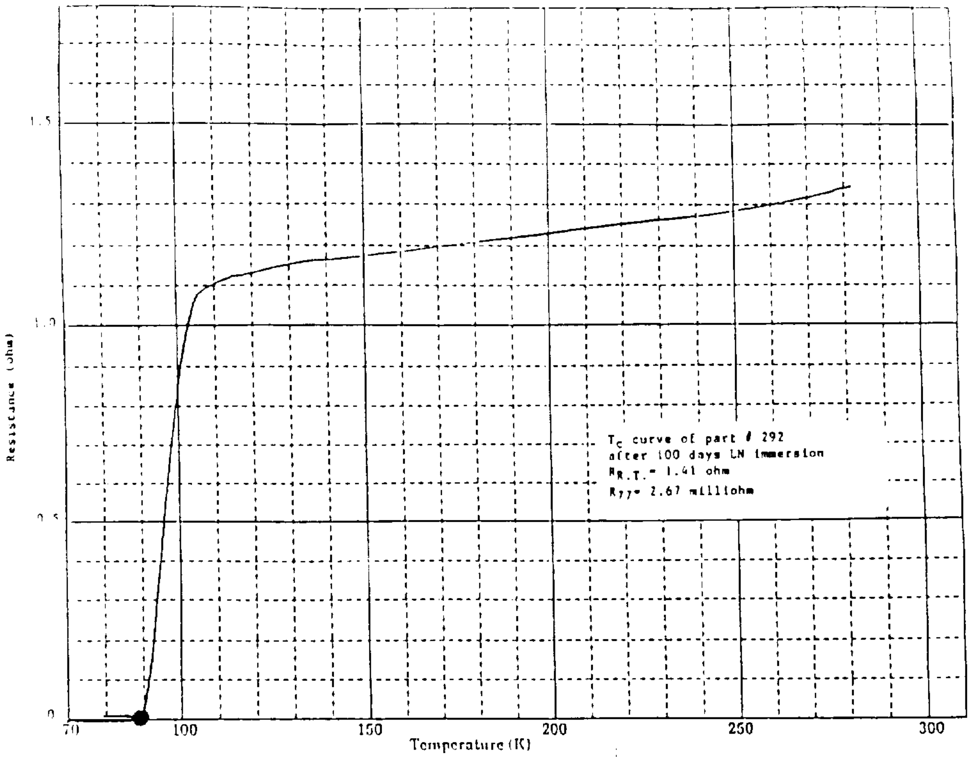
Eight links were immersed in liquid nitrogen for one year (since October 19, 1990). From that time on, the links were pulled out from the liquid nitrogen to measure their resistances and to inspect their mechanical integrity once a week. Table 5 lists selected results in this test. More detailed results are listed in Appendix IV. At room temperature, the resistance of each link has remained constant during one year of liquid nitrogen immersion. Because the pins of sample # 297 and 298 were overheated during soldering (253 immersion days), the connections between the pins and the electrodes of these samples were broken, and consequently were not measured.

Table 5: The resistances of the links in long-term liquid nitrogen immersion. The resistances were measured at room temperature.

unit: Ω

Date	10/19/90	10/26/90	12/09/90	01/27/91	03/18/91	05/05/91	06/30/91	08/18/91	10/04/91	10/18/90
Day	0	7	50	101	151	198	253	302	350	365
Link No.										
291	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
292	1.4	1.4	1.4	1.4	1.4	1.3	1.4	1.4	1.4	1.4
293	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
294	1.9	1.9	1.9	1.9	1.9	1.8	1.9	1.8	1.9	1.9
295	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
296	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
297	1.3	1.3	1.3	1.3	1.2	1.2	1.3	-	-	-
298	1.8	1.6	1.7	1.8	1.8	1.8	1.8	-	-	-

No aging effect was found from the links in this measurement. This may be due to the low immersion temperature of 77K. Figure 14 shows the T_c curve of the link #292 after 100 days and one year liquid nitrogen immersion. All the samples, in this test, had similar temperature vs. resistance curves between the 100 day and one year immersion tests, as shown in Figure 14 and Appendix V.



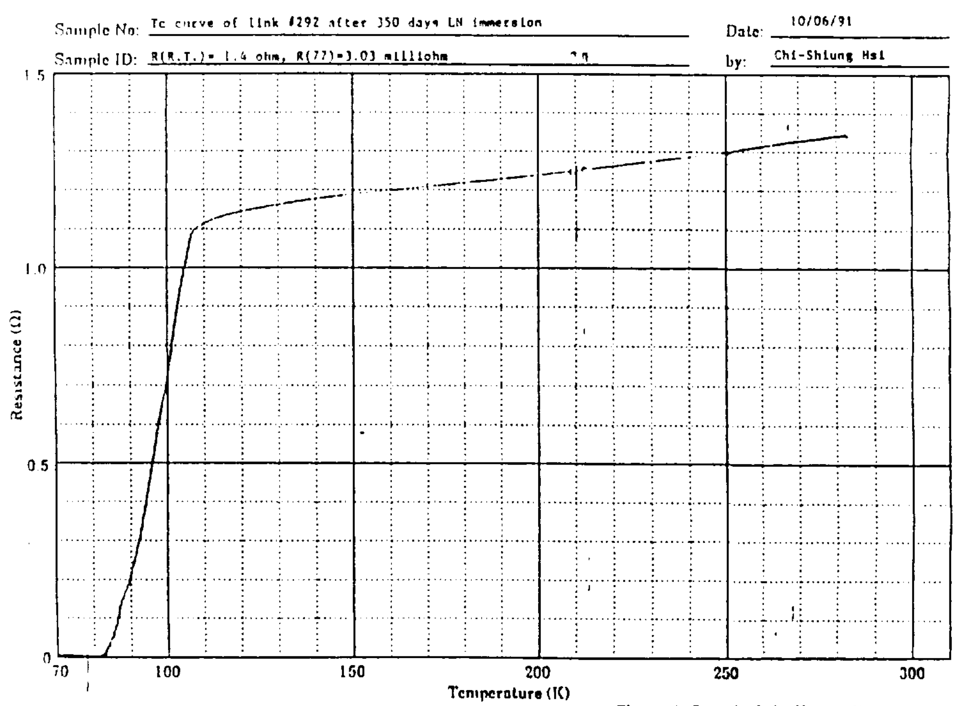


Figure 14: T_c curve of link #292 after 100 days and one year liquid nitrogen immersion.

The cracks on the epoxy as described previously were not found to be present in the samples in this immersion test. Both the structural integrity and electrical properties of the elements were maintained after long term liquid nitrogen immersion.

III.5 Moisture sensitivity.

Water immersion and humidity tests were selected in order to examine the moisture sensitivity of the link.

a. Water immersion test.

In this test, the links were put in a water pan and immersed with distilled water. The pan was kept at room temperature. Figure 15 shows the links after 30 days water immersion. The epoxy of link #205 peeled off. It was caused by the reaction of the water and the superconductor. Because the epoxy thickness along the edge of the superconductor was thinner than at other places, the reaction occurred in this location. Once the epoxy peeled off, the reaction accelerated, and delamination proceeded further as link # 179 in Figure 15 reveals. When the epoxy along the superconductor edge was thick enough, the location on top of the electrodes became the places of weakness due to the thinner epoxy. Thus, the cracks formed at these positions.

Table 6: The resistances of the links in water immersion. The resistances were measured at room temperature.

unit: Ω

Date Link No.	5/16/91 at start	8/14/91 90 days
234	1.3	1.5
238	1.2	1.5
248	1.3	C*
250	1.2	1.3
255	1.4	1.7
259	1.4	1.7
271	1.4	1.8
272	1.5	1.8
273	1.4	1.7
277	1.5	1.8
279	1.6	1.8

C: crack

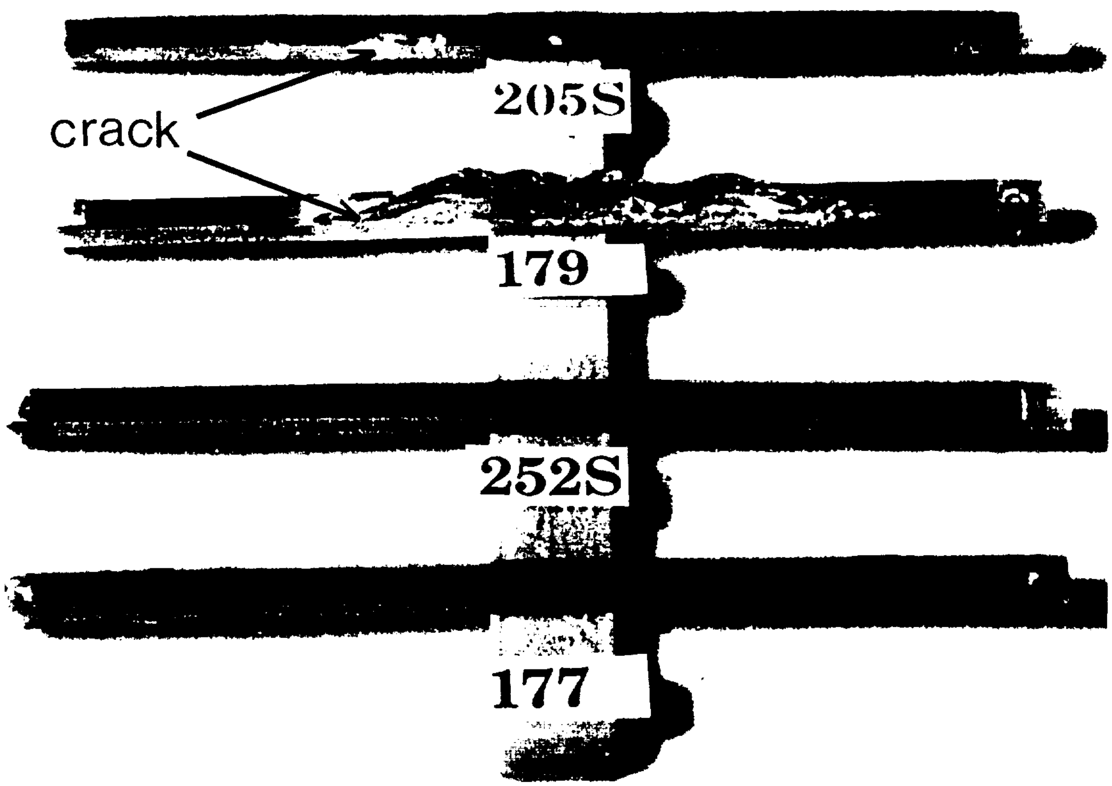


Figure 15: Photograph of the links after 20 days (205S, 252S) and 100 days (179,177) water immersion test.

After increasing the thickness of the epoxy on the top of the superconductor, the link's resistance to water corrosion was enchanced. Table 6 lists the resistance of the links after 90 days water immersion. In this test, only one out of eleven samples had a crack on it. The other samples maintained their structure integrity after 90 testing days. The samples' resistances increased as the links aged at ambient conditions.

b. Humidity test.

A 90% relative humidity environment at 38^{o}C was controlled by a Blue M environmental chamber (Model No. VP-100RAT-1). Two types of the cracks observed in the water immersion test were also found in this test. These are;

a. Type 1

When the epoxy was not thick enough, the epoxy broke at this position. Usually, this position was found along the top edge of the superconductor strips, where there was thinner epoxy thickness in the links.

b. Type 2

When the thickness of the epoxy along the superconductor was thick enough, the epoxy on the top of the solder became the weak link of the element. Type 2 cracks occurred at this position.

However, the MTBF (Mean Time Before Failure) of the samples in this test was shorter than that of the water immersion. The MTBF of the links vs. thickness is shown in Figure 16. The failure time of the link was roughly proportional to the epoxy thickness. Within 40 testing days, the cracks were found on the links having the epoxy thickness less than 0.1875 mm. In addition, some bubbles formed at the interface between the epoxy and the superconductor before the cracks formed.

Table 7 lists the resistances of the links during testing. As can be seen,the resistances of the links increased with the testing time. The links without heat-treatment had a higher sensitivity to humidity than those of the heat treated samples. This is similar to the results obtained from the

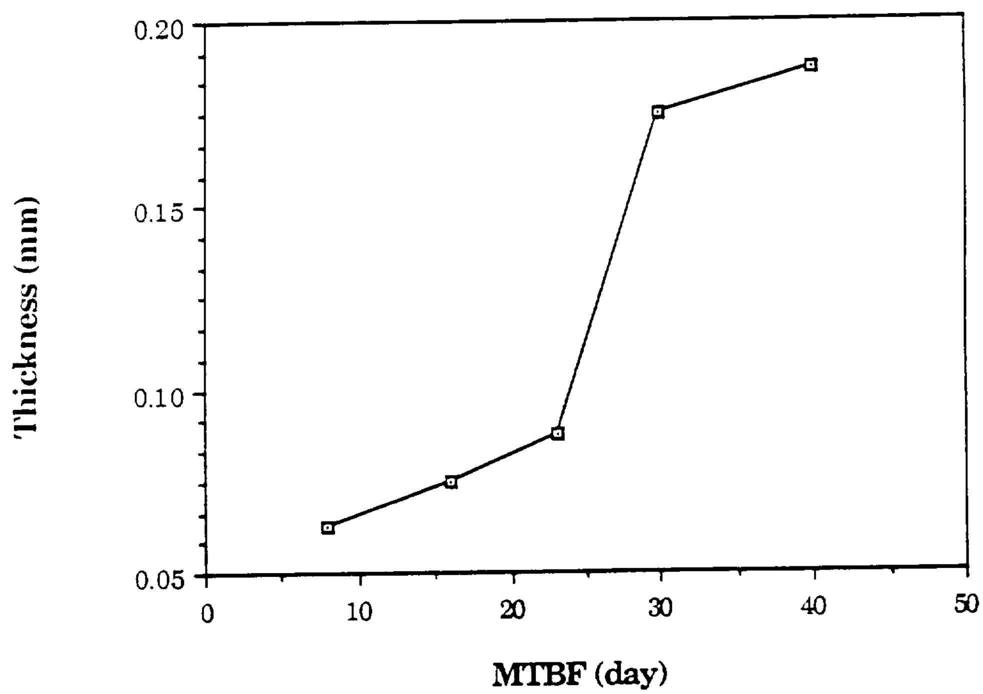


Figure 16: MTBF of the link in the high humidity test

air aged samples (refer to Appendix I).

Table 7: The resistances of the links in the humidity test. (The resistances were measured at room temperature)

unit: Ω

Day / Part #	at start	4	8	17	30	44	52
274[a]	1.6	1.6	1.7	1.9	2.2	-	-
275[a]	1.4	1.5	1.7	-	-	-	-
276[a]	1.2	1.2	1.3	1.4	1.6	1.8	C
278[a]	1.5	1.5	1.6	1.8	-	-	-
280[b]	1.6	1.5	1.6	C*			
281[b]	1.4	1.4	1.4	1.5	1.7	1.9	1.9
282[c]	1.6	1.6	1.6	1.7	1.9	2.1	2.3
283[c]	1.7	1.6	1.7	1.7	2.0	2.1	2.3
303[d]	1.6	1.6	1.6	1.7	1.8		
304[d]	2.6	2.6	2.6	2.7	2.8		

*C: Crack, a: non-heat treatment, b: 0.5 hours heat treatment, c: 1 hour heat treatment, d: 3 hours heat treatment.

When the humidity chamber's temperature was decreased to 32°C, only one out of sixteen samples had crack after 73 test days. The resistances of those links also increased with the testing time, as listed in Appendix VI. In the high humidity conditions, the link's resistance degradation was temperature dependent. Below 32°C, the epoxy protected the superconductor from high moisture for at lease 90 days. If the temperature was higher than 32°C, the links failed within approximately 50 days. The curing conditions of the epoxy was the most important factor in improving the protection time of the epoxy. Especially, when the temperature was higher than 32°C.

From the discussion above, the following conditions are necessary in the fabrication process:

1. The epoxy's thickness should be thicker than 0.2 mm.

2. The samples are to be cured at 110^{o}C for more than one hour.

III.6 Radiation test.

Figure 17 show the T_c curves of the links before and after the gamma radiation test. The curves measured after the radiation test showed the same characteristics as the curves obtained before the test.

Table 8: The resistances of the radiated links at room temperature and liquid nitrogen temperature and their critical temperature(T_c).

Link No.	Before Radiation Test			After Radiation Test		
	$R_{R.T.}$ (Ω)	R_{77} (mΩ)	T_c (K)	$R_{R.T.}$ (Ω)	R_{77} (mΩ)	T_c (K)
222	1.47	1.52	85	1.54	1.46	85
225	1.59	1.11	87	1.64	1.11	86
230	1.75	2.63	84	1.84	2.83	85
244S	1.21	0.36	88	1.27	0.21	84
247S	1.22	0.33	87	1.27	0.20	88
245S	1.24	0.33	89	1.29	0.21	88
242S	1.32	0.44	86	1.32	0.44	88

The resistances of the links at room temperature increased slightly after the test, as indicated in Table 8. Since it was almost 6 months after the samples preparation, this increase in the resistance at room temperature was caused by normal aging, as described previously. The resistance of the links at 77K did not increase, and critical temperatures of the links were in the normal temperature range. The samples also maintained their structural integrity. It can be concluded that radiation exposure had no measurable effect on the grounding links.

III. Drop test.

The resistances of the links before and after the drop test are listed in Table 9. The samples were dropped from different heights; i. e., 3, 6, 12 and 24 foot. The samples which were dropped from 3 foot showed consistent resistances with the samples before test. They also maintained their superconducting behavior, as

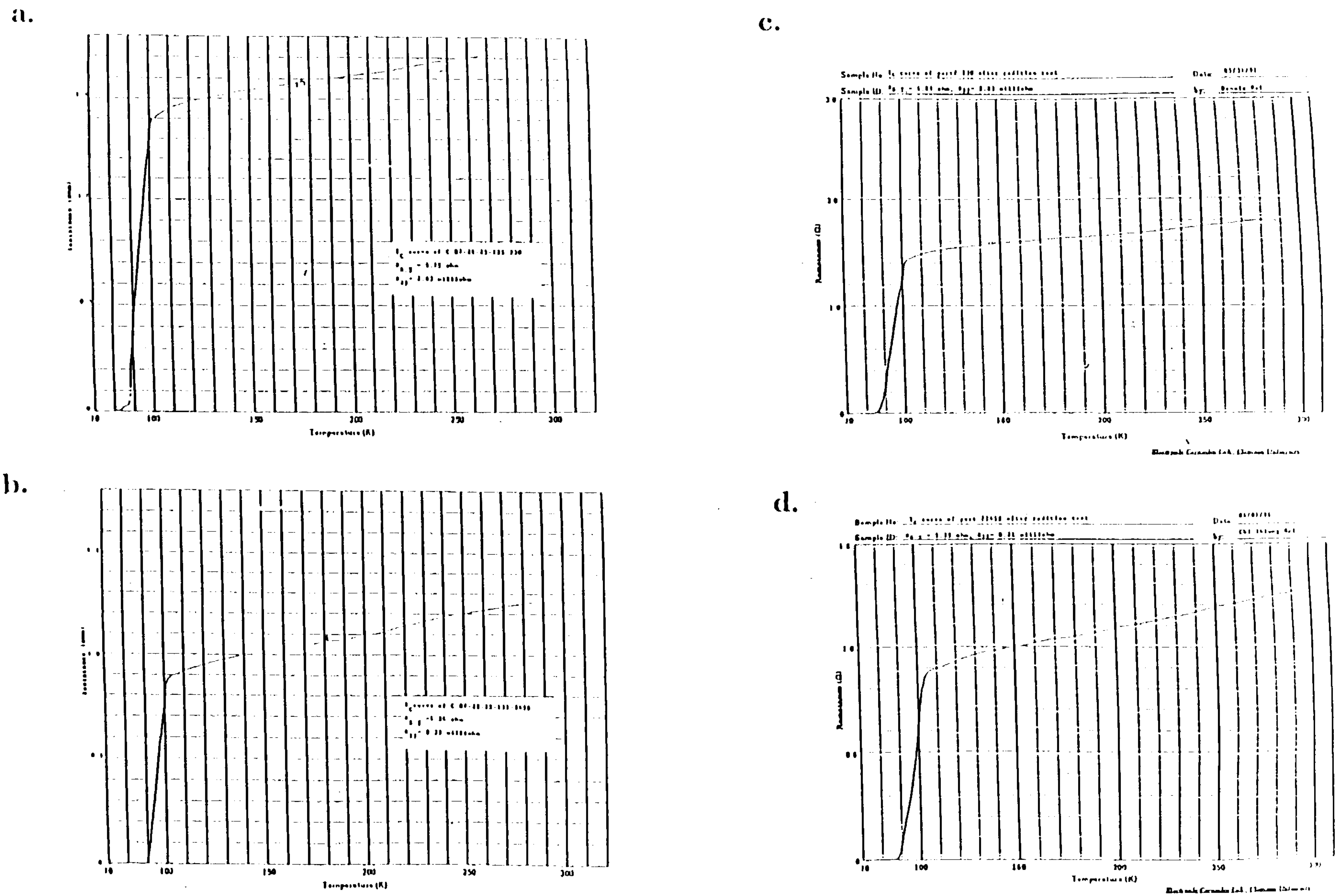


Figure 17: T_c curves of two selected samples before (a, b) and after (c, d) radiation test.

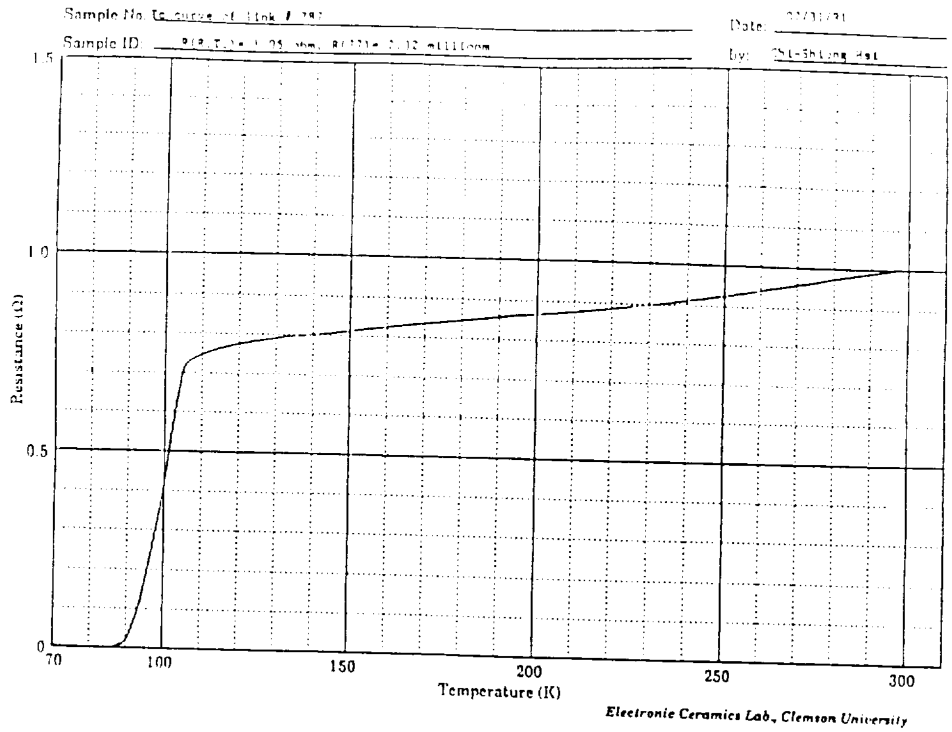
shown in Figure 18. The links dropped from 6 to 24 foot had resistances from 2.0 to 7.3Ω. The drop height did not have much influence on the resistances. In the resistance vs. temperature measurement, those links exhibited semiconductor behavior, as shown in Figure 19 and Appendix VII and were not in the superconducting state at LN temperature. However, there were no cracks found in those samples under microscopic observation.

Table 9 :The resistances of the links before and after the drop test. The resistances were measured at room temperature.

unit: Ω

Link No	Before drop	After drop	Drop height
381	1.5	1.5	3
387	1.0	1.0	3
393	1.0	1.0	3
395	1.4	1.4	3
400	1.3	1.5	3
377	1.5	4.2	6
378	1.4	3.2	6
388	1.0	1.3	6
391	1.4	2.5	6
399	1.0	3.5	6
379	1.4	2.0	12
380	1.3	2.7	12
384	1.7	3.5	12
389	1.5	7.3	12
390	1.5	5.2	12
382	1.4	5.2	24
386	1.6	7.1	24
392	1.6	3.0	24
397	1.5	3.9	24
398	1.4	5.2	24

When the link (#382) was dropped from 24 foot for 10 times, cracks across the superconductor strip were observed under steric microscopy observation, as shown in Figure 20. The resistance of this link was as high as 85.5Ω. Therefore the links' resistances increased in this test were dued to the microcrack inside the superconductor.



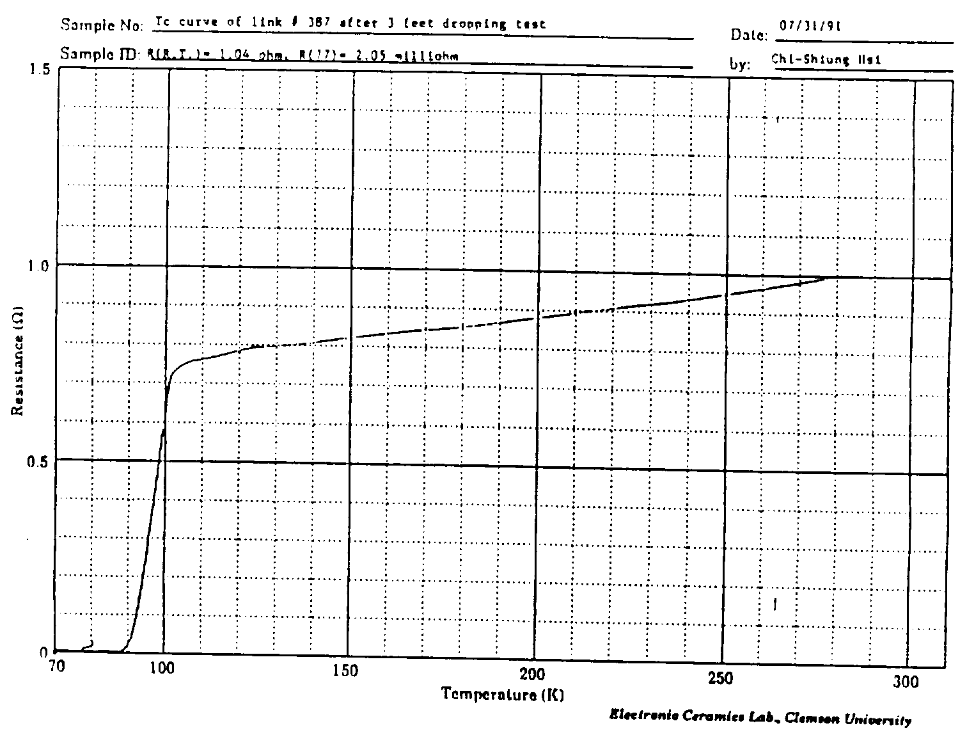
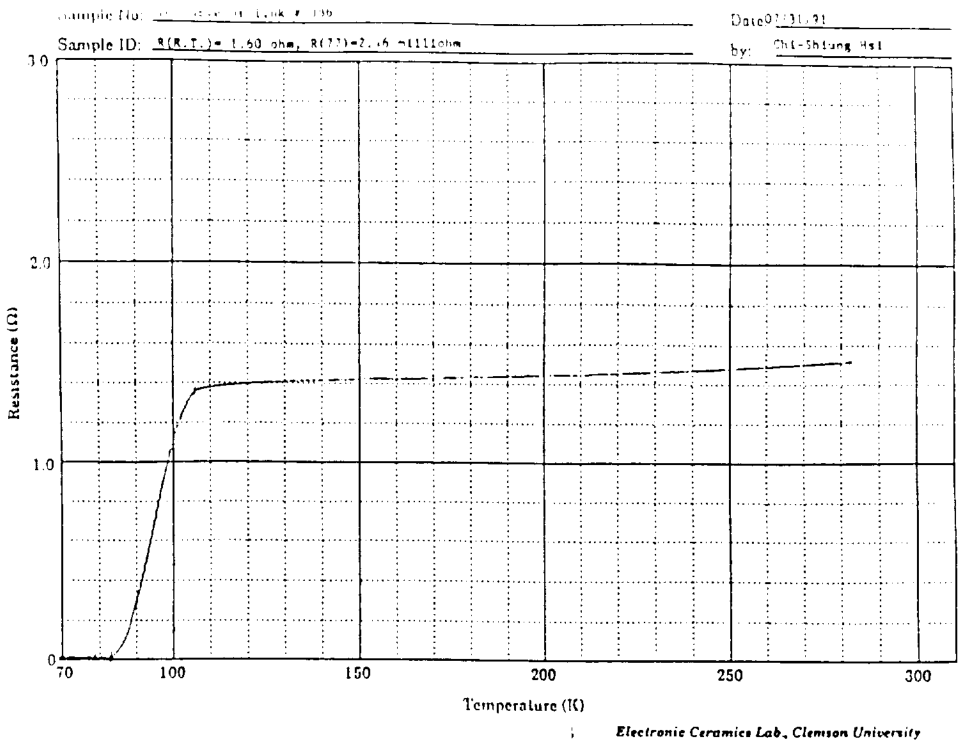


Figure 18: T_c curve of a link before and after the 3 foot drop test.



