ENVIRONMENTAL TEST PROGRAM

FOR

SUPERCONDUCTING MATERIALS AND DEVICES

Mid-Term Report

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

Principal Investigator:
Gene Haertling

Supporting Investigators:
Henry Randolph
Chi-Shiung Hsi
Warren Verbelyi

Contract No. NAG-1-112[illegible]

July 26, 1991

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CLEMSON UNIVERSITY

Department of Ceramic Engineering
College of Engineering

I. Introduction

This mid-term 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. This work was performed in the Ceramic Engineering Department of Clemson University and at the facilities of the Westinghouse Savannah River site 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 YBa2Cu3O7-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_2 immersion
5 ea.	- water immersion
10 ea.	- humidity
12 ea.	- drop test
all	- visual test

Specific tests conducted at Westinghouse/SRS were:

*8 ea.	- long term hi-vac at LN_2 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, so far, are as follows:

1. Overall yields from the tapecast stage to the final elements is approximately 70% - 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 a re-design of the element which significantly improved its performance.

4. Long term LN_2 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, 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.

7. Long term hi-vacuum at LN_2 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_2 temperature and those which had no current applied.

10. Tests yet to be completed are magnetic field, vibration and drop.

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

Since these tests are generating first-time, real-time data, consideration should be given to extending them to time periods beyond the expiration of this contract.

This 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.

Semi-Annual Report

ENVIRONMENTAL TEST FOR SUPERCONDUCTING MATERIALS AND DEVICES

Preliminary Results of Testing Program at Clemson University

to

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

Principal Investigator:
Gene H. Haertling -Clemson University

Supporting Investigator:
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Contract No. NAG-1-1127 July, 1991

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 $YBa_2Cu_3O_{7-x}$ superconductor tape, mounted on a printed circuit board and encapsulated with epoxy resin. This report describes their evaluation under a long term environmental test program. The program includes temperature vs. resistance, liquid nitrogen immersion, water immersion, thermal cycling, humidity and radiation testing. Preliminary results from these tests are reported. To date, the links have maintained their structural and electrical integrity in regard to all tests with the exception of long term humidity and water immersion.

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 implemented. A low noise, low thermal conductivity superconductor grounding link developed at Clemson University uses a PC board and epoxy encapsulant as a rigid support and protective coating in order to maintain the structural integrity and electrical properties of the superconductor(1-3). Two papers had previously been reported on epoxy coating for $YBa_2Cu_3O_{7-x}$(4,5), but these studies were of a more basic nature with no long term results on actual devices. As far as we know, the grounding link is the first announced 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 is now underway at Clemson University and Westinghouse / Savannah River Co. in Aiken, SC. Among the various tests, temperature vs. resistance, thermal cycling, liquid nitrogen immersion, water immersion, and humidity are in progress at Clemson University. The properties of the links after radiation exposure at Westinghouse were also characterized. This report records the sample preparation procedure and preliminary results obtained since May 1, 1990, at Clemson University.

II. Experimental Procedure.

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 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. 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

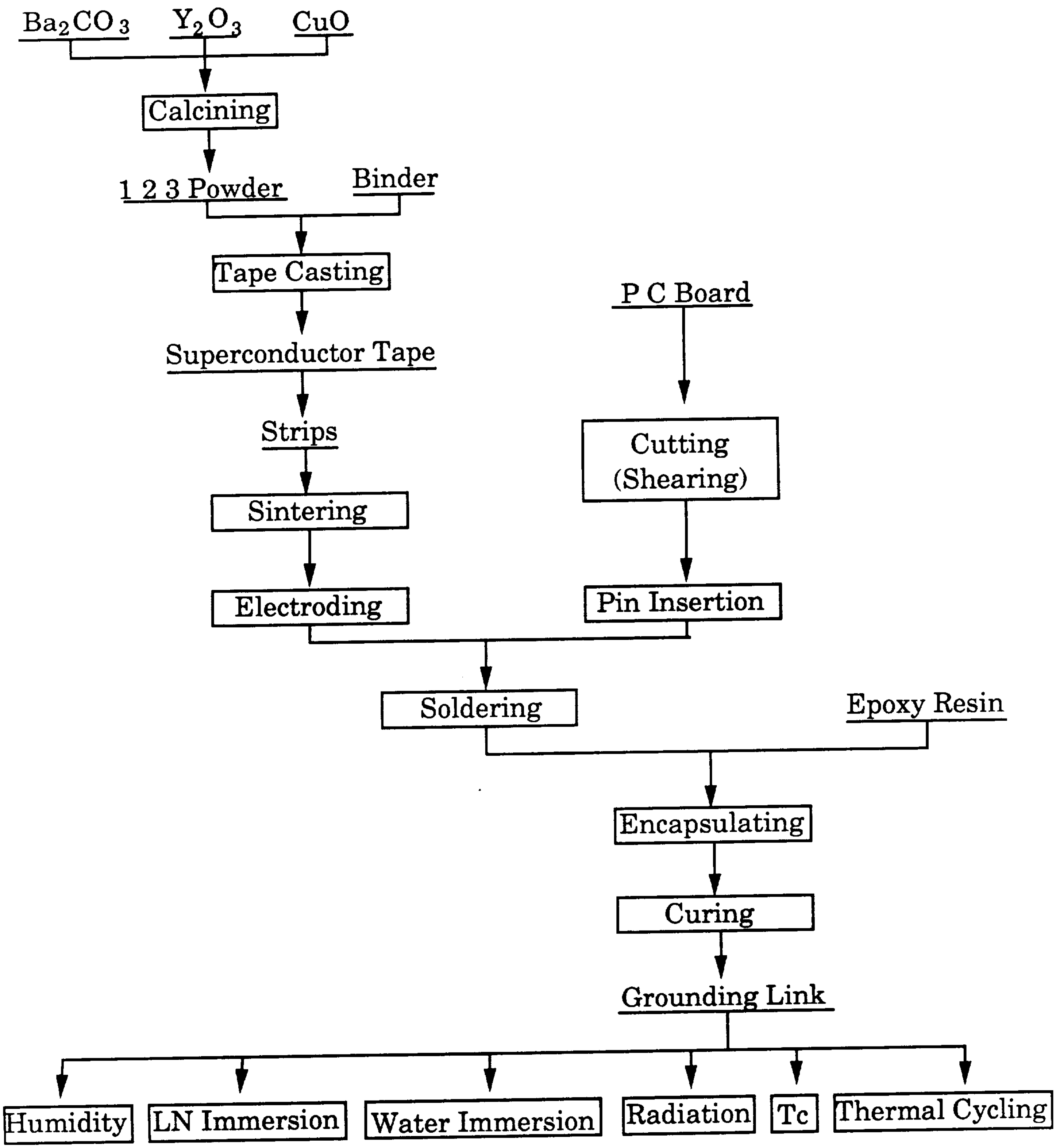


Figure 1: Fabrication process of the grounding links

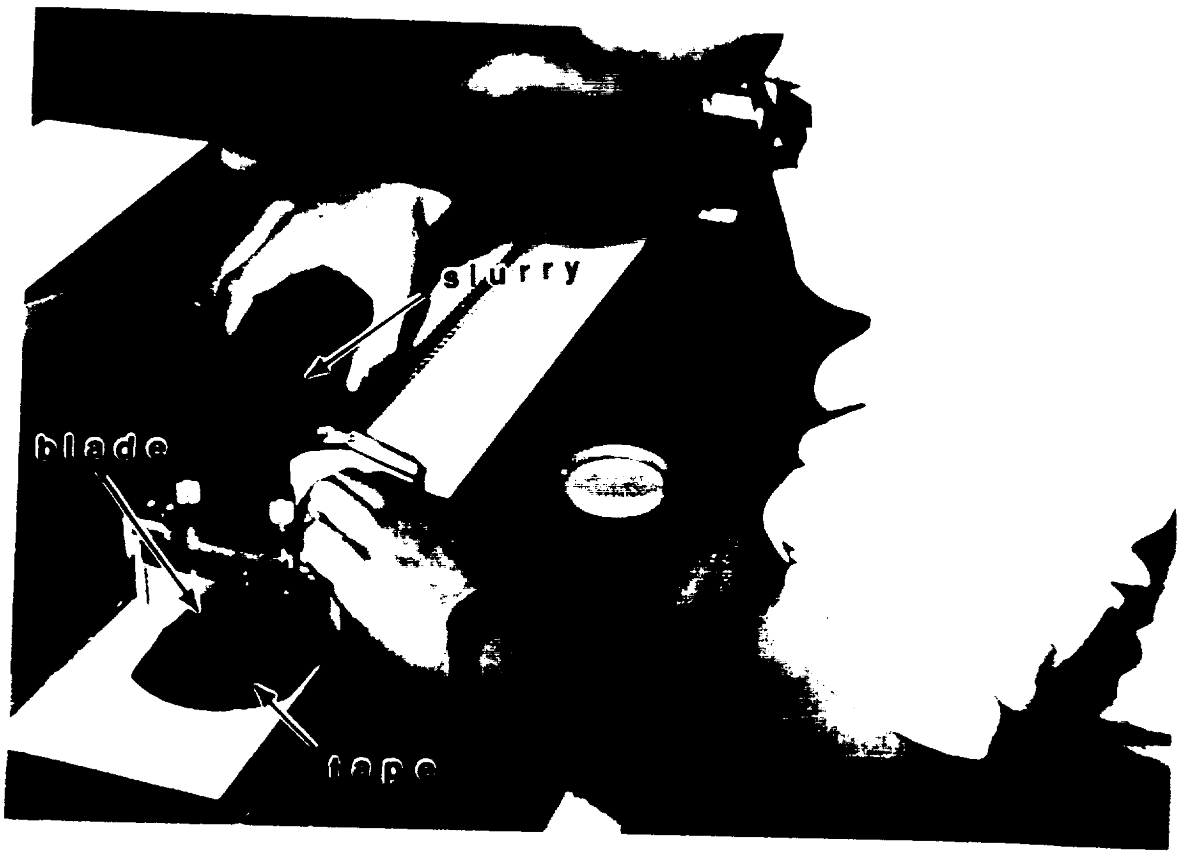


Figure 2: Tape casting of $YBa_2Cu_3O_{7-x}$ superconductor.

hours and annealed at 450°C for another 12 hours before they were cooled to room temperature. An electrode firing process[6] 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 foils 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,
6. radiation test.

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

II.3 Configurations of the sample design.

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

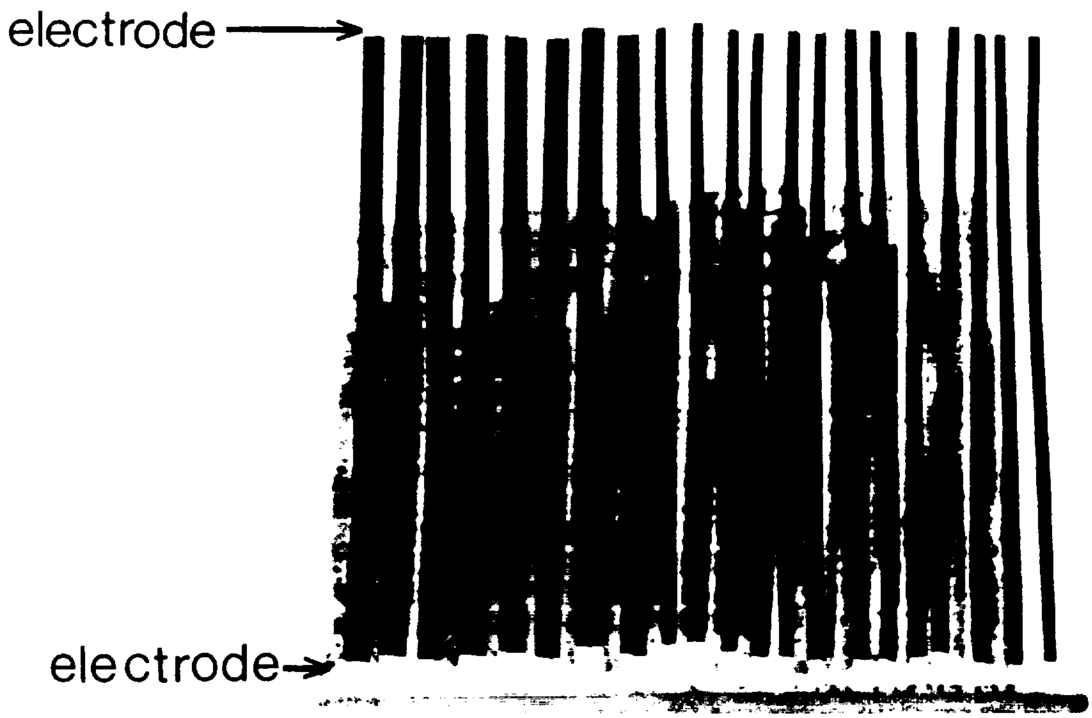


Figure 3: Electroding process for $YBa_2Cu_3O_{7-x}$ superconductor strips.

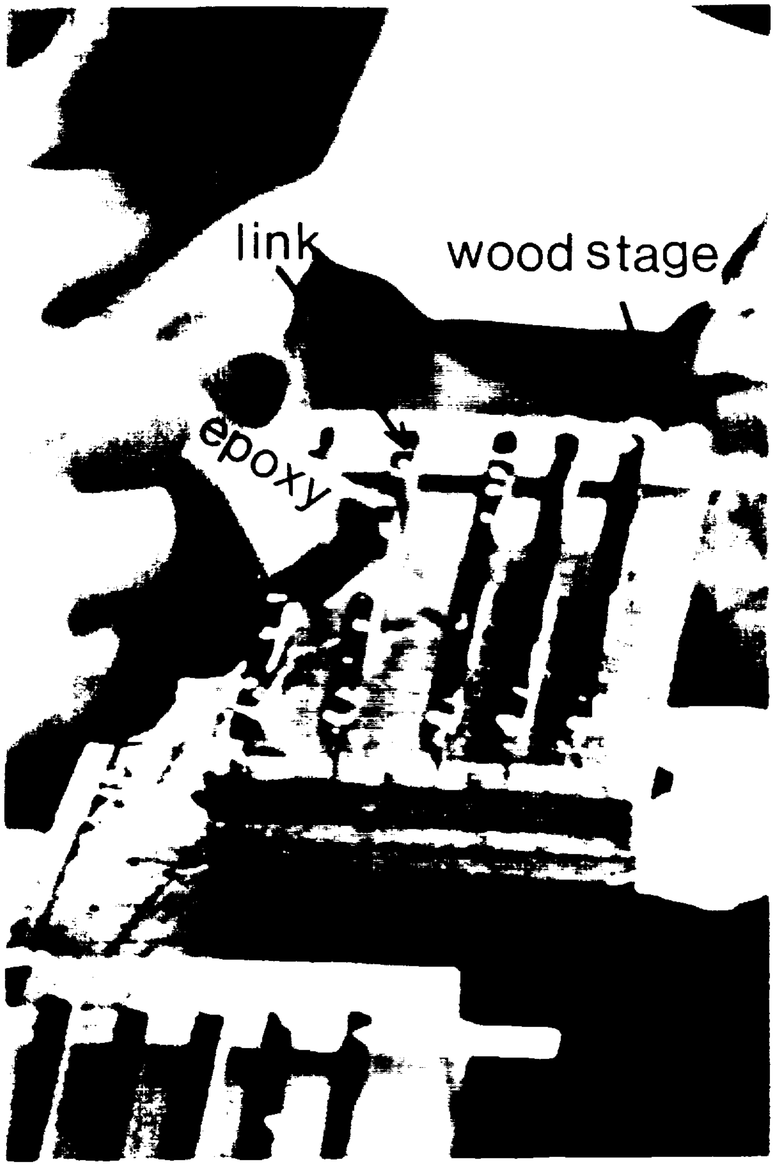


Figure 4: Encapsulating of the superconductor links.

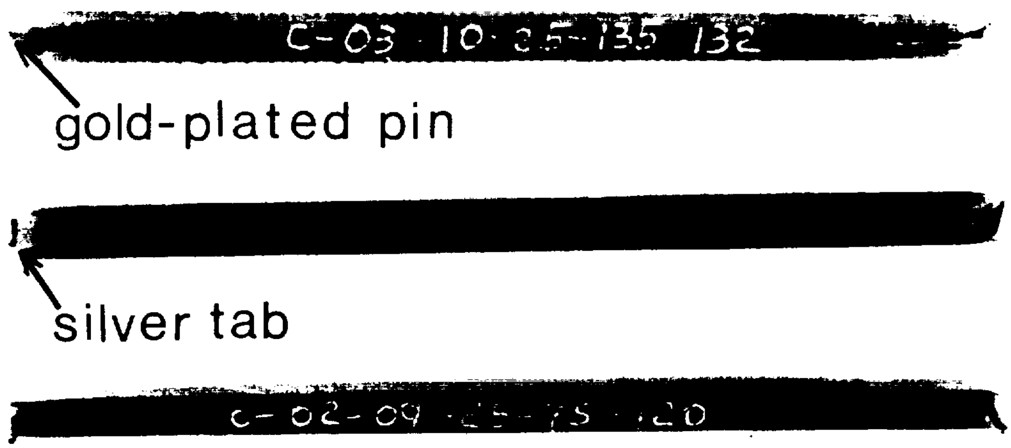


Figure 5: Serial number of grounding links.

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

Properties	Device	Condition
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	$38^{o}C$, 90% R.H.
Thermal cycling	Hand	3 minutes in LN 10 minutes in the air
Radiation test*		Cs_{137} Gamma radiation

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

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, as type I, II and III defects 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.

Type II defects were specified as those due to high stress concentration

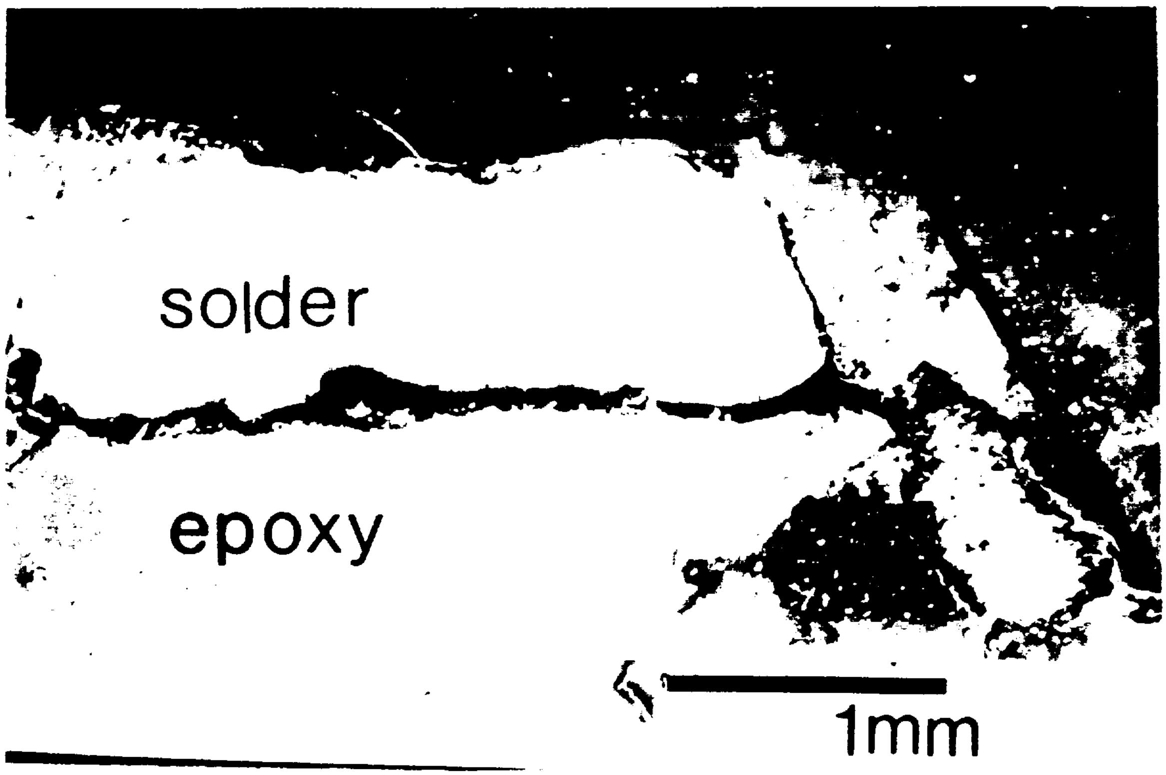


Figure 6: The cracks formed around the electrode area after the LN immersion test.

along the top edges of the $YBa_2Cu_3O_{7-x}$ superconductor strips where less epoxy was presented. When the epoxy was not thick enough to resist the thermal stress, 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.

Table 2: Occurrence and mechanism of different types of defects on 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

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 PC board and superconductor(1), 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 was considered to be the mechanism of 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 in 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.

c. step 3

Another type of defect, which was observed after the proceeding 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,

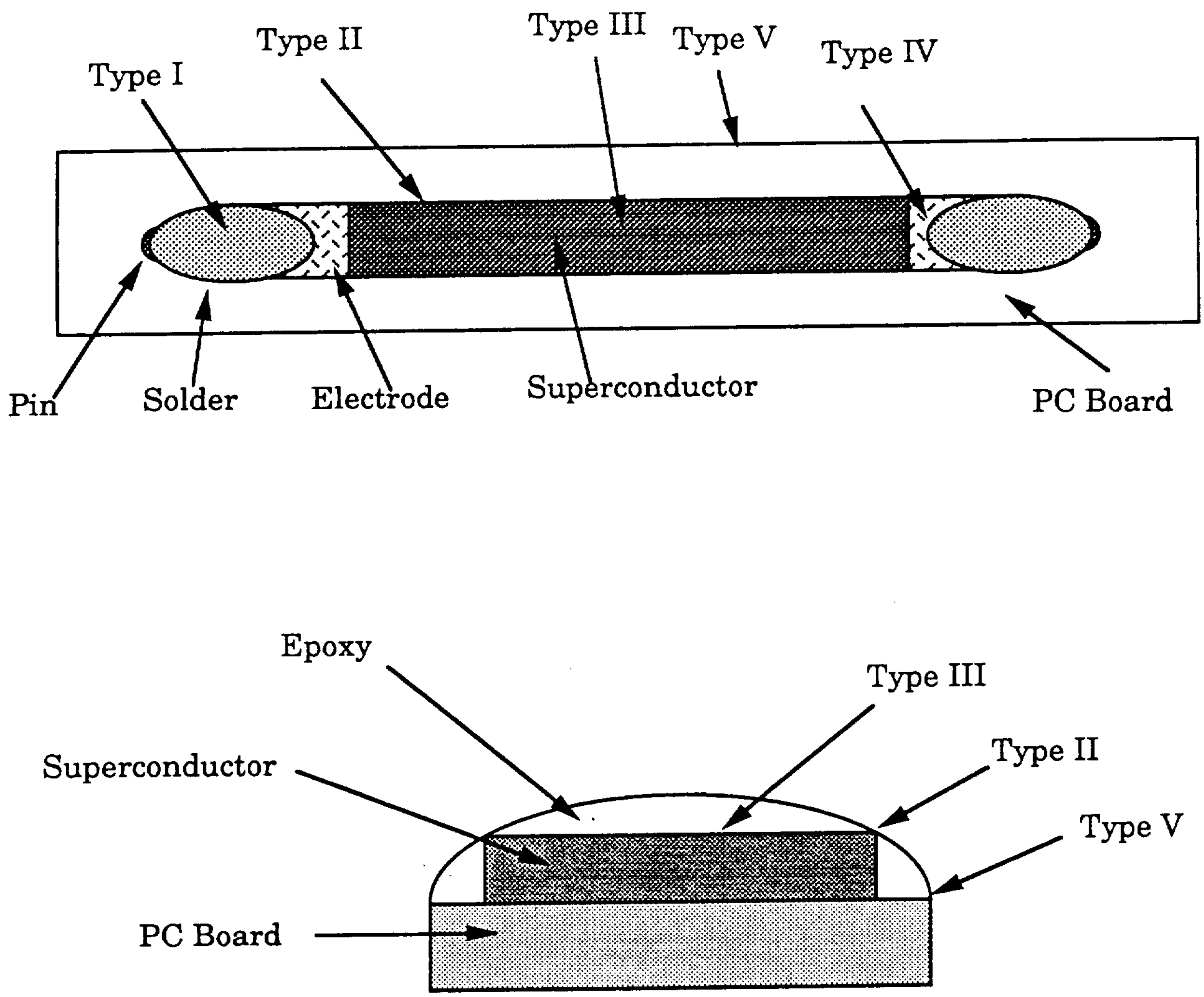


Figure 7: The location of different types of the defects on the links.