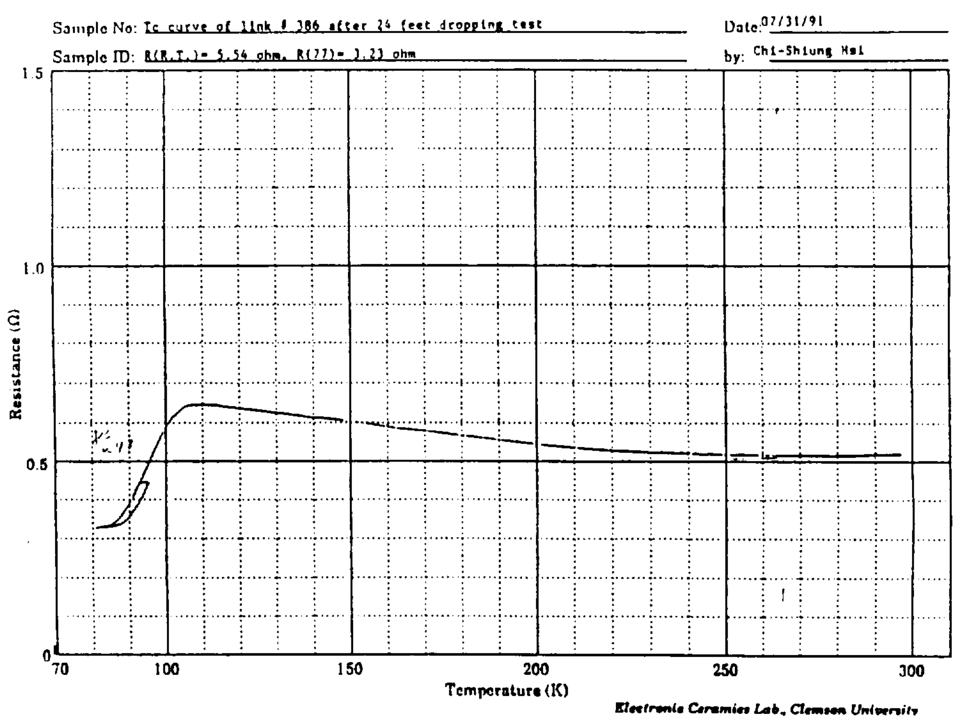


Figure 19: T_c curve of a link before and after the 24 foot drop test.

Figure 20: Cracks across the superconductor strip afer 10 times 24 foot dropping test.

III.8 Control samples.

There were ten control samples maintained at ambient conditions for more than 15 months. These links not only exhibited superconducting behavior at LN temperature, as shown in Appendix VIII, but also maintained their structure integrity. The epoxy coating successfully protected the superconductor from environment.

IV. Conclusions.

The $YBa_2Cu_3O_{7-x}$ superconductor grounding link used in the NASA-sponsored SAFIRE project showed excellent performance after being evaluated in the environmental test program. The electrical properties and structural integrity of the elements at ambient conditions were maintained by the epoxy encapsulation. No degradation was found from long term liquid nitrogen immersion, thermal shock, 3 foot drop test, or exposure to gamma radiation. Nevertheless, the links had high sensitivity to high humidity conditions, especially when the environmental temperature was higher than 32°C. The proposed operating conditions of the links, however, are in a very low humidity environment at 77K. Under these conditions, the elements yielded good results. Therefore, in this rigid-conductor concept, the substrate and epoxy successfully preserves the electrical and physical properties of the $YBa_2Cu_3O_{7-x}$ superconductor. This concept can also be applied to electrical circuit techniques or multi-leaded elements, as shown in Appendix IX.

From the humidity test results, the following fabrication conditions are recommended:

1. An epoxy thickness greater than 0.2 mm,
2. An epoxy curing cycle of 110°C for one hour or more.

Reference

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2. G. H. Haertling, "Development and evaluation of superconducting circuit elements", NASA Final Report, Contract No. NAG-1-820, October, 1990.
3. G. H. Haertling, "Ceramic Superconducting Components", Ceramic Transactions, Vol. 18, 537-546, 1991.
4. G. H. Haertling and J. D. Buckley, "Method of Preforming and Assembling Superconducting Elements", US Patent Application, Serial No.07/666, 536, filed march 6, 1991, NASA Langley Research Center.
5. C. S. Hsi and G. H. Haertling, "Low resistivity contacts to $YBa_2Cu_3O_{7-x}$ superconductors", Ceramic Transactions, Vol. 18, 399-406, 1991.

Appendix I

Table A-1: The variation of the links' resistances after 30 days room temperature aging in air. The $YBa_2Cu_3O_{7-x}$ superconductor strips were sintered by single firing[(5)].

unit:Ω

Link No.	at 07/28/90	at 08/27/90	variation (%)
1*	0.895	0.915	2.2
2*	1.017	1.034	1.7
3*	0.861	0.885	2.8
6*	0.975	0.999	2.5
48*	0.765	0.781	2.1
49*	0.816	0.830	1.7
54*	0.843	0.860	2.0
10	0.883	0.982	11.2
11	0.844	0.964	9.0
14	0.951	1.097	15.4
39	0.682	0.756	10.9
41	0.653	0.738	13.0
44	0.680	0.757	11.3
82	1.100	1.206	9.6
83	0.774	0.835	7.9
85	0.894	0.961	7.5
86	0.785	0.852	8.5
87	2.014	2.198	9.1
88	1.607	1.748	8.8
89	1.644	1.797	9.3
90	1.508	1.635	8.4

*: The links were heat-treated at 110°C for 1 hour.

Appendix II

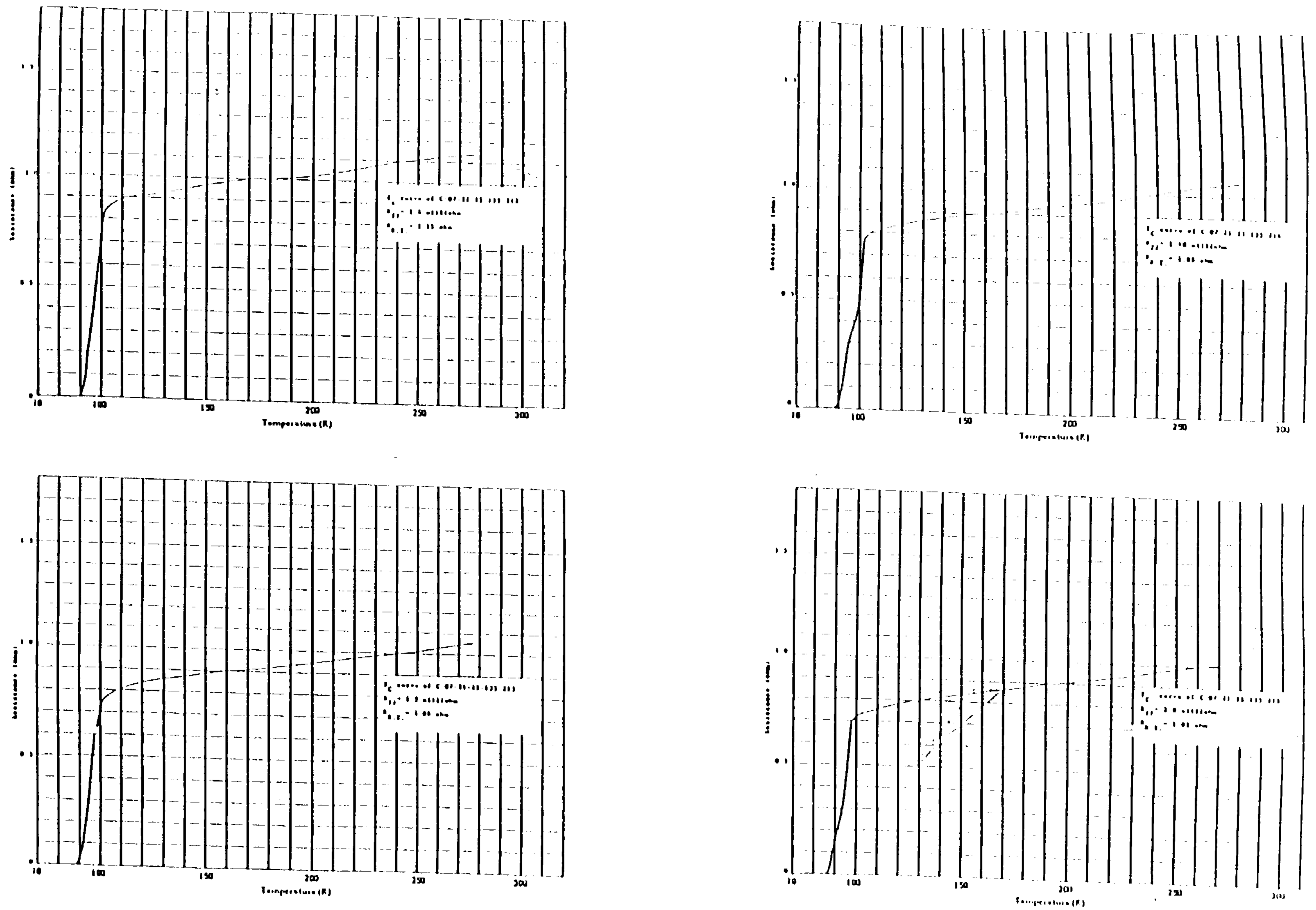
Table A-2: The resistance of some selected links at room temperature and at liquid nitrogen temperature, and their critical temperatures.

Link No.	$R_{R.T.}$ (Ω)	R_{77} (mΩ)	T_c (K)
212	1.15	1.4	90
213	1.08	1.9	88
214	1.08	1.4	86
215	1.02	2.0	86
216	1.02	2.1	86
217	1.09	2.18	88
218	1.10	1.93	85
219	1.11	2.08	88
220	1.14	1.91	88
221	1.82	1.20	86
223	1.24	1.30	84
226	1.41	1.39	85
227	1.34	1.62	86
228	1.31	0.98	87
229	1.29	1.19	87
203S	1.08	0.25	86
204S	1.21	0.36	90
205S	1.10	0.34	89
206S	1.93	0.25	84
207S	1.44	0.4	88
208S	1.09	0.34	87
209S	1.15	0.22	89
231S	1.07	0.45	88
232S	1.11	0.38	87
235S	1.12	0.3	88
240S	1.05	0.45	88
241S	1.17	0.39	88
243S	1.14	0.23	89
246S	1.14	0.34	87

S: silver tab

Appendix III

Figure A-1: The T_c curves of some selected samples.



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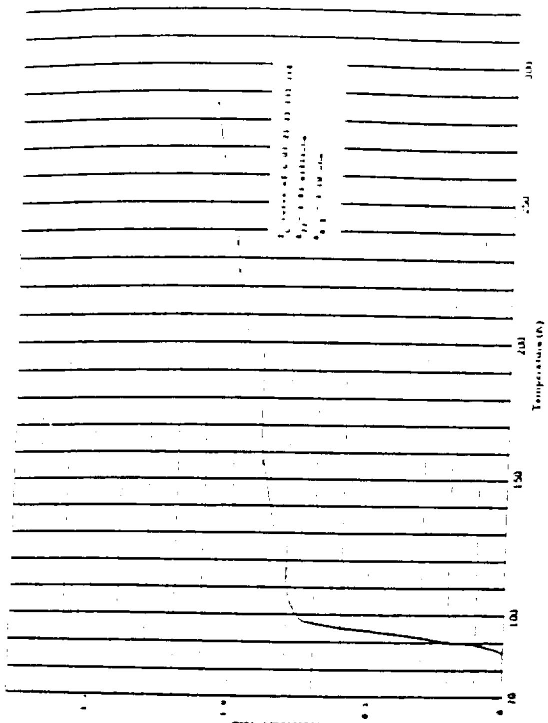
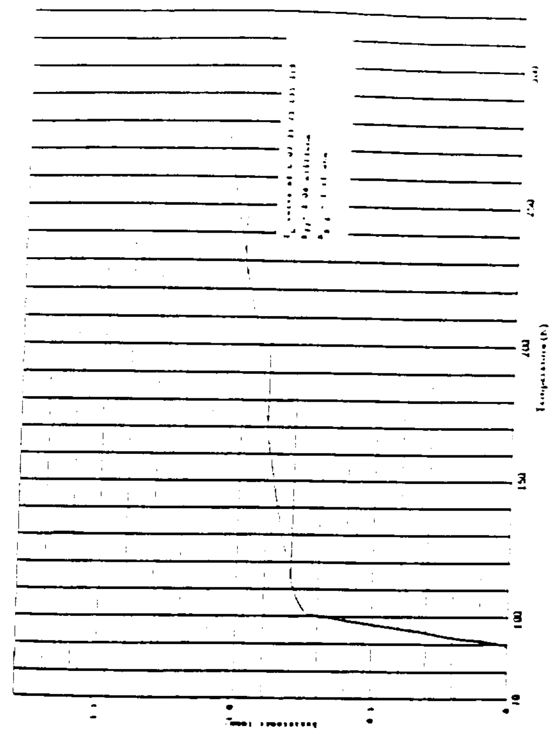
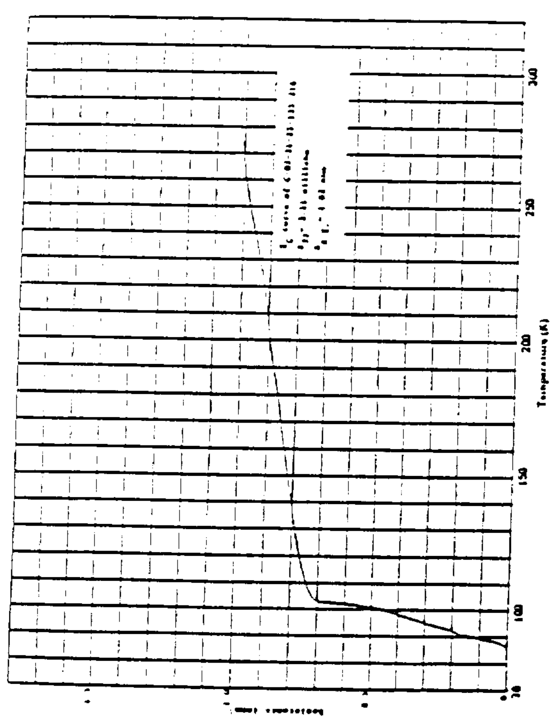
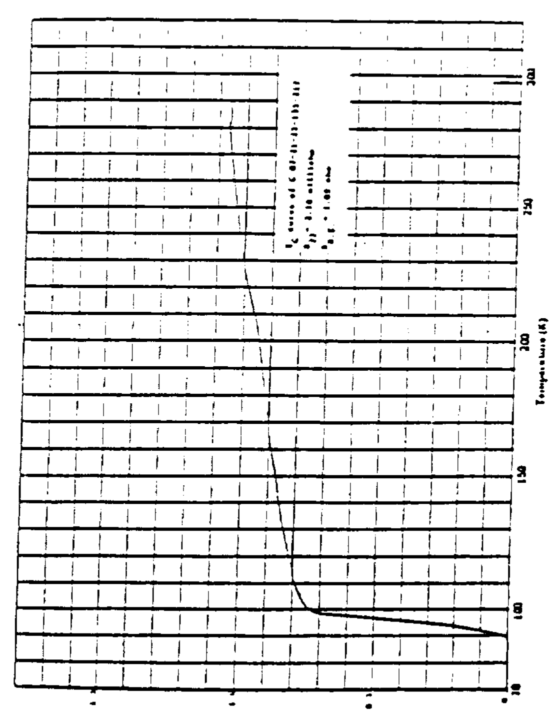
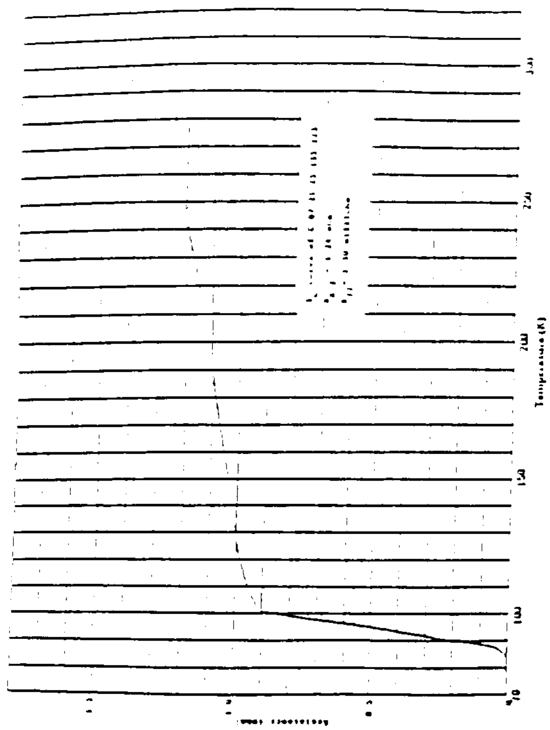
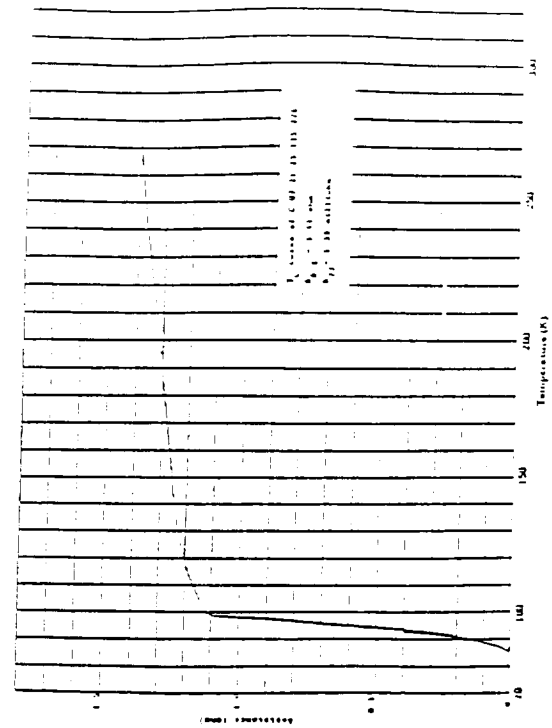


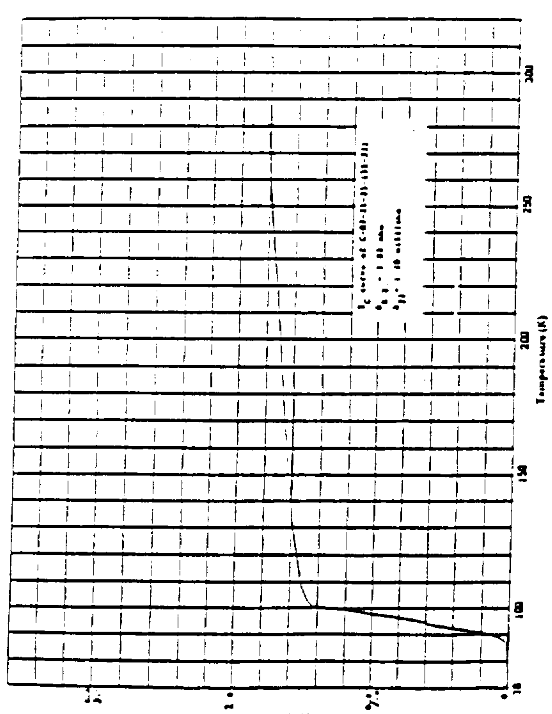


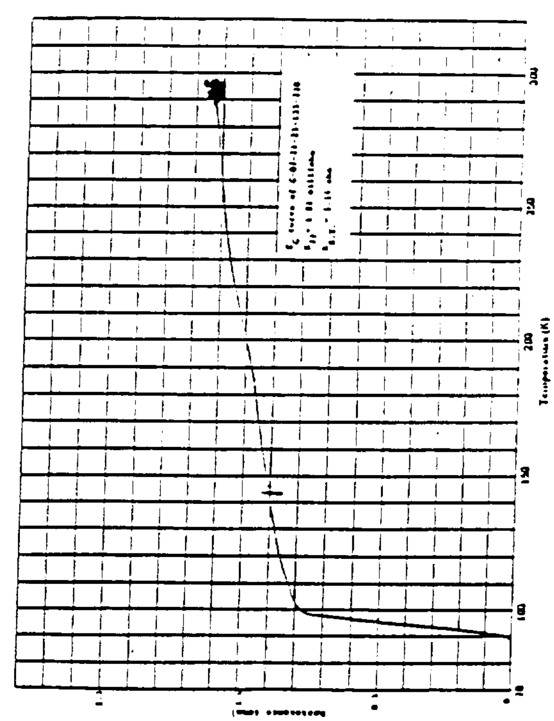


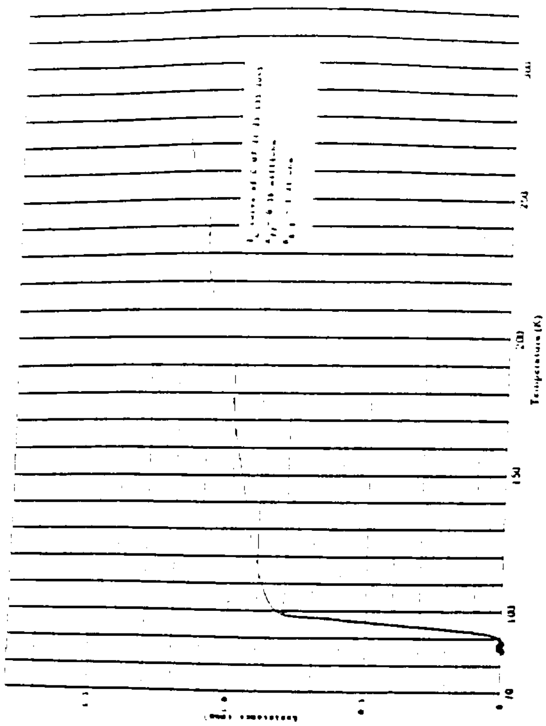


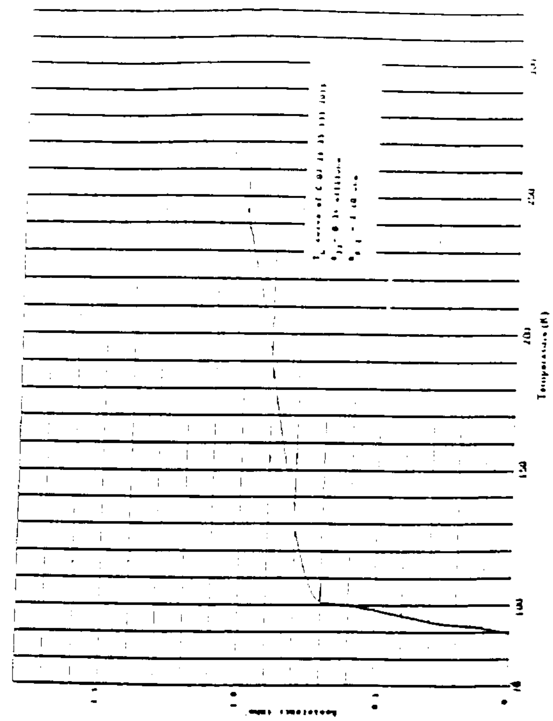


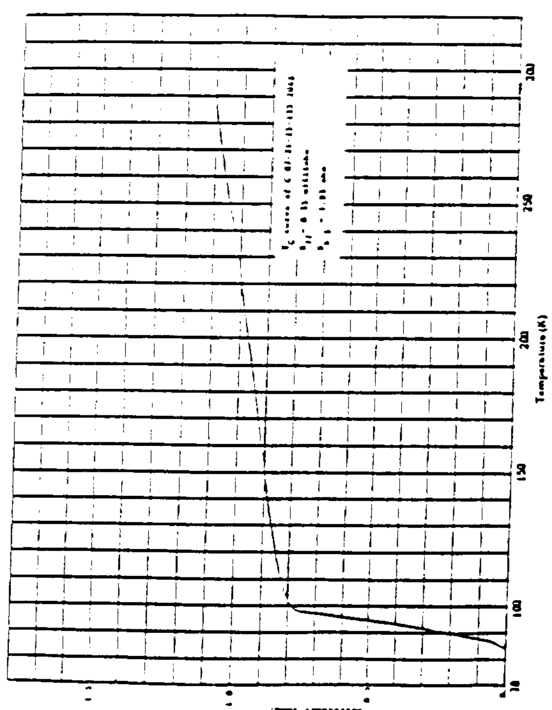


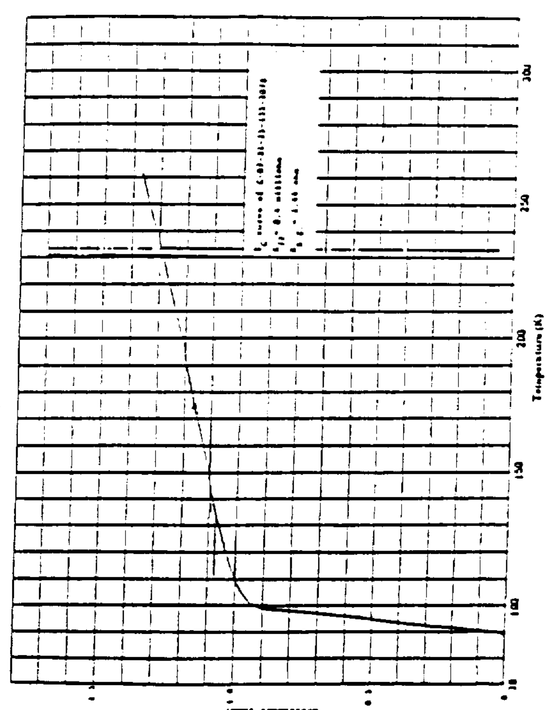


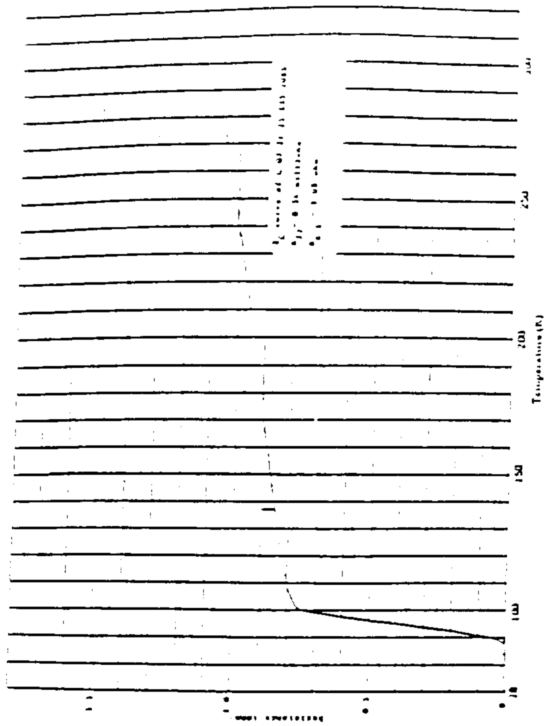


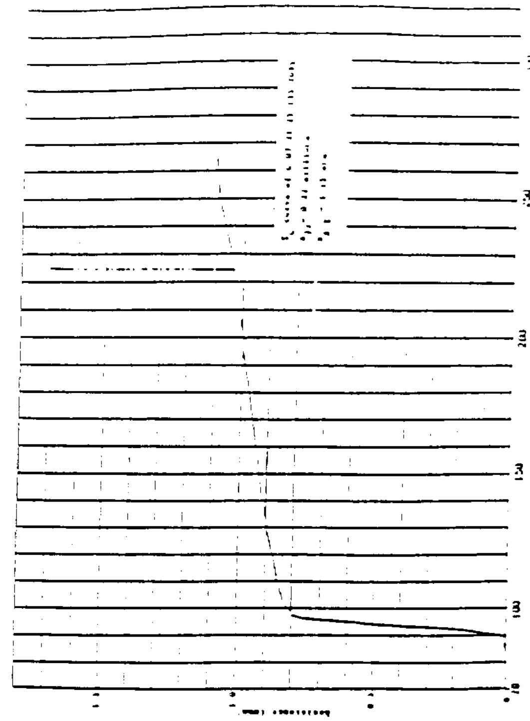


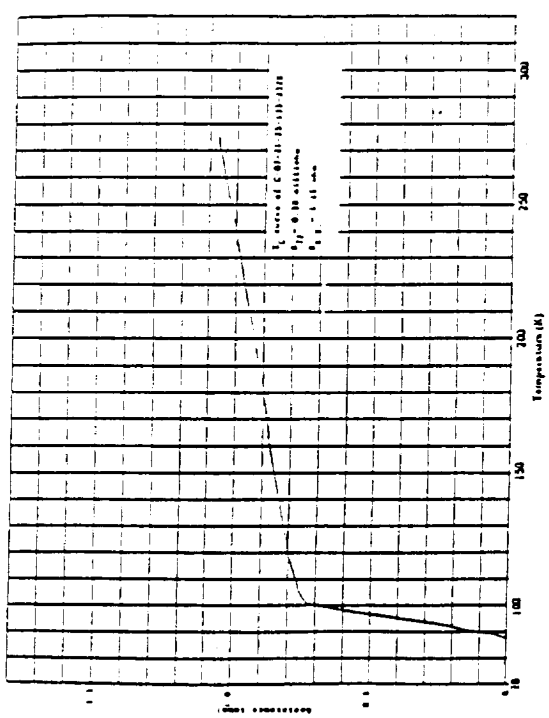


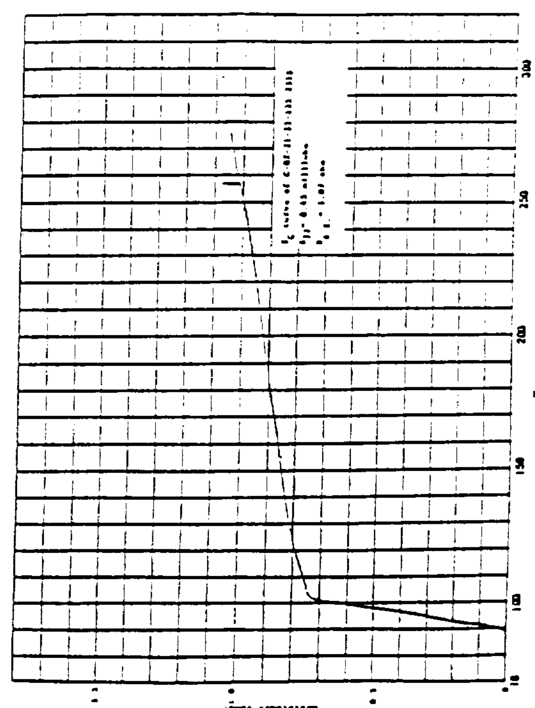


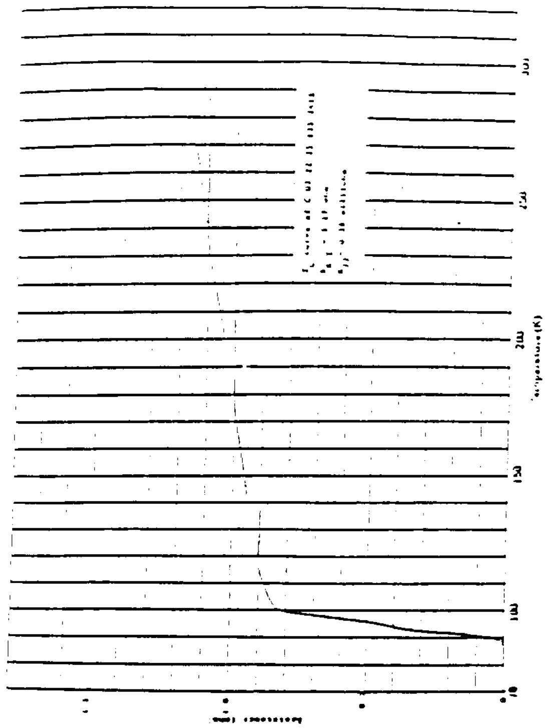


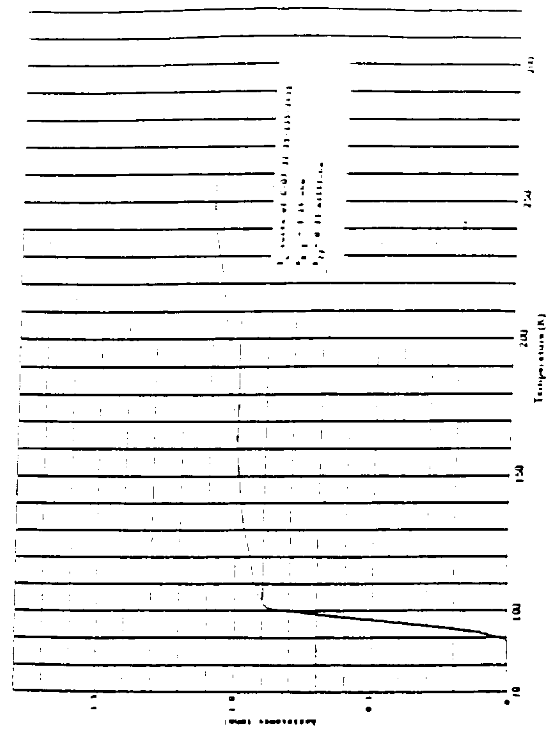


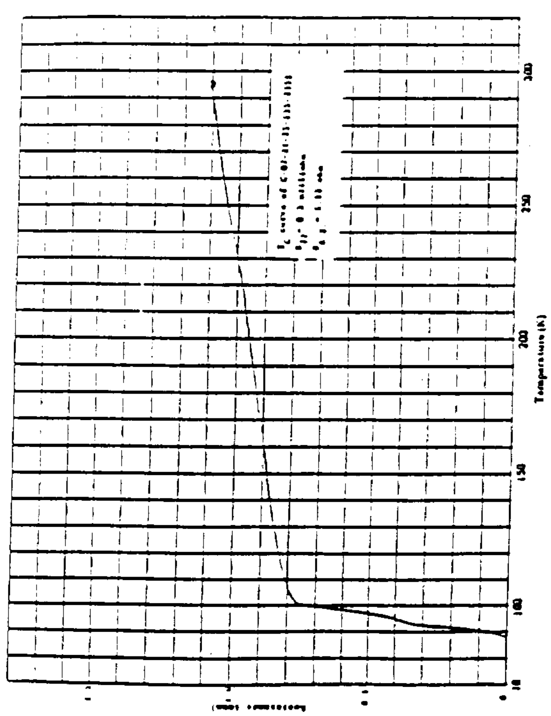


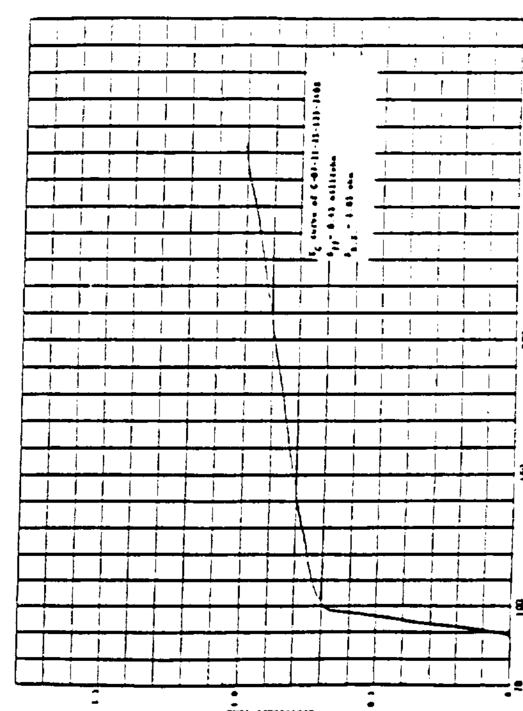












Appendix IV

Table A-3: The resistances of the links in the long-term liquid nitrogen immersion test. The resistances were measured at room temperature.

unit: Ω

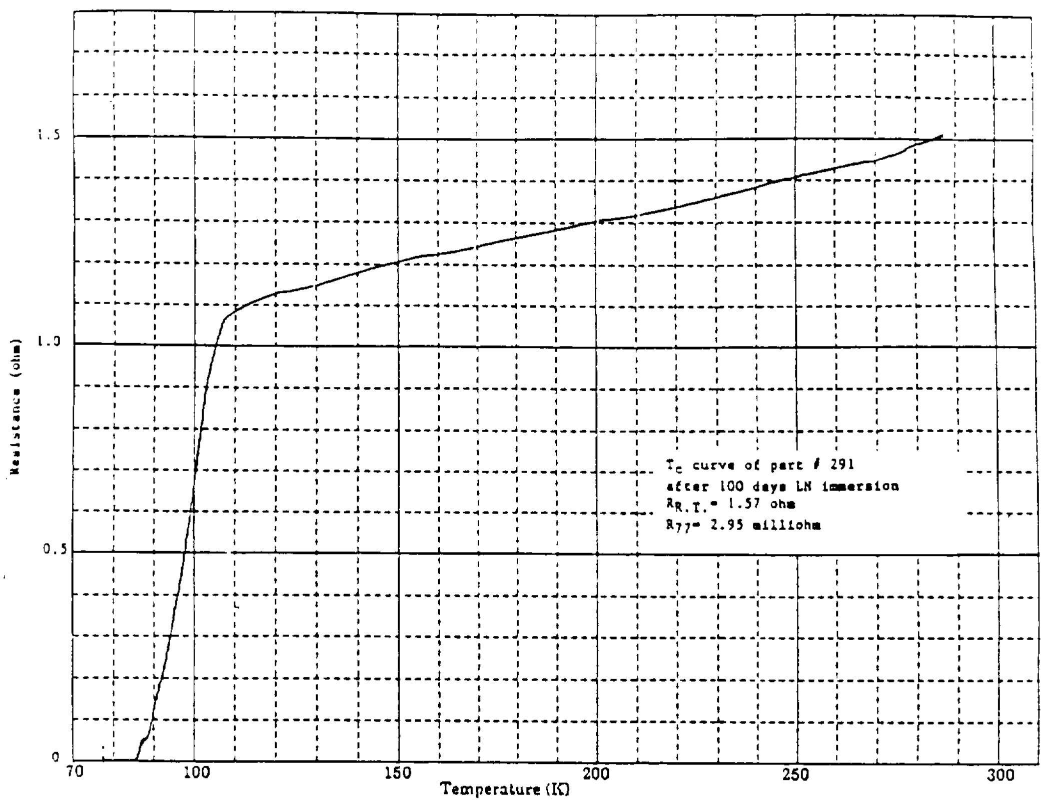
Date	10/19/90	10/26/90	11/04/90	11/18/90	12/02/90	12/17/90	01/01/91	01/13/91	01/27/91	02/10/91
Day	0	7	16	31	45	60	75	87	101	115
Link No.										
291	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
292	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
293	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
294	1.9	1.9	1.8	1.9	1.9	1.9	1.9	1.9	1.9	1.9
295	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
296	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
297	1.3	1.3	1.3	1.4	1.3	1.3	1.2	1.3	1.3	1.3
298	1.8	1.6	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8

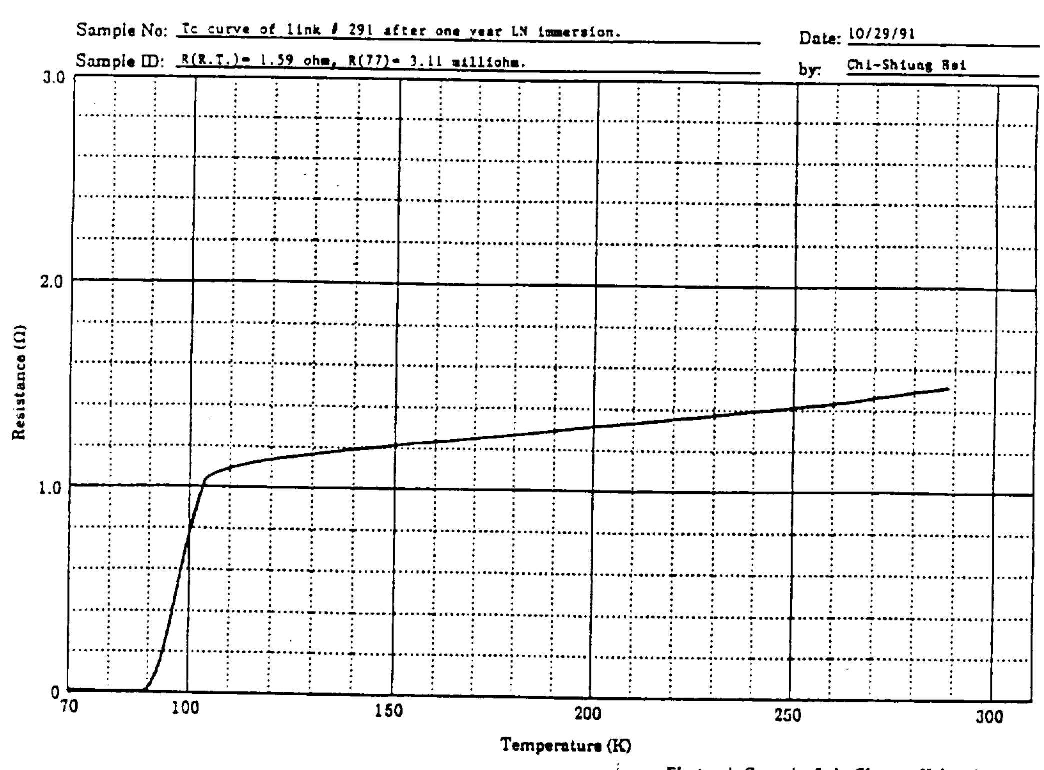
Date	02/26/91	03/10/91	03/24/91	04/14/91	04/28/91	05/19/91	06/03/91	06/16/91	06/30/91	07/14/91
Day	136	143	157	178	192	212	227	240	253	267
Link No.										
291	1.6	1.6	1.6	1.5	1.5	1.6	1.6	1.5	1.6	1.6
292	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
293	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
294	1.9	1.9	1.9	1.9	1.9	1.9	1.8	1.9	1.9	1.9
295	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
296	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
297	1.3	1.3	1.2	1.2	1.2	1.2	1.3	1.2	1.2	-
298	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	-

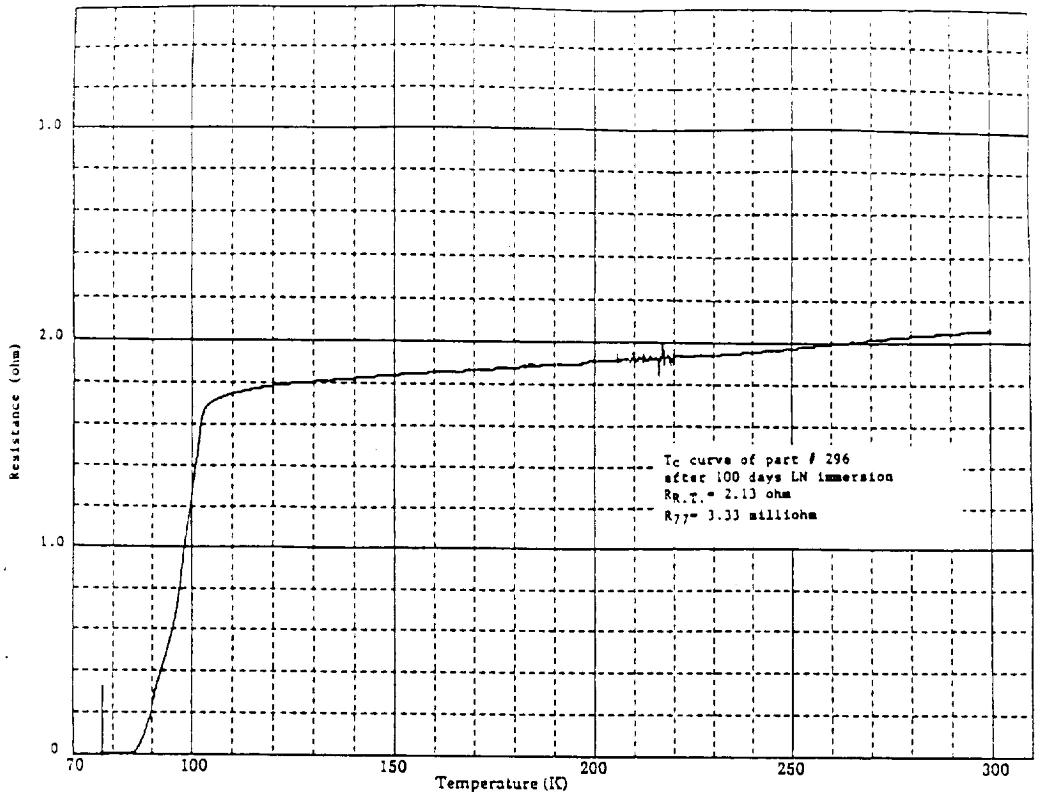
Date	07/28/91	08/11/91	08/18/91	08/25/91	09/01/91	09/09/91	09/16/91	09/23/91	10/06/91	10/18/91
Day	281	295	302	309	316	324	331	338	353	365
Link No.										
291	1.6	1.6	1.6	1.6	1.6	1.6	1.5	1.6	1.6	1.6
292	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
293	2.1	2.1	2.1	2.1	2.1	2.1	2.0	2.1	2.1	2.1
294	1.9	1.9	1.8	1.8	1.8	1.8	1.8	1.8	1.9	1.9
295	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
296	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
297	-	-	-	-	-	-	-	-	-	-
298	-	-	-	-	-	-	-	-	-	-

Appendix V

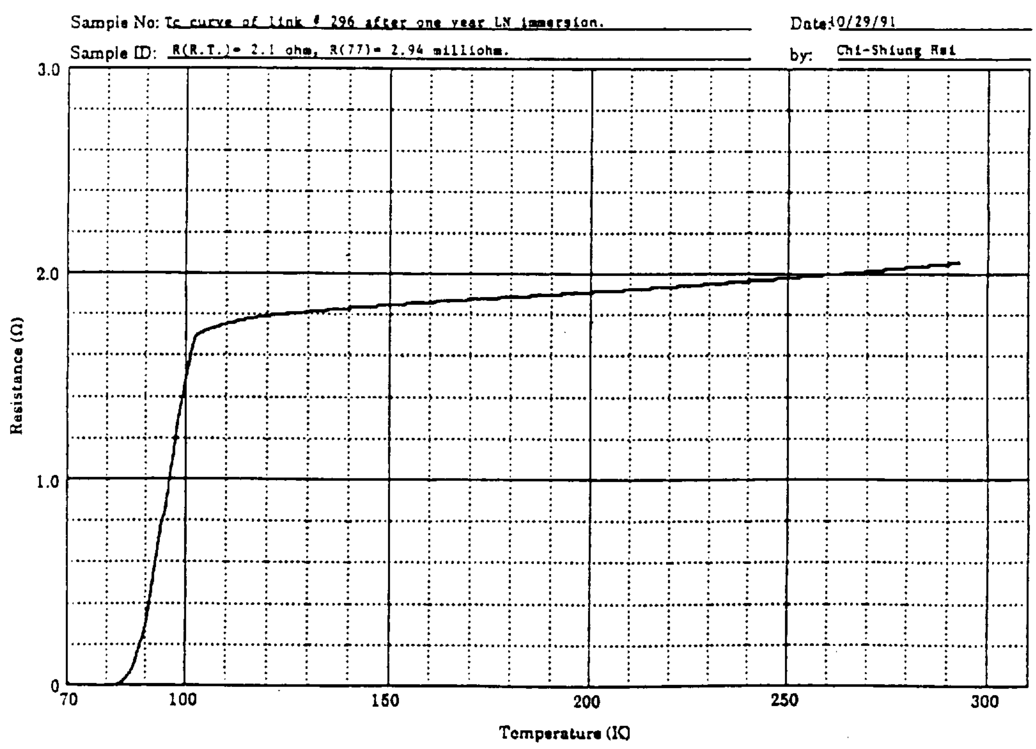
Figure A-2: The T_c curves of the links after 100 days and one year liquid nitrogen immersion.



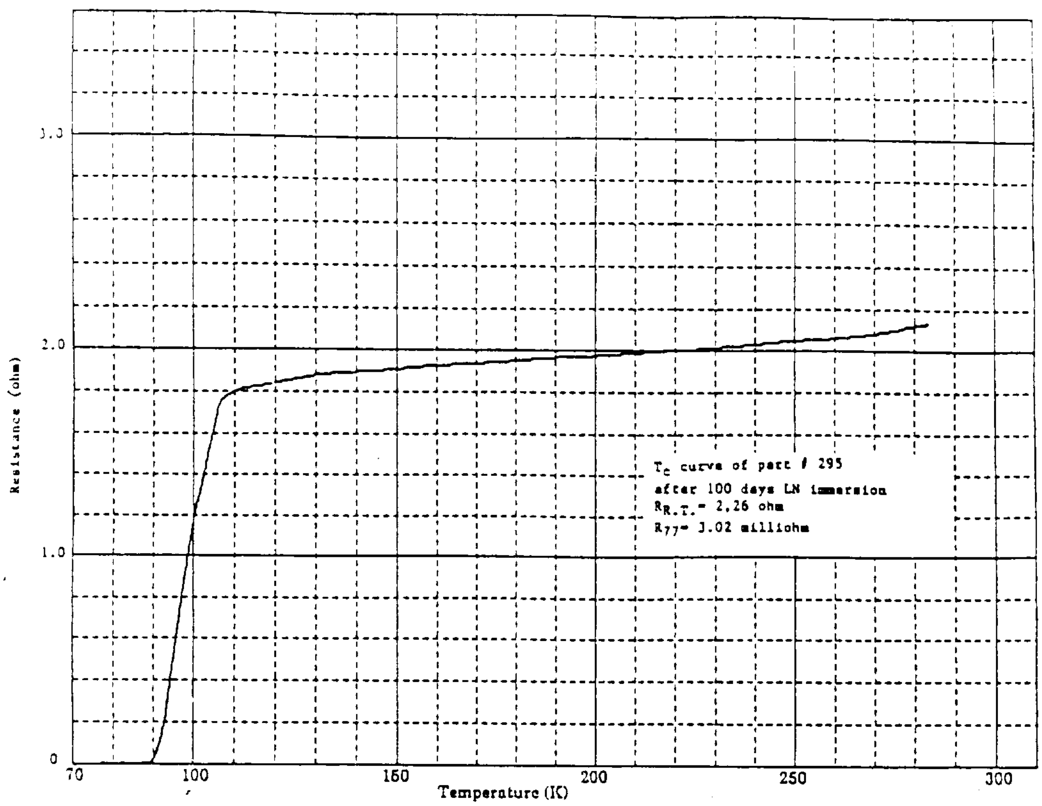




3.0
2.0
1.0
0
70
100
150
200
250
300
Resistance (ohm)
Temperature (K)
Tc curve of part # 296
after 100 days LN immersion
R R.T. = 2.13 ohm
R77 = 3.33 milliohm

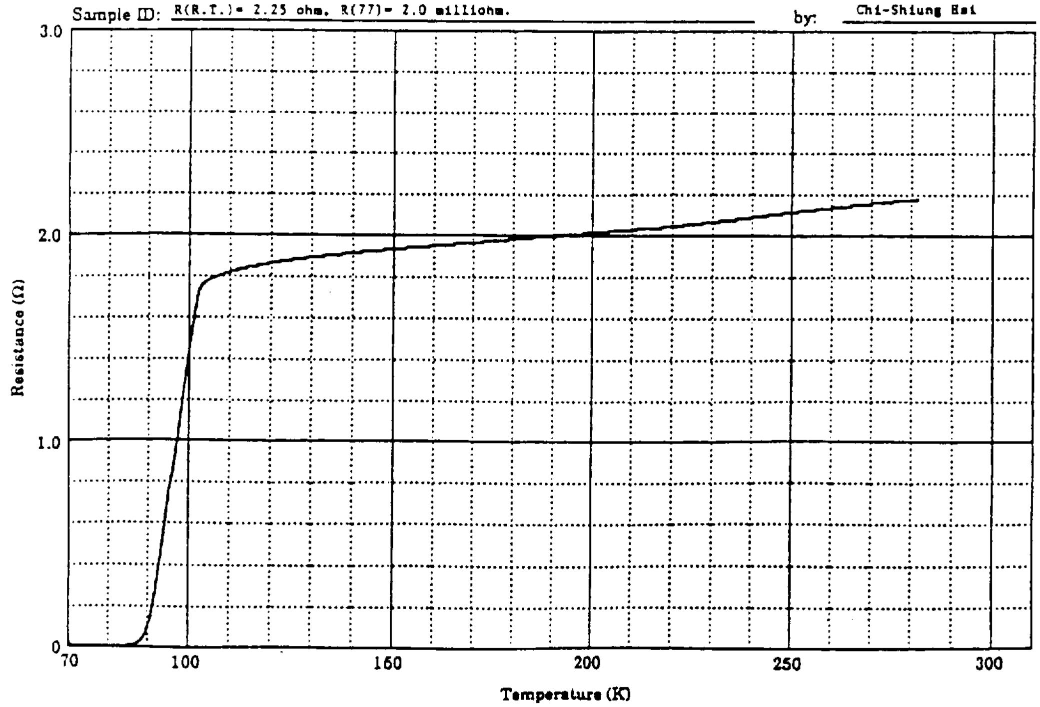


Sample No: Tc curve of link # 296 after one year LN immersion.
Date: 10/29/91
Sample ID: R(R.T.) = 2.1 ohm, R(77) = 2.94 milliohm.
by: Chi-Shiung Hsi
3.0
2.0
1.0
0
70
100
150
200
250
300
Resistance (Ω)
Temperature (K)
Electronic Ceramics Lab., Clemson University



Sample No: Tc curve of link # 295 after one year LN immersion. Date: 10/30/91

Sample ID: R(R.T.)= 2.25 ohm, R(77)= 2.0 milliohm. by: Chi-Shiung Hsi



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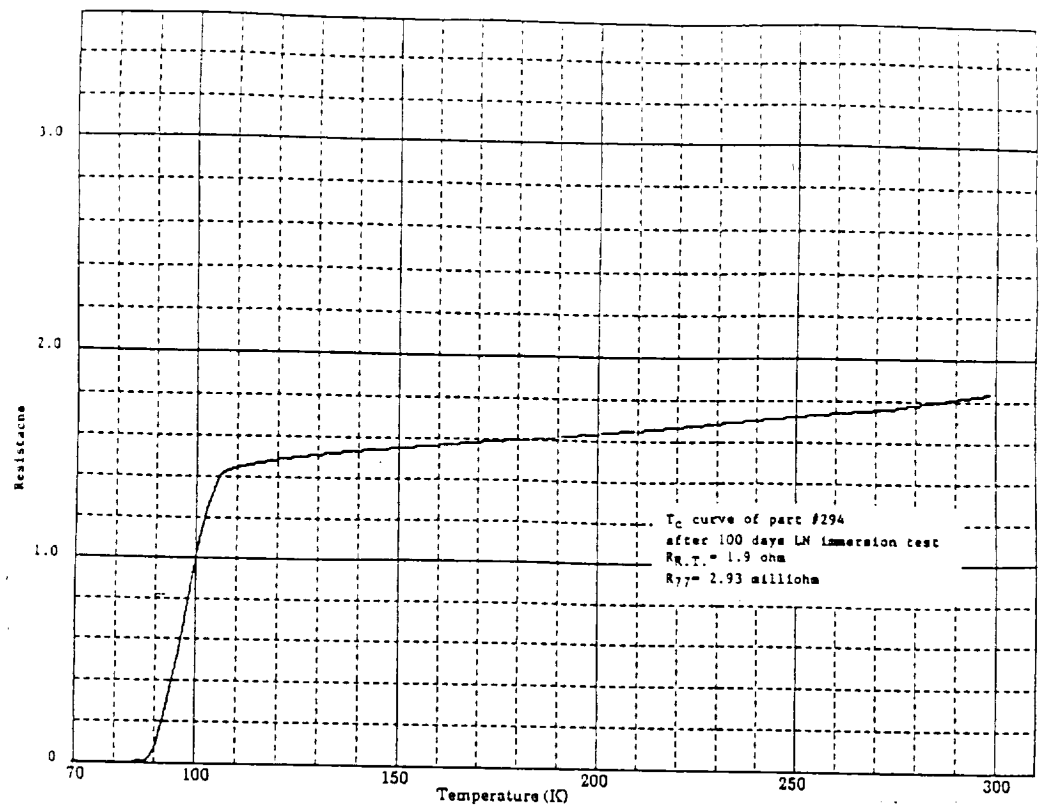
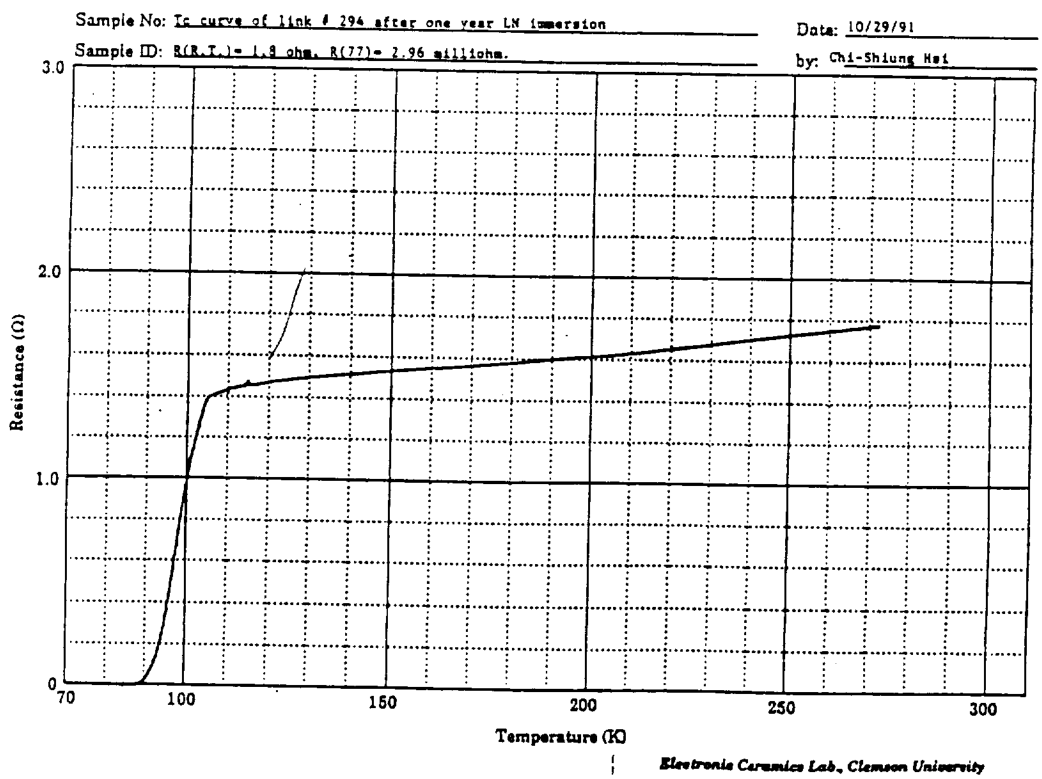
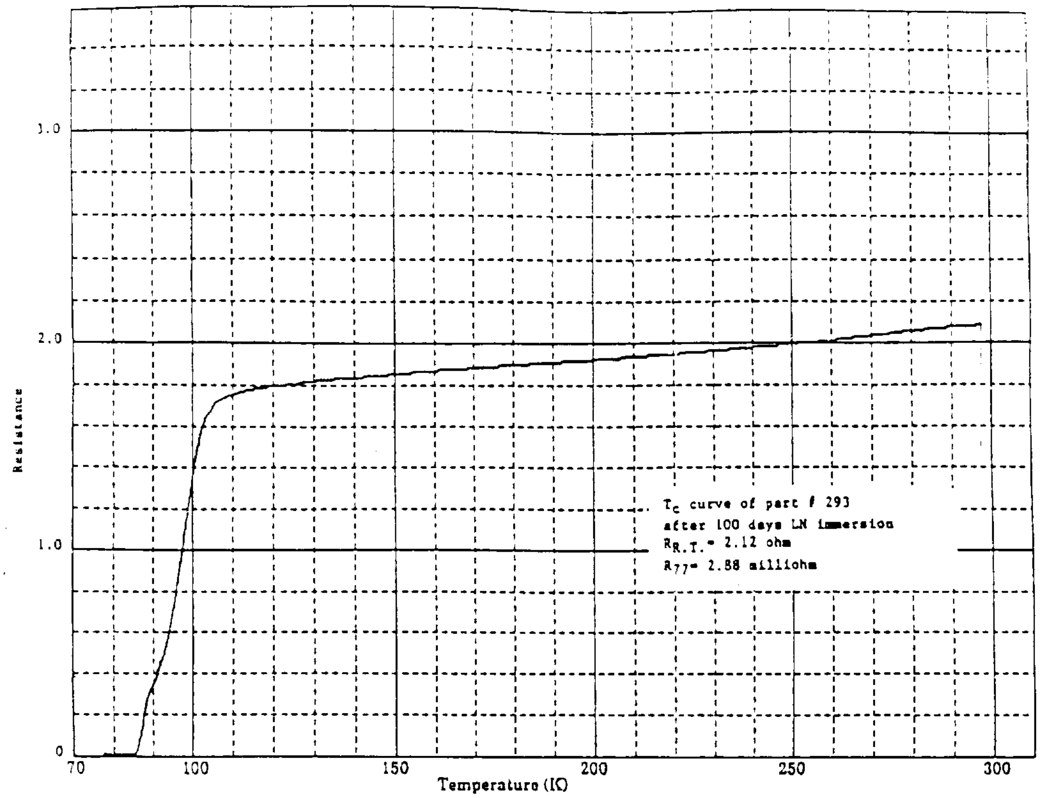
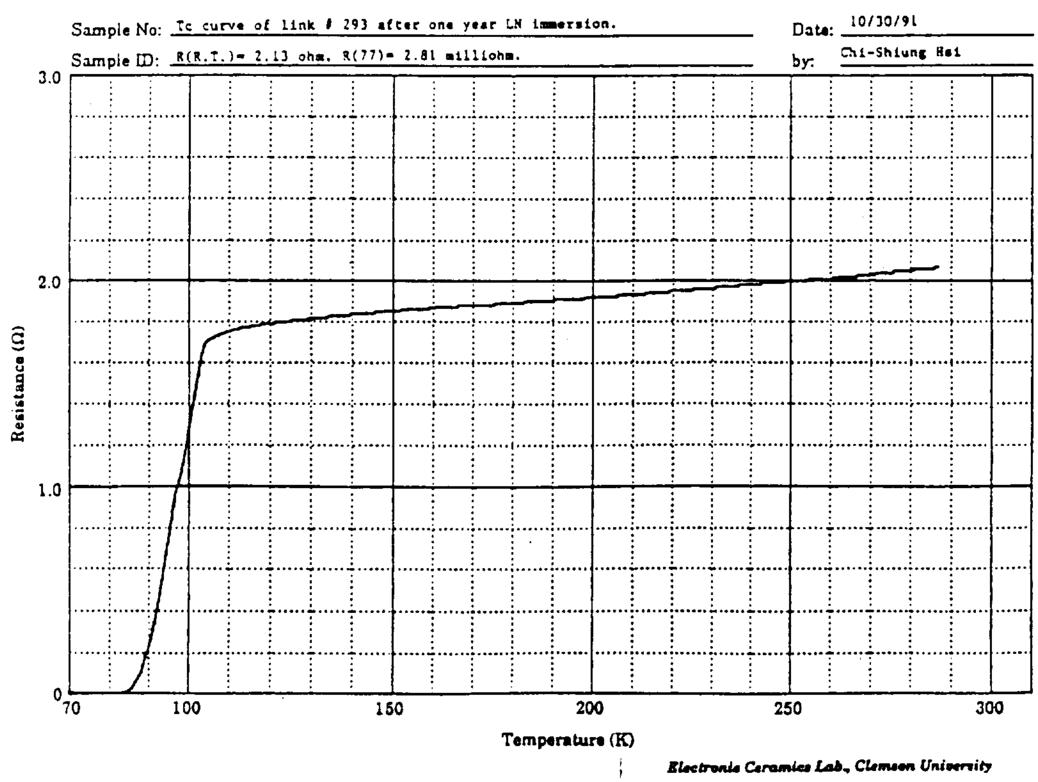