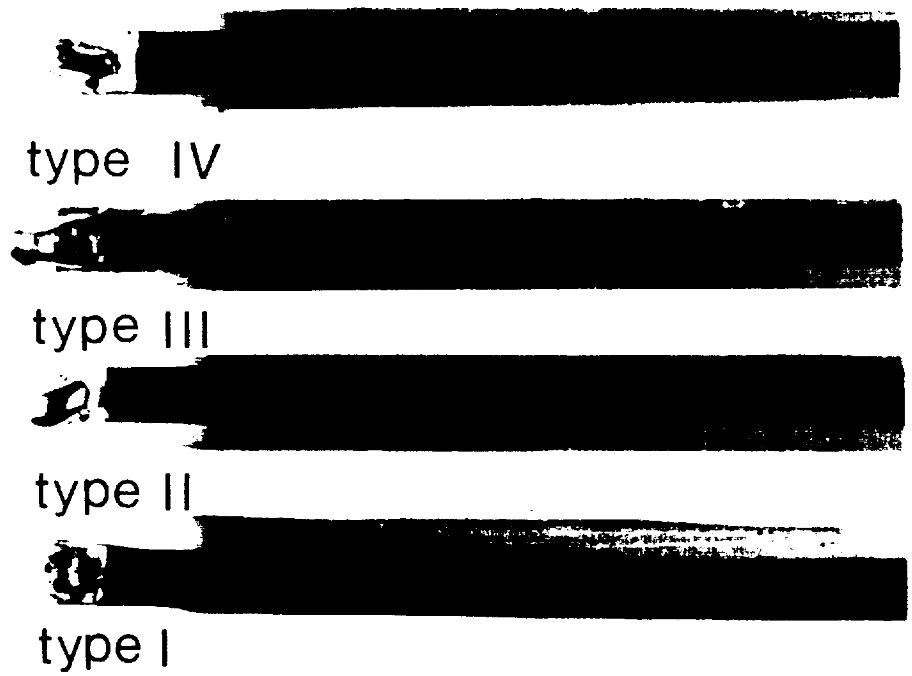


Figure 8: Examples of the type I, II, III and IV defects.

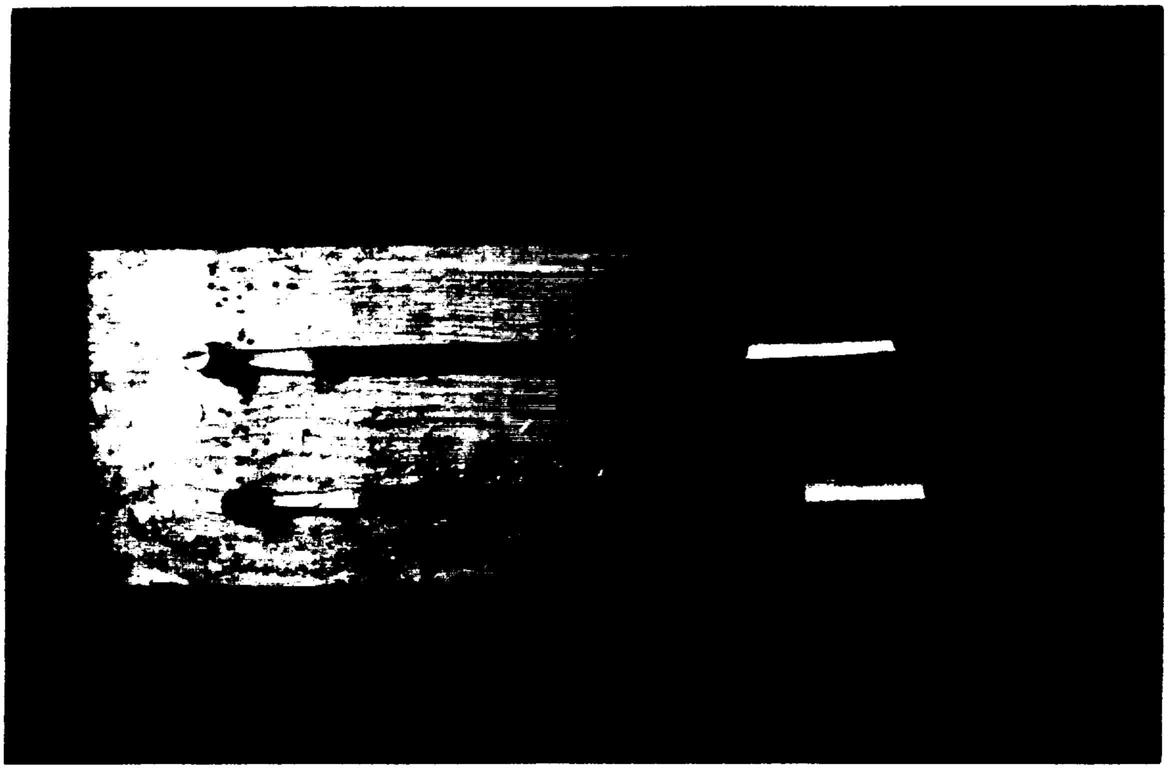


Figure 9: The encapsulation step of the mold process.

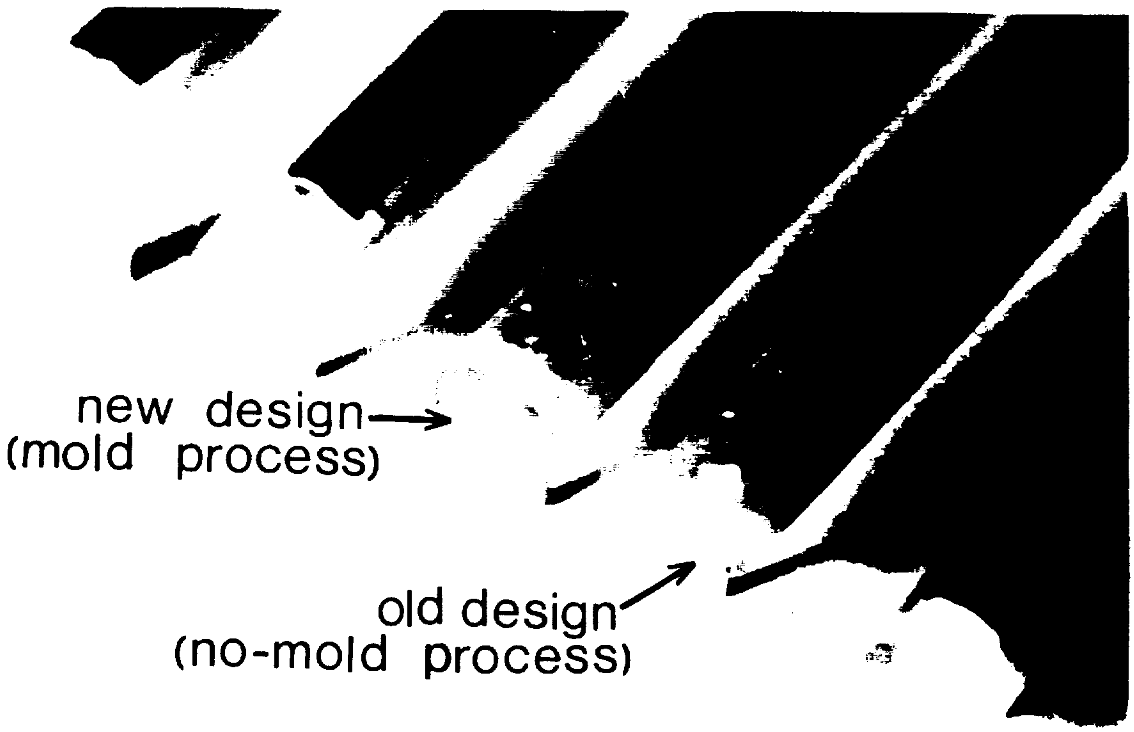


Figure 10: Side view of the links made by the mold and no-mold process.

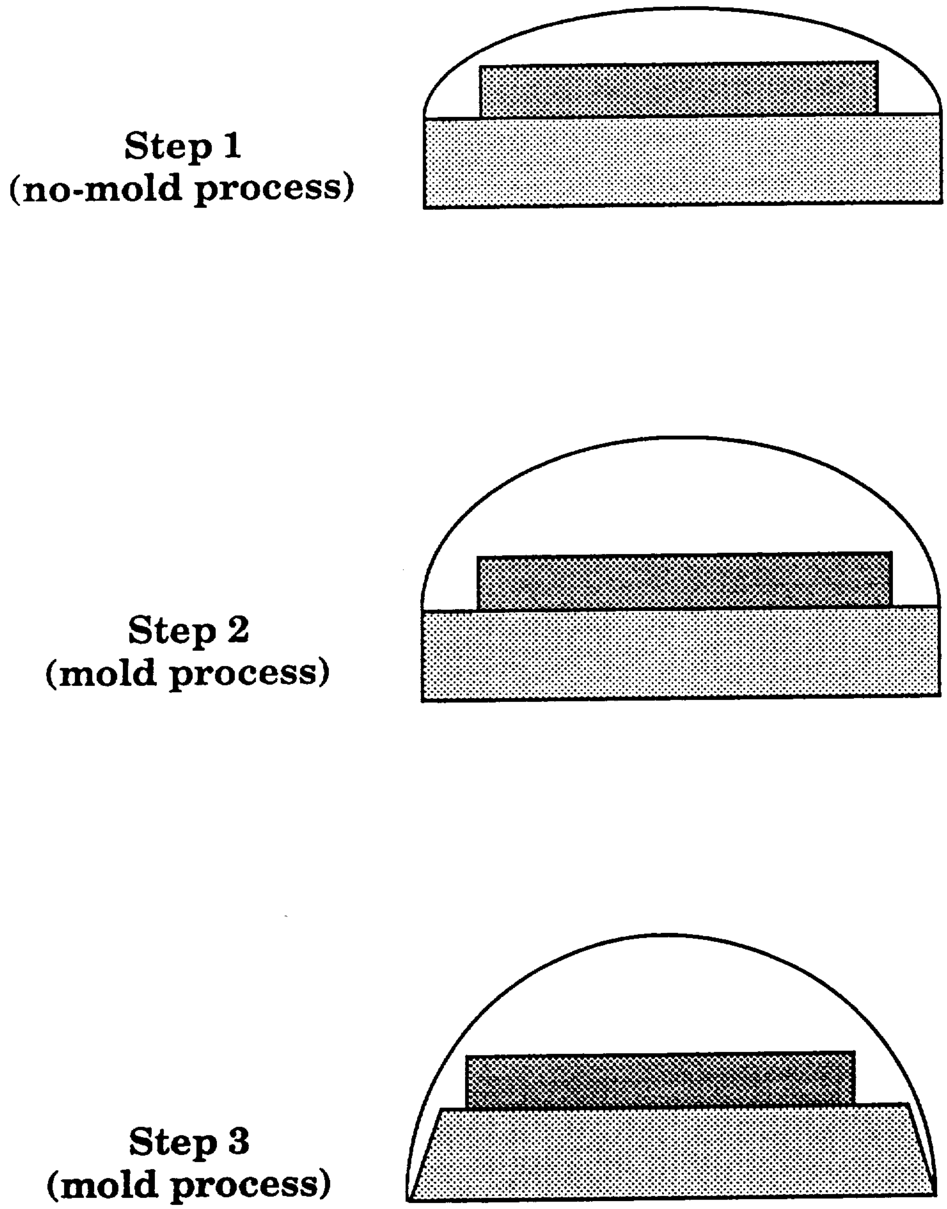


Figure 11: Cross section of the links at each step.

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

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

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°C for 1 hour. The links which were not heat treated had a similar 10.8% resistance increase, as shown in Appendix 1, 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% resistance increase before the epoxy became stable. The reason for the resistance increase during aging has not yet been determined and is still under investigation.

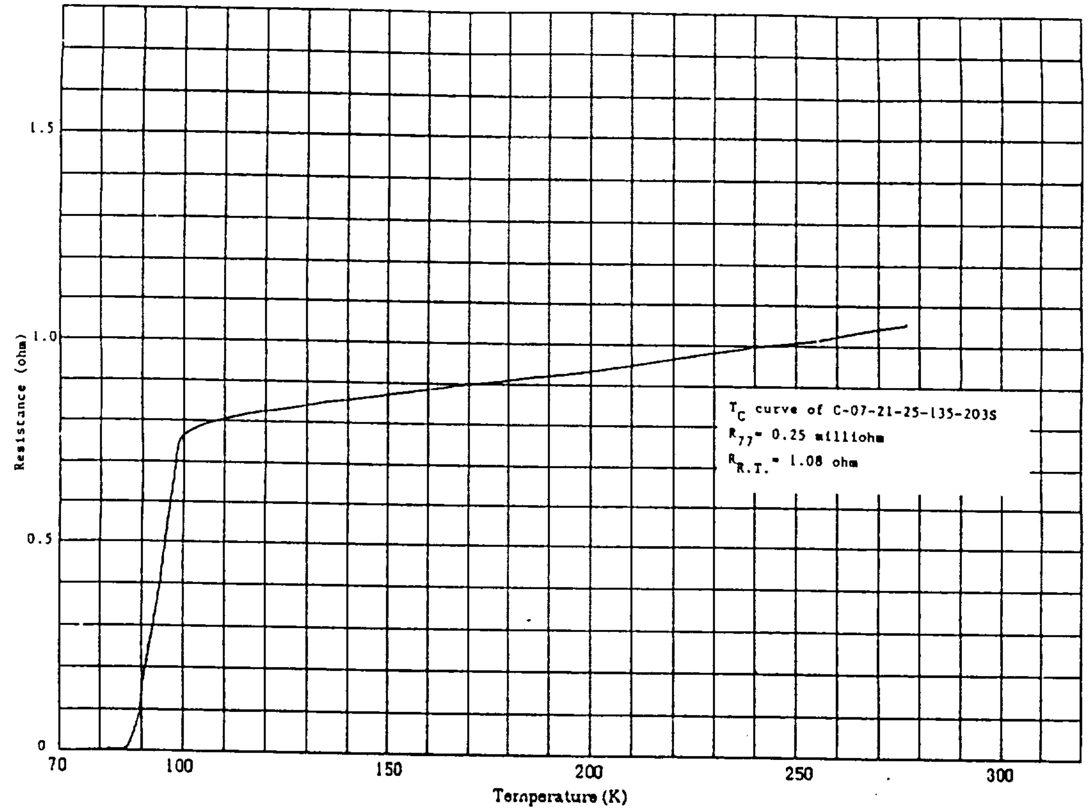
III.2 Temperature Vs. resistance- T_c

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 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, as shown in Appendix II. There are some temperature vs. resistance results included in Appendix III. All of them show a similar shape of the T_c curve.

The resistance of the links at 77K were not influenced by the resistance of the links at room temperature. The links with gold-plated pins had resistances from 1.0 to 2.5 milliohms below the transition temperature. The links with silver



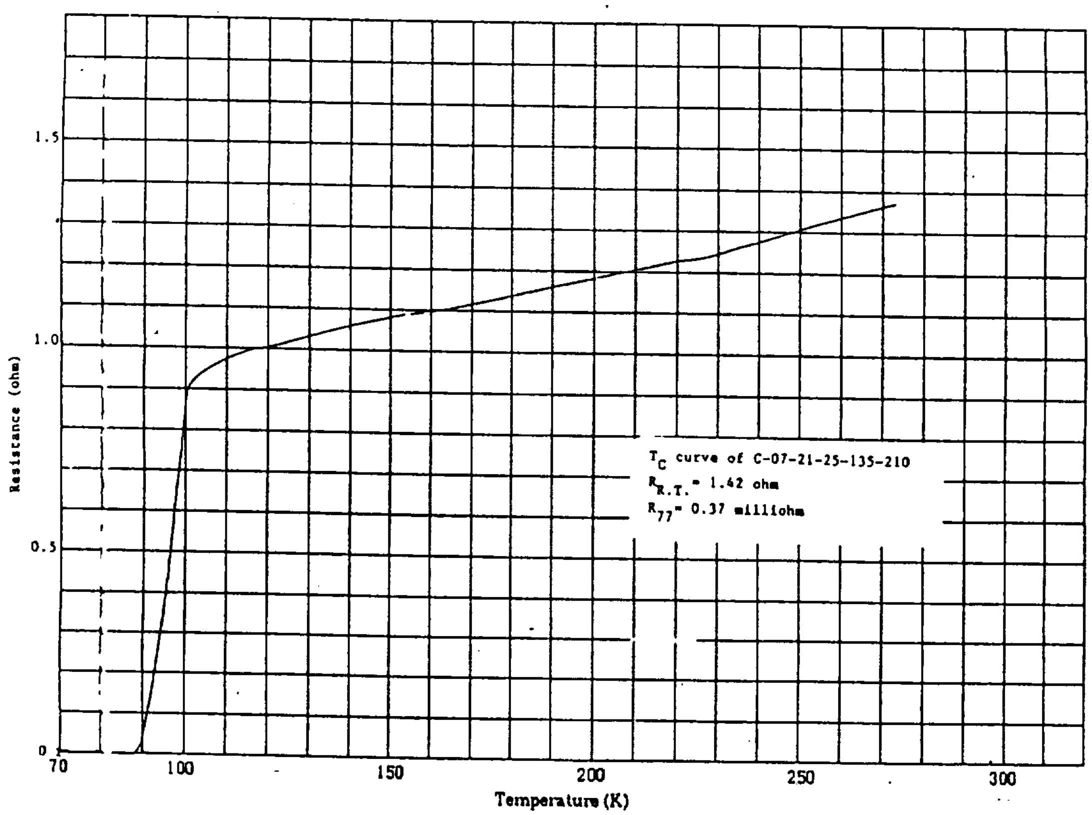
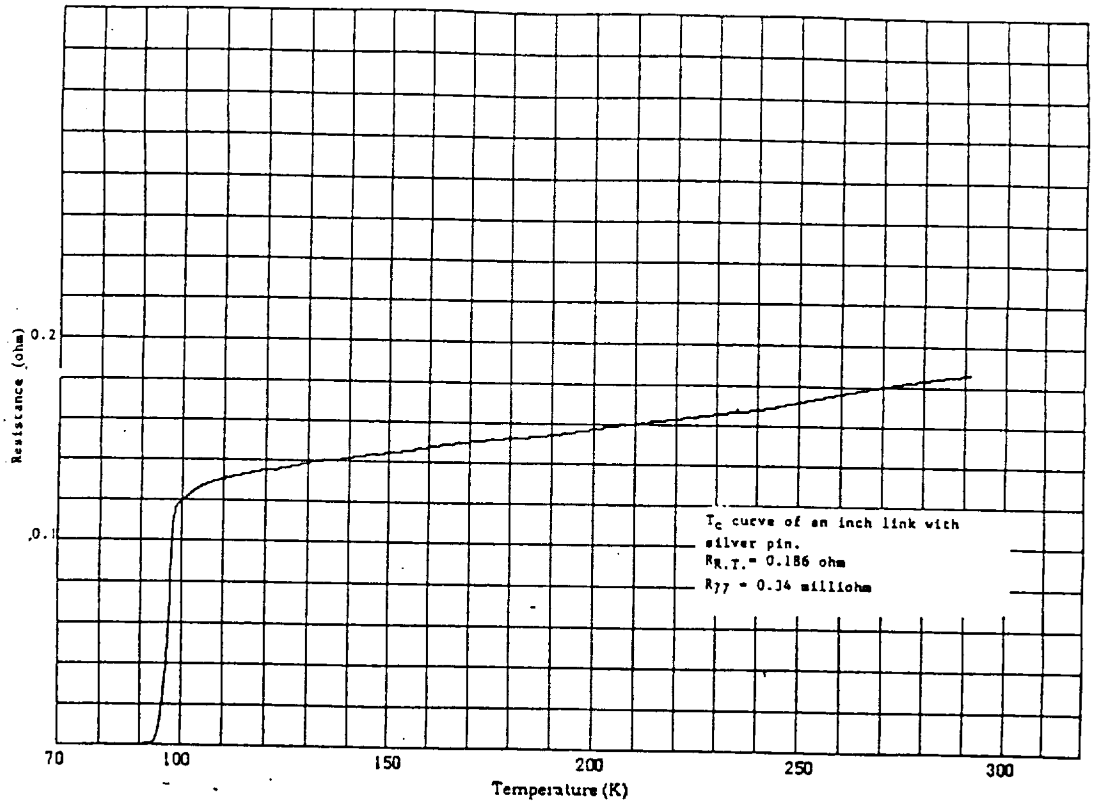


Figure 12: T_c curves of the links with silver tabs (top) and gold-plated pins (bottom).



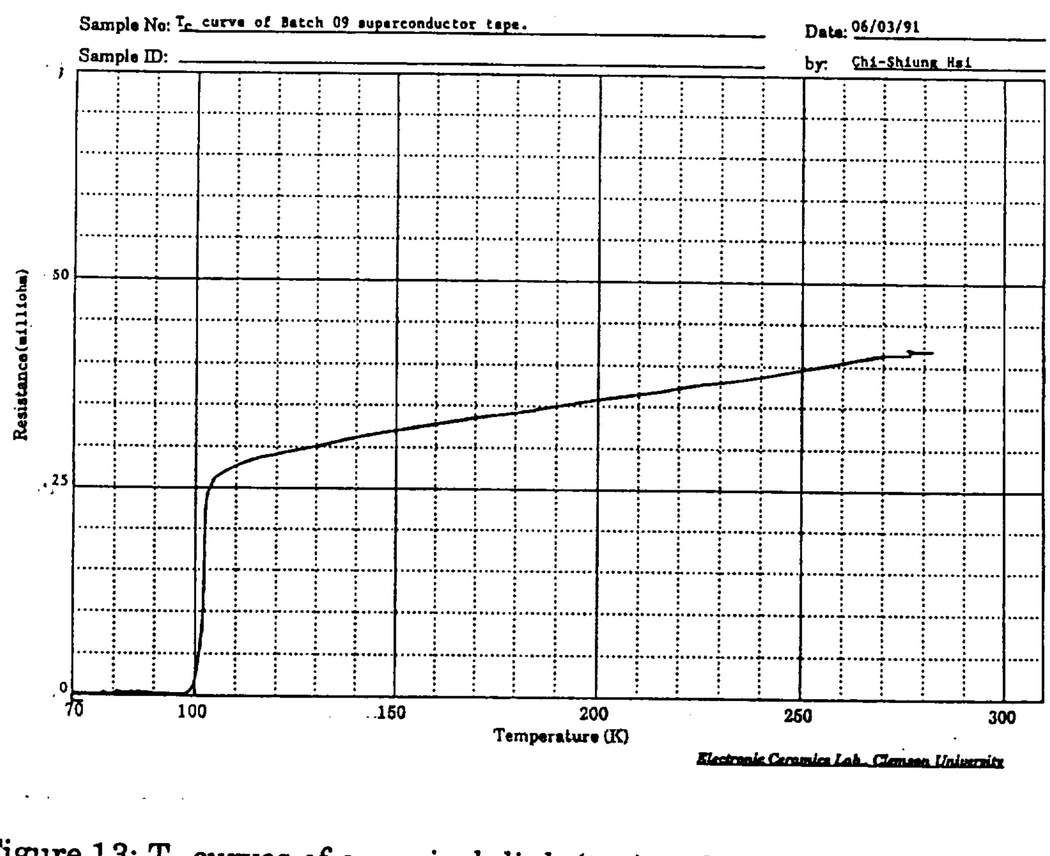


Figure 13: T_c curves of a one inch link (top) and a superconductor tape (bottom).

tabs exhibited resistances between 0.23 and 0.5 milliohms at 77K. 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 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 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.