3.0
2.0
1.0
0
Resistacne
70
100
150
200
250
300
Temperature (K)
T_c curve of part #294
after 100 days LN immersion test
$R_{R.T.}$= 1.9 ohm
R_{77}= 2.93 milliohm

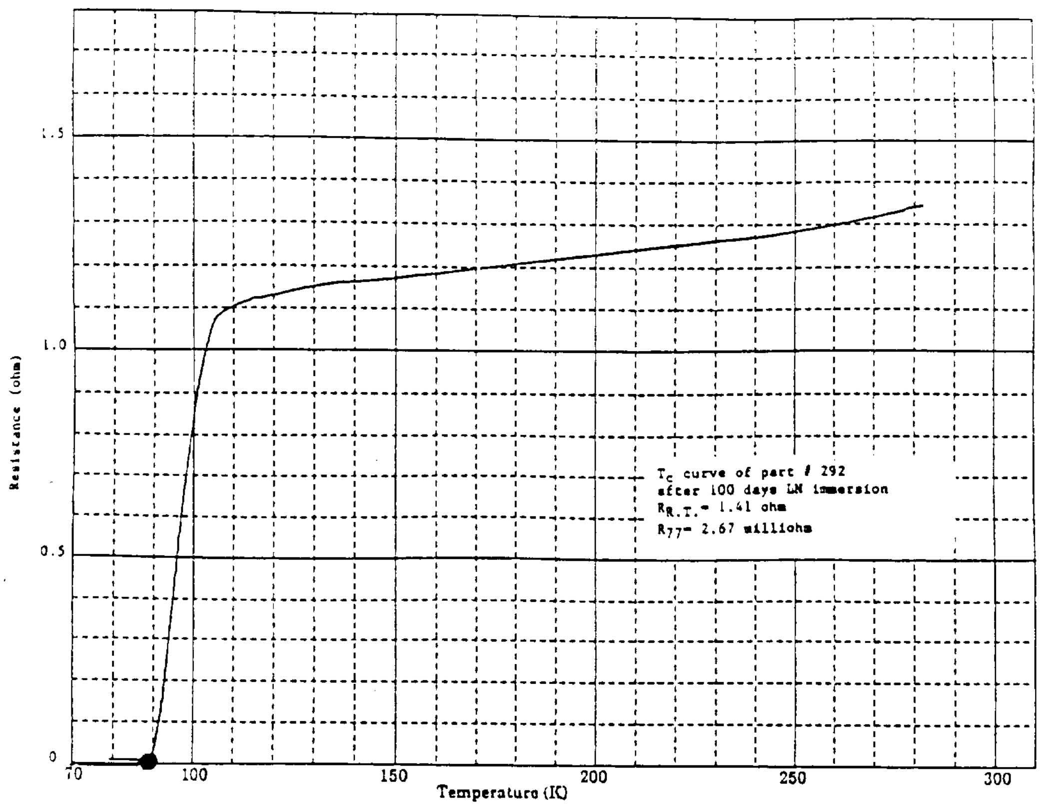

Sample No: Tc curve of link # 294 after one year LN immersion
Date: 10/29/91
Sample ID: R(R.T.)= 1.8 ohm, R(77)= 2.96 milliohm.
by: Chi-Shiung Hsi
3.0
2.0
1.0
0
Resistance (Ω)
70
100
150
200
250
300
Temperature (K)
Electronic Ceramics Lab., Clemson University

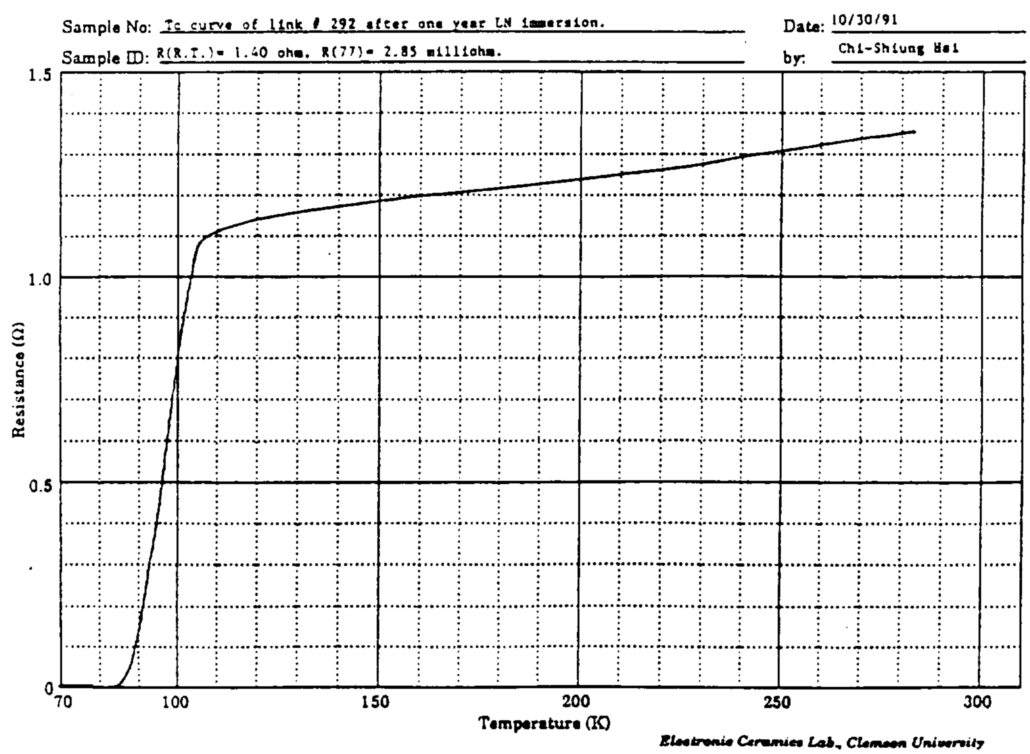


3.0
2.0
1.0
0
Resistance
70
100
150
200
250
300
Temperature (K)
T_c curve of part # 293
after 100 days LN immersion
$R_{R.T.}$= 2.12 ohm
R_{77}= 2.88 milliohm



Sample No: Tc curve of link # 293 after one year LN immersion.
Date: 10/30/91
Sample ID: R(R.T.)= 2.13 ohm. R(77)= 2.81 milliohm.
by: Chi-Shiung Hsi
3.0
2.0
1.0
0
Resistance (Ω)
70
100
150
200
250
300
Temperature (K)
Electronic Ceramics Lab., Clemson University


Resistance (ohm)
1.5
1.0
0.5
0
70
100
150
200
250
300
Temperature (K)
Tc curve of part # 292
after 100 days LN immersion
RR.T.= 1.41 ohm
R77= 2.67 milliohm


Sample No: Tc curve of link # 292 after one year LN immersion.
Sample ID: R(R.T.)= 1.40 ohm. R(77)= 2.85 milliohm.
Date: 10/30/91
by: Chi-Shiung Hsi
Resistance (Ω)
1.5
1.0
0.5
0
70
100
150
200
250
300
Temperature (K)
Electronic Ceramics Lab., Clemson University

Appendix VI

Table A-4: The resistances of the links in the humidity test at 32 oC, 90% R. H..
The resistances were measured at room temperature.

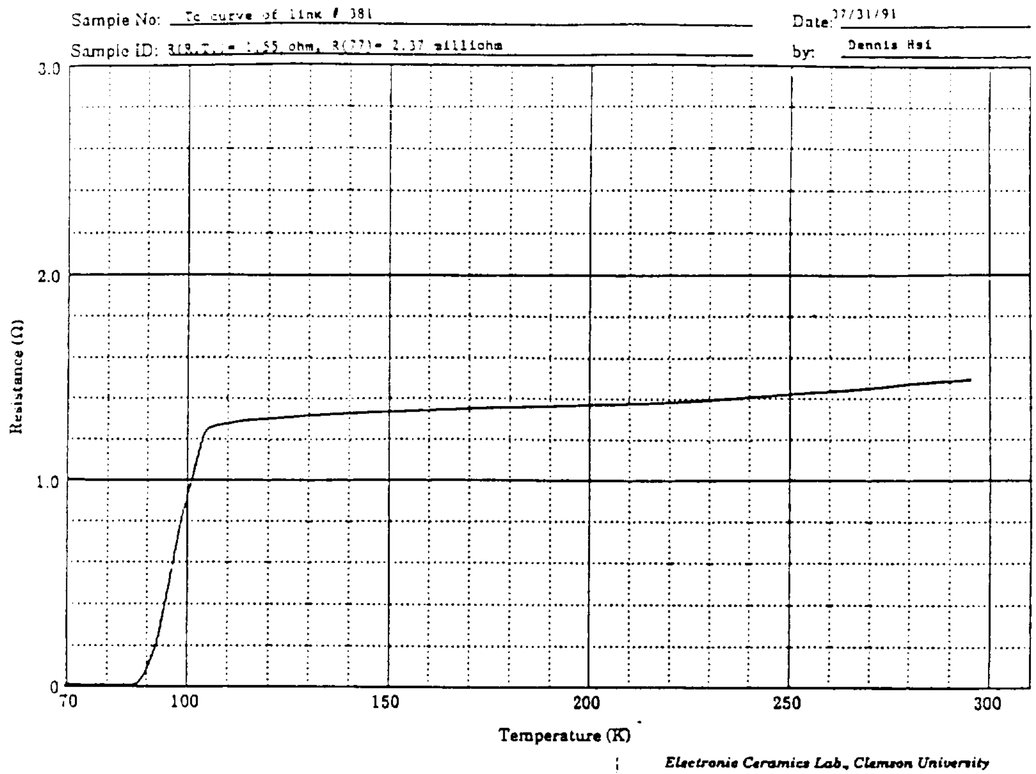
unit: Ω

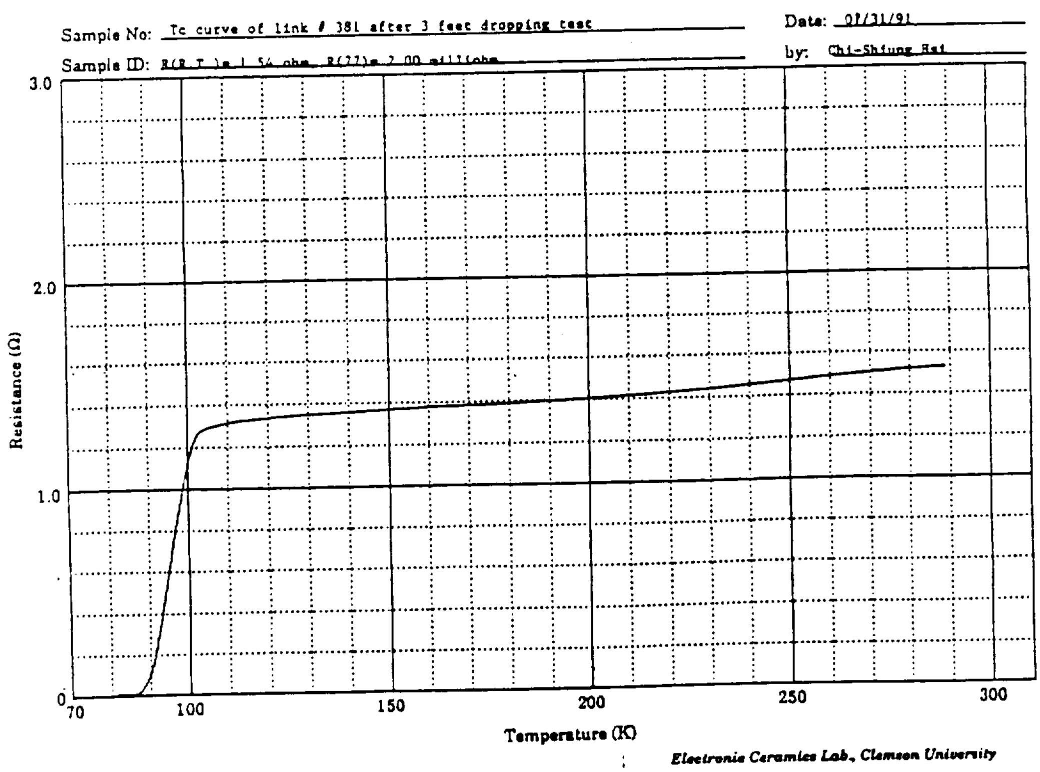
date	07/29/91 at start	08/11/91 17 days	08/25/91 31 days	09/09/91 46 days	09/23/91 60 days	10/06/91 73 days
link #						
368[a]	1.1	1.1	1.2	1.3	1.3	1.4
369[a]	1.0	1,0	1.1	1.15	1.2	1.3
370[a]	1.5	1.5	1.5	1.65	1.7	1.9
371[a]	1.6	1.6	1.7	1.9	1.95	2.1
372[a]	1.5	1.5	1.7	1.8	1.9	2.0
373[b]	1.2	1.2	1.2	1.3	1.4	1.5
374[b]	1.7	1.7	1.8	2.0	2.0	2.1
375[b]	1.7	1.7	1.8	1.9	2.0	2.2
376[b]	1.8	1.7	1.8	1.8	2.0	2.1
401[c]	1.6	1.6	1.7	1.8	1.9	2.0
402[c]	2.0	2.0	2.1	2.2	2.4	2.5
403[c]	1.2	1.2	1.2	1.3	1.4	1.4
405[d]	1.5	1.6	C*			
406[d]	1.6	1.6	1.7	1.7	1.9	1.9
407[d]	1.5	1.5	1.6	1.8	1.9	1.9
408[d]	1.8	1.8	1.8	1.9	2.0	2.1

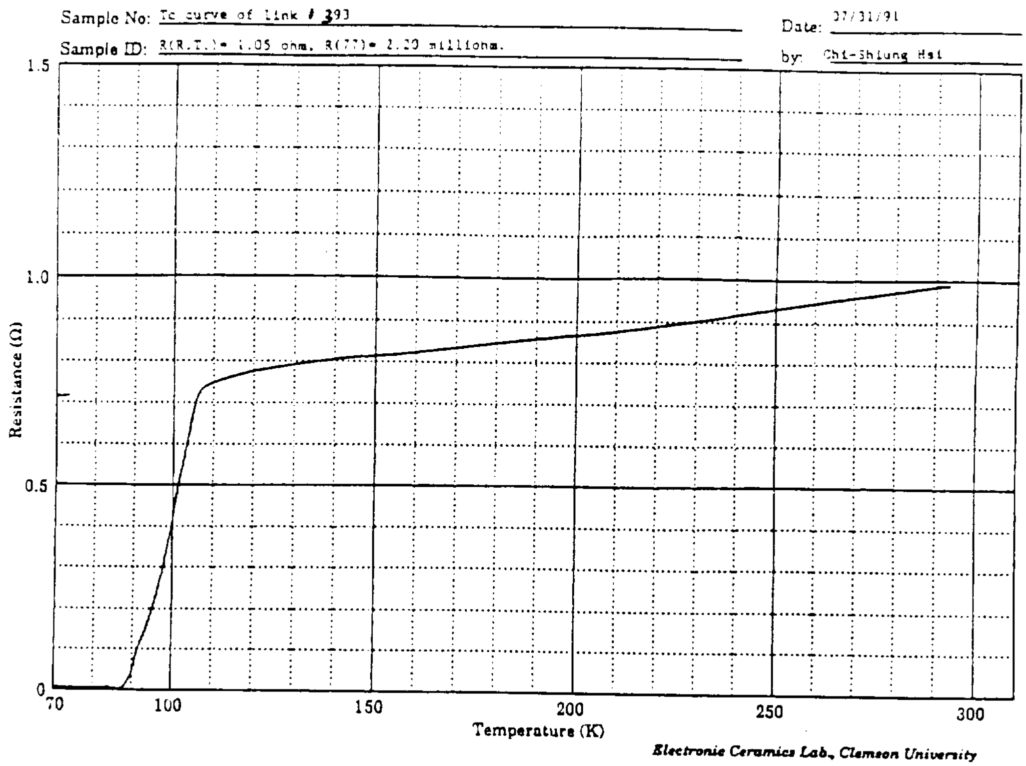
C: crack, a: samples were cured at 110oC for 2 hours, b: samples were cured at 110oC for 12 hours, c: samples were cured at 110oC for 24 hours, d: samples were cured at 115oC for 4 hours.

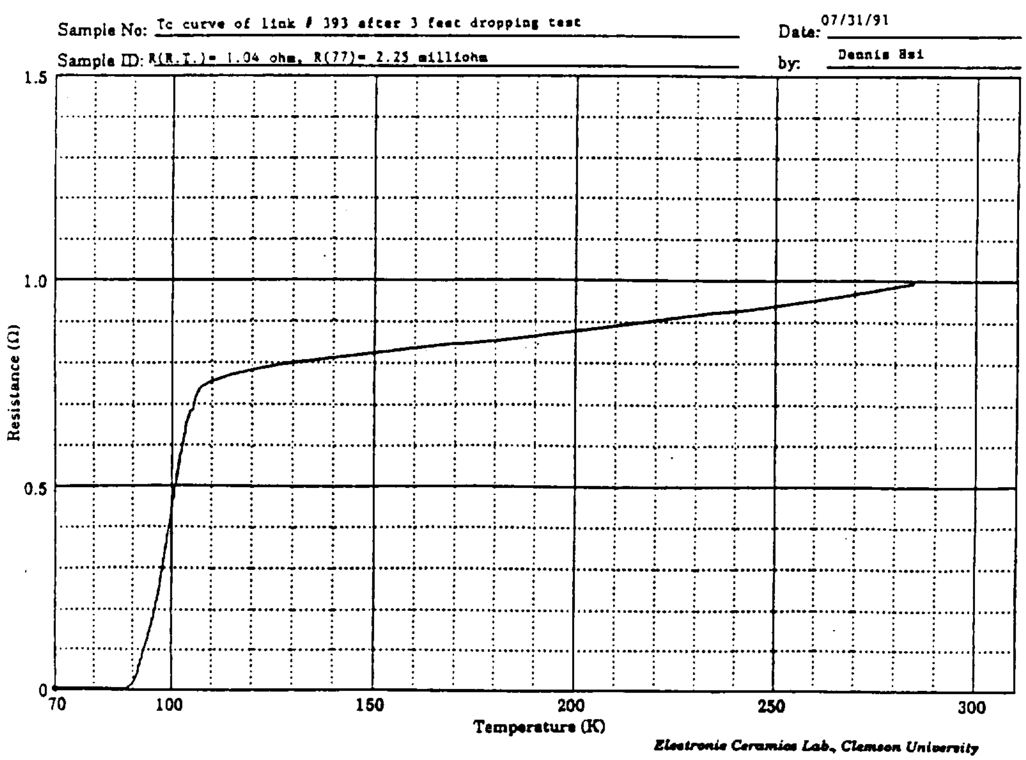
Appendix VII

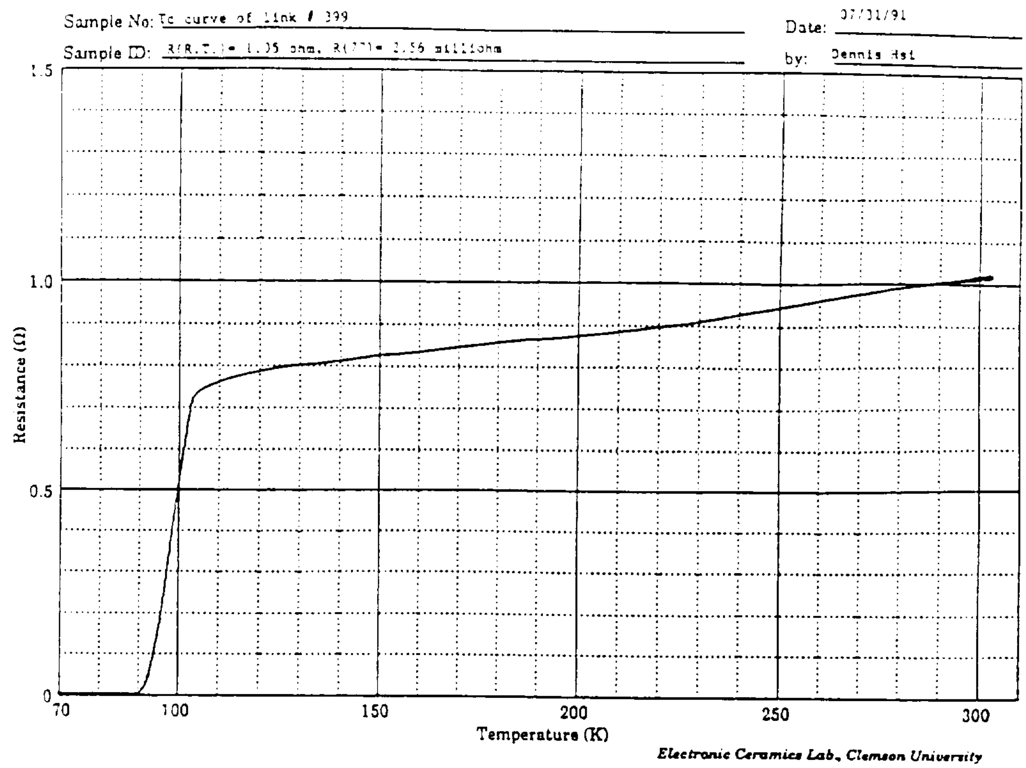
Figure A-3: T_c curve of selected results of dropping test samples.

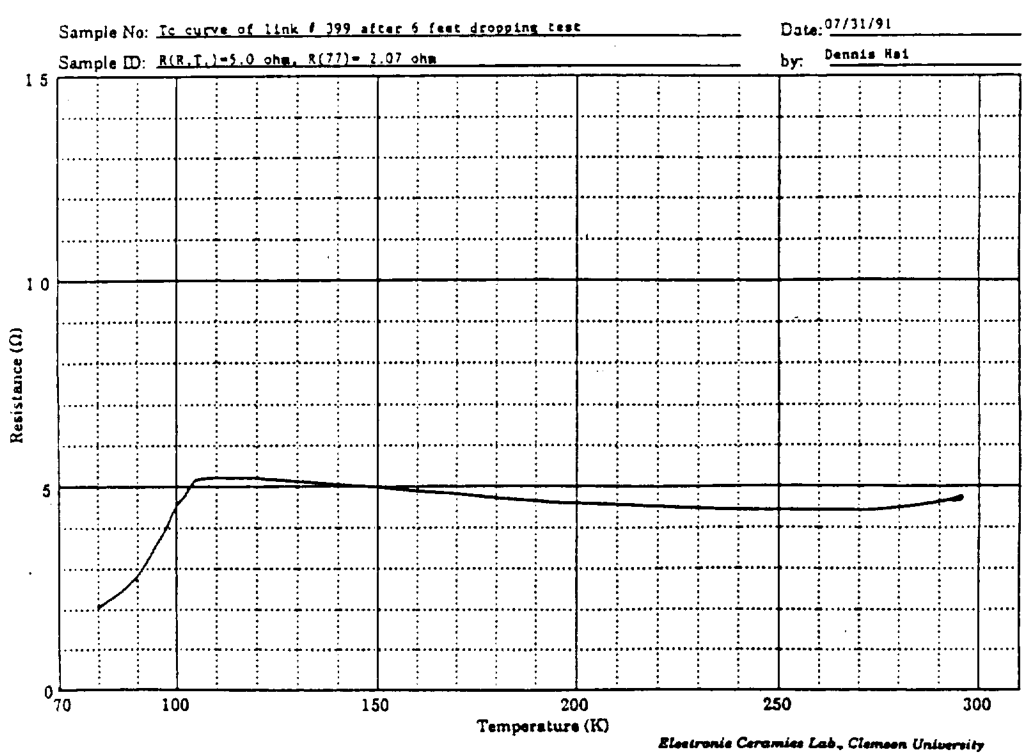





Sample No: Tc curve of link # 393
Date: 07/31/91
Sample ID: R(R.T.)= 1.05 ohm, R(77)= 2.20 milliohm.
by: Chi-Shiung Hsi
1.5
1.0
0.5
0
Resistance (Ω)
70
100
150
200
250
300
Temperature (K)
Electronic Ceramics Lab, Clemson University

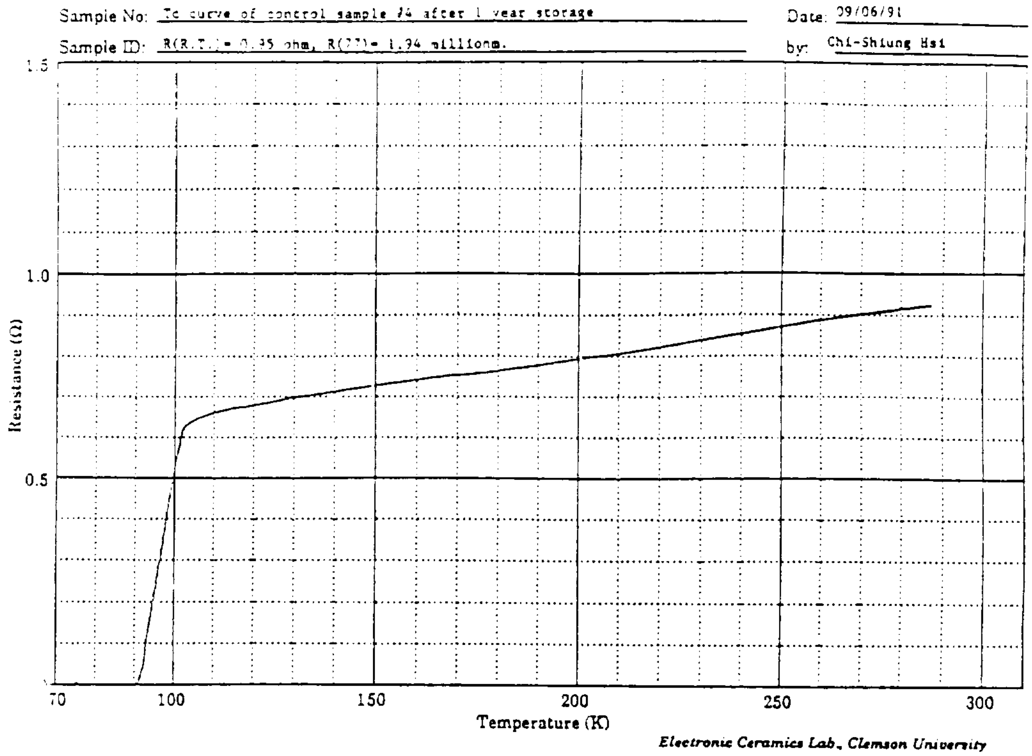

Sample No: Tc curve of link # 393 after 3 feet dropping test
Date: 07/31/91
Sample ID: R(R.T.)= 1.04 ohm, R(77)= 2.25 milliohm
by: Dennis Hsi
1.5
1.0
0.5
0
Resistance (Ω)
70
100
150
200
250
300
Temperature (K)
Electronic Ceramics Lab, Clemson University

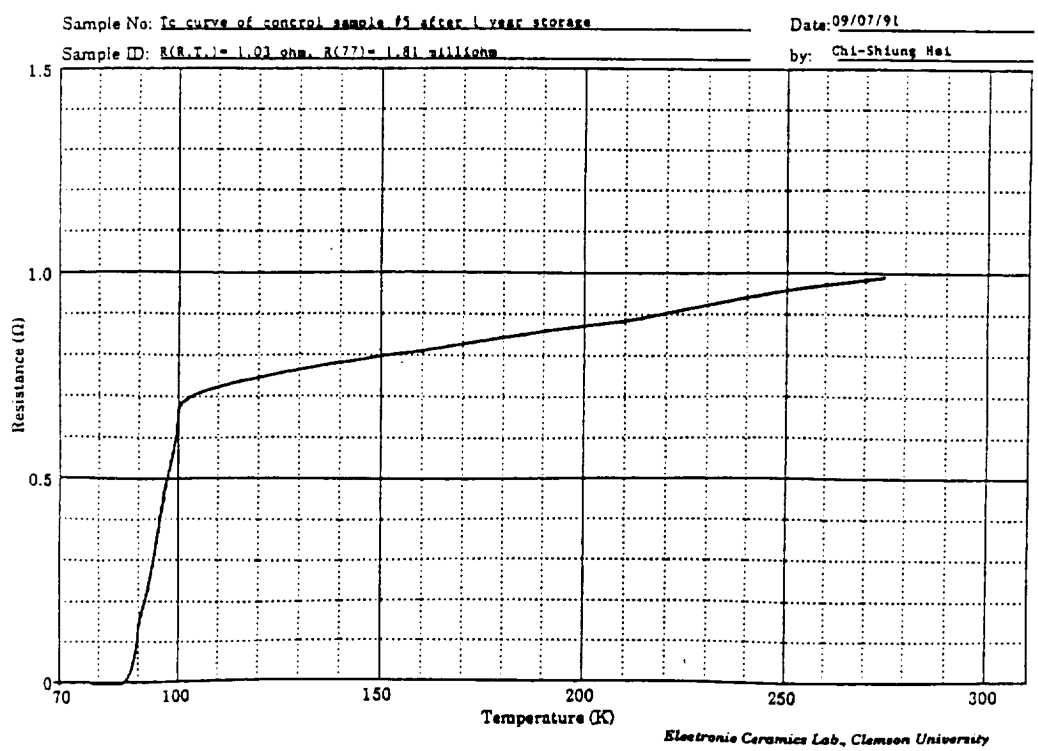

Sample No: Tc curve of link # 399
Date: 07/31/91
Sample ID: R(R.T.)= 1.35 ohm, R(77)= 2.56 milliohm
by: Dennis Hsi
1.5
1.0
0.5
0
Resistance (Ω)
70
100
150
200
250
300
Temperature (K)
Electronic Ceramics Lab., Clemson University

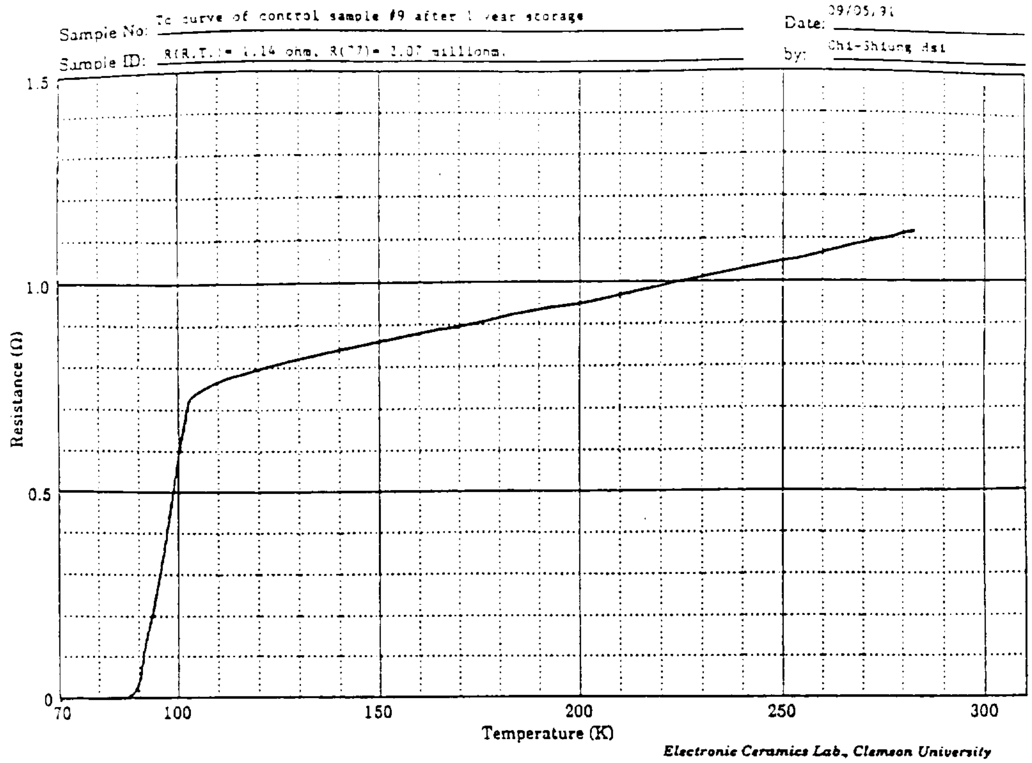

Sample No: Tc curve of link # 399 after 6 feet dropping test
Date: 07/31/91
Sample ID: R(R.T.)=5.0 ohm, R(77)= 2.07 ohm
by: Dennis Hsi
1 5
1 0
5
0
Resistance (Ω)
70
100
150
200
250
300
Temperature (K)
Electronic Ceramics Lab., Clemson University

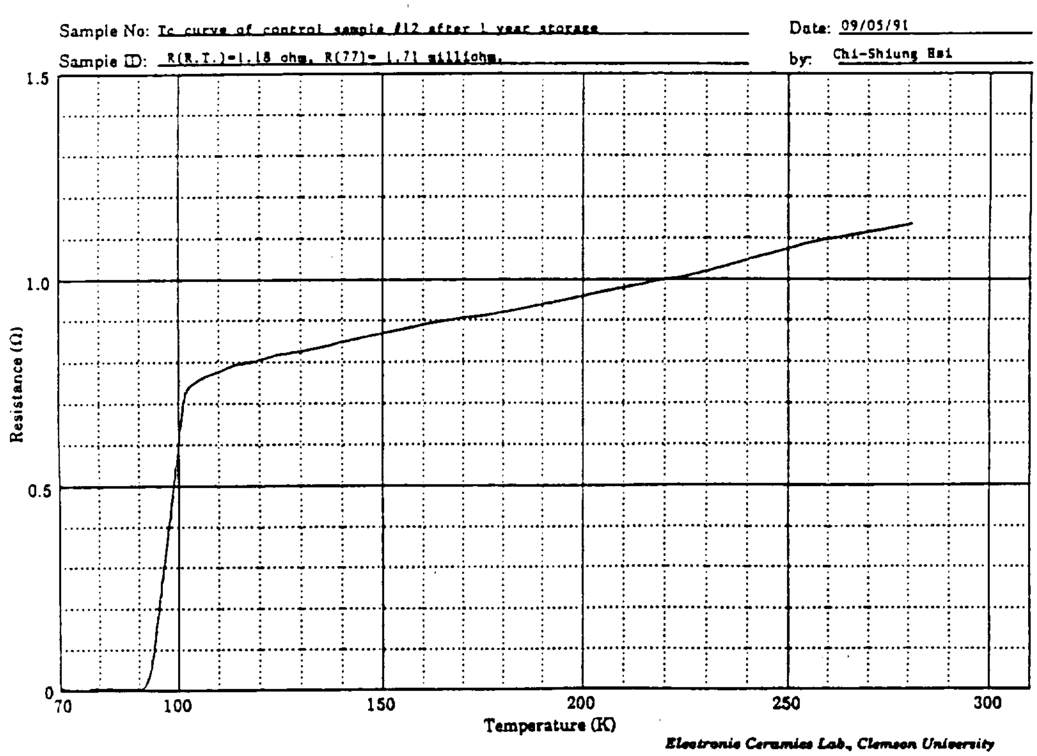
Appendix VIII

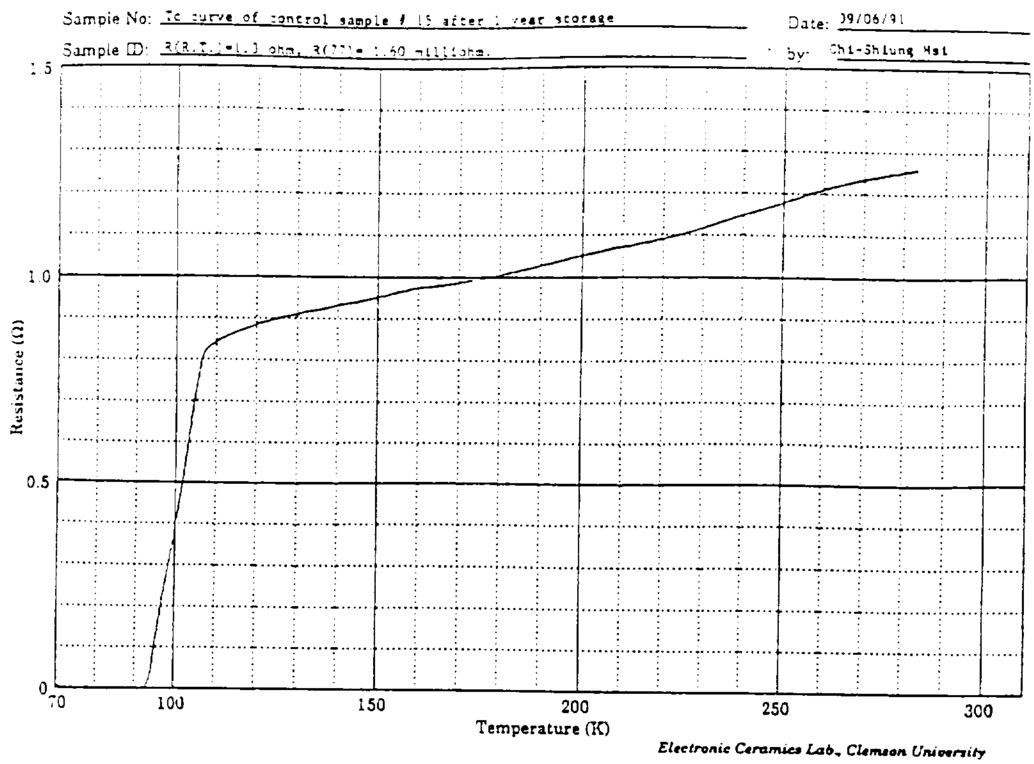
Figure A-4 T_c curves of the control samples after one year storage at ambient conditions.



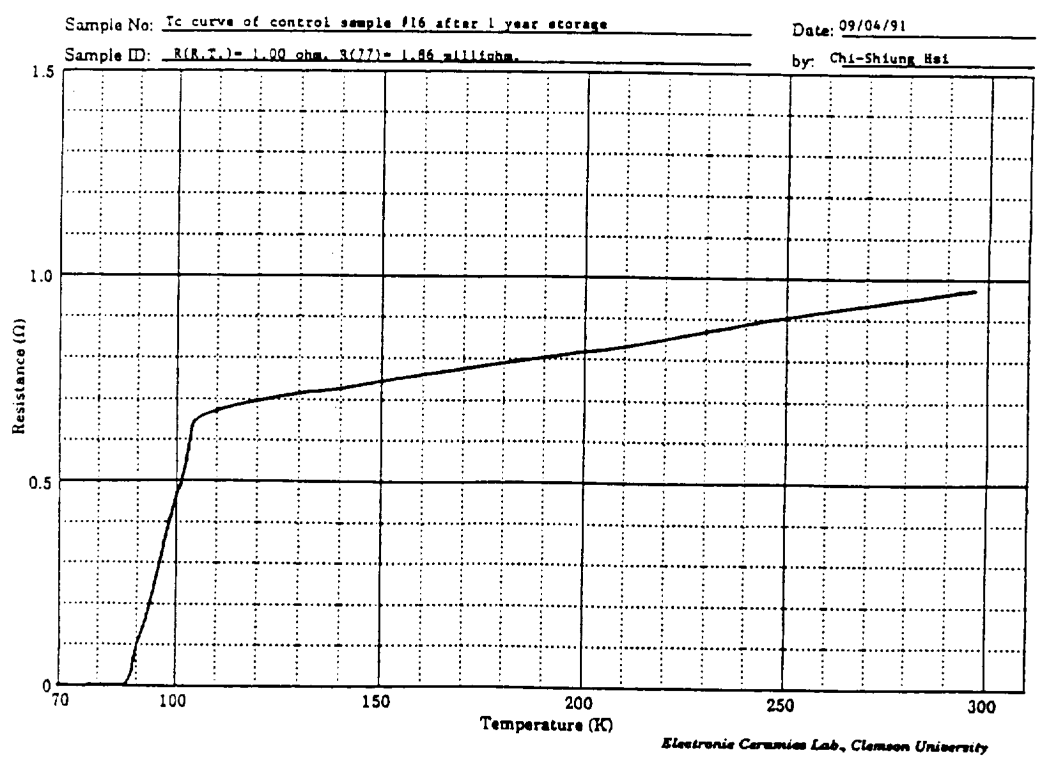



Sample No: Tc curve of control sample #9 after 1 year storage
Date: 09/05/91
Sample ID: R(R.T.)= 1.14 ohm, R(77)= 1.07 milliohm.
by: Chi-Shiung Hsi
Resistance (Ω)
Temperature (K)
Electronic Ceramics Lab., Clemson University

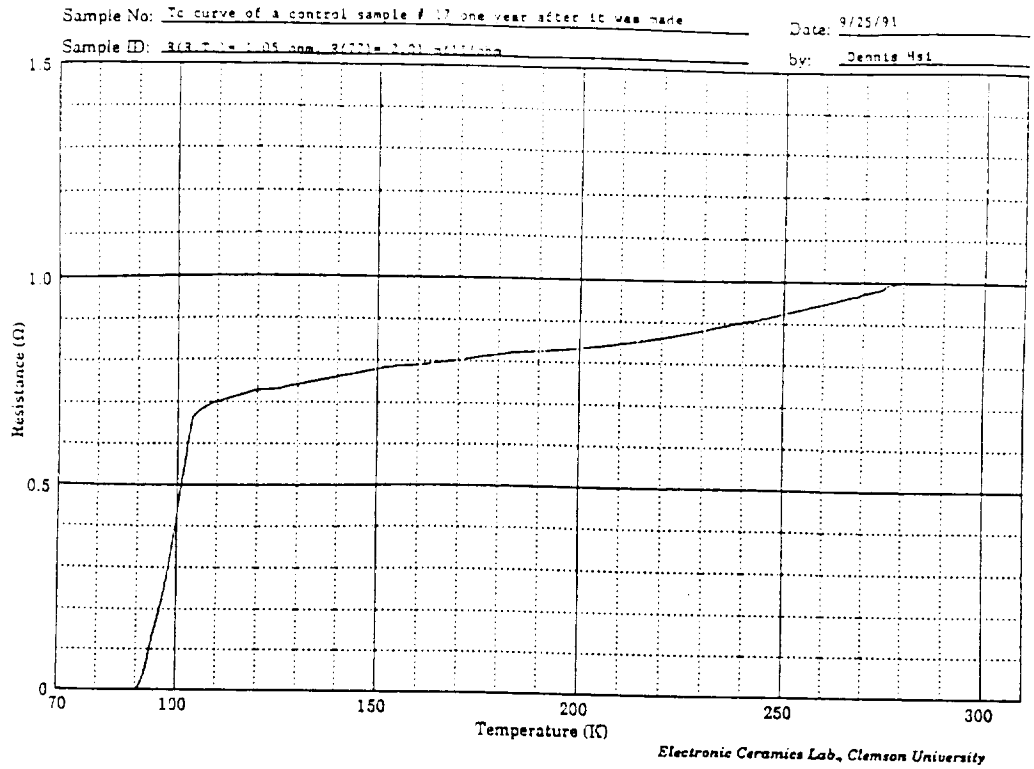

Sample No: Tc curve of control sample #12 after 1 year storage
Date: 09/05/91
Sample ID: R(R.T.)=1.18 ohm, R(77)= 1.71 milliohm.
by: Chi-Shiung Hsi
Resistance (Ω)
Temperature (K)
Electronic Ceramics Lab., Clemson University

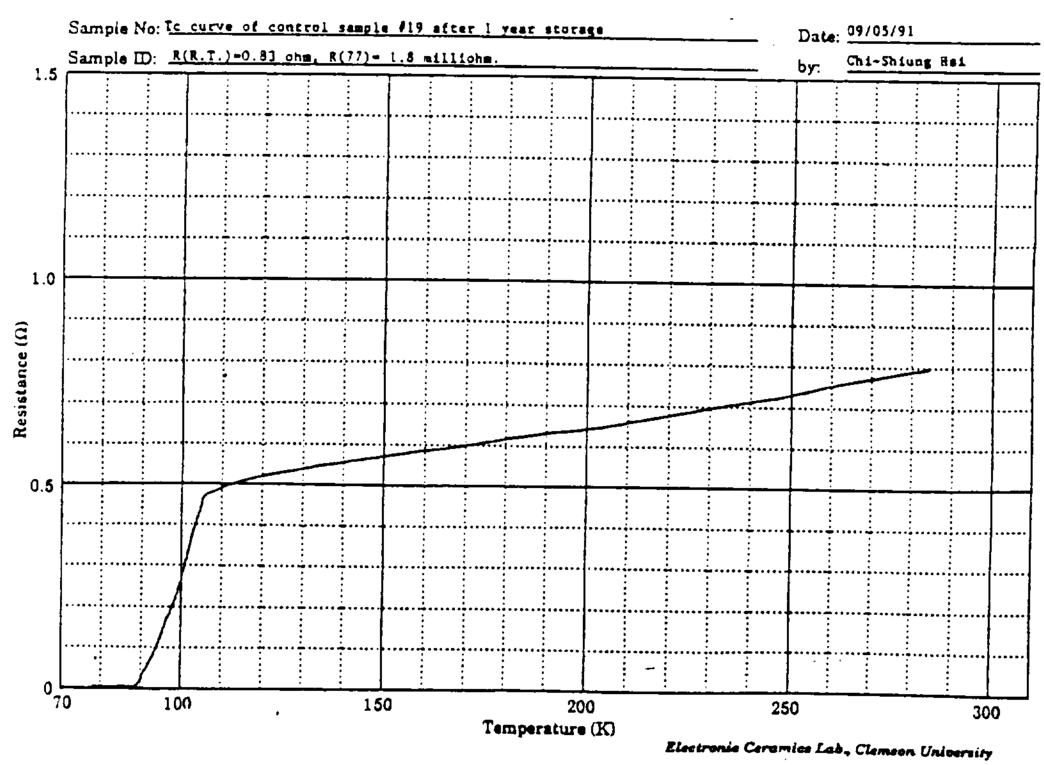


Sample No: Tc curve of control sample # 15 after 1 year storage
Date: 09/06/91
Sample ID: R(R.T.)=1.1 ohm, R(77)= 1.60 milliohm.
by: Chi-Shiung Hsi
Resistance (Ω)
1.5
1.0
0.5
0
70
100
150
200
250
300
Temperature (K)
Electronic Ceramics Lab., Clemson University



Sample No: Tc curve of control sample #16 after 1 year storage
Date: 09/04/91
Sample ID: R(R.T.)= 1.00 ohm, R(77)= 1.86 milliohm.
by: Chi-Shiung Hsi
Resistance (Ω)
1.5
1.0
0.5
0
70
100
150
200
250
300
Temperature (K)
Electronic Ceramics Lab., Clemson University





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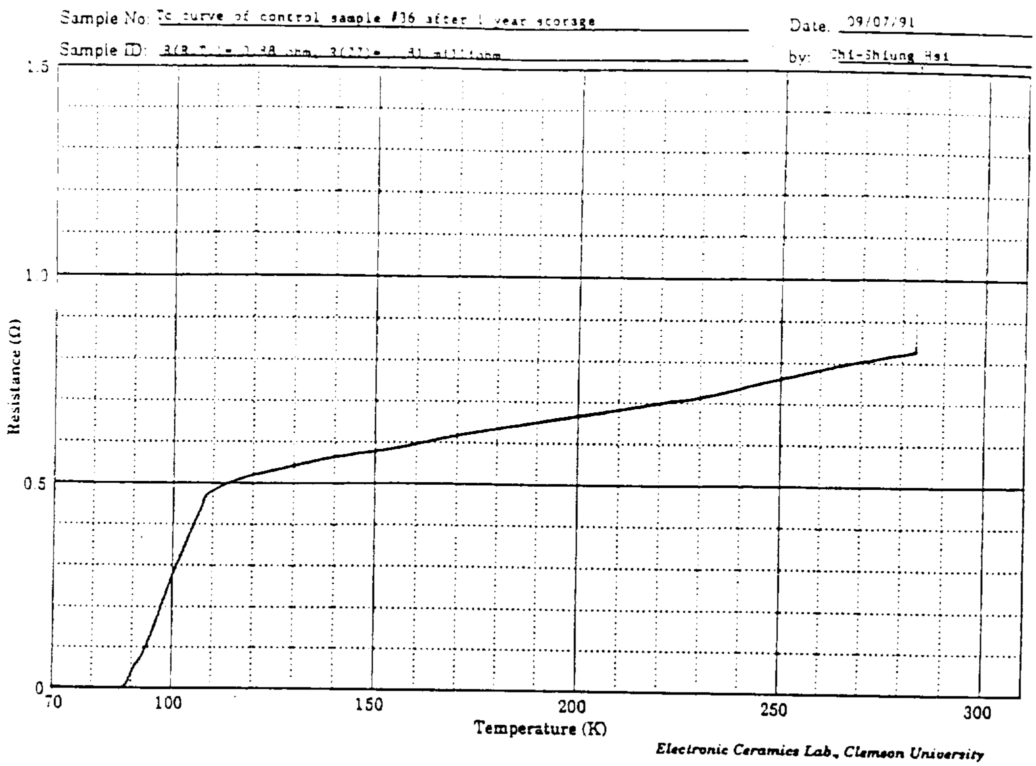
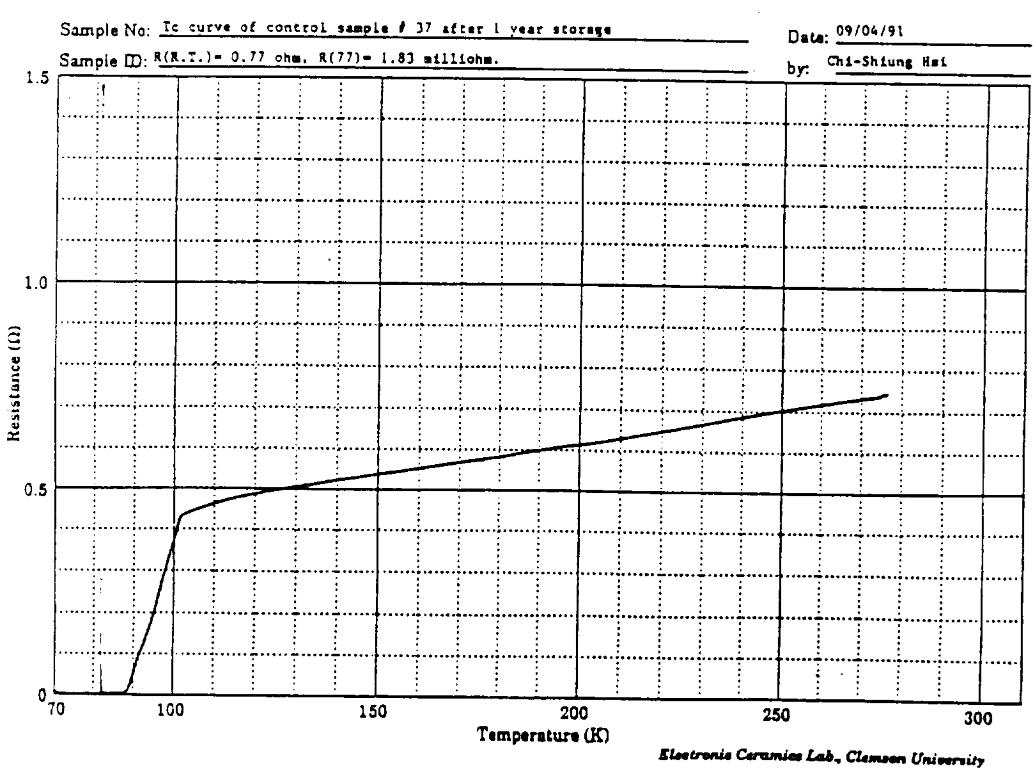
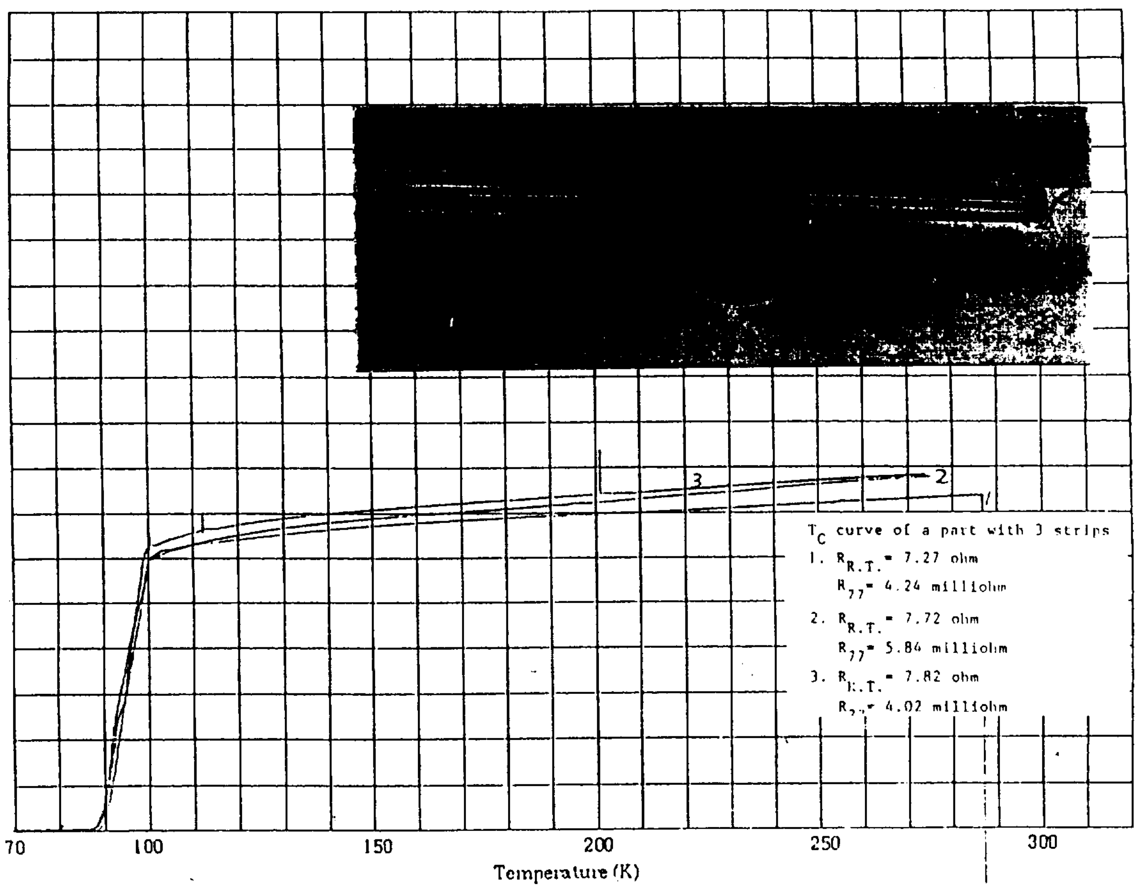

Sample No: Tc curve of control sample #36 after 1 year storage
Date. 09/07/91
Sample ID:
by: Chi-Shiung Hsi
1.5
1.0
0.5
0
Resistance (Ω)
70
100
150
200
250
300
Temperature (K)
Electronic Ceramics Lab., Clemson University


Sample No: Tc curve of control sample # 37 after 1 year storage
Date: 09/04/91
Sample ID: R(R.T.)= 0.77 ohm, R(77)= 1.83 milliohm.
by: Chi-Shiung Hsi
1.5
1.0
0.5
0
Resistance (Ω)
70
100
150
200
250
300
Temperature (K)
Electronic Ceramics Lab., Clemson University

Appendix IX

Figure A-5: T_c curve of a link with three $YBa_2Cu_3O_{7-x}$ superconductor strips.



V. PART II

WESTINGHOUSE SAVANNAH RIVER CO.

Annual Report

ENVIRONMENTAL TEST FOR SUPERCONDUCTING MATERIALS AND DEVICES

Results of Testing Program at SRS

to

Dr. Gene H. Haertling
Ceramic Engineering, Clemson University
Clemson, SC 29634-0907

Investigators:

Henry Randolph	- Westinghouse Savannah River Co.
Darren Verebelyi	- Westinghouse Savannah River Co.
	- Clemson University

Contract No. NAG-1-1127
WSRC-TR91-403

Introduction

The properties of $YBa_2Cu_3O_{7-x}$ superconducting tapes designed and fabricated into SAFIRE-type, encapsulated, grounding links by the Ceramic Engineering Department at Clemson University were investigated(NASA Contract No. NAG-1-1127). Testing at the Savannah River Site included gamma irradiation, vibration, magnetic field, and long-term evaluation. Irradiation and vibration did not change the physical or electrical properties of the tested samples. An applied magnetic field of 1000 Gauss increased the superconducting resistance and invoked semiconductor electrical properties of some samples. The long-term testing began in January 91 and resistance data showed no increases. No gaseous decomposition has been found.