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

III.4 Long term liquid nitrogen immersion.

Eight links have been immersed in the liquid nitrogen for 226 days (since October 19, 1990), in a 4 liter LN dewar. 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. The resistance of each link has remained constant for 226 days of liquid nitrogen immersion. Figure 14 shows

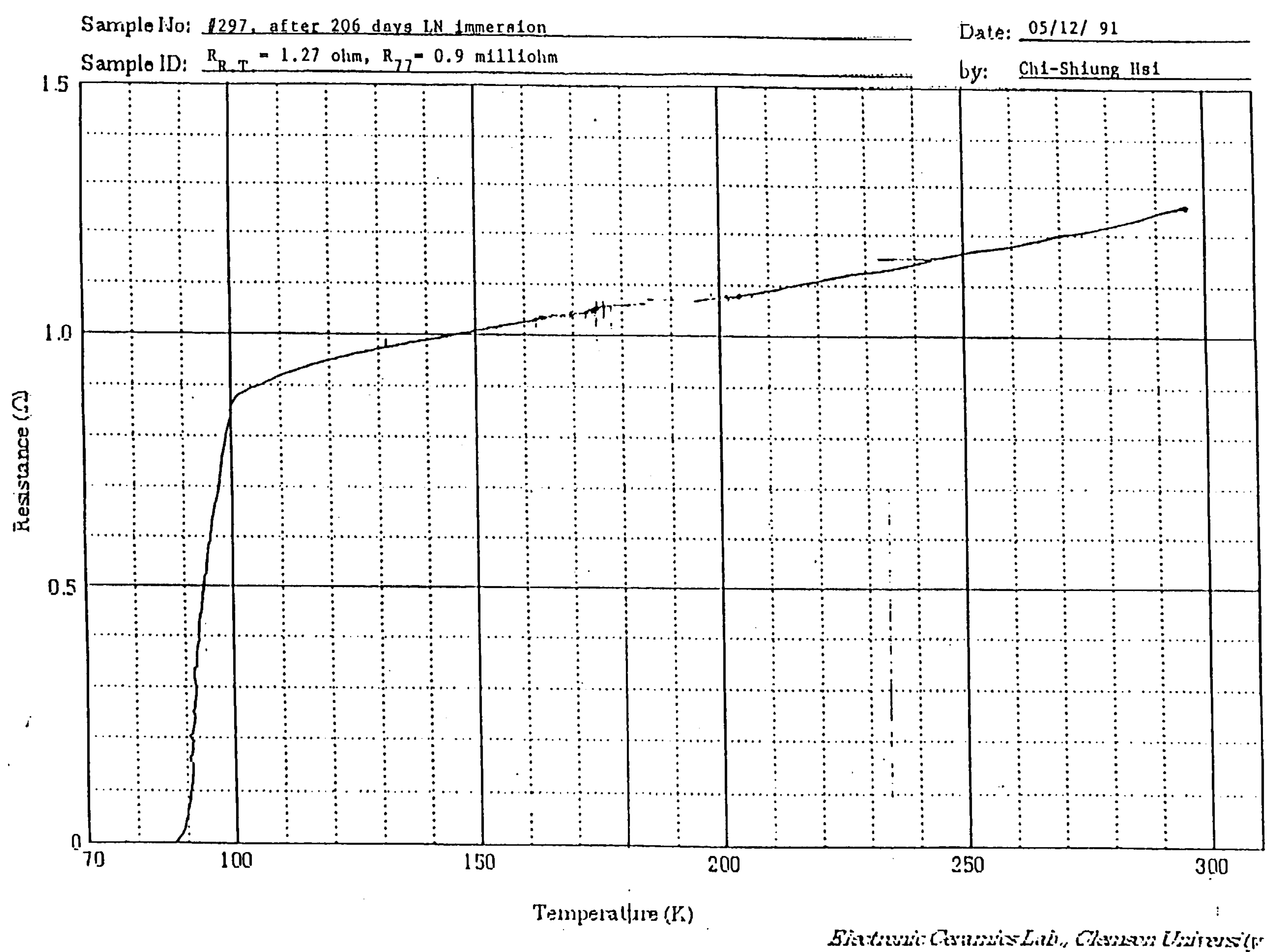


Figure 14: T_c curve of link #297 after 206 days liquid nitrogen immersion.

the T_c curve of link #297 after 206 days of liquid nitrogen immersion. The curves of this link after 50, 100 and 150 liquid nitrogen immersion are shown in Appendix V. These curves are similar to those shown in Appendix III. Currently, all the links have maintained their structural integrity.

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	06/02/91
Day	0	7	50	101	151	199	226
Link No.							
291	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
293	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	1.8
295	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
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

III.5 Moisture sensitivity.

Water immersion and humidity tests were selected 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 and in the ambient atmosphere. Figure15 shows the links after 30 days water immersion. The epoxy of link #205 peeled off. It was caused by 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 where the epoxy was thinner, became the weak point. Thus, cracks formed at these positions.

b. Humidity test.

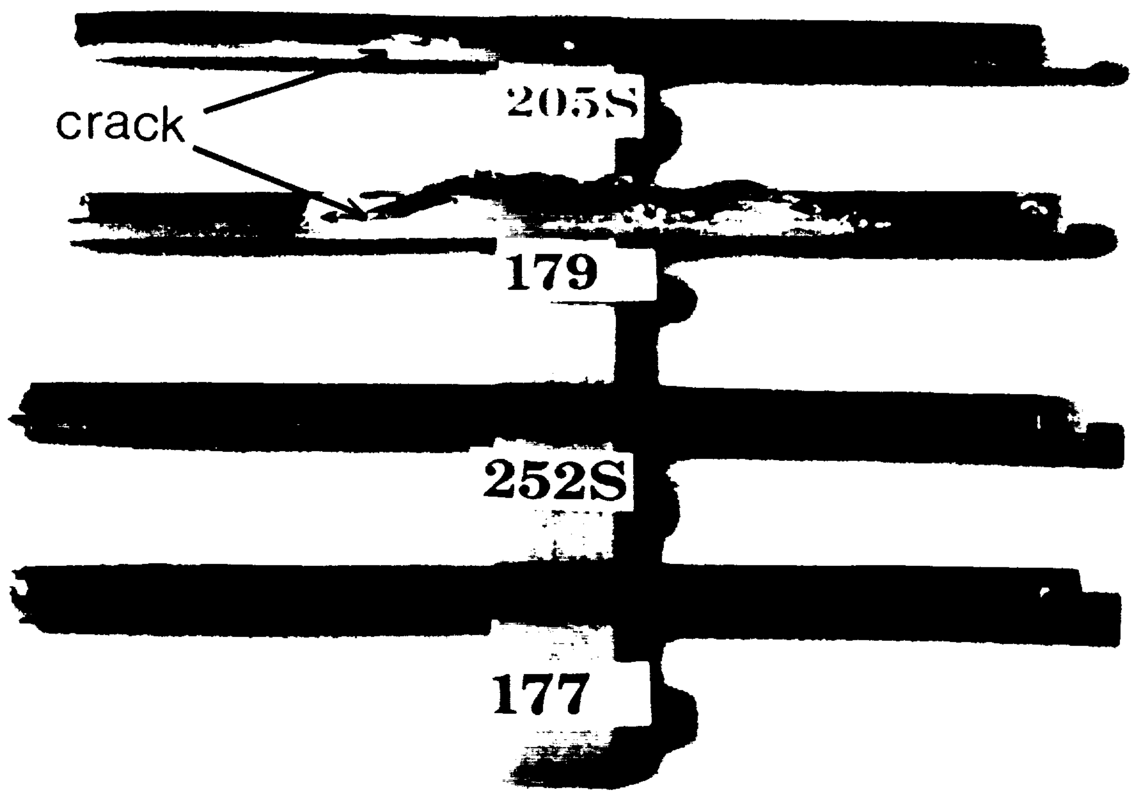


Figure 15: Photograph of the links after 20 days (205S, 252S) and 100 days (179,177) water immersion test.

A 90% relative humidity environment at 38°C was controlled by a Blue M environmental chamber (Model No. VP-100RAT-1). The type of cracks observed in the water immersion test were also found in this test. However, the MTBF (Mean Time Before Failure) of the samples in this test was shorter than that of the water immersion. In addition, some bubbles formed at the interface between the epoxy and the superconductor before the cracks formed.

Table 6 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 just like the results obtained from the air aged samples (refer to Appendix I). From the discussion above, two types of failure modes in the moisture sensitivity test can be concluded. These are;

Table 6: The resistances of the links in the humidity test. (The resistances were measure 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.

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.

In order to obtain appropriate conditions for curing the links, 15 samples were cured at different conditions and have been tested since May 8, 1991. Up to the present, these links have maintained their structural integrity.

III.6 Radiation test.

Figure 16 shows the T_c curves of selected samples before and after gamma radiation test. The curves measured after the radiation test showed the same characteristics as the curves obtained before the test. The resistances of the links at room temperature increased after the test, as indicated in Table 7. Since it was

Table 7: The resistances of the radiated links at room temperature, 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
224	1.44	0.96	88			
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

almost 6 months after the samples were prepared, 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 a.

c.

b.

d.

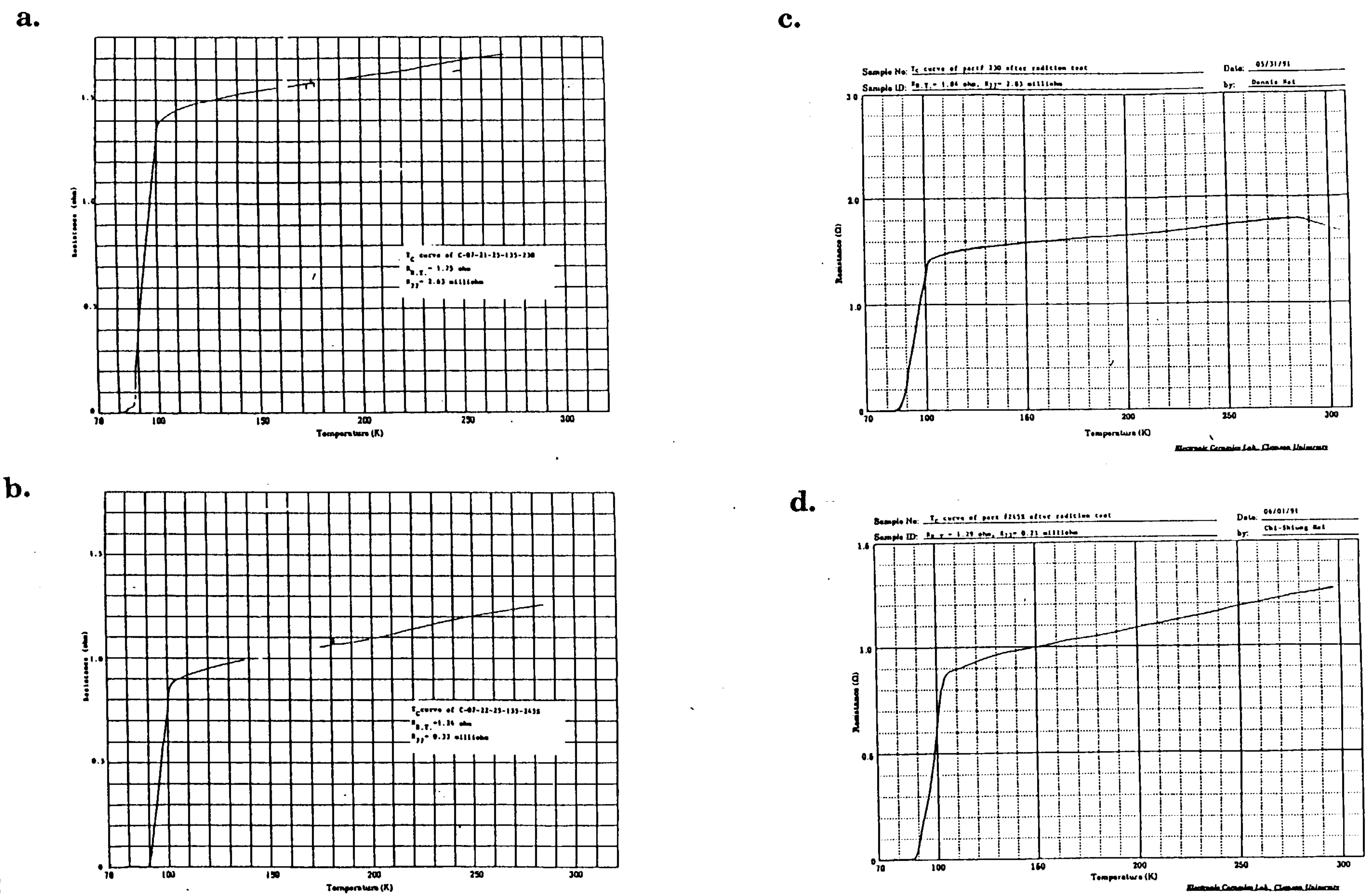


Figure 16: T_c curves of two selected samples before (a, b) and after (c, d) radiation test.

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.

IV. Summary.

The grounding link used in the NASA-sponsored SAFIRE project showed good performance results in the liquid nitrogen immersion, temperature vs. resistance, thermal shock and radiation tests. After testing, the links maintained not only their structural integrity, but also their electrical characteristics. Currently some of these tests are still in progress.

However, the cracks which developed in the links during the moisture sensitivity test and the resistance increase during aging must be eliminated. In order to reach this objective, more study of the curing conditions is in progress. The best fabrication process and overall test results will be included in the final report.

Reference

1. G. H. Haertling, "Development and evaluation of superconducting circuit elements", NASA Final Report, Contract No. NAG-1-820, October, 1990.
2. G. H. Haertling, "Ceramic superconducting components", Ceramic Transactions, Vol. 18, 1991.
3. 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.
4. M. R. de Guire, I. Manas-Zloczower, M. Tabib-Azar, D. E. Farrell, C. J. Kim, W. H. Lu, H. Ng and F. Rayal, "Thermosetting epoxy as a moisture-resistant coating for $YBa_2Cu_3O_7$", Journal of Materials Science, 25, 2881-2885, 1990.
5. M. R. de Guire, C. J. Kim, W. H. Lu, D. E. Farrell and D. Boyne, in "Ceramic Superconductors II", edited by M. F. Yan (American Ceramics Society, Columbus, Ohio, 1988) 343-355.
6. C. S. Hsi and G. H. Haertling, "Low resistivity contacts to $YBa_2Cu_3O_{7-x}$ superconductors", Ceramic Transactions, Vol. 18, 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[(6)].

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

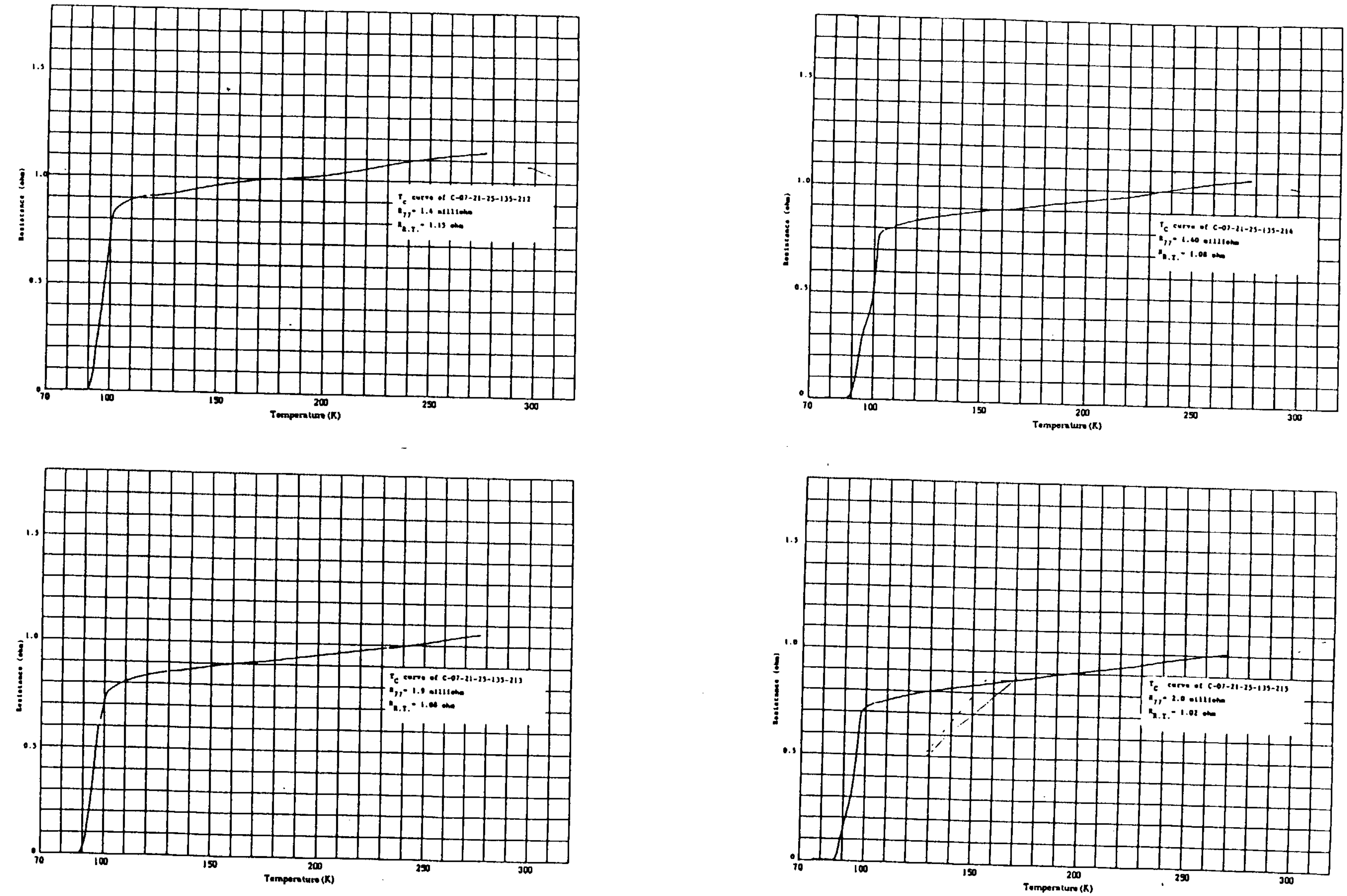
Table A-2: The resistance of some selected links at room temperature and at liquid nitrogen temperature, and their critical temperatures.

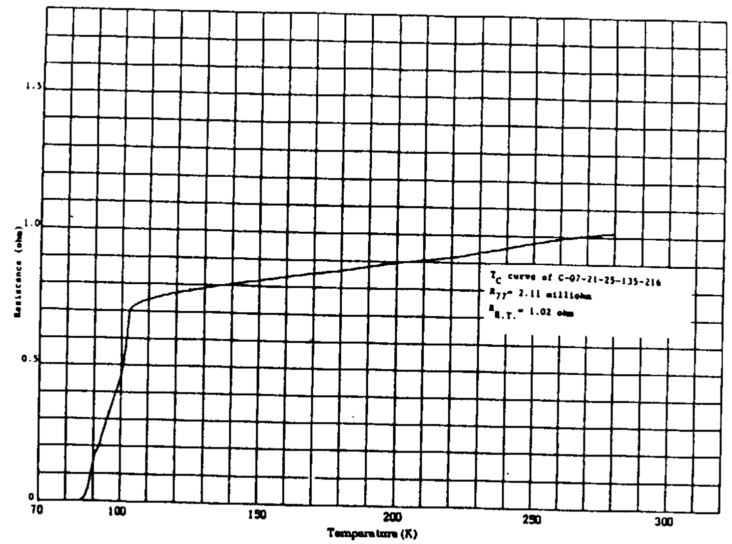
Link No.	$R_{R.T.}$ (Ω)	R_{77} (mΩ)	T_c (K)
212	1.15	1.4	90
213	1.08	1.9	88
214	1.08	1.4	86
215	1.02	2.0	86
216	1.02	2.1	86
217	1.09	2.18	88
218	1.10	1.93	85
219	1.11	2.08	88
220	1.14	1.91	88
221	1.82	1.20	86
223	1.24	1.30	84
226	1.41	1.39	85
227	1.34	1.62	86
228	1.31	0.98	87
229	1.29	1.19	87
203S	1.08	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

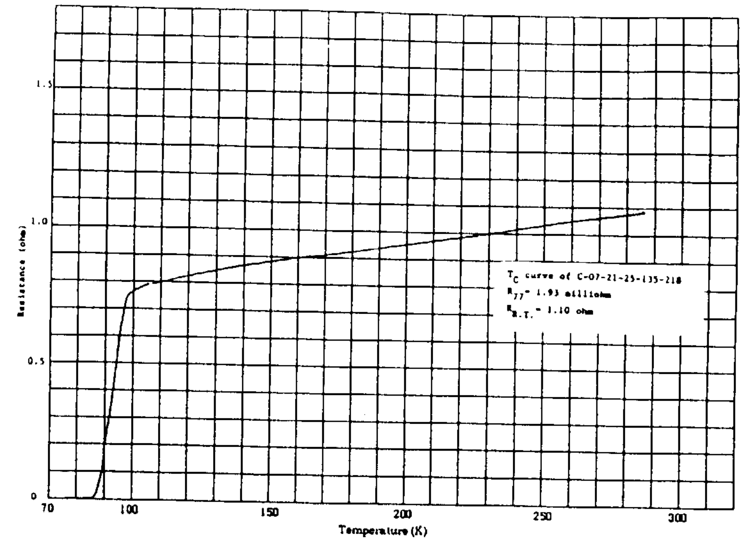
Appendix III

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

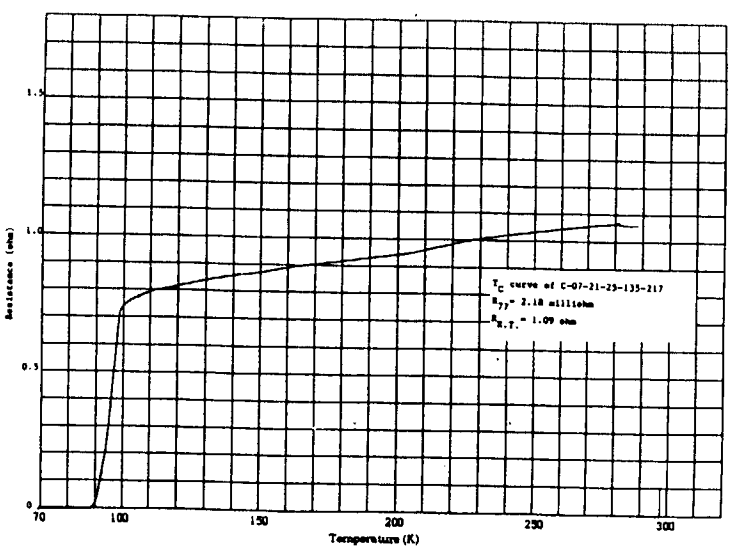




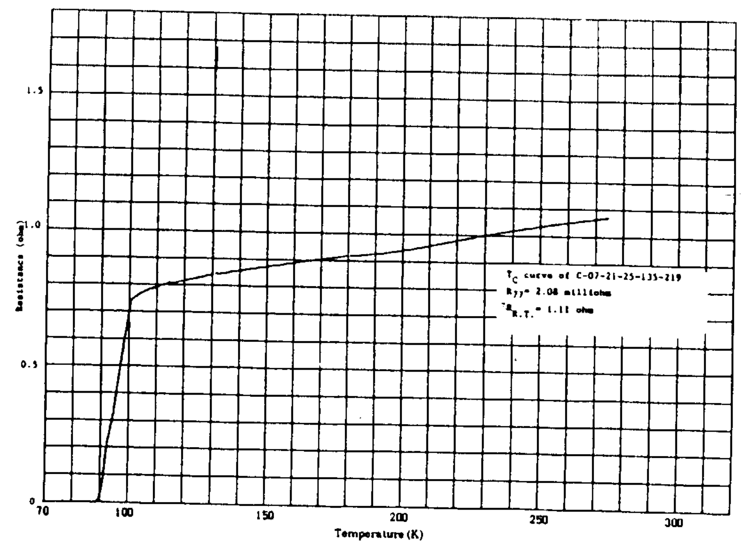
Resistance (ohm)
Temperature (K)
T_C curve of C-07-21-25-135-216
R_{77} = 2.11 milliohm
$R_{R.T.}$ = 1.02 ohm



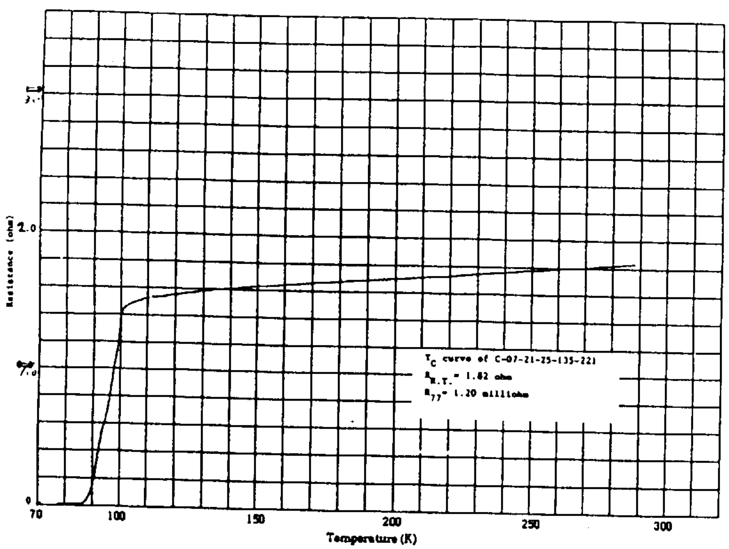
Resistance (ohm)
Temperature (K)
T_C curve of C-07-21-25-135-218
R_{77} = 1.93 milliohm
$R_{R.T.}$ = 1.10 ohm



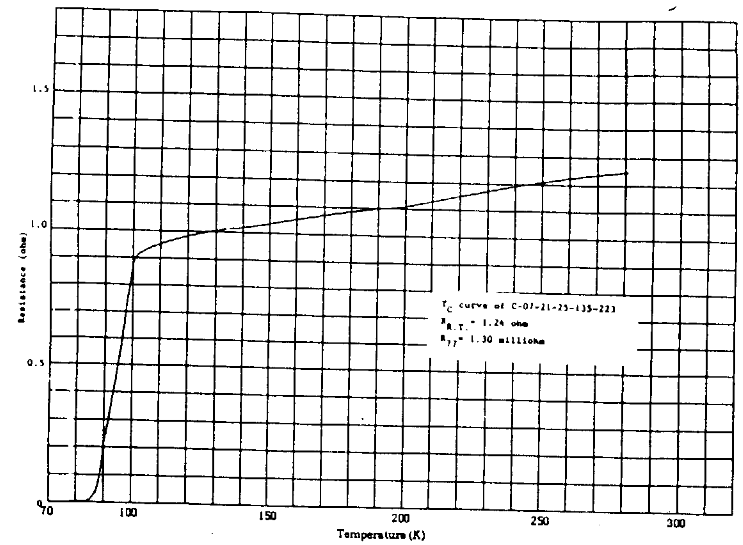
Resistance (ohm)
Temperature (K)
T_C curve of C-07-21-25-135-217
R_{77} = 2.18 milliohm
$R_{R.T.}$ = 1.09 ohm



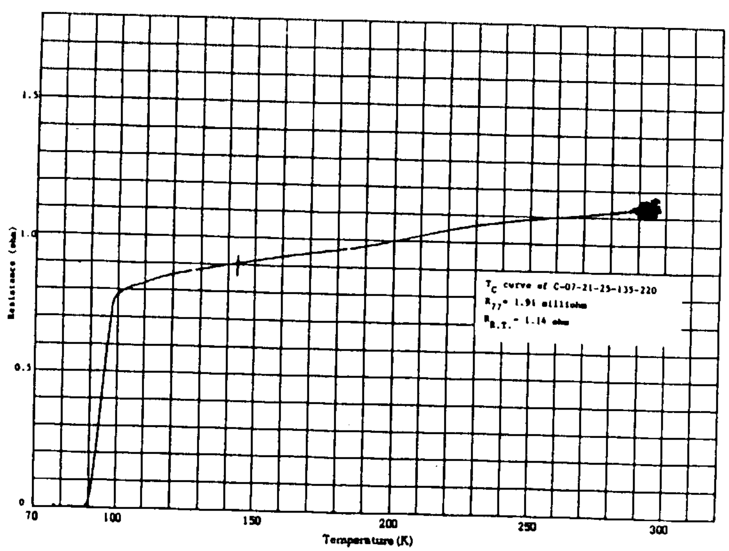
Resistance (ohm)
Temperature (K)
T_C curve of C-07-21-25-135-219
R_{77} = 2.08 milliohm
$R_{R.T.}$ = 1.11 ohm



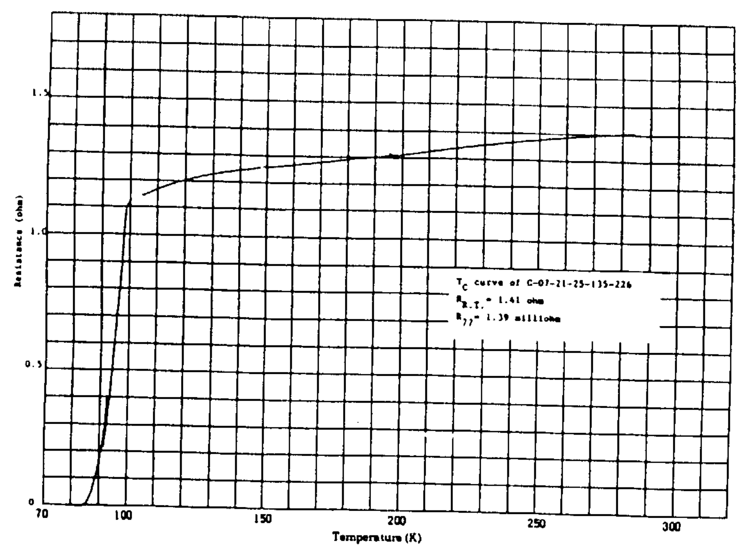
T_c curve of C-07-21-25-135-221
$R_{R.T.}$ = 1.82 ohm
R_{77} = 1.20 milliohm
Resistance (ohm)
Temperature (K)



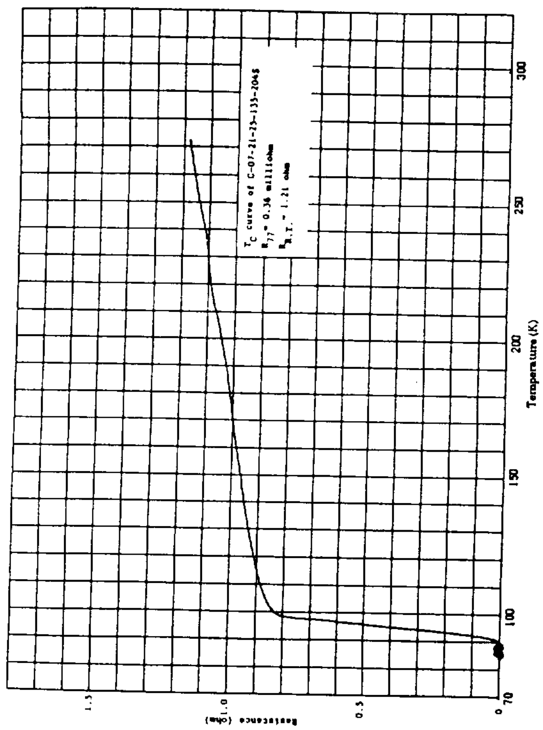
T_c curve of C-07-21-25-135-223
$R_{R.T.}$ = 1.24 ohm
R_{77} = 1.30 milliohm
Resistance (ohm)
Temperature (K)

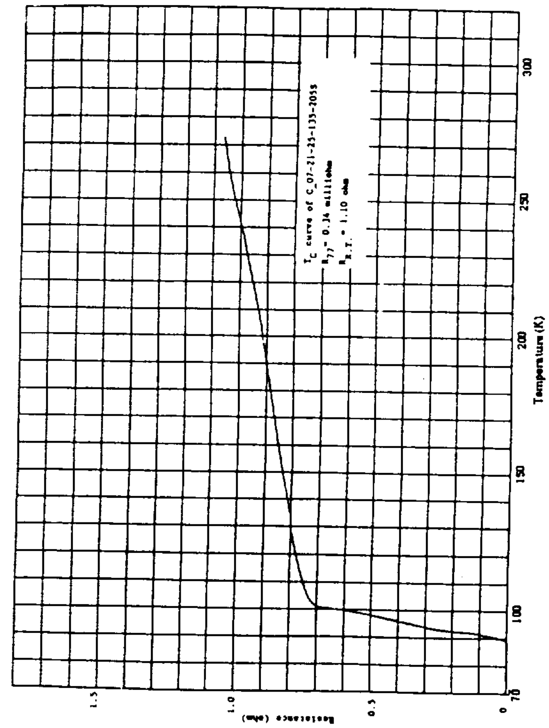


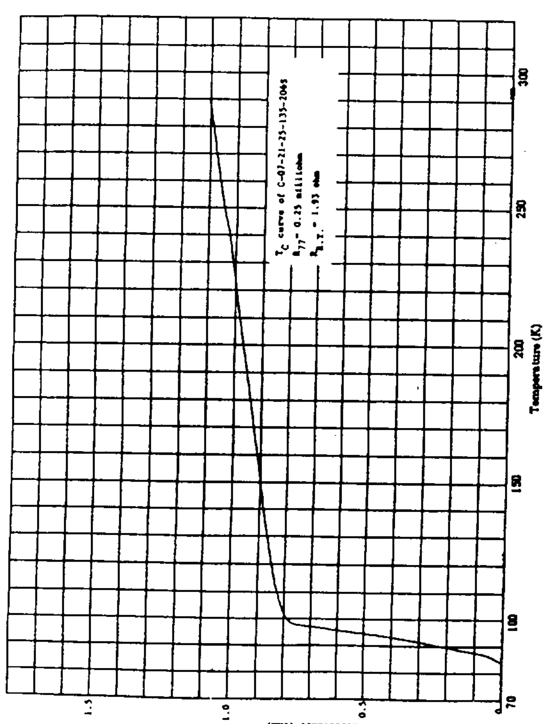
T_c curve of C-07-21-25-135-220
R_{77} = 1.91 milliohm
$R_{R.T.}$ = 1.14 ohm
Resistance (ohm)
Temperature (K)

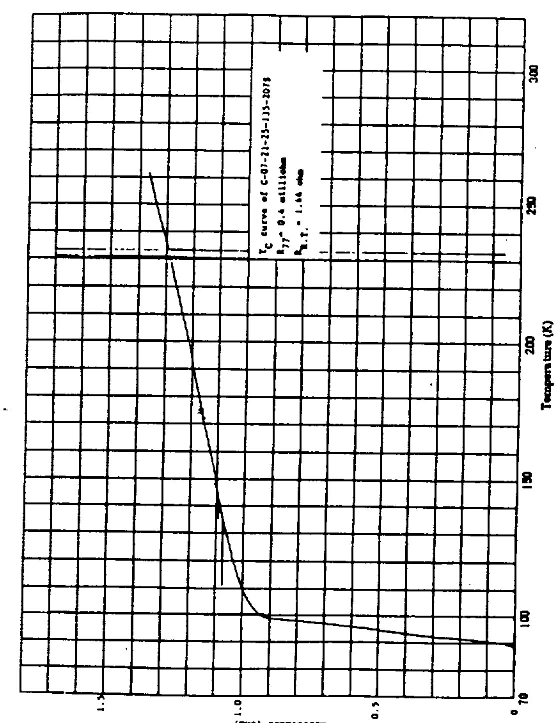


T_c curve of C-07-21-25-135-226
$R_{R.T.}$ = 1.41 ohm
R_{77} = 1.39 milliohm
Resistance (ohm)
Temperature (K)









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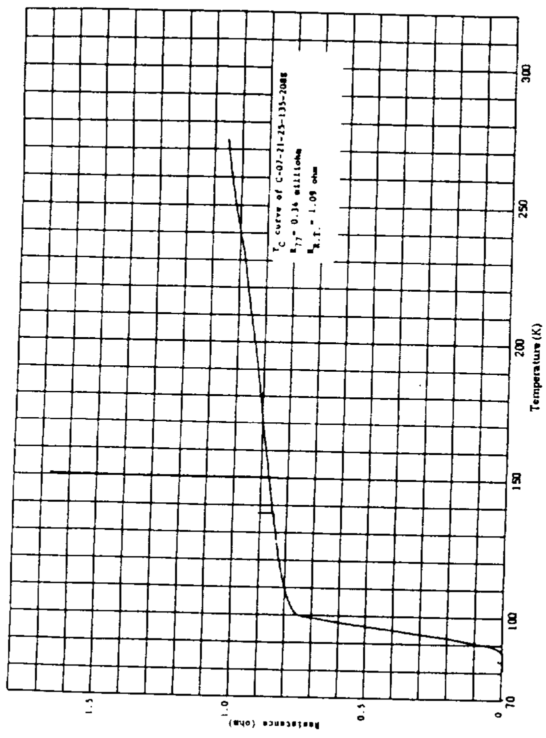
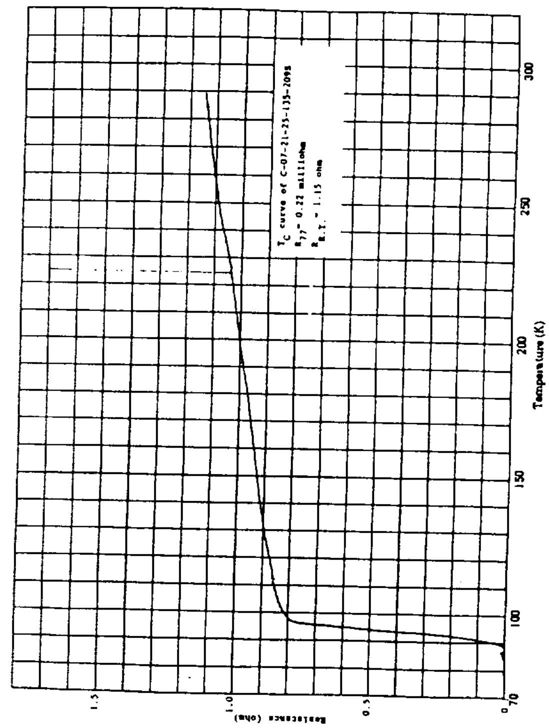
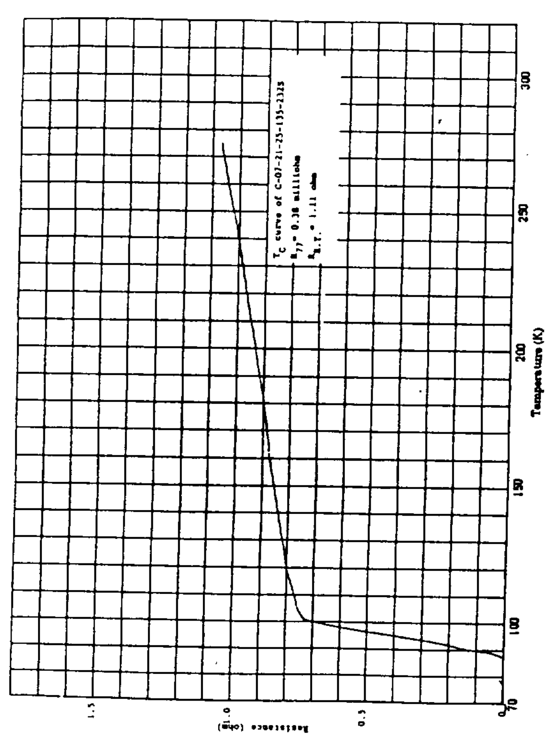


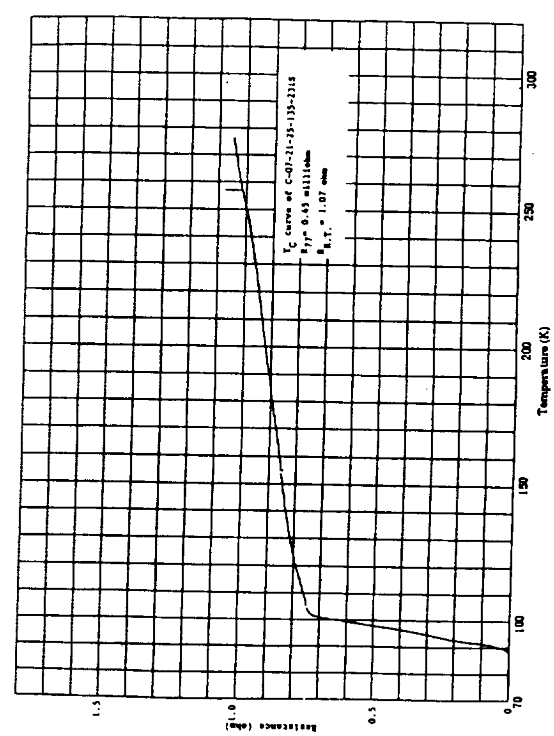
T_C curve of C-07-21-25-135-208S
R_77 = 0.34 milliohm
R_R.T. = 1.09 ohm
Temperature (K)
Resistance (ohm)
70
100
150
200
250
300
0
0.5
1.0
1.5



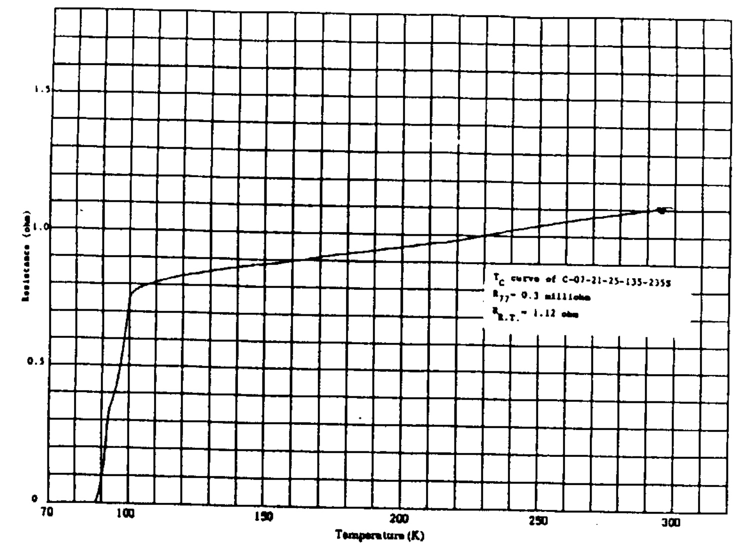
T_C curve of C-07-21-25-135-209S
R_77 = 0.22 milliohm
R_R.T. = 1.15 ohm
Temperature (K)
Resistance (ohm)
70
100
150
200
250
300
0
0.5
1.0
1.5



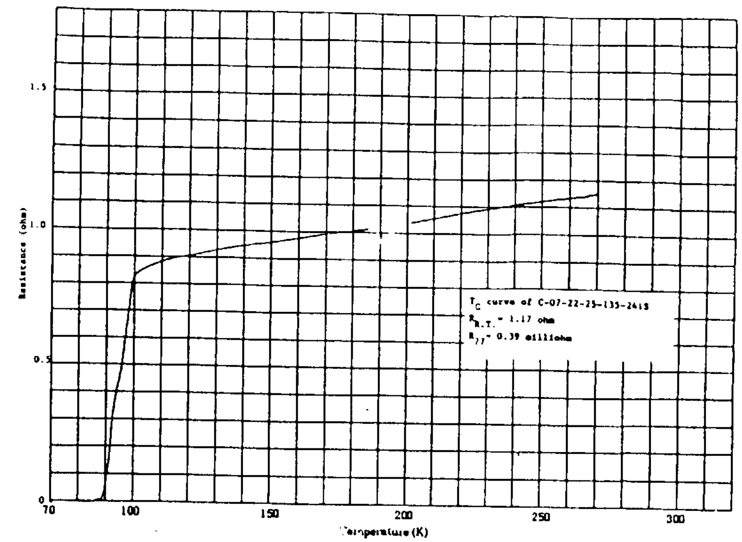
T_C curve of C-07-21-25-135-232S
R_77 = 0.38 milliohm
R_R.T. = 1.11 ohm
Temperature (K)
Resistance (ohm)
70
100
150
200
250
300
0
0.5
1.0
1.5



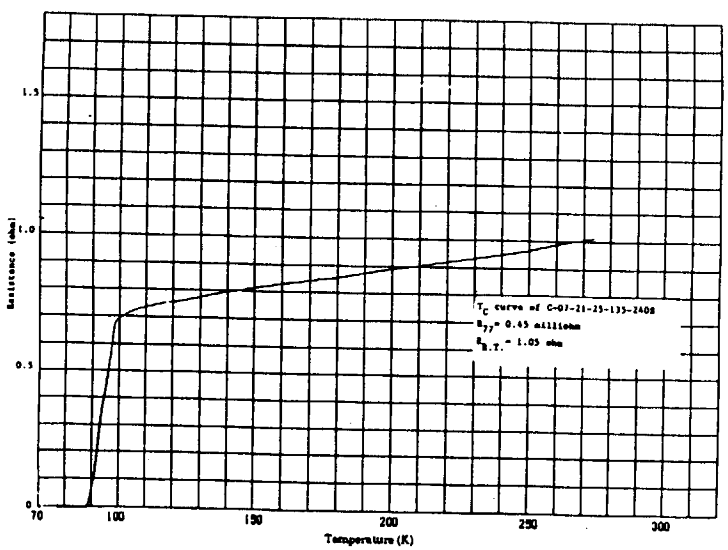
T_C curve of C-07-21-25-135-231S
R_77 = 0.45 milliohm
R_R.T. = 1.07 ohm
Temperature (K)
Resistance (ohm)
70
100
150
200
250
300
0
0.5
1.0
1.5



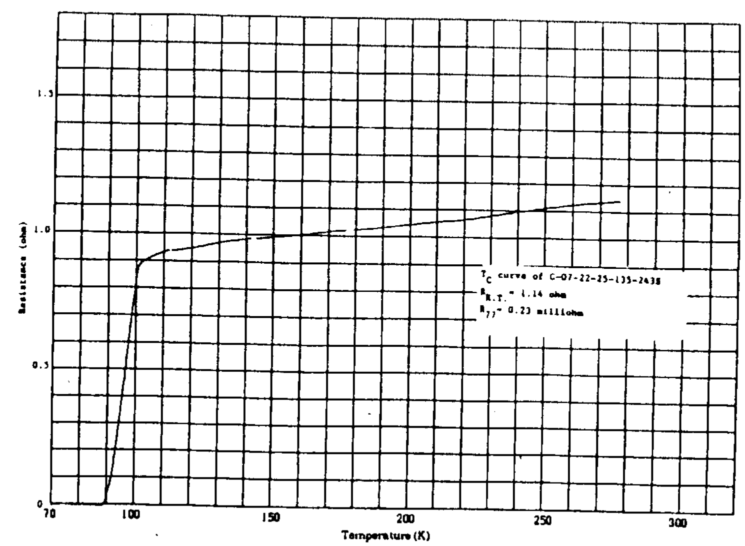
T_C curve of C-07-21-25-135-235S
R_{77} = 0.3 milliohm
$R_{R.T.}$ = 1.12 ohm
Resistance (ohm)
Temperature (K)



T_C curve of C-07-22-25-135-241S
$R_{R.T.}$ = 1.17 ohm
R_{77} = 0.39 milliohm
Resistance (ohm)
Temperature (K)



T_C curve of C-07-21-25-135-240S
R_{77} = 0.45 milliohm
$R_{R.T.}$ = 1.05 ohm
Resistance (ohm)
Temperature (K)



T_C curve of C-07-22-25-135-243S
$R_{R.T.}$ = 1.14 ohm
R_{77} = 0.23 milliohm
Resistance (ohm)
Temperature (K)

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.