Radiation Test

Eight samples were irradiated in a high level gamma well. These samples were received from Clemson with known resistance vs. temperature curves. Before irradiation the samples were videotaped. The full screen view equaled the width of the sample. The samples were then immersed in liquid Nitrogen(LN_2) and exposed to ^{137}Cs for 126 total hours over a 10 day period. The main energy peak of the ^{137}Cs spectrum is at 661.66 keV. The calibrated exposure rate was 96.940 R/hr. The equivalent gamma radiation dose in water is equal to 11,000 rad. The cross section for gamma absorption in superconducting material is greater. Therefore, the dose would be greater than 11,000 rad.

After irradiation these samples were videotaped again in the same manner as before exposure. The only physical change resulting from the treatment, was minor epoxy separation from the superconductor. This effect has been observed at Clemson on some samples during long periods of LN_2 immersion. The samples were returned to Clemson for comparison resistance vs. temperature curves. These curves showed no change from the pre-test curves.

Vibration Test

Resistance vs. temperature curves on four unused samples were taken before vibration. Figures 1 and 2 are the original curves. All four samples had well defined transitions to the superconducting state and had a 80K resistance of less than 5 milliohms. Using the first derivative of the resistance data curves similar to Figure 3 show two distinct transitions. These two transitions are compiled in Table 1.

Sample	T_{C1}(K)	T_{C2}(K)
364	94	89
365	94	90
366	92	87
367	93	90

Table 1 Original Critical Temperatures of the Four Vibration Test Samples

Samples 364, 365, 366, and 367 were then vibrated perpendicular to their face as shown in Figure 4. The samples were fixed to table supports at each end. All samples were in the same configuration when vibrated simultaneously. The elapsed time of vibration with the corresponding frequency and acceleration are shown in Table 2.

Time (seconds)	Frequency (Hertz)	Acceleration (m/s)	Acceleration (g's)
750	15	70	7
350	16	50	5

Table 2 Vibration Test Variables
Total time: 18.5 minutes

After vibration, the samples had resistance vs. temperature curves taken again. These curves were compared to the previous curves and no major differences were found. Table 3 compares the original data to the post-vibration data. The post-vibration curves are shown in Figures 5 and 6. Overlays of the post-vibration curves on the original curves show the transition region in detail. Overlays are shown in Figures 7 and 8.

Sample	T_{C1} (K)		T_{C2} (K)	
	Original	Post-Test	Original	Post-Test
364	94	93	89	86
365	94	94	90	90
366	92	93	87	87
367	93	93	90	90

Table 3 Original vs. Post-Vibration Critical Temperatures of the Four Test Samples

Magnetic Field Test

Resistance vs. temperature curves on four unused samples were first taken with no applied magnetic field. Figures 9 and 10 show the original curves of the four samples. Two of the samples were found to be poor, 362 and 363, and had superconducting resistances of several hundred milliohms.

Samples 360, 361, 362, & 363 were then placed in a 1000 Gauss magnetic field and then cooled to LN_2 temperature. The magnetic field was perpendicular to the face of the sample and is shown in Figure 11. The excitation current used during a 4-wire ohm measurement was 10 milliamps.

The comparison data with and without the applied field is shown in Table 4. The first poor sample, 362, was slightly changed by the applied field. However, sample 363 became worse and exhibited semiconductor properties. Sample 360 was unchanged in the field and had a T_c of 91K. Sample 361 was severely changed by the field and also exhibited a semiconductor-like increase in resistance during cooling. Figures 12 and 13 show the resistance vs. temperature curves to room temperature in an applied field. Figures 14 and 15 compare the curves at the transition with and without a field.

Sample	T_c(K)		Resistance(milliohms)	
	Zero Gauss	1K Gauss	Zero Gauss	1K Gauss
360	91	92	<5	<5
361	90	91	<5	480*
362	93	93	110	103
363	93	93	440	1060*

* Exhibited Semiconductor Properties

Table 4 Zero vs. 1000 Gauss comparison of the Four Samples

Long-Term Test

The long-term test monitored for decomposition by-products and changes in resistance while maintaining low temperature(77K) and high vacuum(10-7 torr). The equipment to perform measurements included a cryostat and a vacuum system consisting of stainless steel piping configured to accommodate two, 20-pin, electronic signal feedthroughs, an ion pump, and a mass spectrometer head. Figures 16 and 17 show the vacuum system configuration. The cryostat is immersed in LN_2 from a 50 liter dewar. LN_2 is replenished to the 50 liter dewar by an interchangeable 160 liter dewar.

Continuous data acquisition by computer control compiled measurements of current, voltage, temperature, pressure, and partial pressure. Data were taken at 15 minute intervals and written into two text files along with a date and time stamp. Measurements were taken by a Hewlett Packard 3457A Multimeter, Hewlett Packard Scanner, and a Dycor Quadrupole Mass Spectrometer. The multimeter was certified and is NIST traceable.

Voltage and current measurements were written to disk and resistance was calculated from Ohm's law. Temperature was calculated from the resistance measurement of a calibrated ceramic Platium RTD. Pressure was calculated from a voltage measurement on the ion pump controller. Partial pressures of 12 masses were normalized to the ion pump pressure in torr.

A current of 10 milliamps was applied to all eight samples for the first week, then the current was removed from four samples for the balance of the test. Samples were arranged in two groups of four as given in Table 5. The one inch diameter cryostat holds the samples as shown in Figure 18. This orientation allows the temperature measurement to be an upper limit for the samples. The continuous current samples are at a lower temperature due to their position at the bottom of the cryostat. The thermal transfer of the tube produces a temperature gradient of approximately 7K from the bottom of the cryostat to the RTD.

	Sample	Type*	Constant Current
Group 1:	203	Tab	Yes
	204	Tab	Yes
	212	Pin	Yes
	213	Pin	Yes
Group 2:	232	Tab	No
	209	Tab	No
	214	Pin	No
	217	Pin	No

* Tab = Silver foil tab connector
Pin = Gold plated pin connector

Table 5 The Two Groups of Samples in the Long-Term Test

The long term test portion of the program has been in progress for more than 6700 hours. Data were collected each minute during the initial cooling of the samples on 15 Jan 91. Data from sample number 212 were omitted due to its failure to go superconducting after its initial testing on 21 Dec 90. The major abnormality found during the experiment was a negative potential from sample 204. This negative potential of several µvolts disappeared after 700 hours of testing. At this point the samples were at an abnormally high temperature of 110K. The normal state resistance of a sample is approximately one ohm. There is a measured superconducting resistance for each sample due to the two-wire configuration of the samples. This superconducting resistance is several hundred µohms.

Resistance data is the primary focus of the long-term experiment. The three samples to be evaluated are the constant current samples. These samples are 203, 204 and 214. Data segments 10 hours long were used for evaluation. These segments were chosen between dewar fills so no transients were present in the data. The temperature increase over a 10 hour segment was quite small in the beginning and has grown because of the better vacuum present in the system. The pressure is currently in the lower 10 torr range. Data segments were taken at 366, 2915 and 6670 hours. Over this span of time the resistance of the samples showed no sign of increase. Figure 19 shows the sample's resistance for each data segment. Figure 20 is a bar graph of the average resistances for each sample and segment.

Physical degradation of the superconductors and encapsulant was evaluated through the use of gas analysis. The vacuum system was attached to a gas analyzer which could see the spectrum of masses up to 200 amu. Normal masses corresponding to water, nitrogen, carbon dioxide and hydrogen were seen. The change in concentration of these gases over a period of time is shown in Figure 21. Other gases were not continuously detected with partial pressures greater than $10^{[illegible]}$ torr. At $10^{[illegible]}$ torr, gas decomposition would not provide a measurable total mass loss from a sample.

Conclusion

Comprehensive testing was performed on 24 encapsulated superconductors provided by Clemson University under NASA Contract No. NAG-1-1127. Of the samples, three were found defective before testing. Twelve samples were gamma irradiated and vibrated with no permanent damage inflicted. A magnetic field was found to cause substantial interruption in the electrical properties of some samples. The primary effect was the induced semiconductor phases.

The long-term testing has not lead to the destruction of the samples investigated. The encapsulant has protected the superconductor from a high vacuum at LN_2 temperature. Overall, the samples tested were durable physically and electrically and have withstood exposure to the adversities of a space environment.

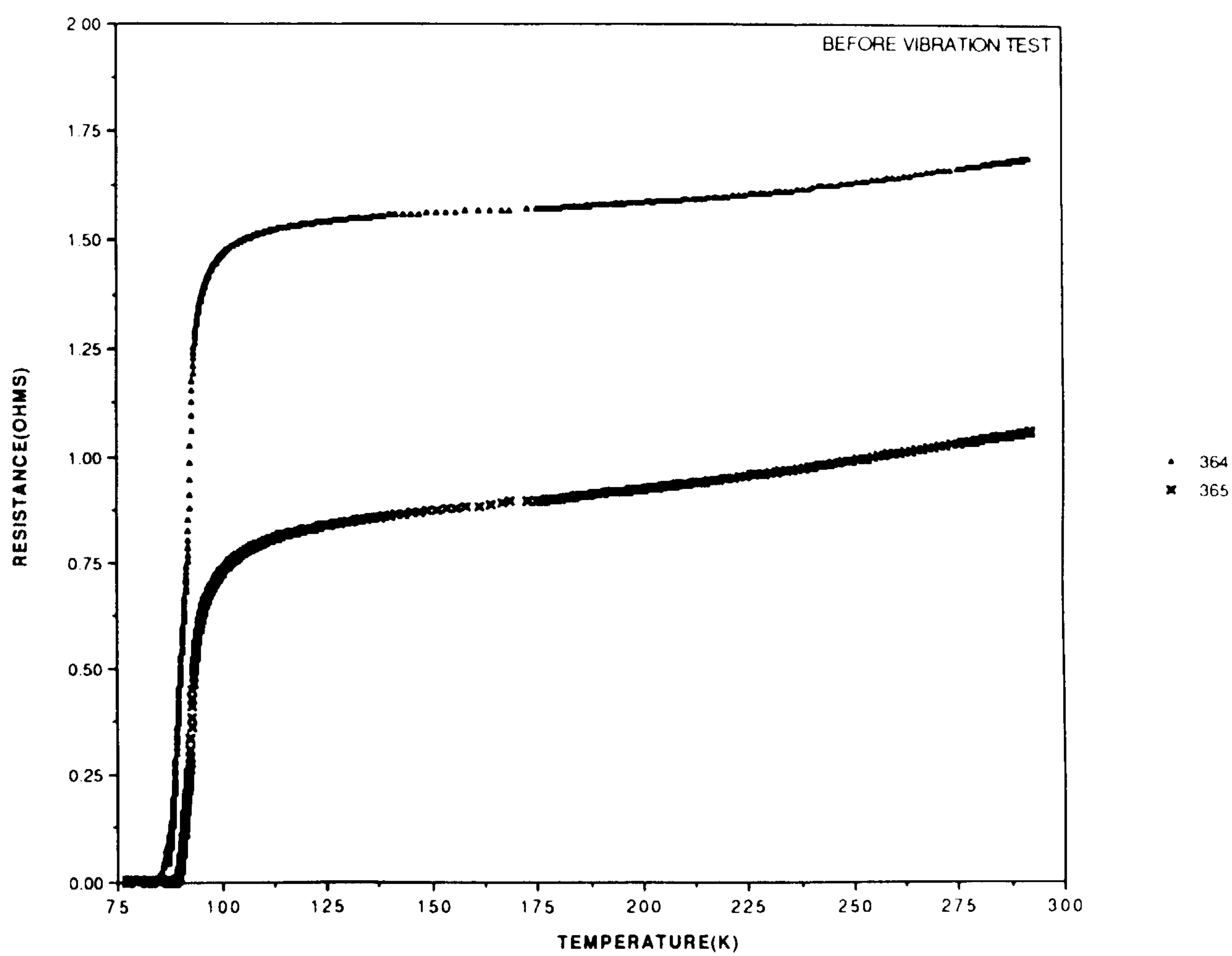


Figure 1 Sample 364 and 365 Resistance vs. Temperature Curves Before Vibration

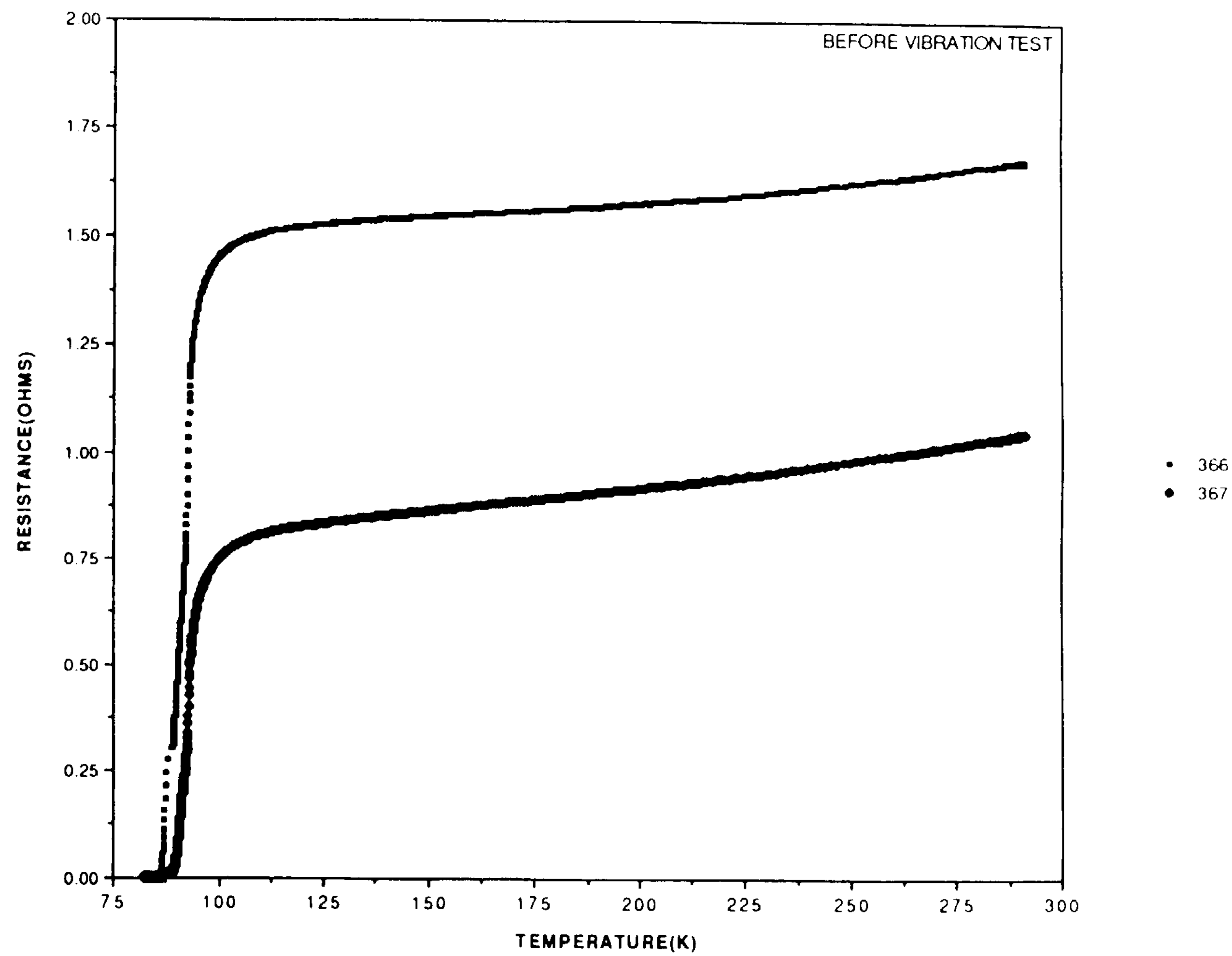


Figure 2 Sample 366 and 367 Resistance vs. Temperature Curves Before Vibration

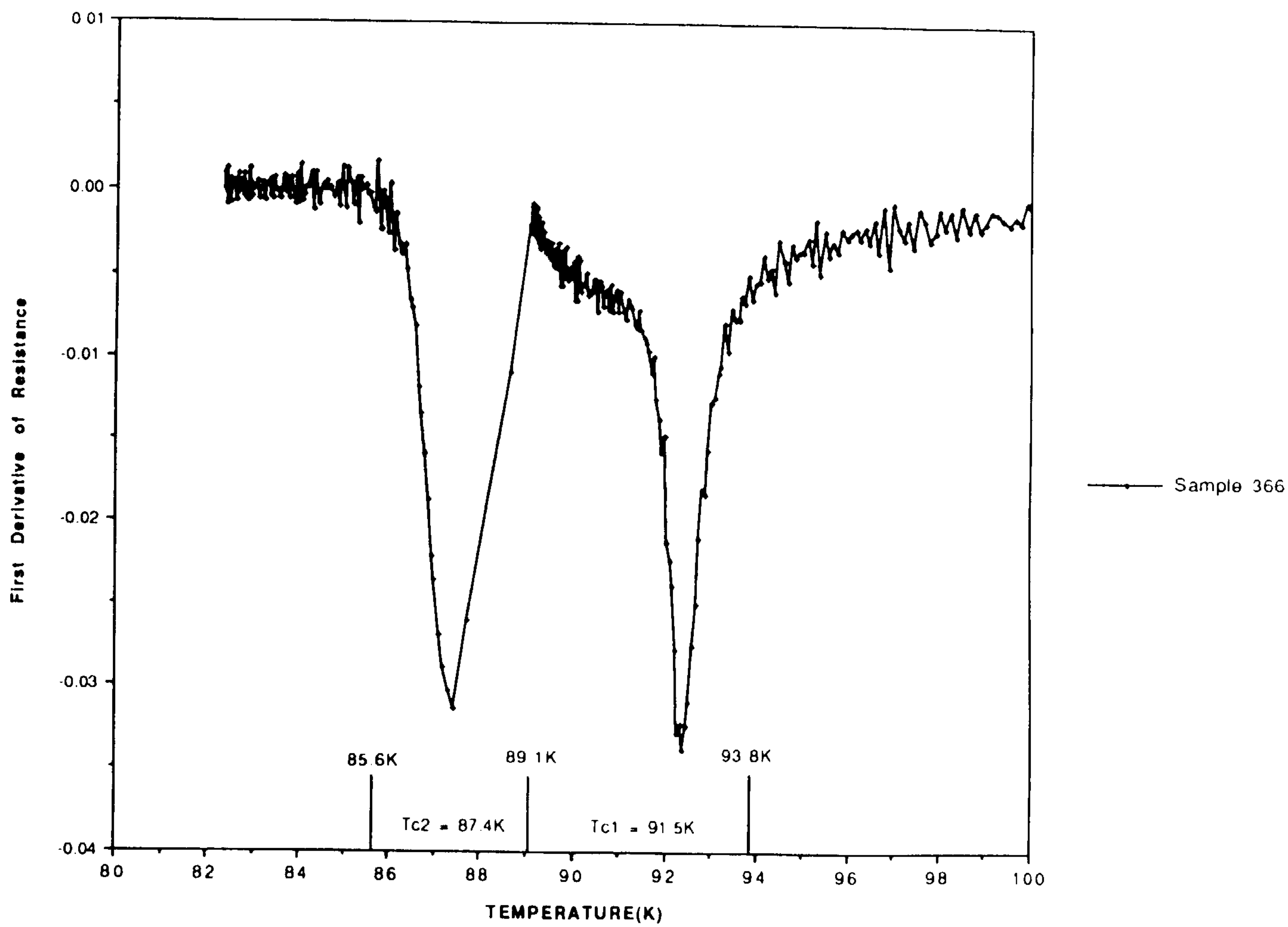
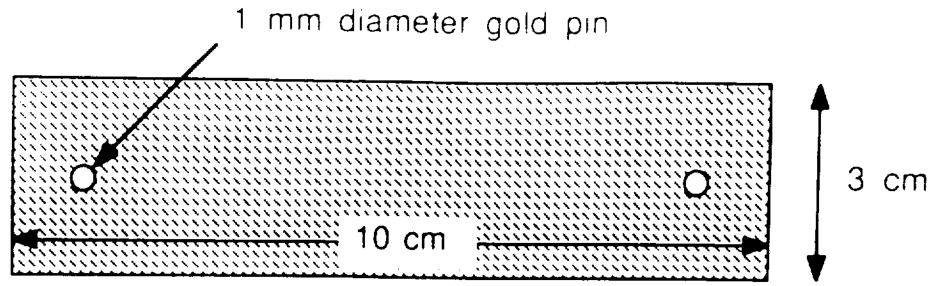
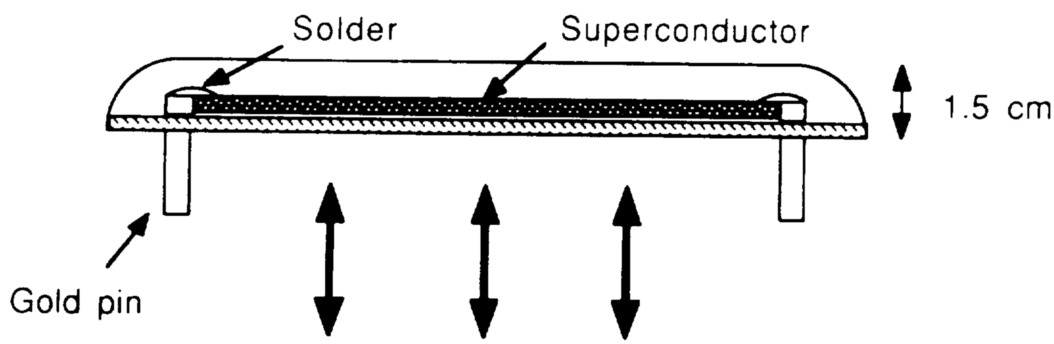


Figure 3 Typical Derivative of Resistance vs. Temperature Curve



Side view of sample on vibration table
(motion is in and out of page)



Top view of sample on vibration table
(each end of the sample was fixed to the table)

Figure 4 Configuration of sample on the Vibration Table.