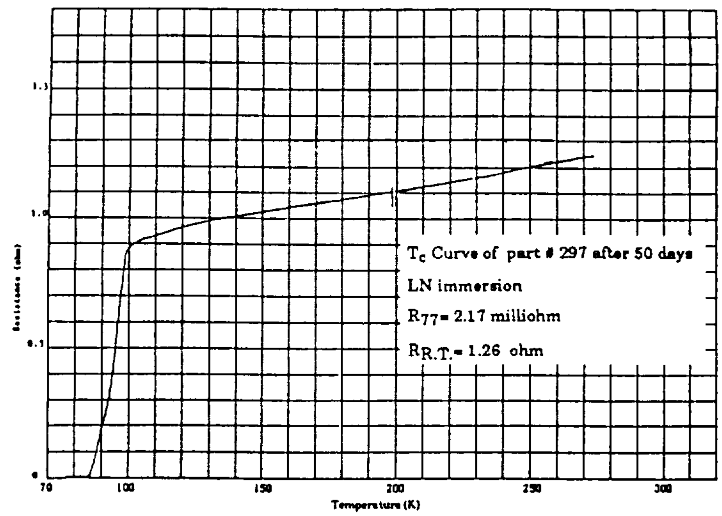
Resistance: Ω

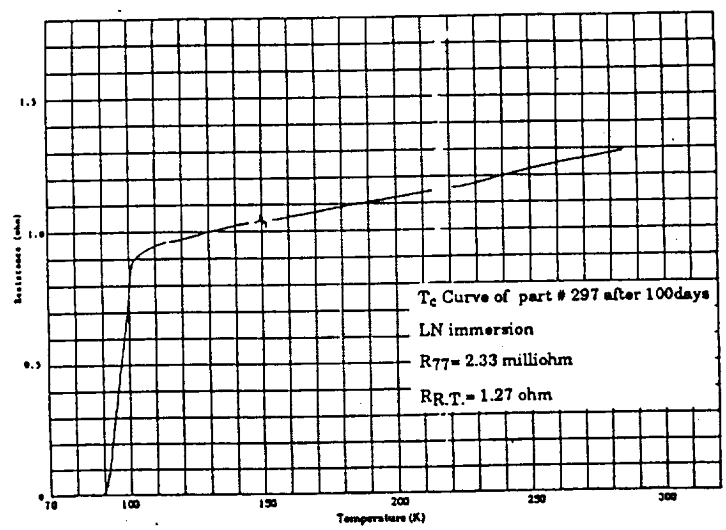
Date	10/19/90	10/20/90	10/22/90	10/26/90	11/04/90	11/26/90	12/24/90
Days / Part No.	at start	1	3	7	16	38	66
291	1.57	1.61	1.56	1.55	1.55	1.56	1.57
292	1.40	1.40	1.45	1.38	1.37	1.38	1.40
293	2.11	2.11	2.10	2.10	2.10	2.12	2.11
294	1.87	1.87	1.91	1.90	1.80	1.86	1.88
295	2.23	2.23	2.24	2.24	2.22	2.22	2.23
296	2.09	2.11	2.17	2.09	2.09	2.08	2.11
297	1.26	1.42	1.28	1.27	1.26	1.27	1.27
298	1.77	1.77	1.76	1.76	1.76	1.77	1.78

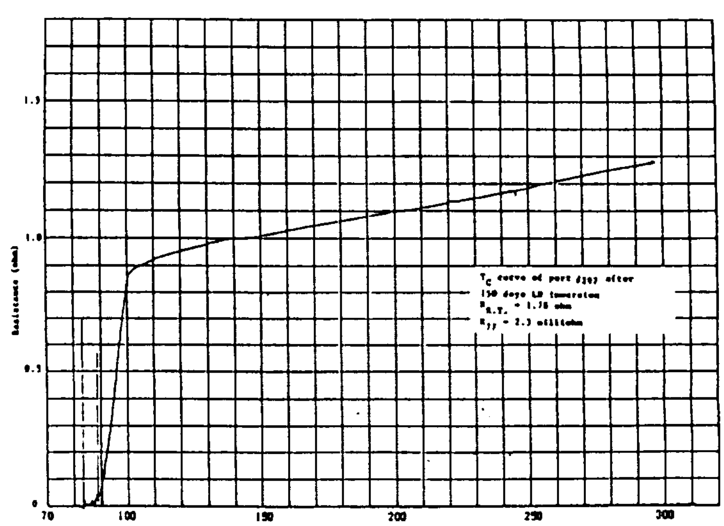
Date	01/13/91	01/27/91	02/17/91	03/18/91	04/21/91	05/05/91	6/ 2/91
Days / Part No.	87	101	122	151	185	199	226
291	1.57	1.57	1.57	1.6	1.5	1.6	1.6
292	1.39	1.39	1.40	1.4	2.1	1.3	1.4
293	2.11	2.11	2.11	2.1	1.4	2.1	2.1
294	1.86	1.87	1.87	1.9	1.9	1.8	1.8
295	2.23	2.26	2.24	2.2	2.2	2.2	2.2
296	2.10	2.10	2.10	2.1	2.1	2.1	2.1
297	1.26	1.26	1.27	1.2	1.2	1.2	1.3
298	1.78	1.78	1.78	1.8	1.8	1.8	1.6

Appendix V

Figure A-2: T_c curve of link #297 after 50, 100 and 150 days liquid nitrogen immersion.







Semi-Annual Report

ENVIRONMENTAL TEST FOR SUPERCONDUCTING MATERIALS AND DEVICES

Preliminary Results of Testing Program at SRS

to

Dr. Gene H. Haertling
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Clemson, SC 29634-0907

Investigators:

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- Clemson University

Contract No. NAG-1-1127 July, 1991

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 are under investigation(NASA Contract No. NAG-1-1127). Testing at the Savannah River Site will include gamma irradiation, vibration, and long-term evaluation. The gamma irradiation portion of testing has been completed. The long-term testing began in January and will continue. The vibration test has yet to be started.

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 with the full screen of a monitor equaling the width of the sample. The samples were then immersed in liquid nitrogen and exposed to ^{137}Cs for 126 total hours 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 as shown in Table 1. The equivalent gamma radiation dose in water is equal to 11,000 rad. The cross section for gamma absorption in 123 material is greater than water so this dose would be a lower limit.

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 liftoff from the 123 material. This has also been observed at Clemson on some samples during long periods of liquid nitrogen immersion. The samples were returned to Clemson for comparison resistance vs. temperature curves.

Long-Term Test

The long-term test is monitoring for decomposition by-products and changes in resistance while maintaining low temperature(77K) and high vacuum(10-7 torr). The equipment to perform measurements includes 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. The cryostat is immersed in liquid nitrogen from a 50 liter dewar. Liquid nitrogen is replenished to the 50 liter dewar by an interchangeable 160 liter dewar.

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

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

A current of 10ma 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 2. The one inch diameter cryostat holds the samples as shown in Figure 1. This orientation allows the temperature measurement to be an upper limit. 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 ceramic RTD.

Results

The long term test portion of the program has been in progress for more than 3000 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. These data were plotted as resistance vs. temperature for each sample and are given in Figures 2,3, and 4. The pressure during the superconducting transition changed for an unexplained reason, with an increase in pressure from 1E-5 to 5E-2 torr. The transition temperature is defined as the point in which the resistance is10 milliohms. The seven samples all exhibited transitions at approximately 79K. This transition temperature is 9K below a similar curve, shown in Figure 5, which was taken at Clemson. Curves from similar samples tested at SRS in the past have shown transitions at about 89K. A typical example is given in Figure 6.

Resistance data for the three constant current samples are graphed in Figures 7-15. The three samples produced data that were very consistent. The only anomaly was during the first 700 hours of sample number 204. Shortly after the initial cooling of sample number 204, a negative potential of approximately 5 microvolts was recorded. This effect disappeared 700 hours later during a section of data loss. Raw data are missing for various reasons and the corresponding times are recorded in Table 3. The current supply was interrupted only once. This 24 hour period on 27 Feb 91 was due to a power outage.

Degradation evaluation of 123 material is of prime importance in the long-term portion of testing. Analysis of degradation of the samples was done by using six data sets each 10 hours in length. These sets are chosen at stable sections of the data at approximately 84K. Figure 16 shows the average resistance divided by the average temperature for the six ranges. The resistance range of 200-400 microhms is comparable to the lead and contact resistance expected. The fact that these values do not increase is an indication that there is no degradation of the 123 material's superconducting properties.

Data for pressure and temperature of the system are also graphed in Figures 17, 18, & 19. Pressure is presently less than 8E-8 torr. This is down from a typical 3E-7 torr in February. Partial pressure data plotted for particular masses of interest are given in Figure 20. The decrease in pressure over time is normal and is due to the continuous pumping of surface sorbed gases. The ratios change as material is removed from surfaces at different rates.

Continuing work

Data will continue to be obtained and is expected to show a continuing decrease in water content of the vacuum system and a slow decline in hydrogen pressure. Full scans of all masses will be taken periodically and compared to data with the isolation valve closed so an assessment of any by-products from decomposition can be analyzed. The vibration test will be performed when equipment becomes available.

TABLE 1

GAMMA WELL CALIBRATION

SRL EXPERIMENT -- March 1991

Calibrated by: W. H. Wilkie   Reviewed by______________________
Date: 3/05/91

Date:______________________

Temperature (Celsius): 21.5
Pressure (mm Mercury): 750.6
T/P Correction Factor: 1.0108

	Keithley Model 35617	Capintec PM-30	Capintec PM-500	Thermometer -1 to 51 C	Barometer B&W dig.
Serial Number:	36996	C1130.7065	C1152.7095		
M&TE Number:	34002-4493	34002-1923	34002-4459		
SRS Gauge DPN#:	HP-507			HP-1024	SL-3708
Certification Date:	2/15/91	12/07/90	12/08/90	5/10/90	4/30/90
Expiration Date:	2/15/92	12/07/91	12/08/91	5/10/91	1/91
Calibration Factor (R/C):		1.15e8	6.167e6		
Six-month Decay Factor:	.9886				

SHIELD OPEN -- 2.75 INCHES ABOVE LUCITE TROLLEY
Well Setting (ft)
Exposure Rate (mR/h)

	************** PM-30 Uncorrected **************						
	START		STOP				
Well Setting (ft)	n	coulombs (nC)	n	coulombs (nC)	ion ch. current (pA)	PM-30 Corrected (mR/h)	
.35	3	5.0260	27	61.2700	234.35	96950	Inside dewer
.35	3	5.0470	27	61.2800	234.30	96931	Inside dewer
.35	3	5.2420	12	27.2200	244.20	101025	Outside

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OF POOR QUALITY

TABLE 2

	SAMPLE	TYPE*	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
PIN = Gold plated pin

TABLE 3

MISSING DATA SEGMENTS

DATE	START	STOP	HOUR
15 Feb	8:55		737
19 Feb		9:10	834
27 Feb	18:52		1036
28 Feb		19:07	1055
8 Mar	19:06		1259
11 Mar		16:14	1328
12 Apr	7:36		2089
13 Apr		7:12	2112
25 Apr	12:45		2406
1 May		0:45	2539

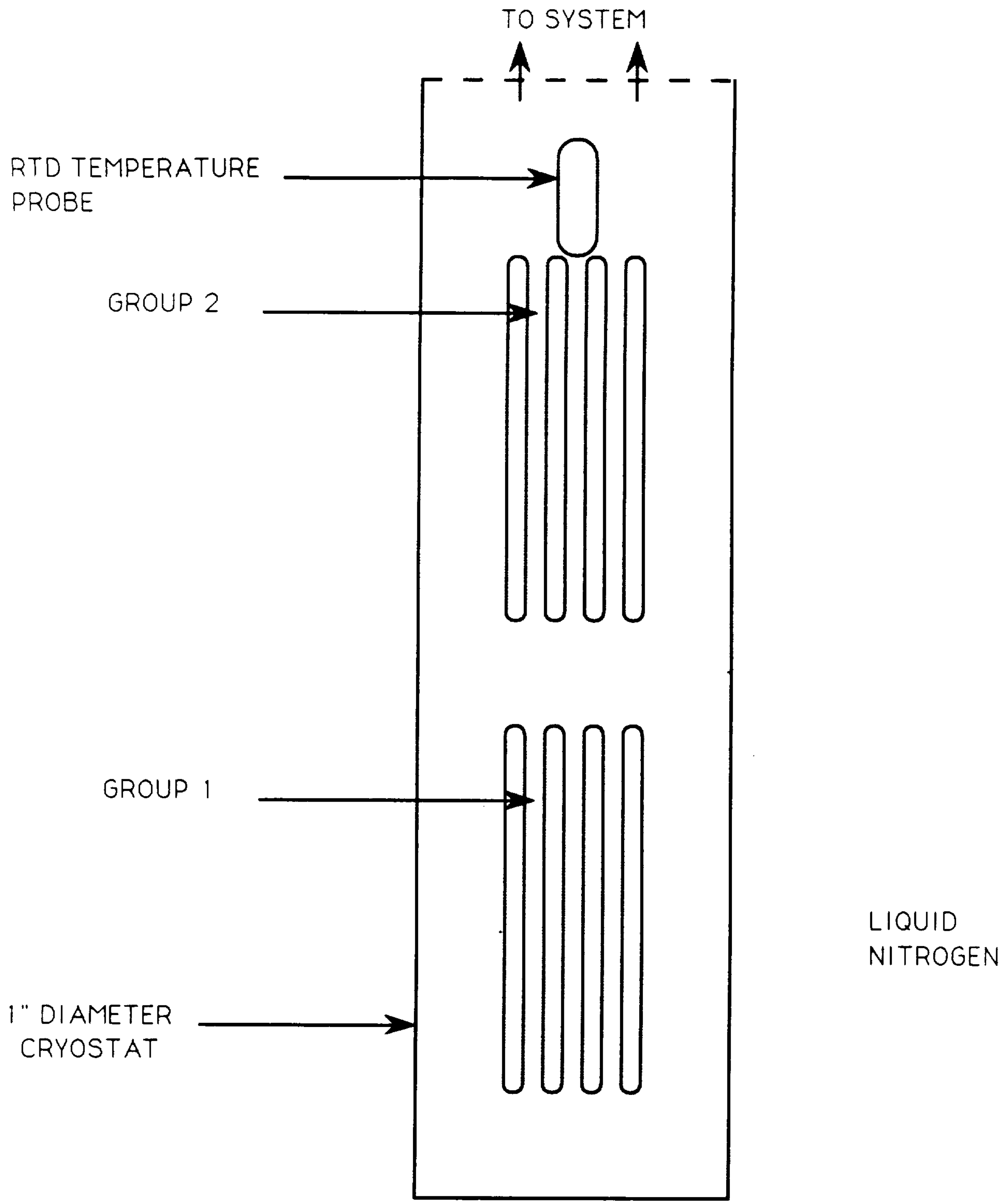


FIGURE 1 SCHEMATIC ORIENTATION OF SAMPLES IN CRYOSTAT

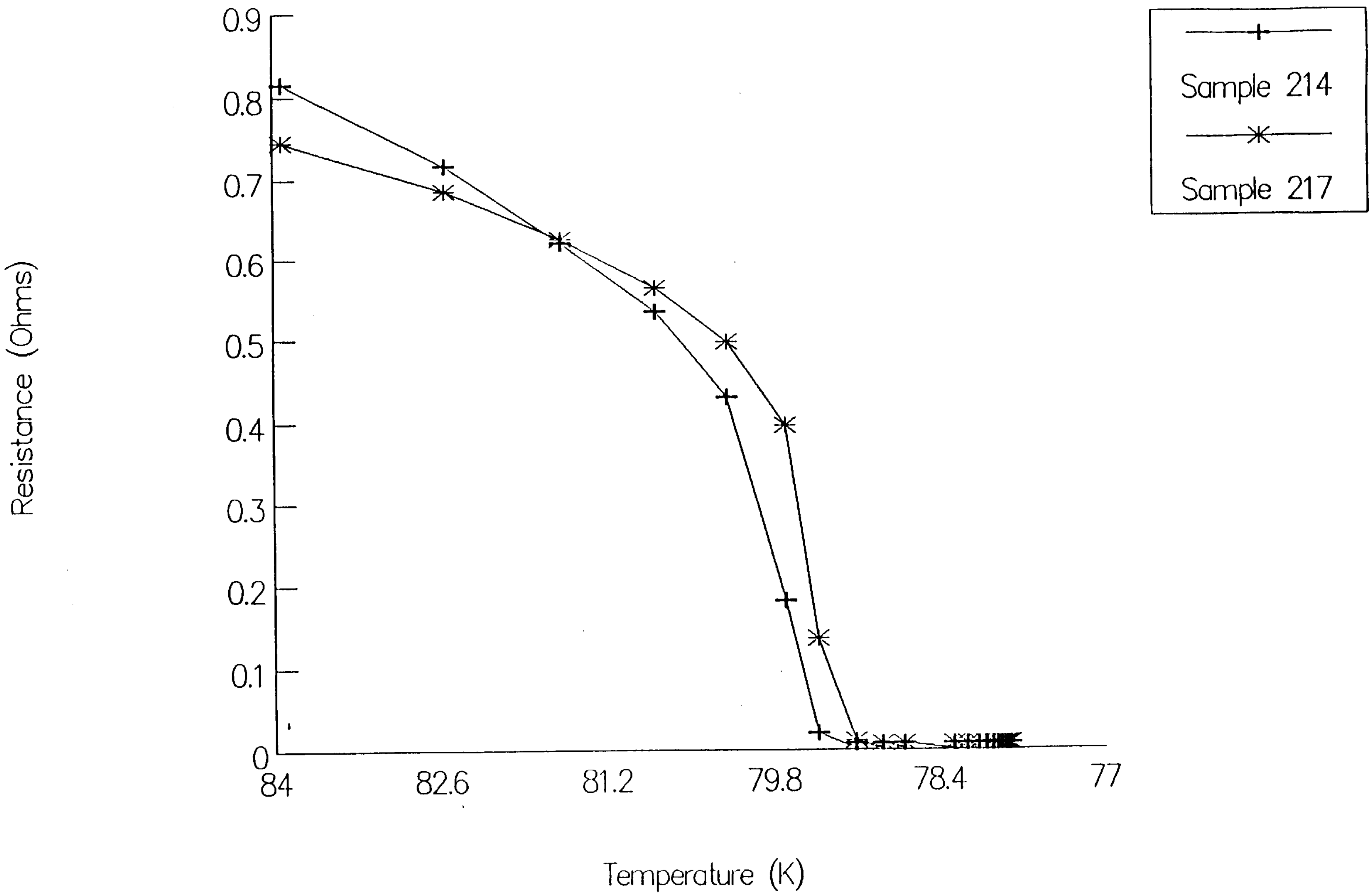


FIGURE 2 INITIAL RESISTANCE VS. TEMPERATURE (Tc) CURVE FOR SUPERCONDUCTING GROUNDING LINKS

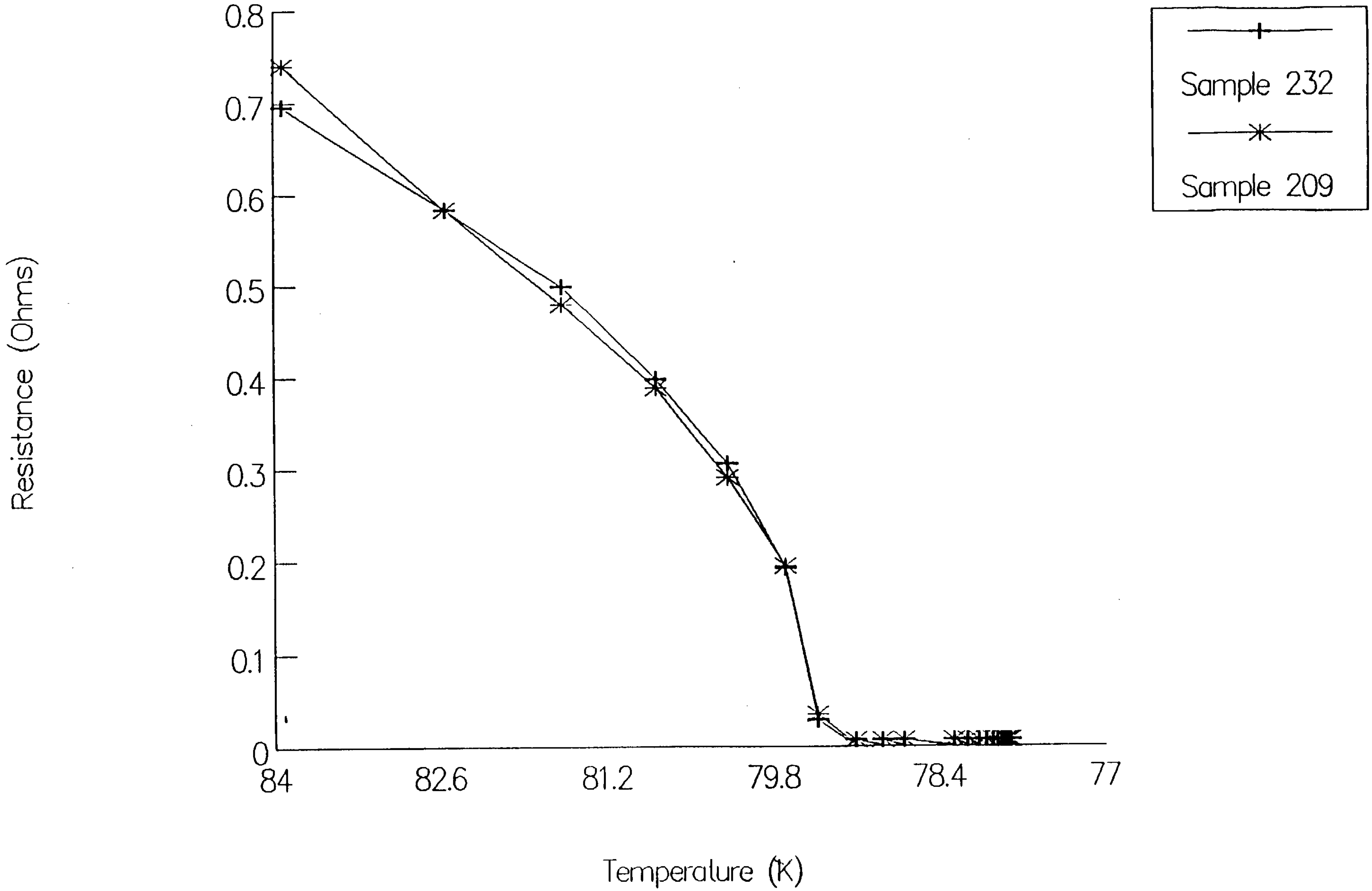


FIGURE 3 INITIAL RESISTANCE VS. TEMPERATURE (Tc) CURVE FOR SUPERCONDUCTING GROUNDING LINKS

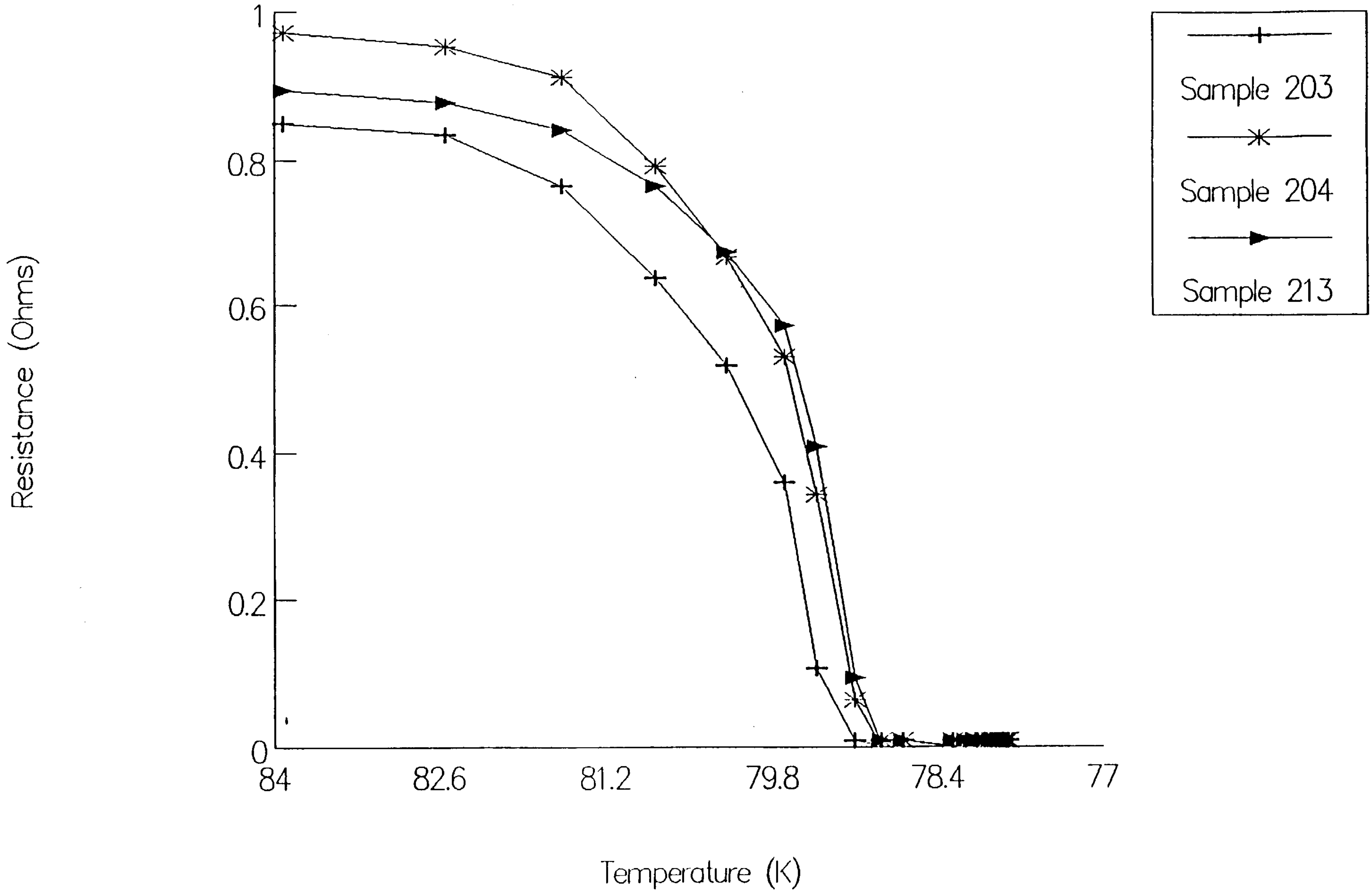


FIGURE 4 INITIAL RESISTANCE VS. TEMPERATURE (Tc) CURVE FOR SUPERCONDUCTING GROUNDING LINKS

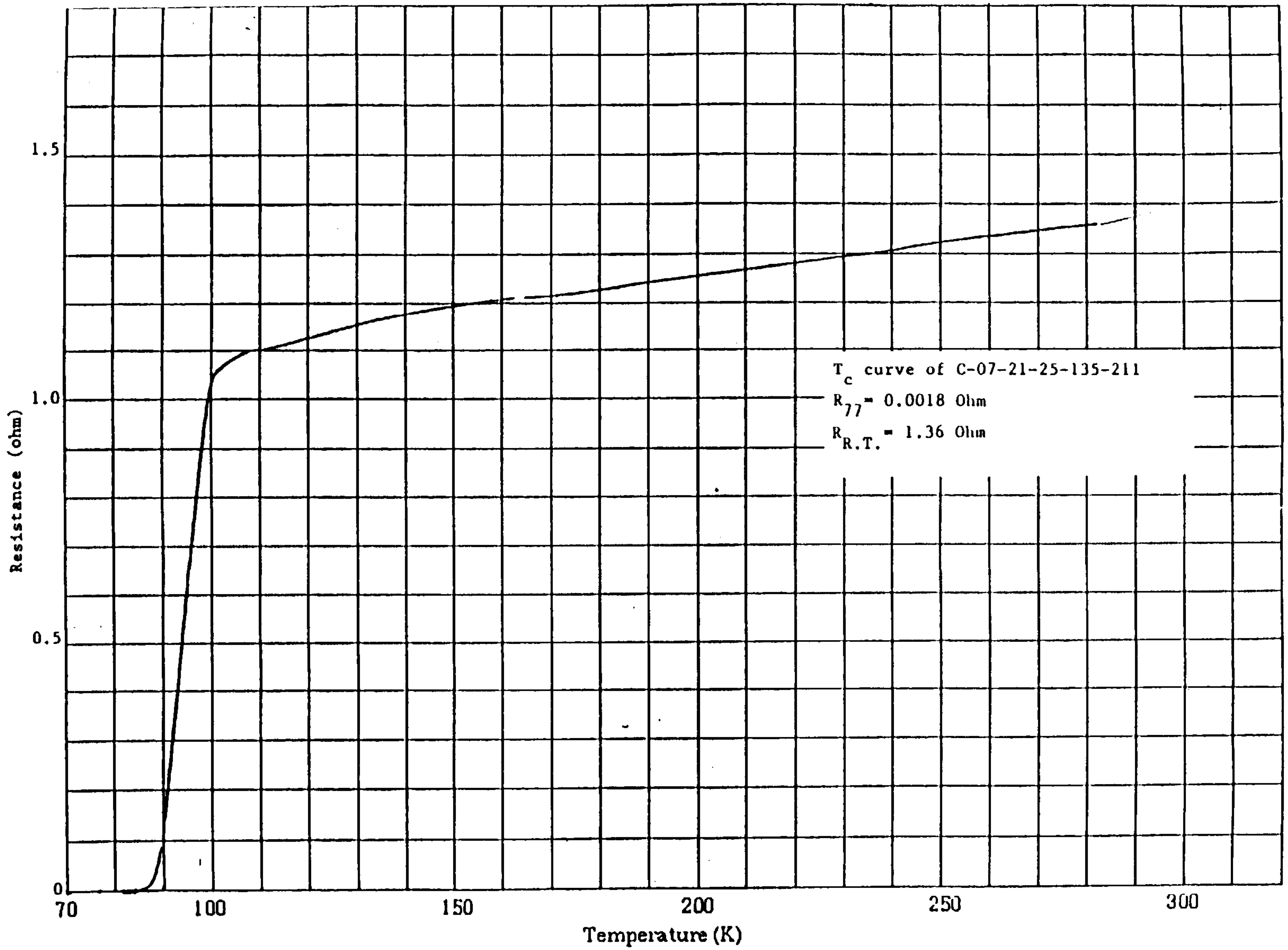


FIGURE 5 TYPICAL TRANSITION CURVE OF A SUPERCONDUCTING GROUNDING LINK TAKEN AT CLEMSON (Tc - 88K)

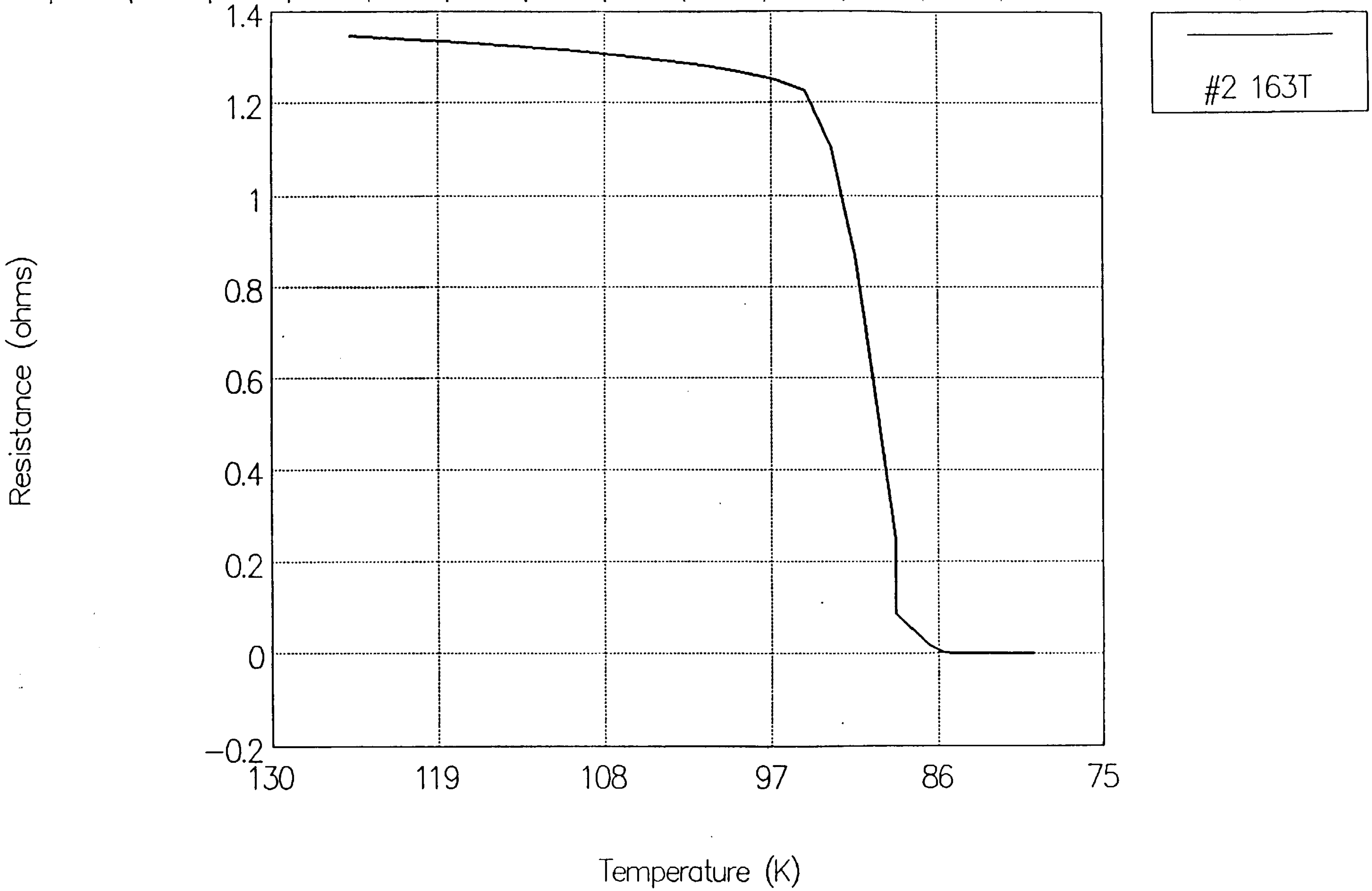


FIGURE 6 TYPICAL TRANSITION CURVE OF A SUPERCONDUCTING GROUNDING LINK TAKEN AT SRS (Tc - 89K)

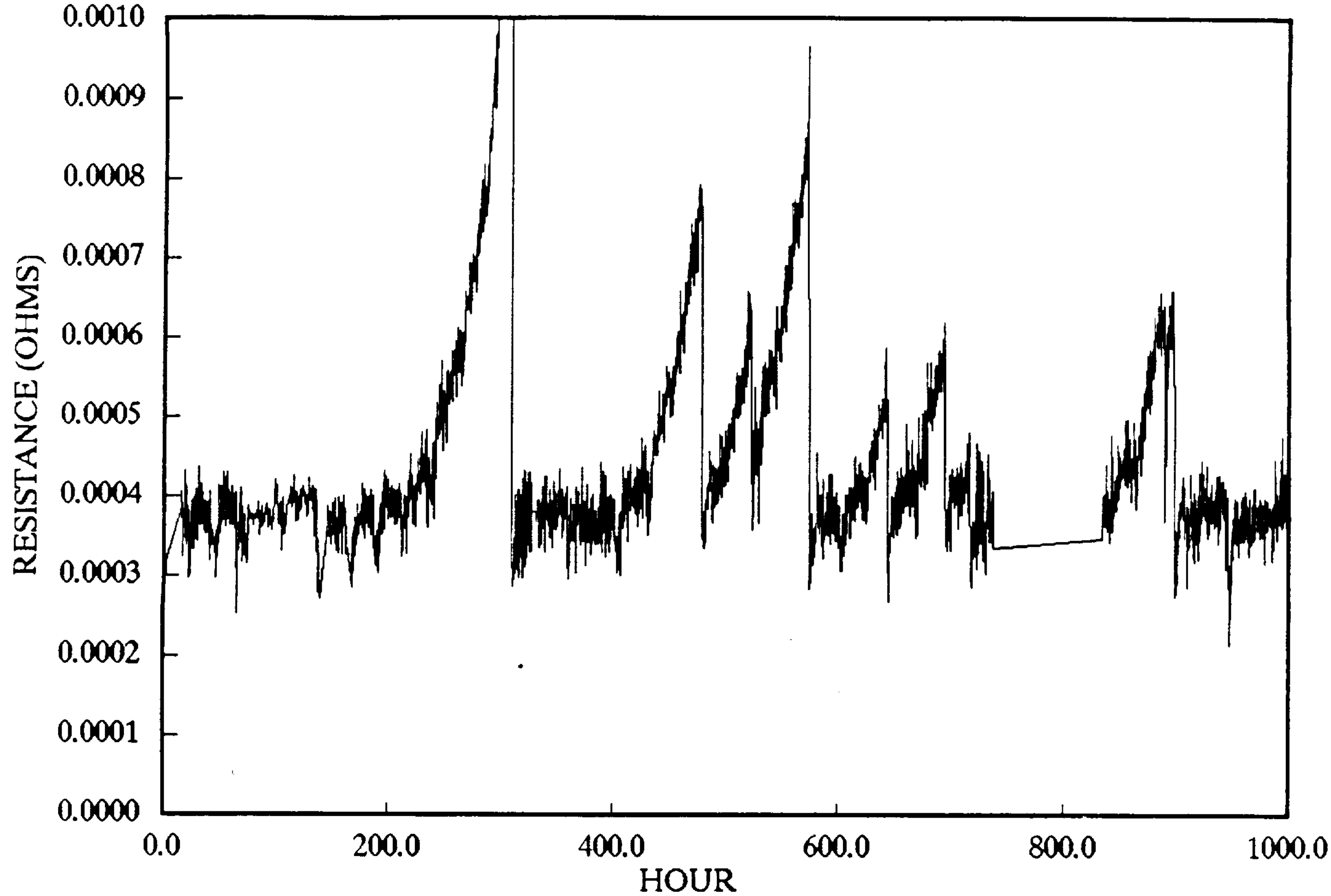
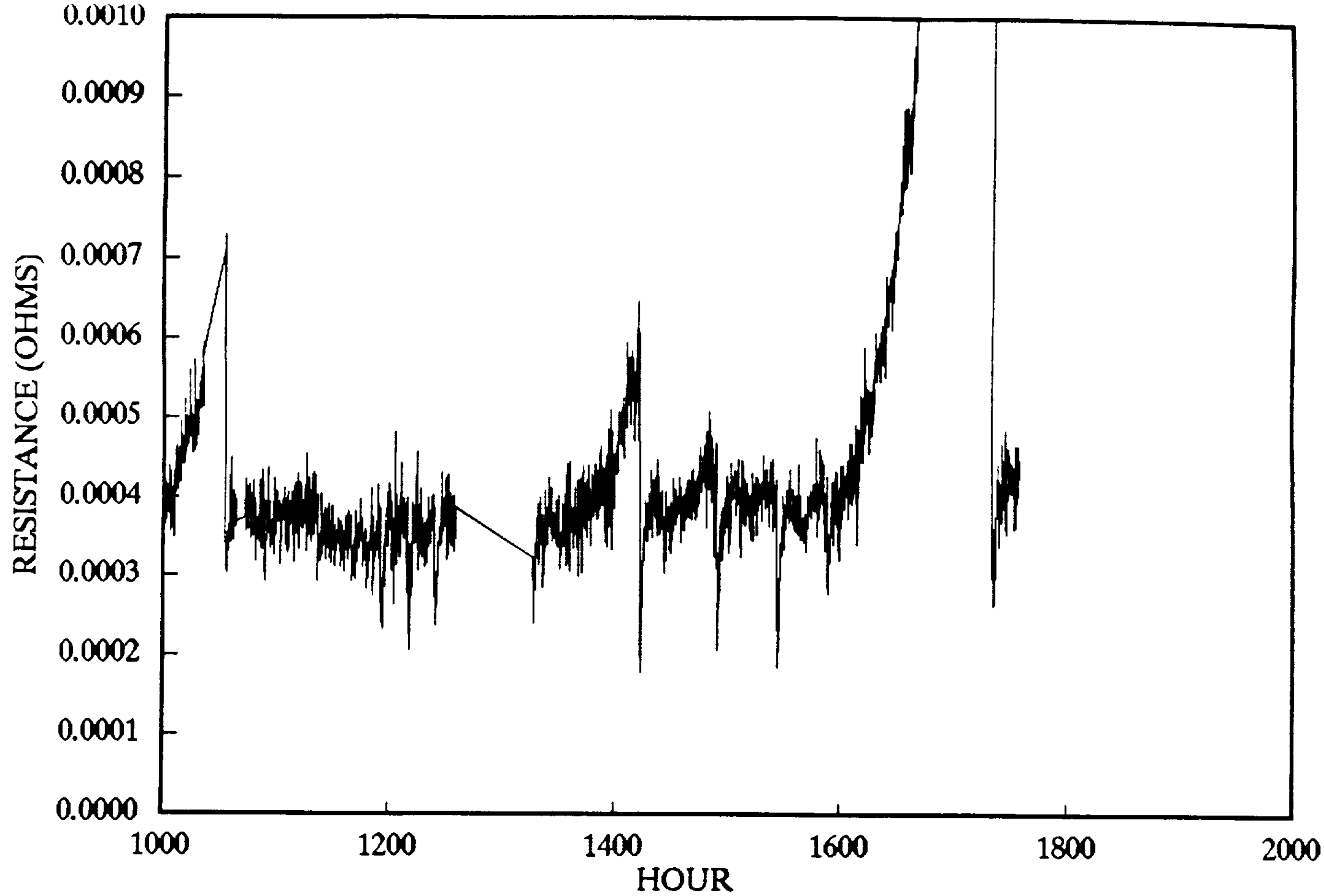