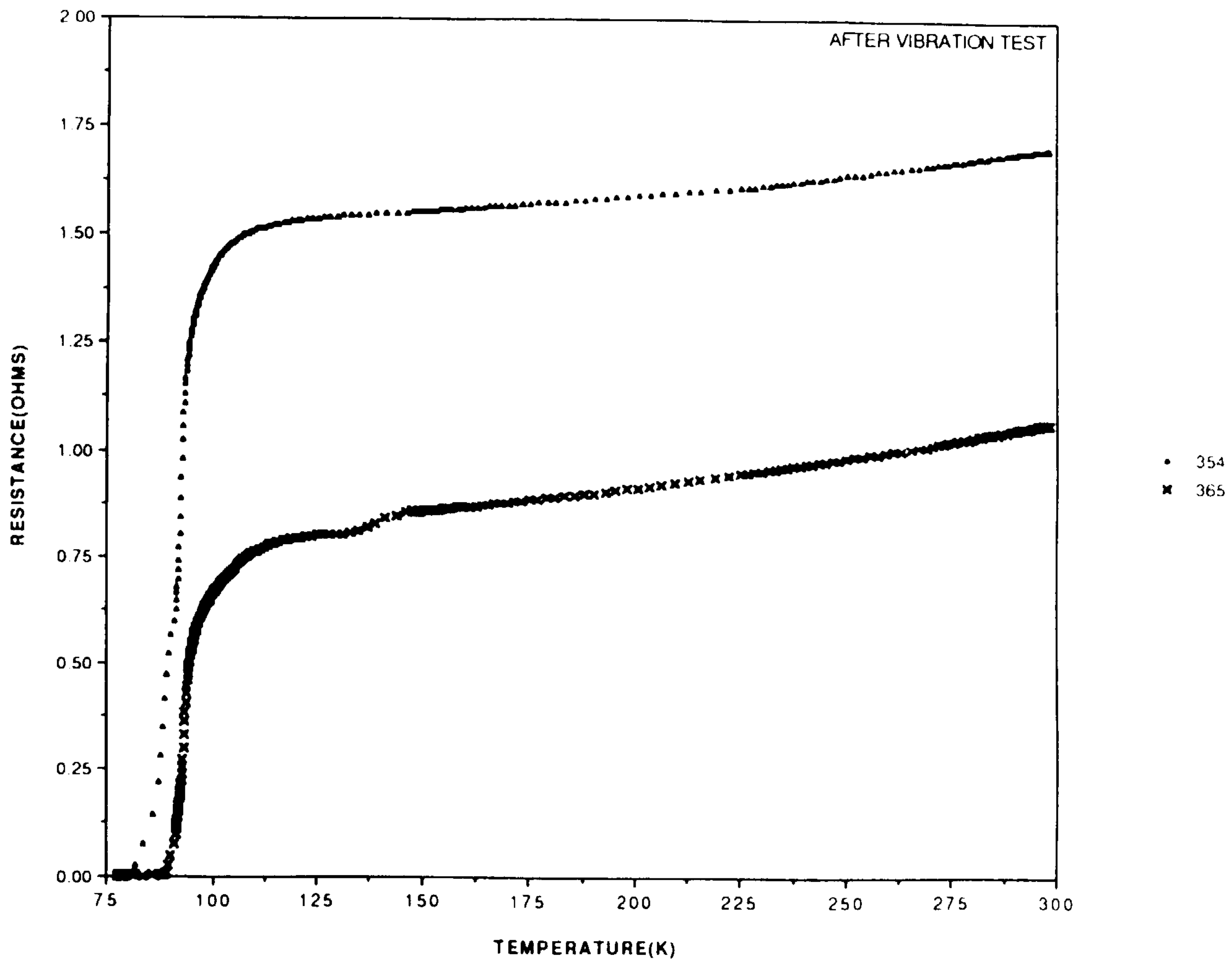


Figure 5 Sample 364 and 365 Resistance vs. Temperature Curves After Vibration

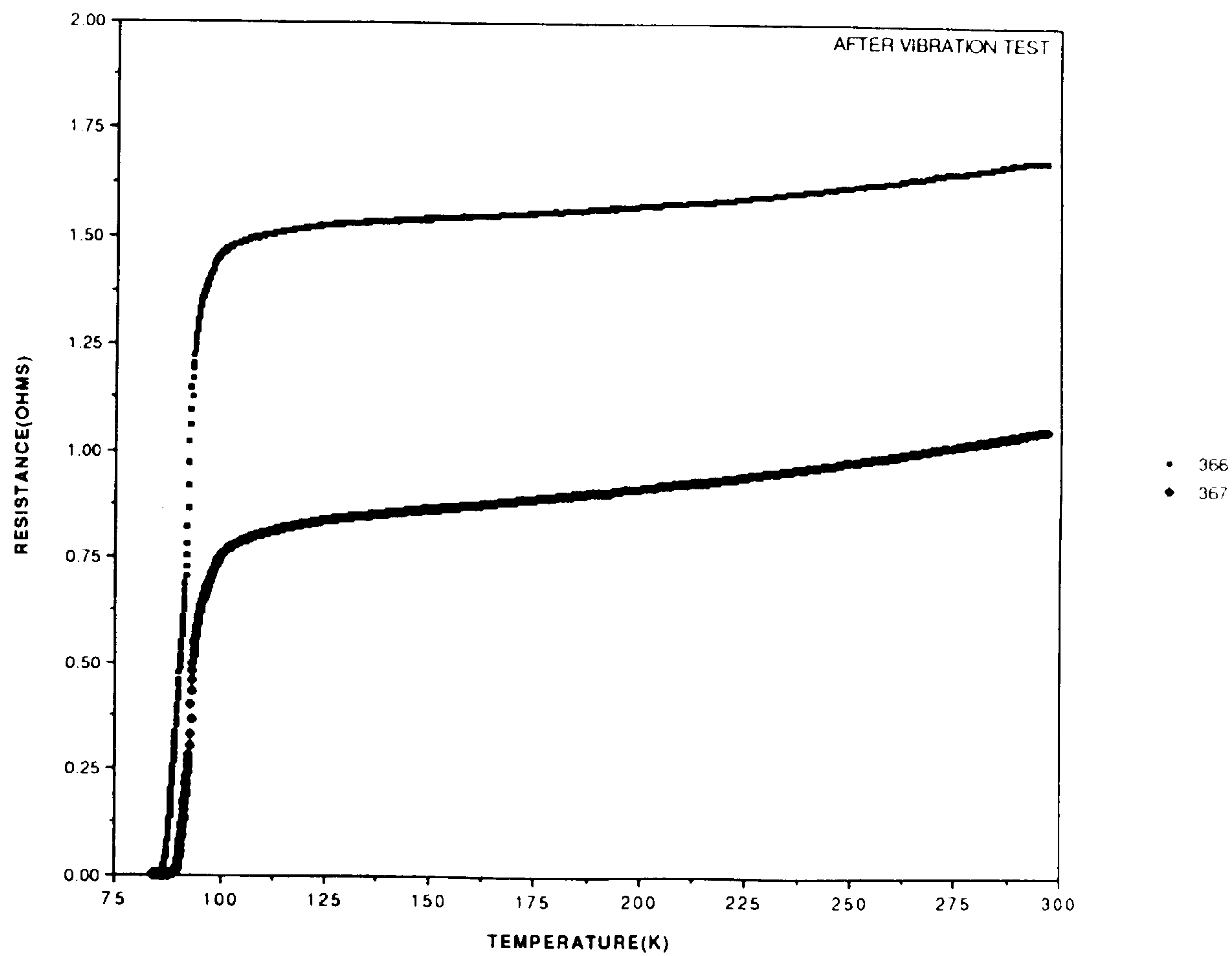


Figure 6 Sample 366 and 367 Resistance vs. Temperature Curves After Vibration

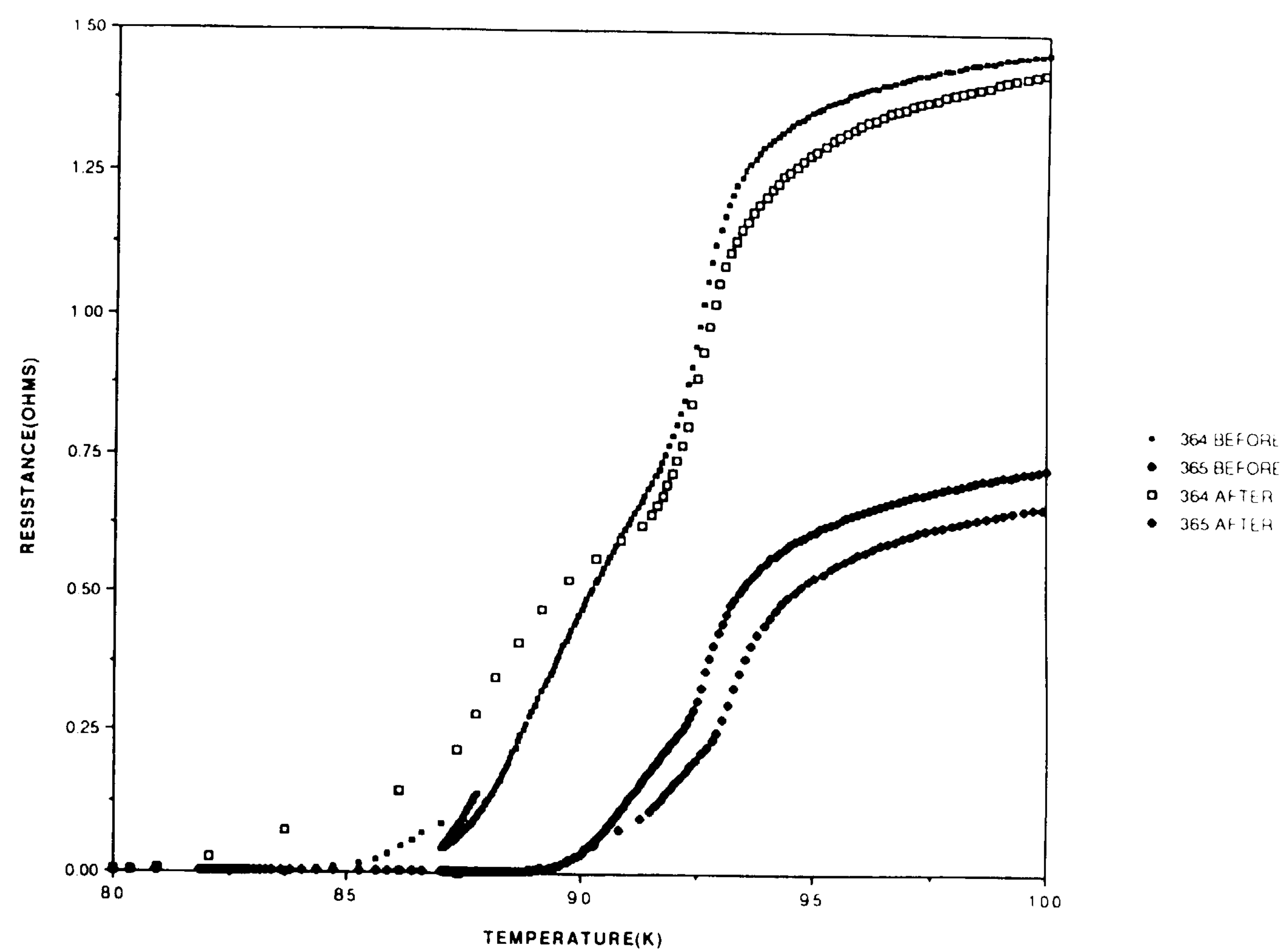


Figure 7 Comparison of Samples 364 and 365 Before and After Vibration

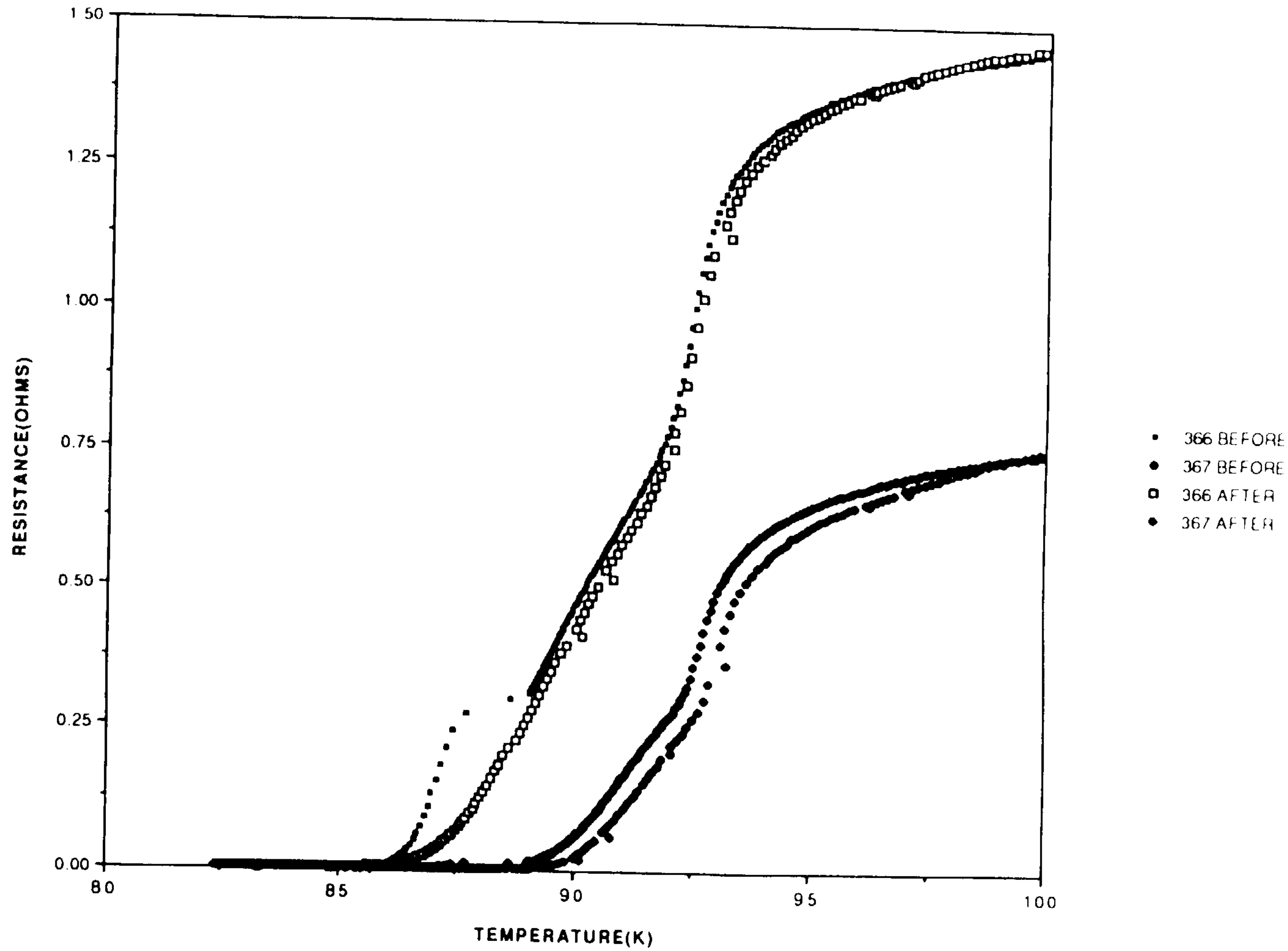


Figure 8 Comparison of Samples 366 and 367 Before and After Vibration

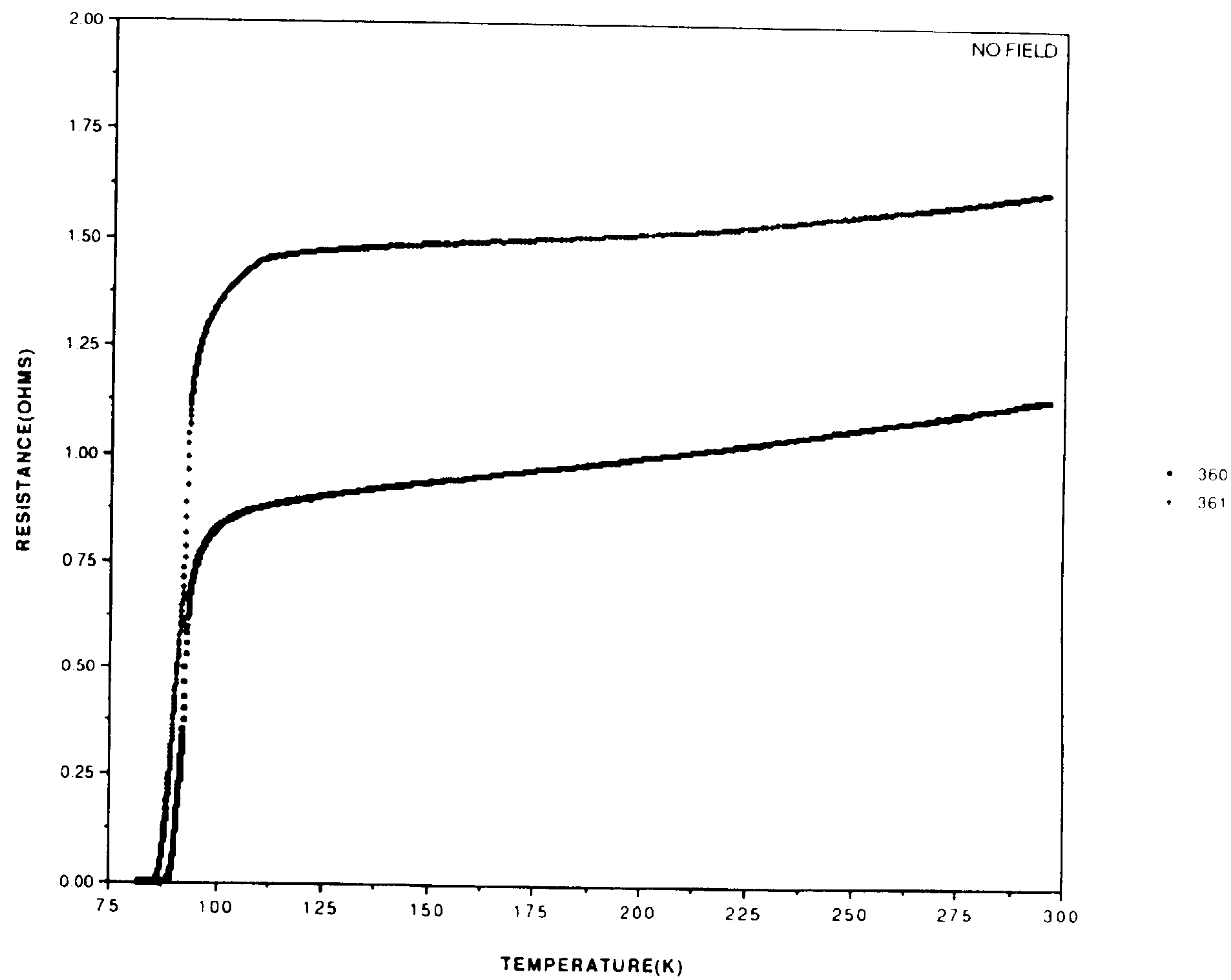


Figure 9 Zero Field Resistance vs. Temperature Curves for Samples 360 and 361

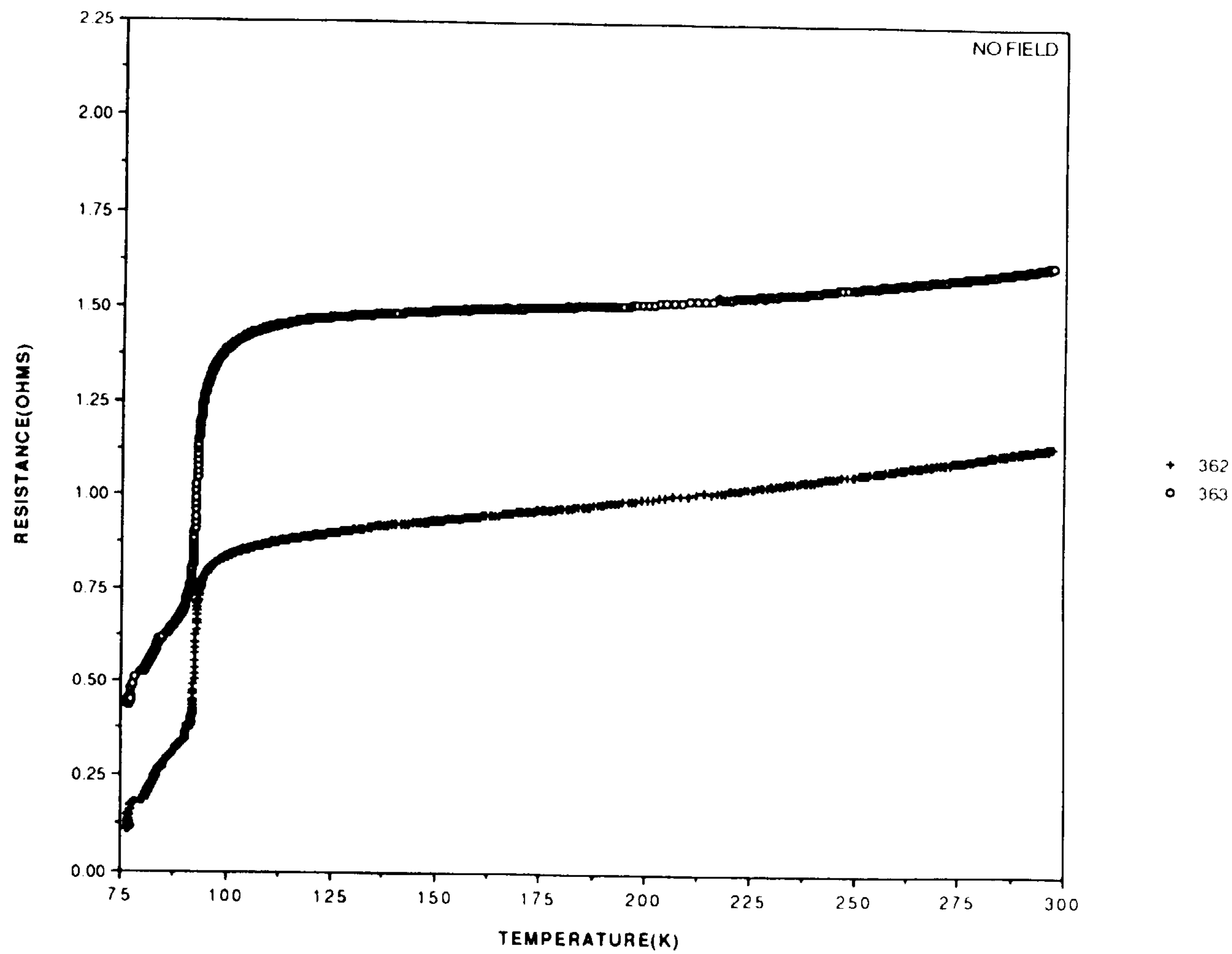


Figure 10 Zero Field Resistance vs. Temperature Curves for Samples 362 and 363

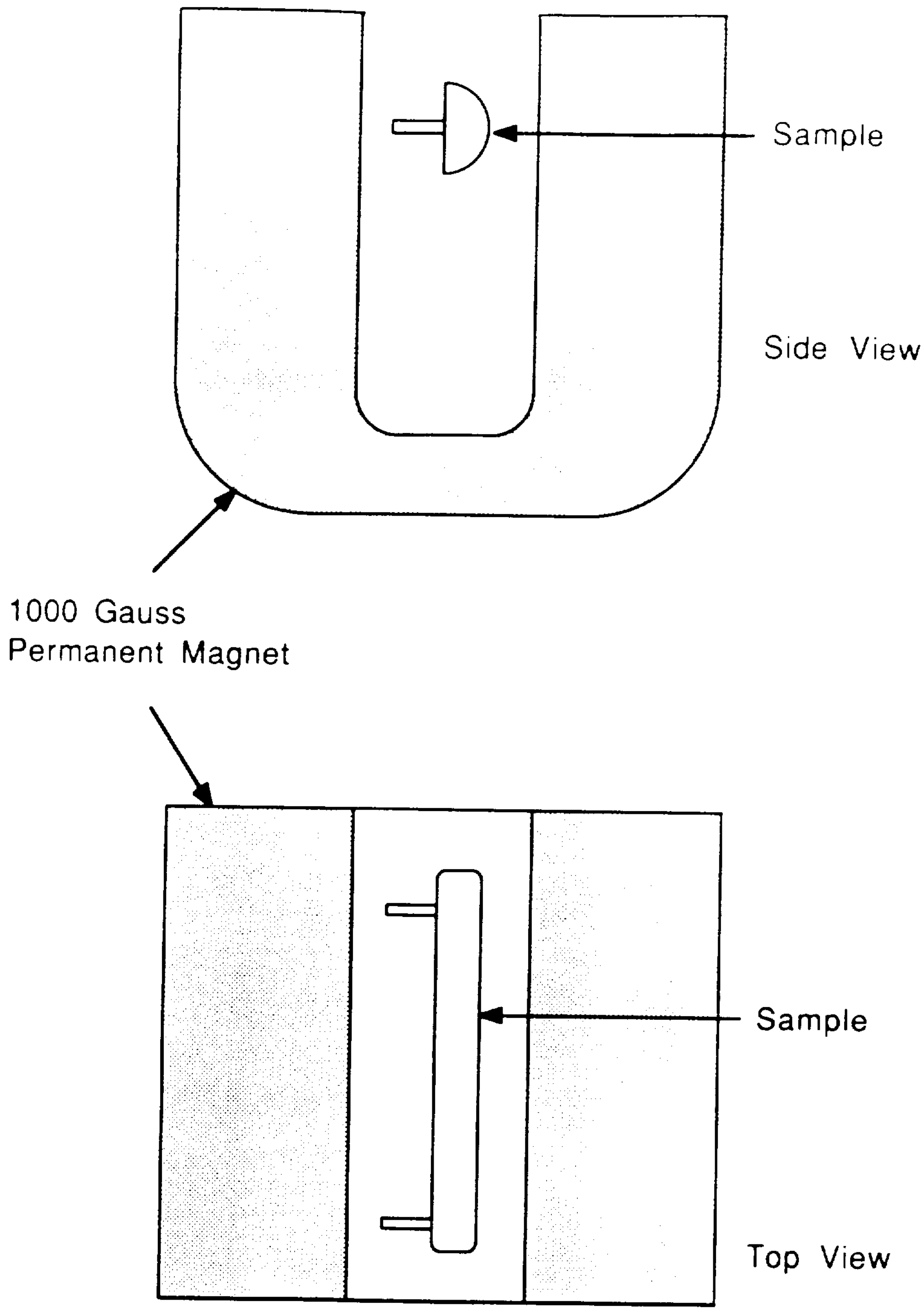


Figure 11 Schematic of Sample Surrounded by Permanent Magnet

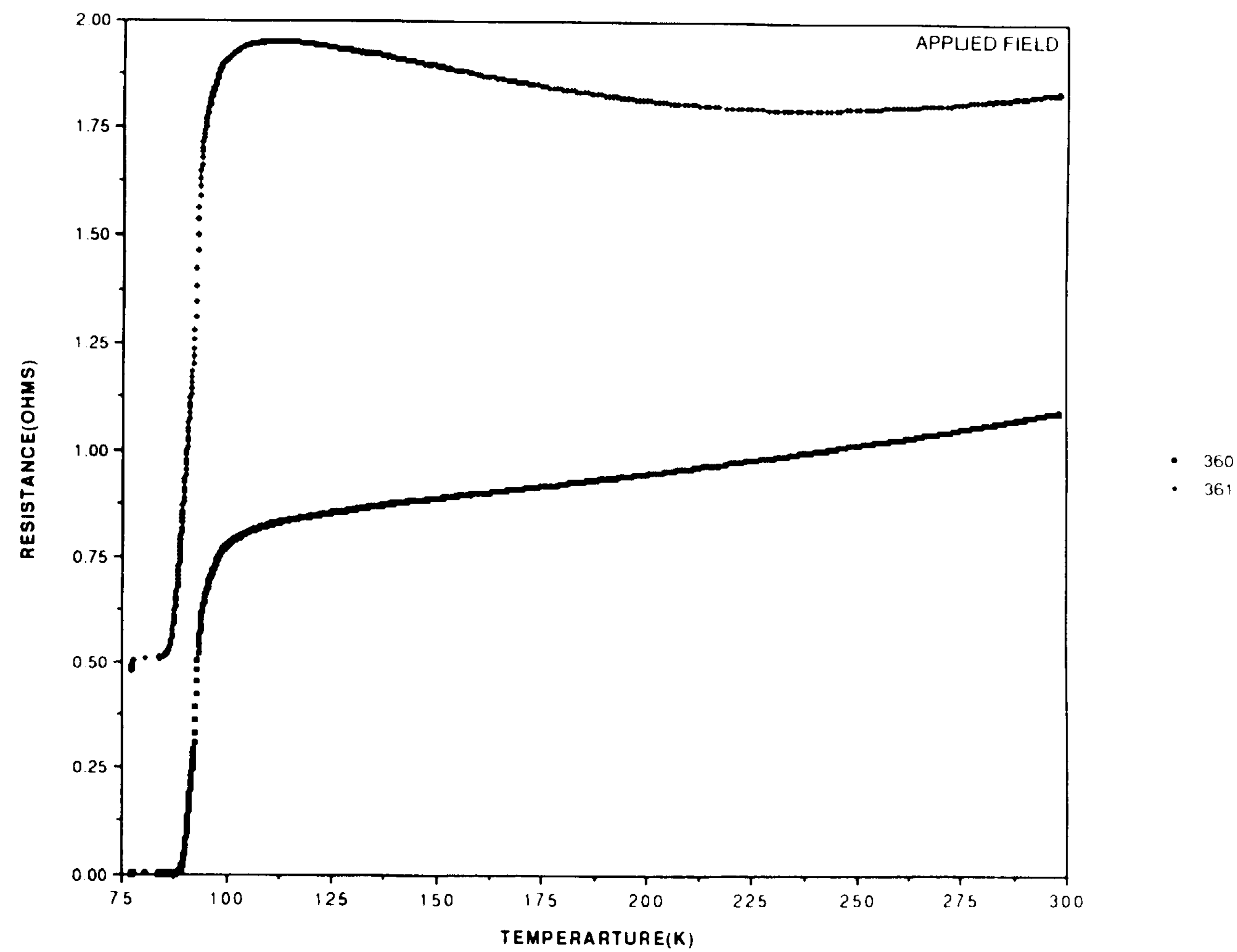


Figure 12 1000 Gauss Field Resistance vs. Temperature Curves for Samples 360 and 361

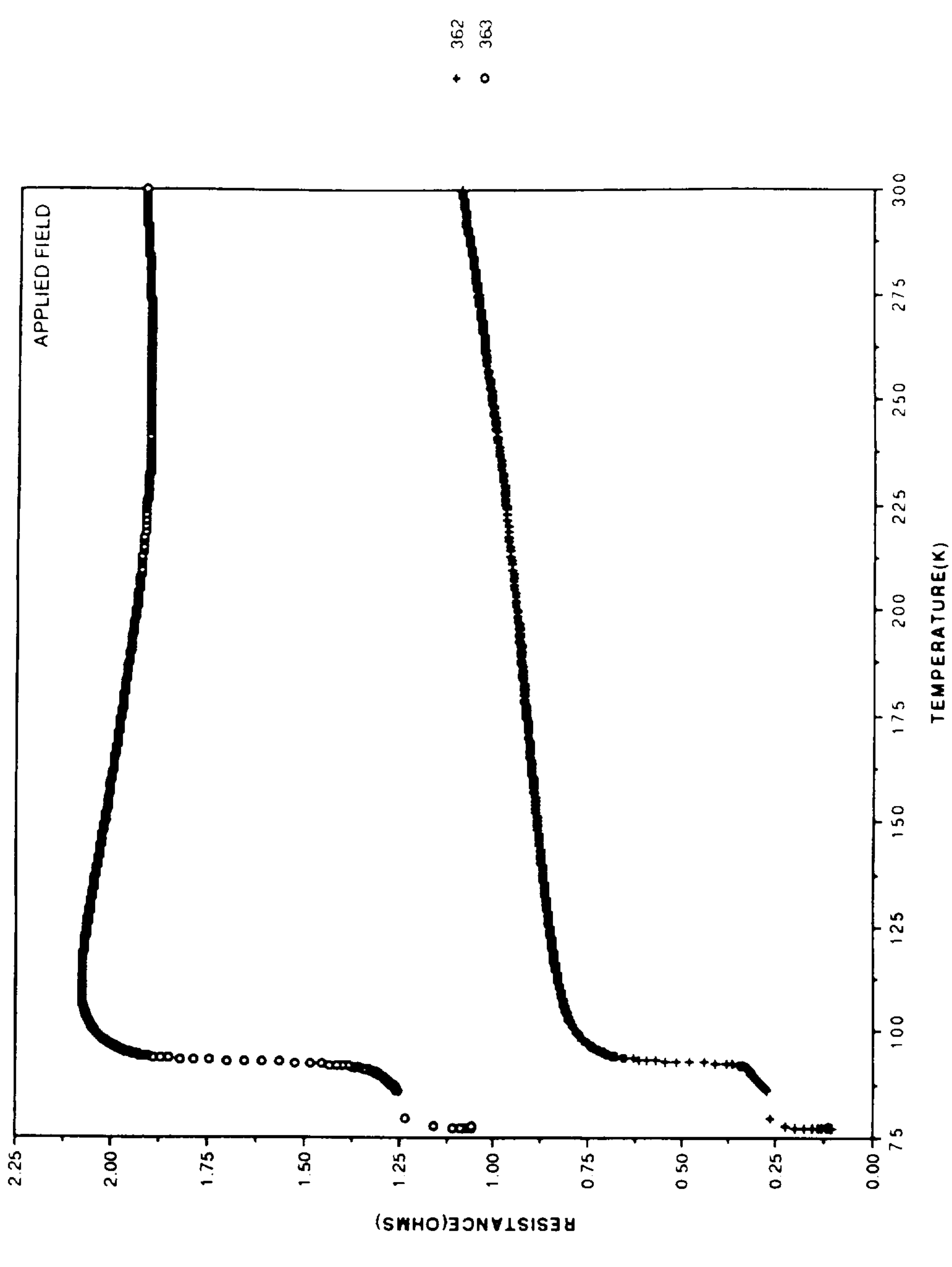


Figure 13 1000 Gauss Field Resistance vs. Temperature Curves for Samples 362 and 363