FIGURE 7 RESISTANCE VS. HOURS FOR SAMPLE 203
0-1000 HOURS



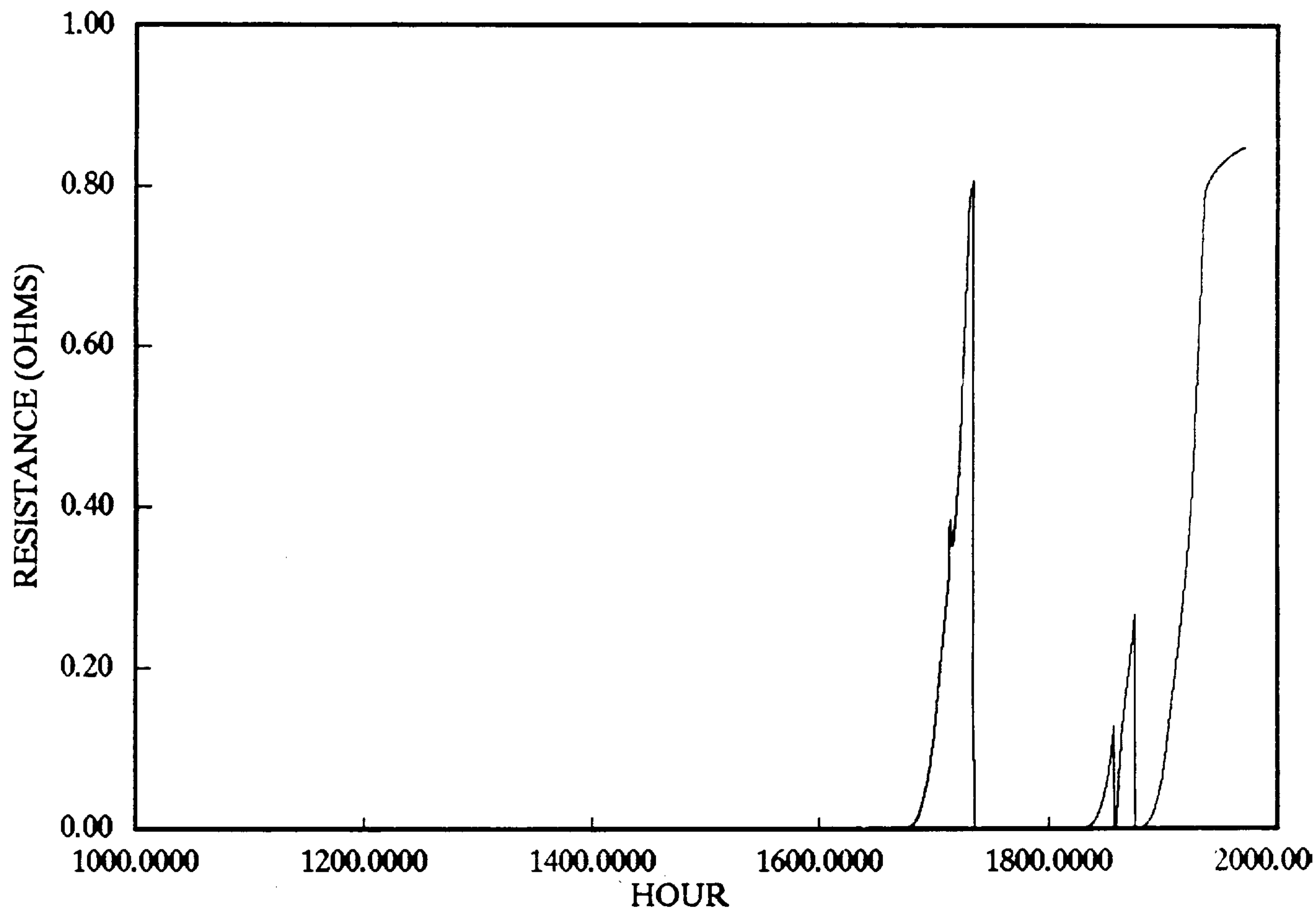


FIGURE 8 RESISTANCE VS. HOURS FOR SAMPLE 203
1000-2000 HOURS

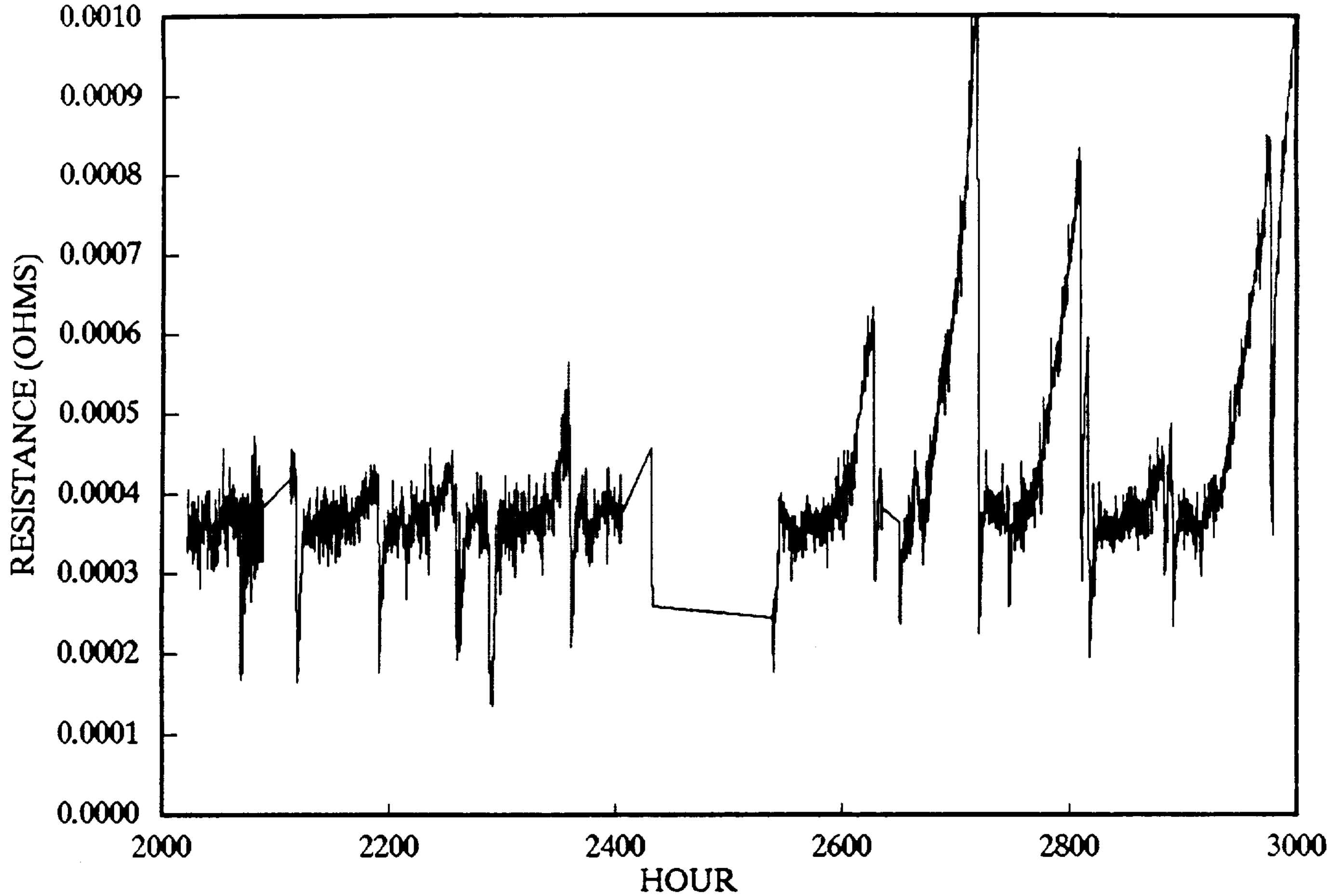


FIGURE 9 RESISTANCE VS. HOURS FOR SAMPLE 203
2000-3000 HOURS

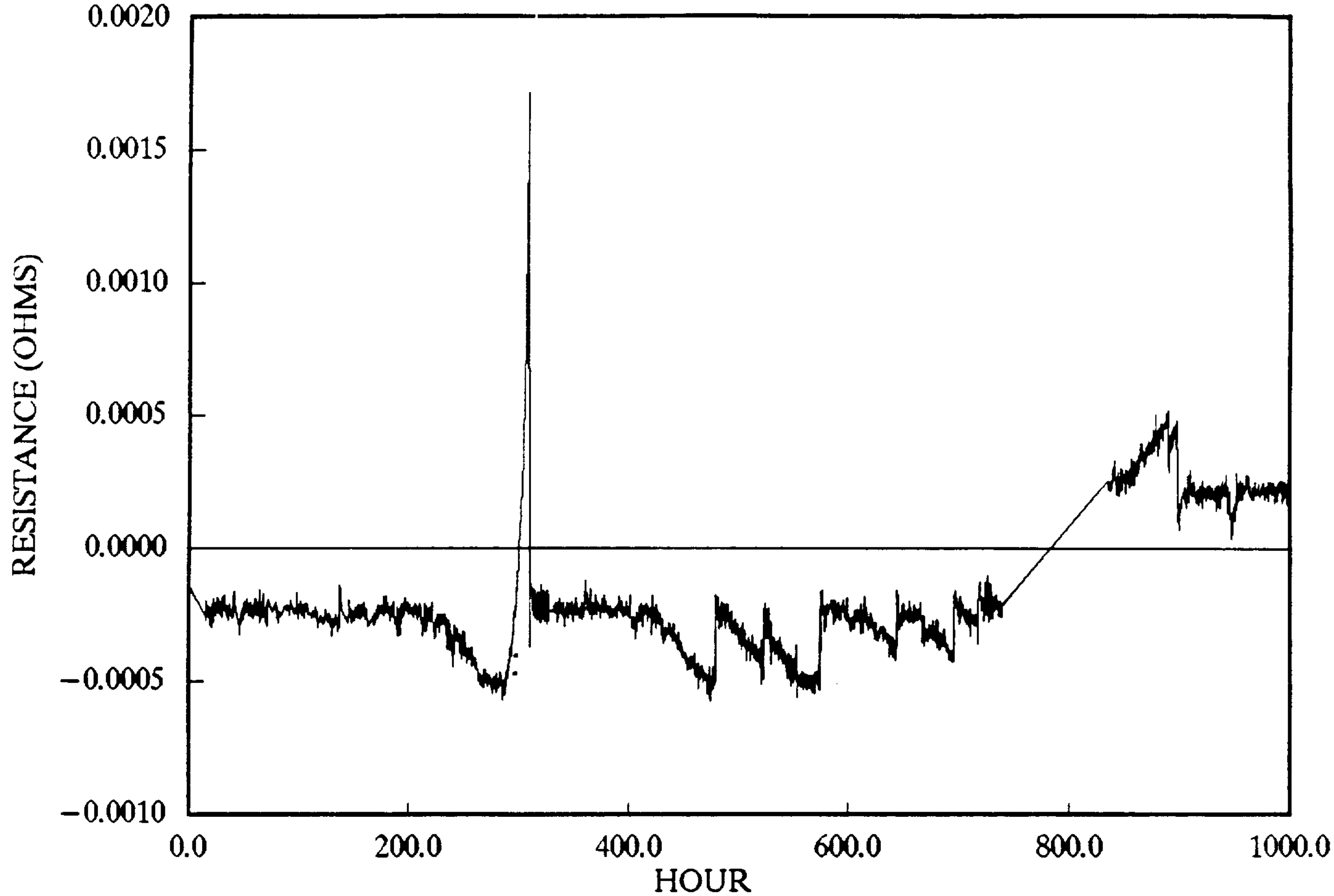
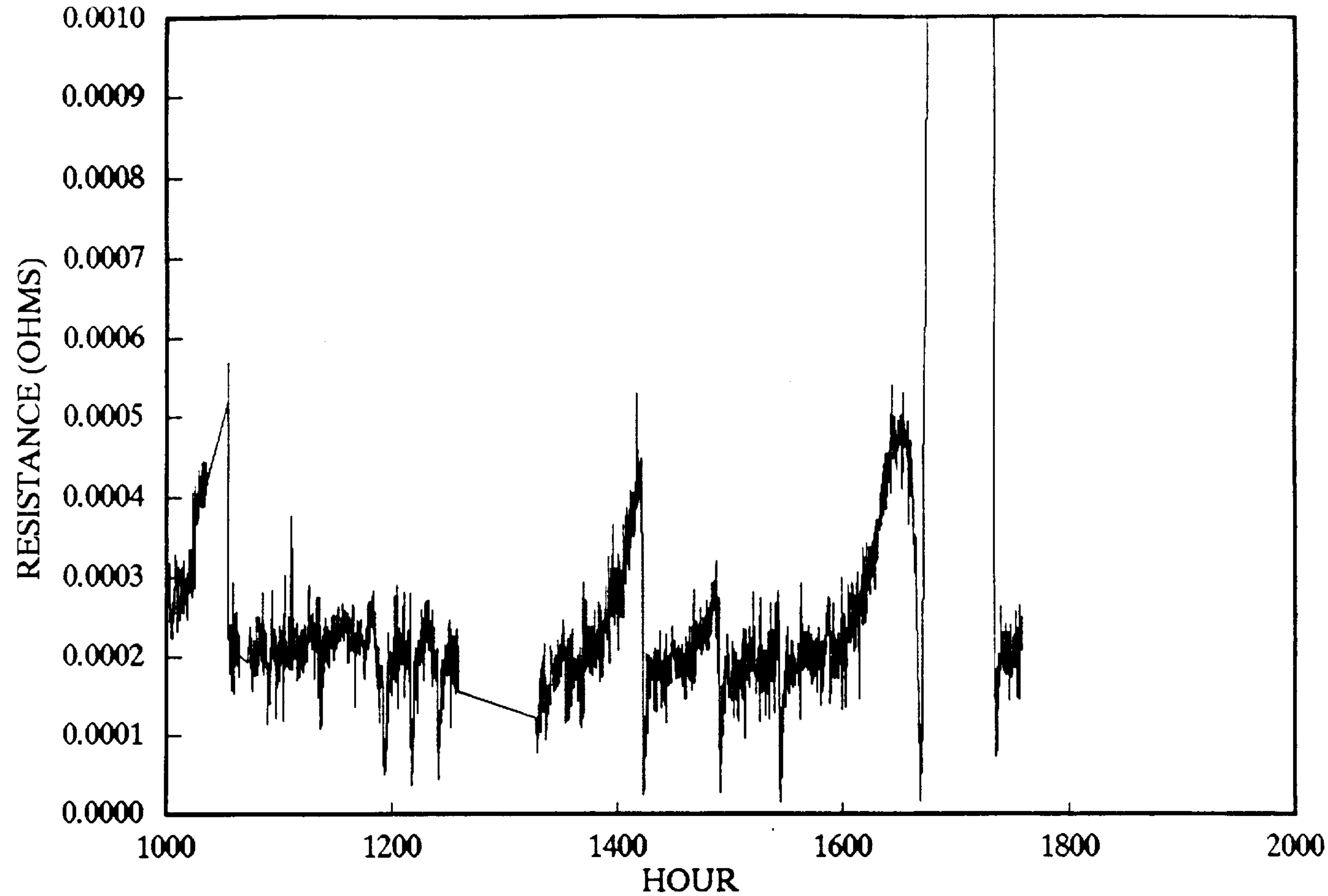