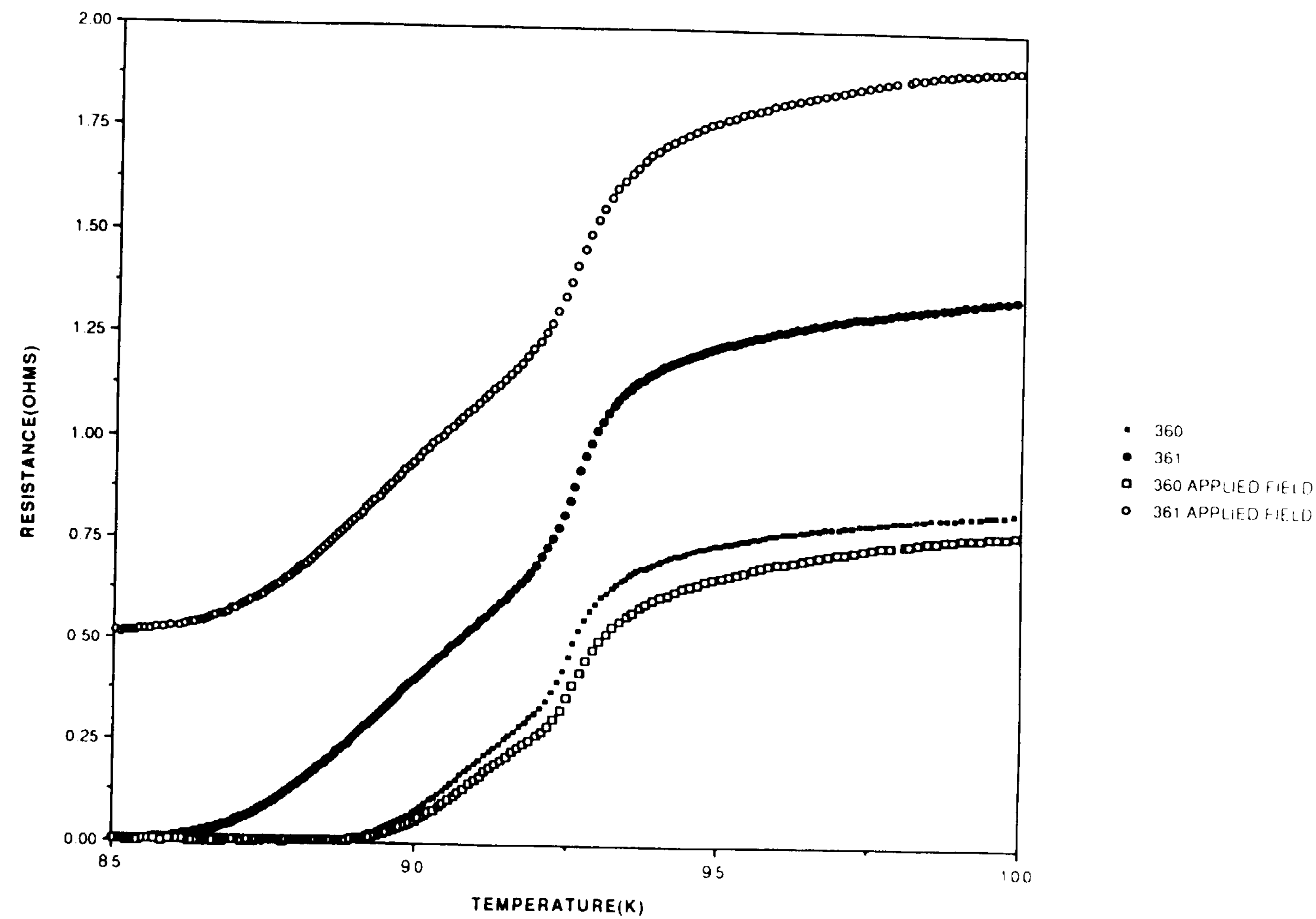


Figure 14 Comparison of Samples 360 and 361 with and without a Magnetic Field

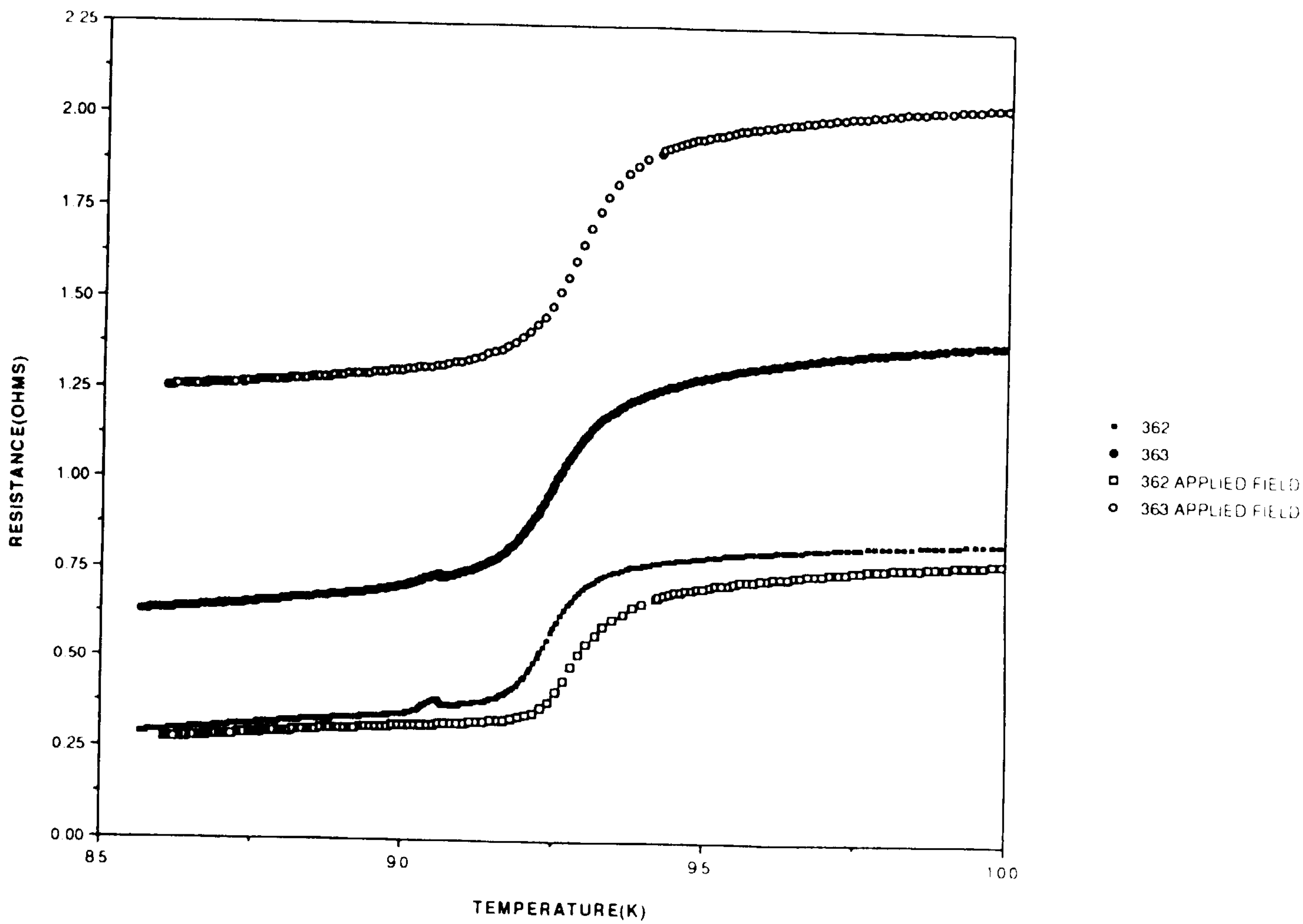


Figure 15 Comparison of Samples 362 and 363 with and without a Magnetic Field

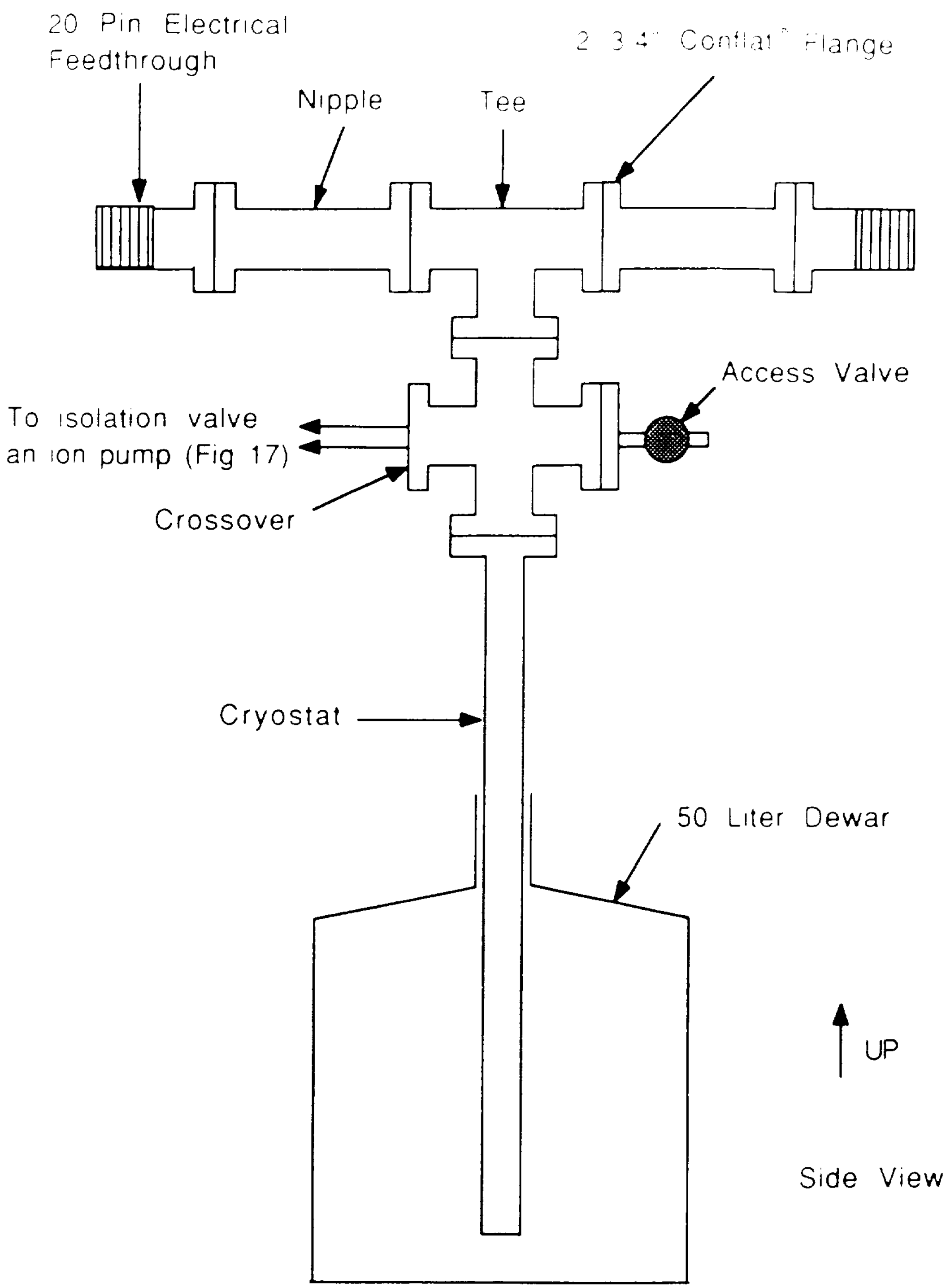


Figure 16 Vacuum System Chamber with Cryostat and Electrical Feedthroughs

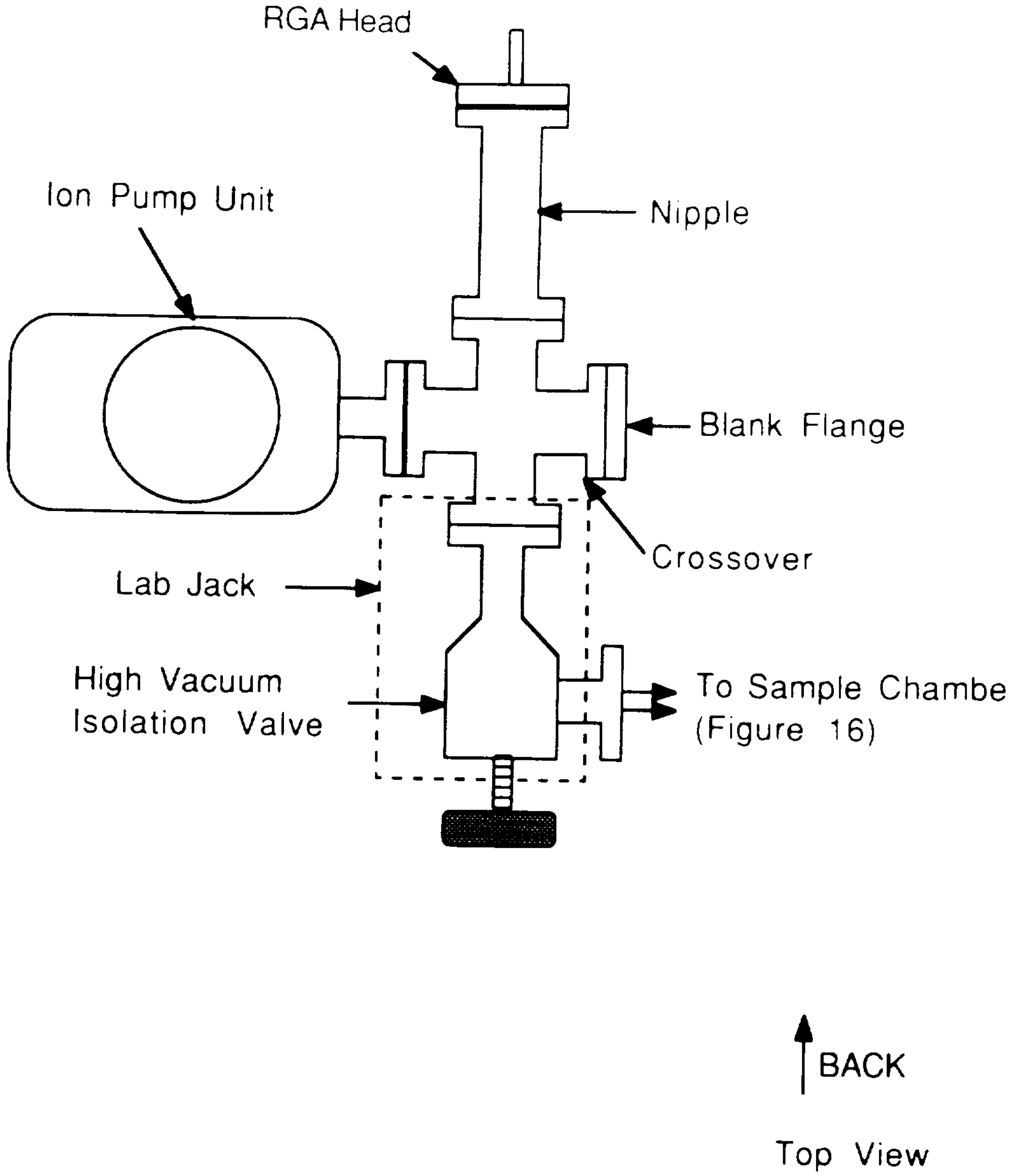


Figure 17 Ion Pump Section of Vacuum System with RGA Head

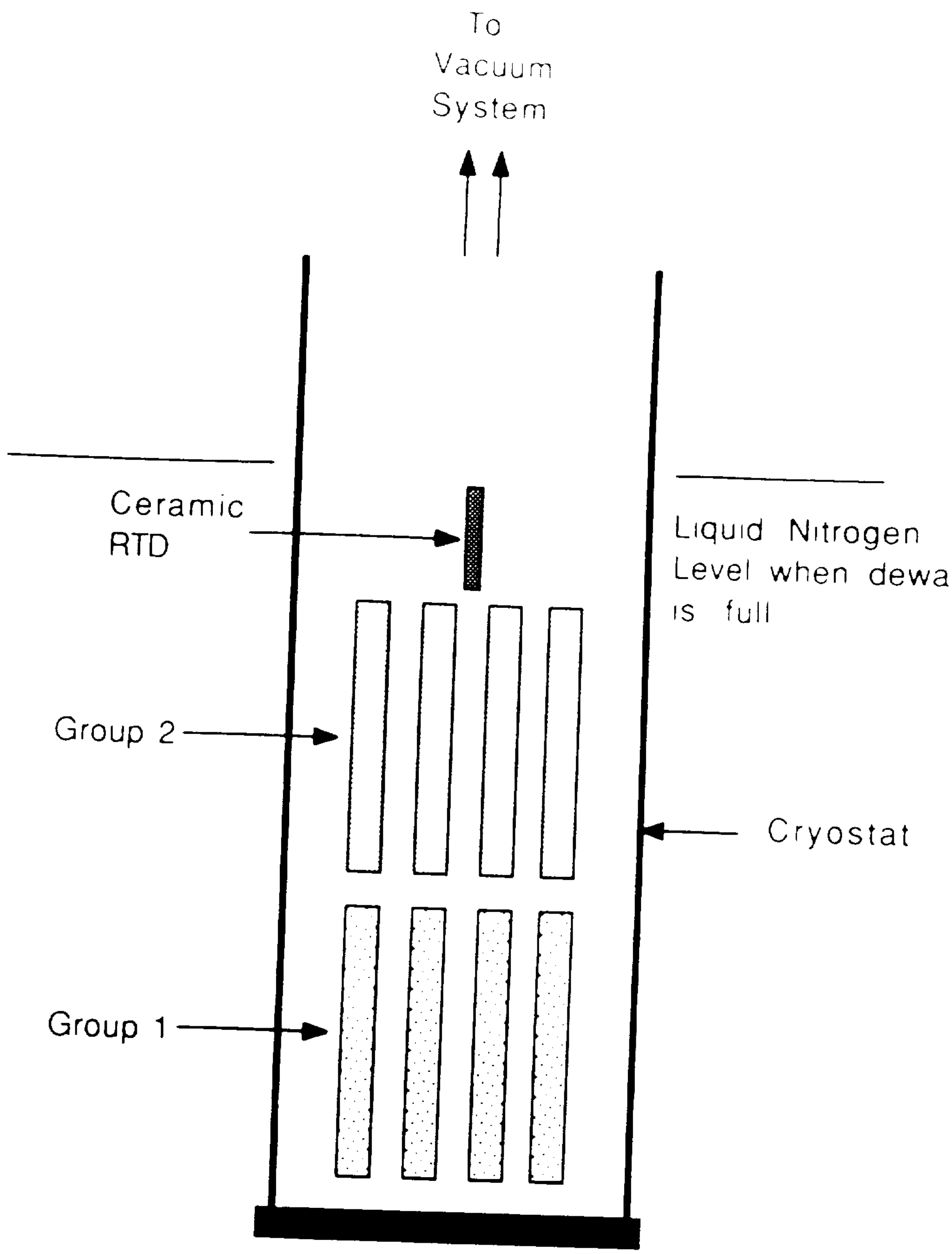


Figure 18 Schematic Orientation of Samples in Cryostat

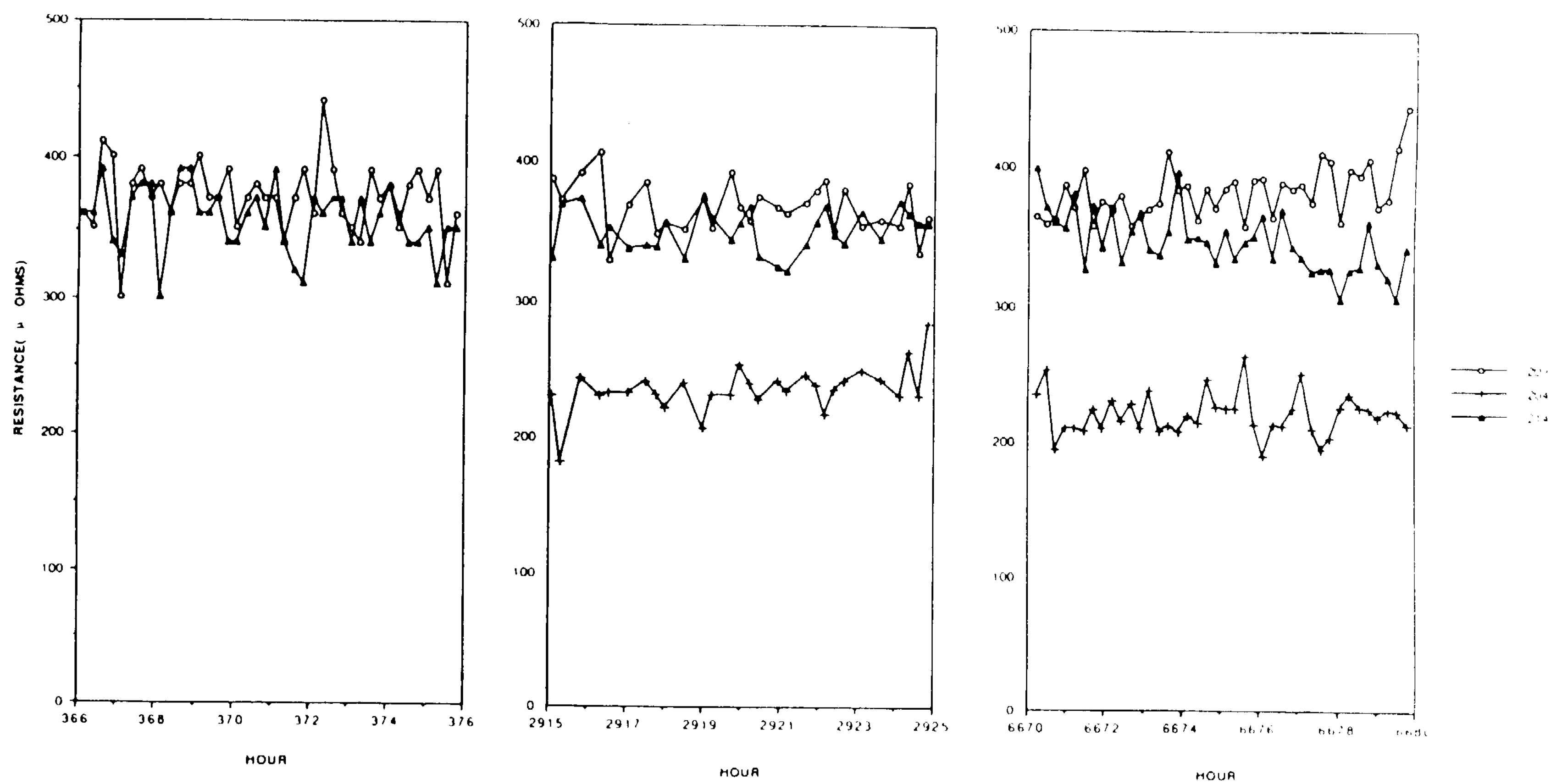


Figure 19 Resistance Data of Samples 203, 204, and 214 over 6700 Hours

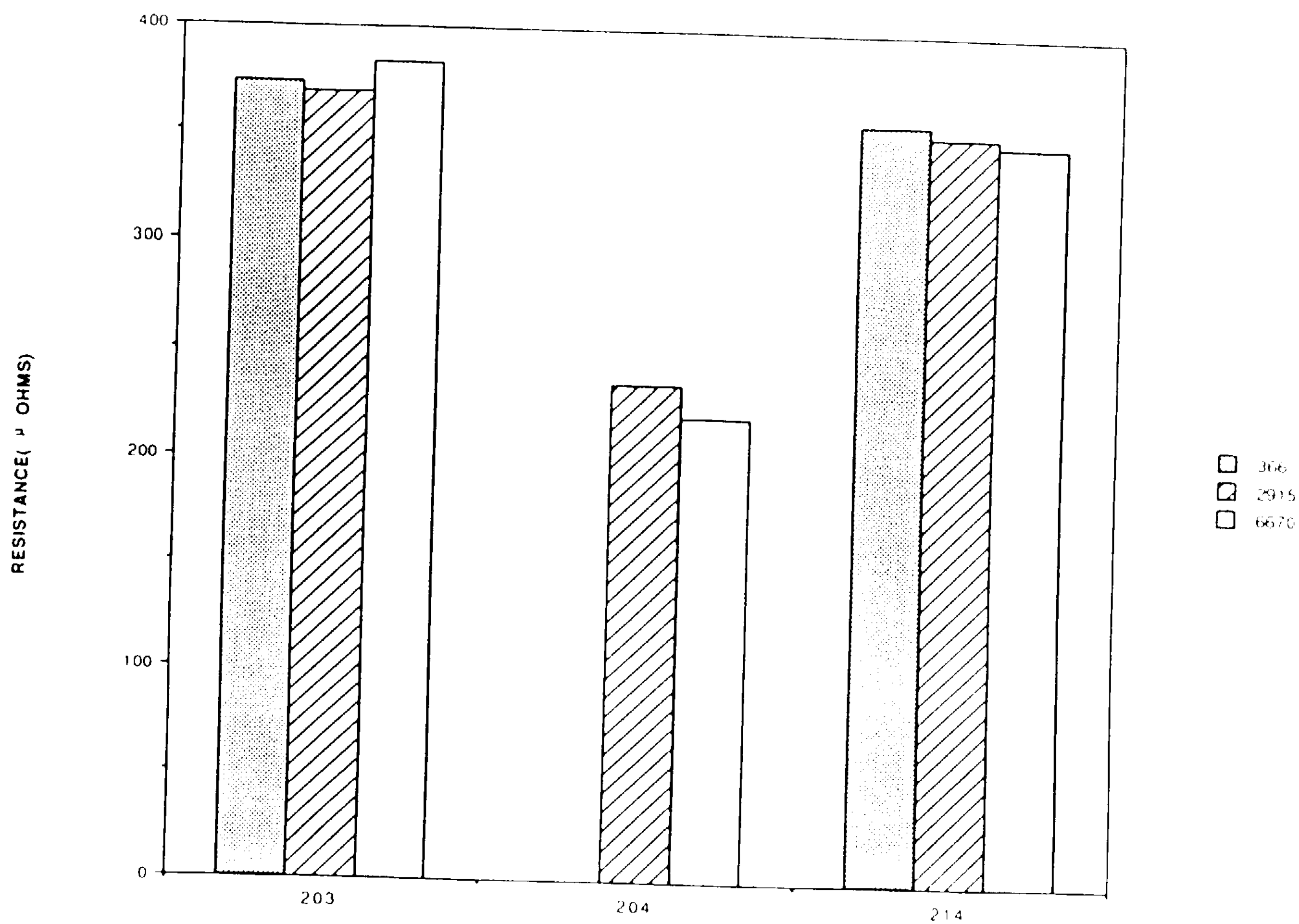


Figure 20   Average Resistance for Each Data Segment for Samples 203, 204, and 214

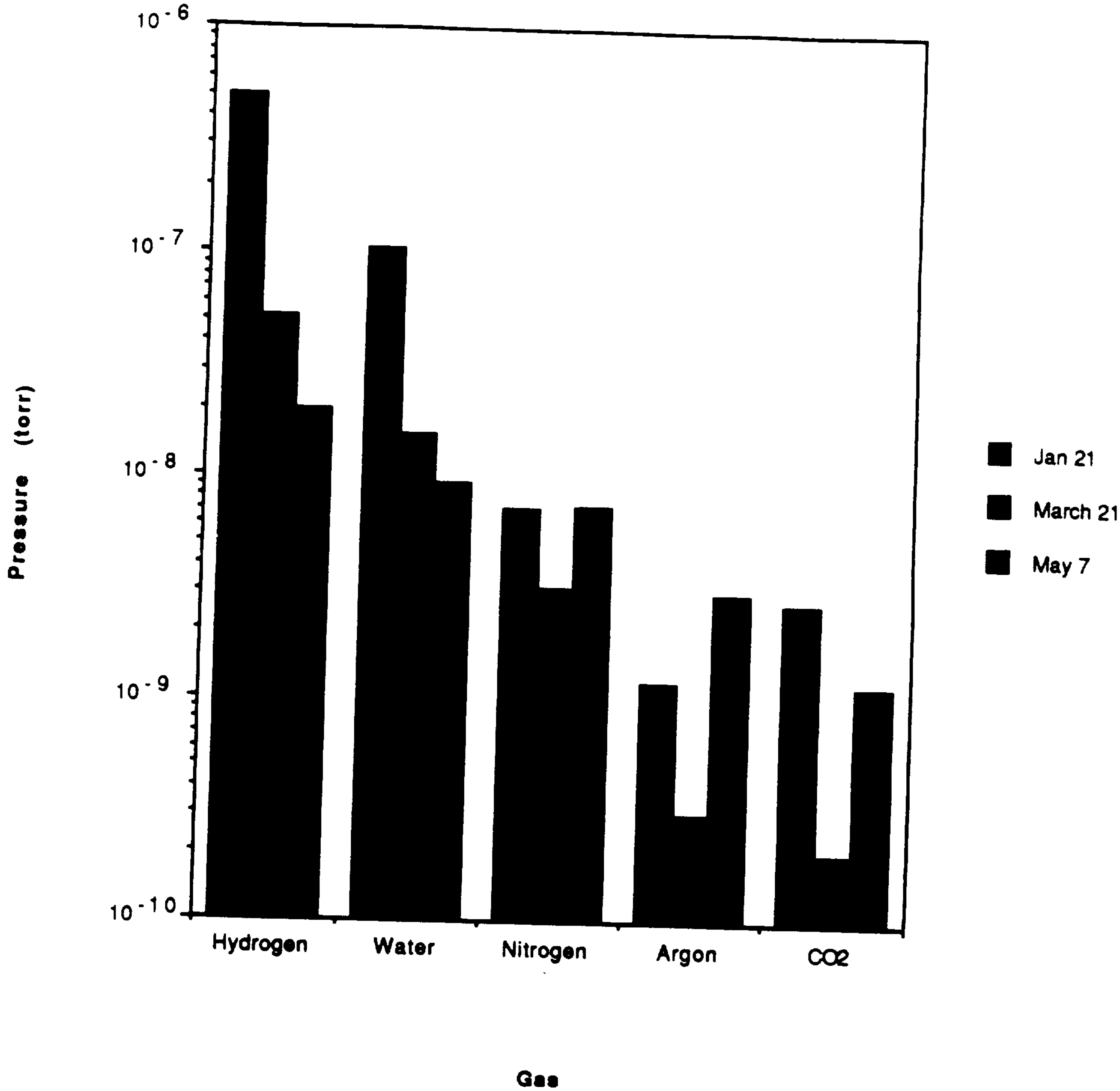


Figure 21 The Partial Pressures of Various Gases Present in the Vacuum System and Their Change with Time

Exploratory Test Series for Clemson Superconducting Shunt

Operational Test(Eight Shunts)

1. Measure initial charactaristics of material
   - Photograph
   - Total weight
   - Dimensions
   - Resistance vs. Temperature curve(-195C to 40C)

2. Irradiate samples to 1E4 Rad (SI) at -195C using Cs^{137} Gamma

3. Measure material characteristics
   - Photograph
   - Total weight
   - Dimensions
   - Resistance vs. Temperature curve(-195C to 40C)

4. Measure resistance vs. temperature curve(-195C to 40C) in 1000 Gauss field

5. Mount 8 shunts in vacuum chamber
   (Four shunts will have 10 ma dc current flow)

6. Lower pressure to 1E-7 torr

7. Lower temperature to -195C

8. Analyze off-gas by quadrupole gas analyzer
   - Continuously for one week
   - Repeat at 2,4,8,16,32, and 64 weeks

9. Measure resistance vs. temperature curve each 6 months

10. Monitor resistance and temperature hourly for duration of test
    (except when 8 & 9 are in progress)

11. Conclusion of test
    - Measure resistance vs. temperature curve at one atmosphere
    - Measure resistance vs. temperature curve in 1000 Gauss field
    - Measure material characteristics

Vibration Test(Four Shunts)

1. Measure initial charactaristics of material
   - Photograph
   - Total weight
   - Dimensions
   - Resistance vs. Temperature curve(-195C to 40C)
     - no external field
     - 1000 gauss field

2. Mount shunt on vibration table

3. Vibrate for 15 minutes at 5 g's(100Hz frequency)

4. Conclusion of test measure
   - Photograph
   - Total weight
   - Dimensions
   - Resistance vs. Temperature curve(-195C to 40C)
     - no external field
     - 1000 gauss field

Humidity Test(Four Shunts)

1. Measure initial charactaristics of material
   - Photograph
   - Total weight
   - Dimensions
   - Resistance vs. Temperature curve(-195C to 40C)
     - no external field
     - 1000 gauss field

2. Mount shunts in chamber at 20% R.H. for four hours

3. Move shunts to chamber at 80% R.H. for four hours

4. Repeat steps 2 & 3 nine times

5. Conclusion of test measure
   - Photograph
   - Total weight
   - Dimensions
   - Resistance vs. Temperature curve(-195C to 40C)
     - no external field
     - 1000 gauss field

VI. Presentations

1. Haertling, G.H., "Ceramic Superconducting Components," Paper No. 58-SIII-90C, Ceramic Science and Tech. Congress, Orlando, FL, November 12-15, 1990.

2. Hsi, C-S and Haertling, G.H., "Environmental Testing of YBa Cu O Superconducting Grounding Link," Paper No. 20-SII-91F, Electronics Division Meeting of the Am. Ceram. Soc., Arlington, VA, October 20-23, 1991.

VII. Publications

1. Haertling, Gene H., "Superconducting Ceramic Components," Ceramic Transactions, Vol. 18, 537-545, 1991.