FIGURE 10 RESISTANCE VS. HOURS FOR SAMPLE 204
0-1000 HOURS



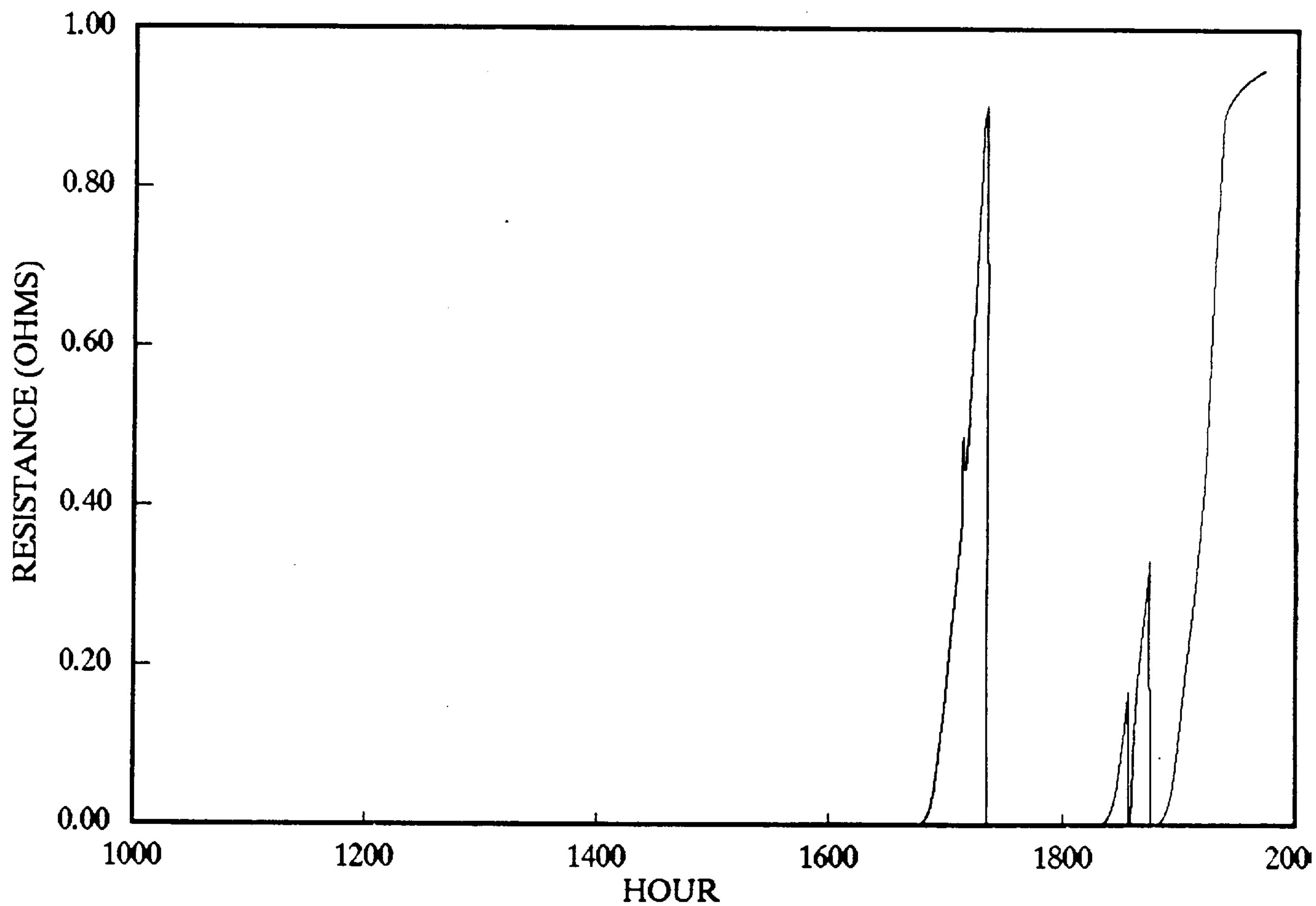


FIGURE 11 RESISTANCE VS. HOURS FOR SAMPLE 204
1000-2000 HOURS

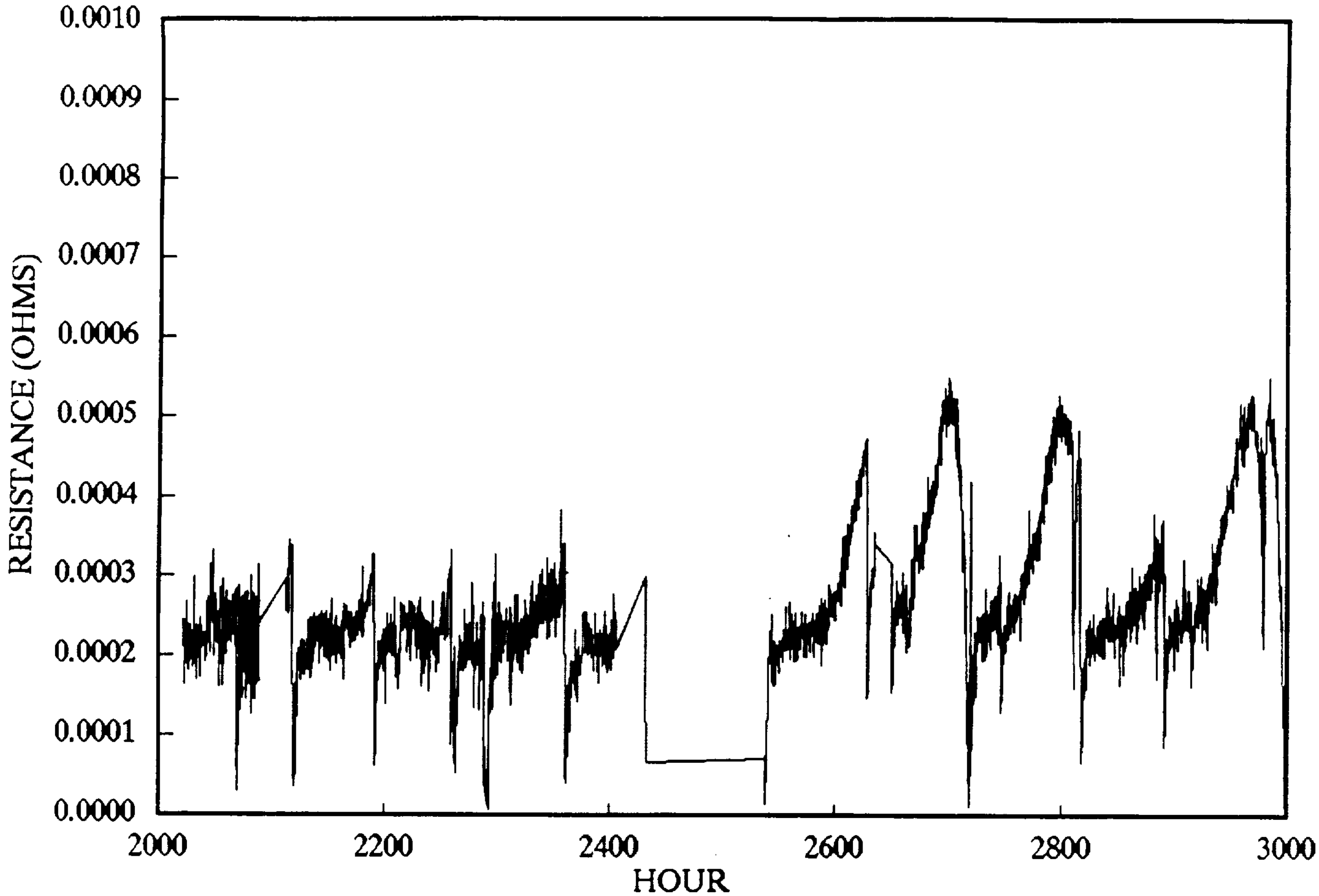


FIGURE 12 RESISTANCE VS. HOURS FOR SAMPLE 204
2000-3000 HOURS

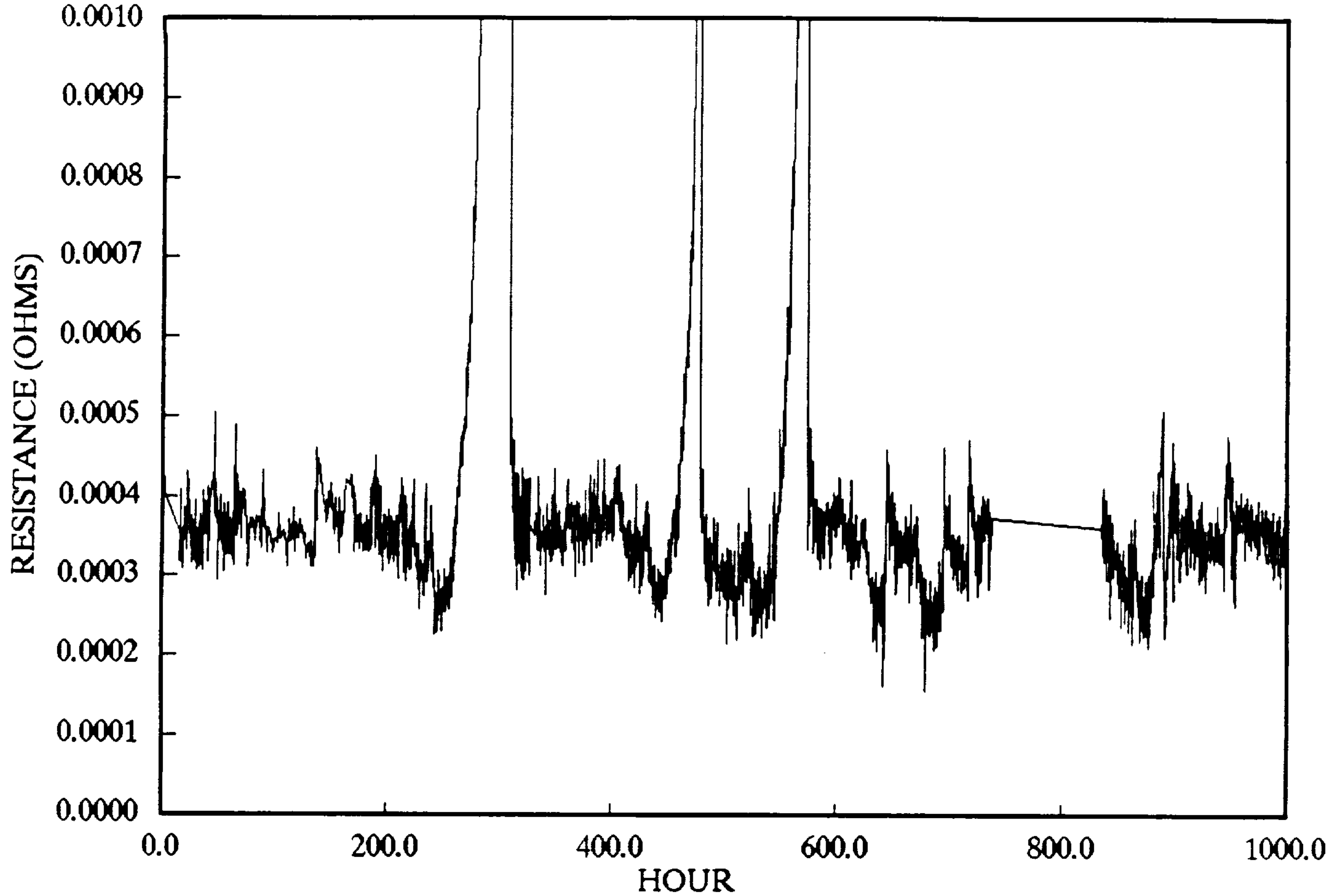
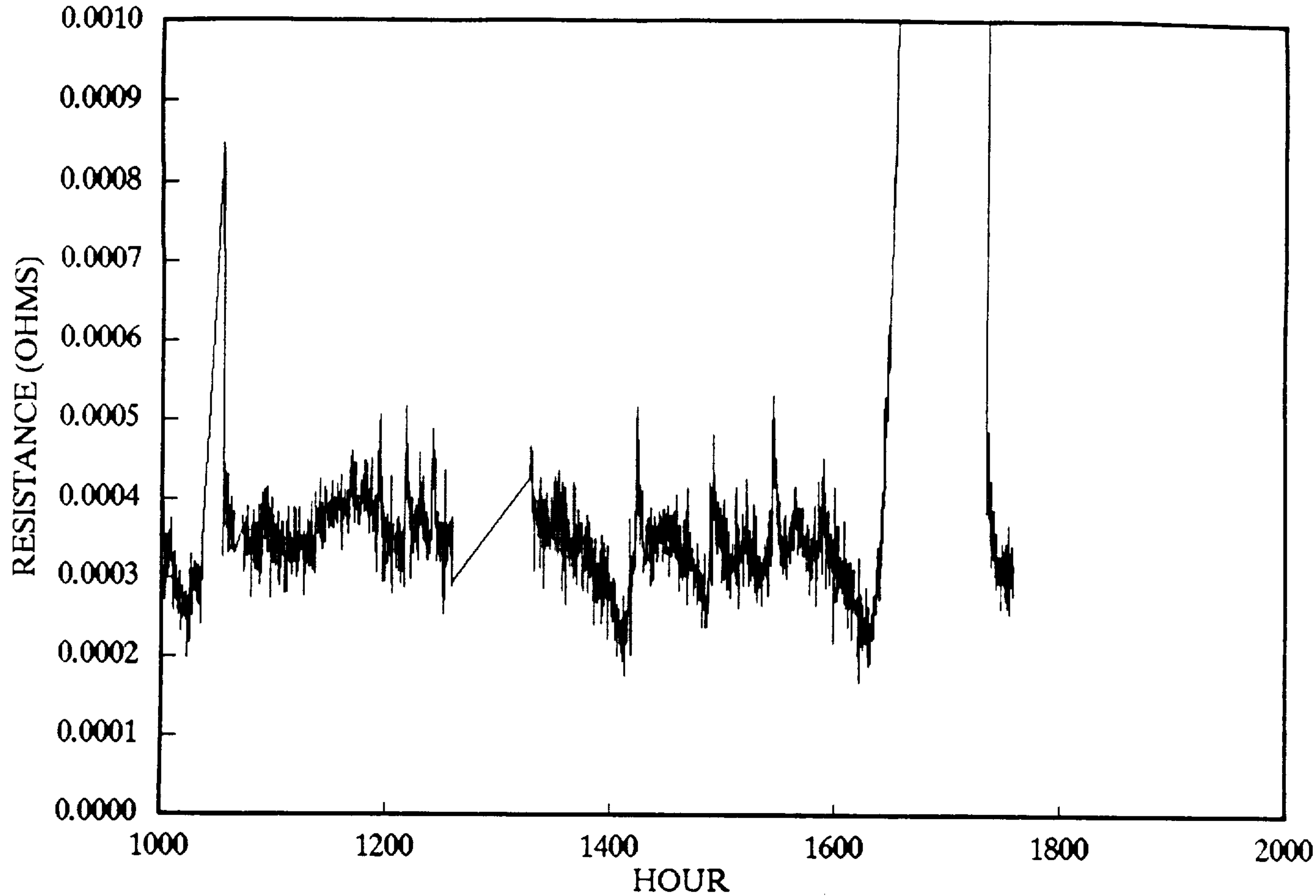


FIGURE 13 RESISTANCE VS. HOURS FOR SAMPLE 213
0-1000 HOURS



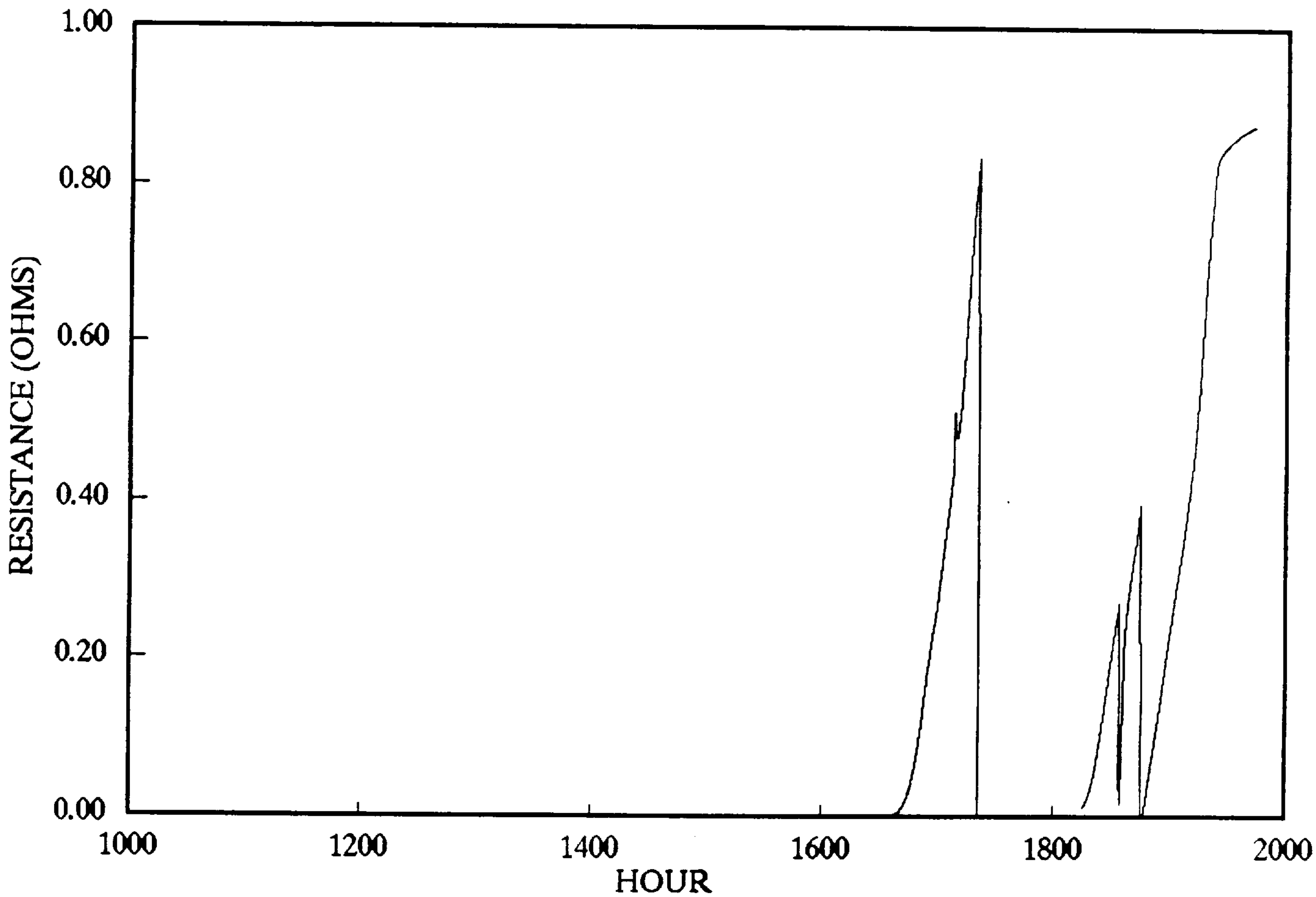


FIGURE 14 RESISTANCE VS. HOURS FOR SAMPLE 213
1000-2000 HOURS

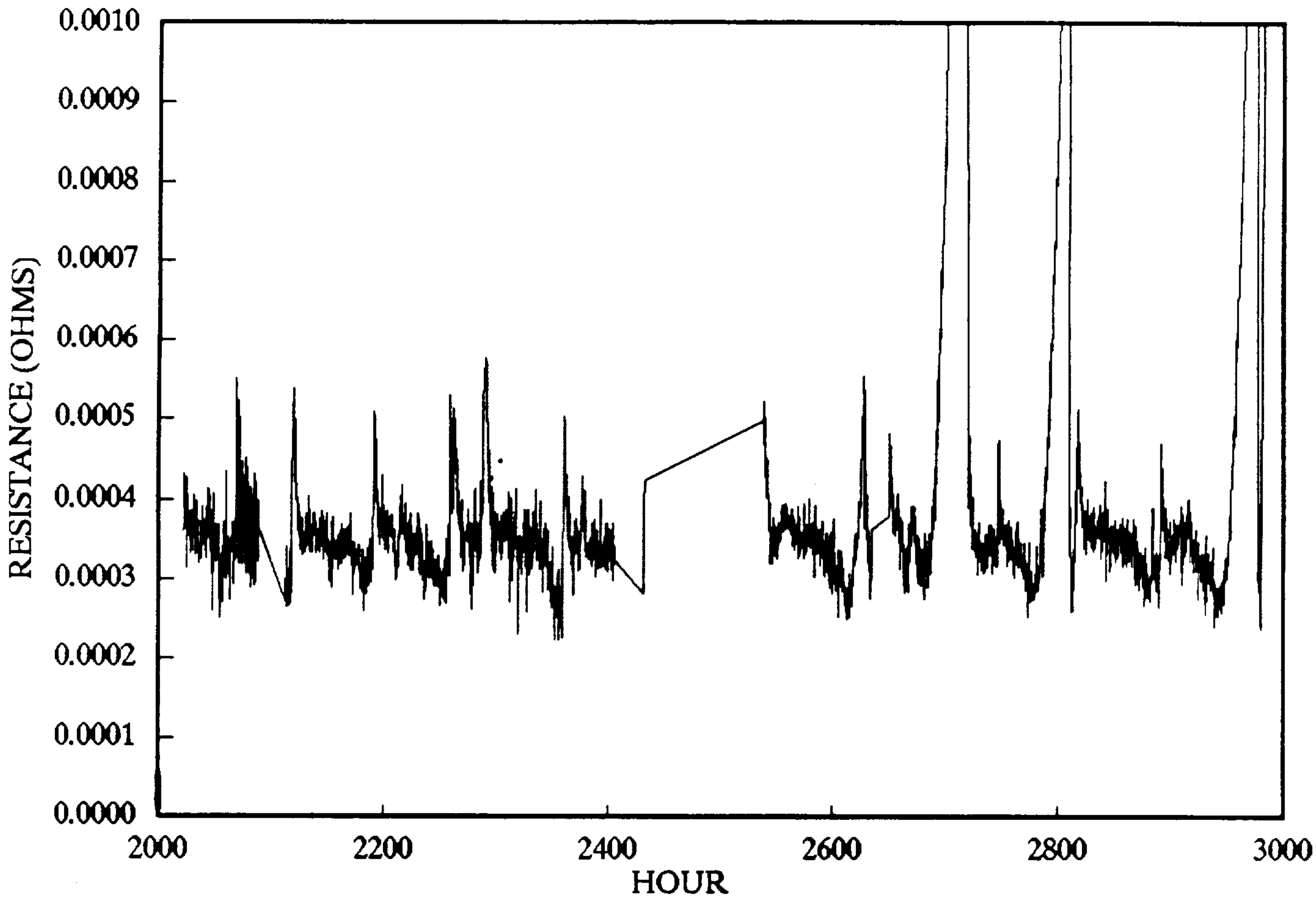


FIGURE 15 RESISTANCE VS. HOURS FOR SAMPLE 213
2000-3000 HOURS

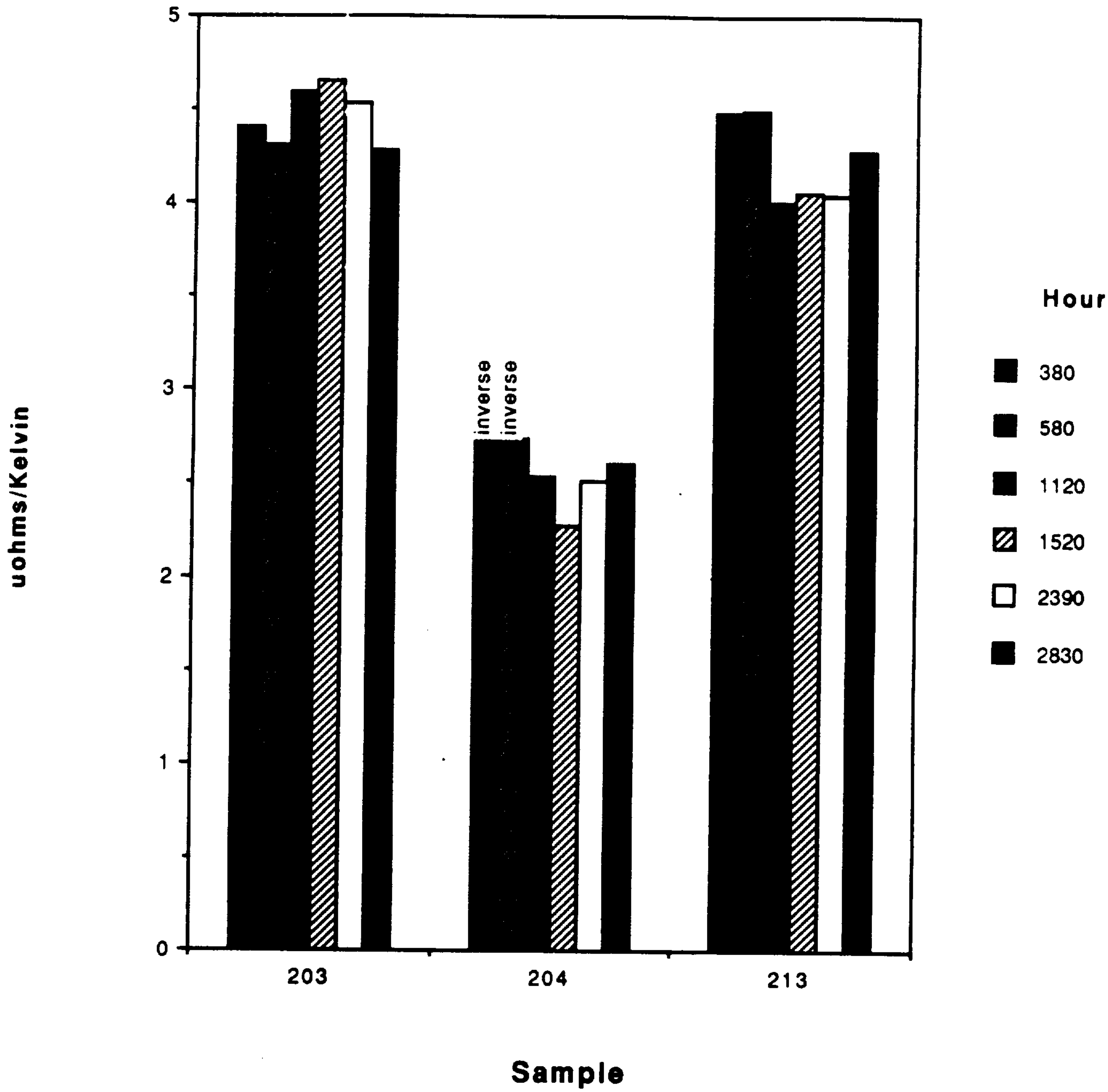


FIGURE 16 123 MATERIAL DEGADATION CHECK OF SAMPLES 203, 204, AND 213.

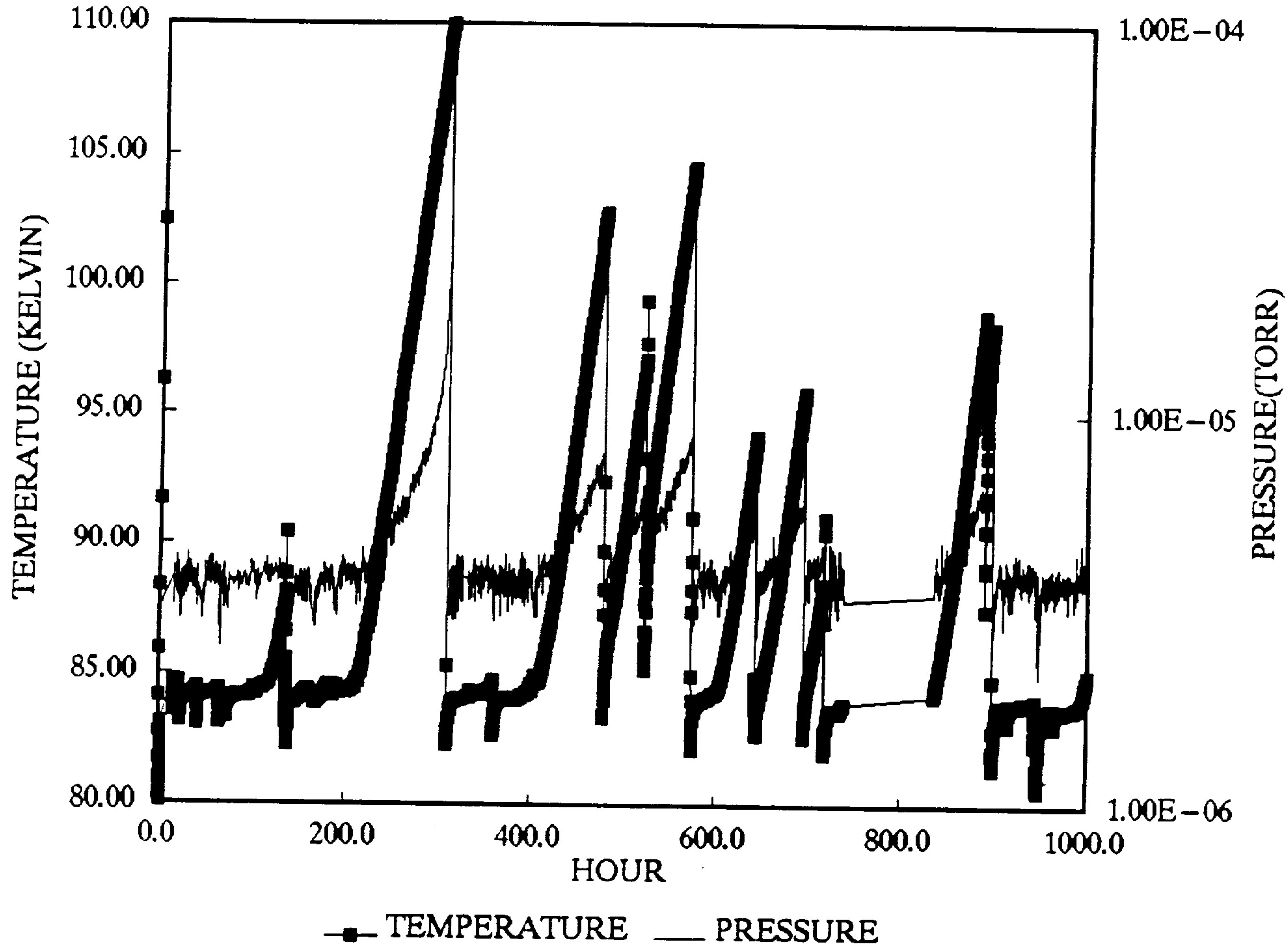


FIGURE 17 TEMPERATURE AND SYSTEM PRESSURE VS. HOURS
0-1000 HOURS

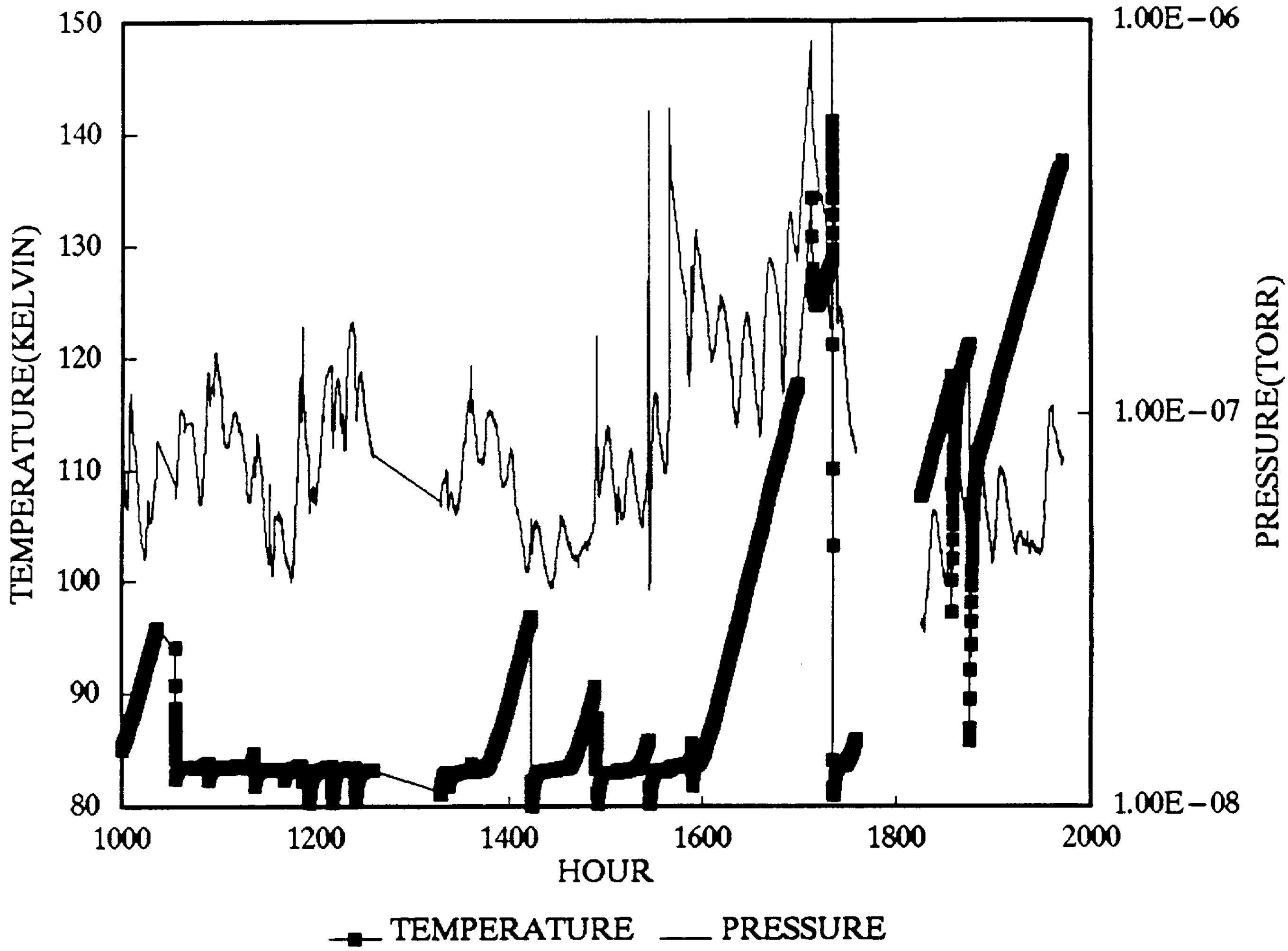


FIGURE 18 TEMPERATURE AND SYSTEM PRESSURE VS. HOURS
1000-2000 HOURS

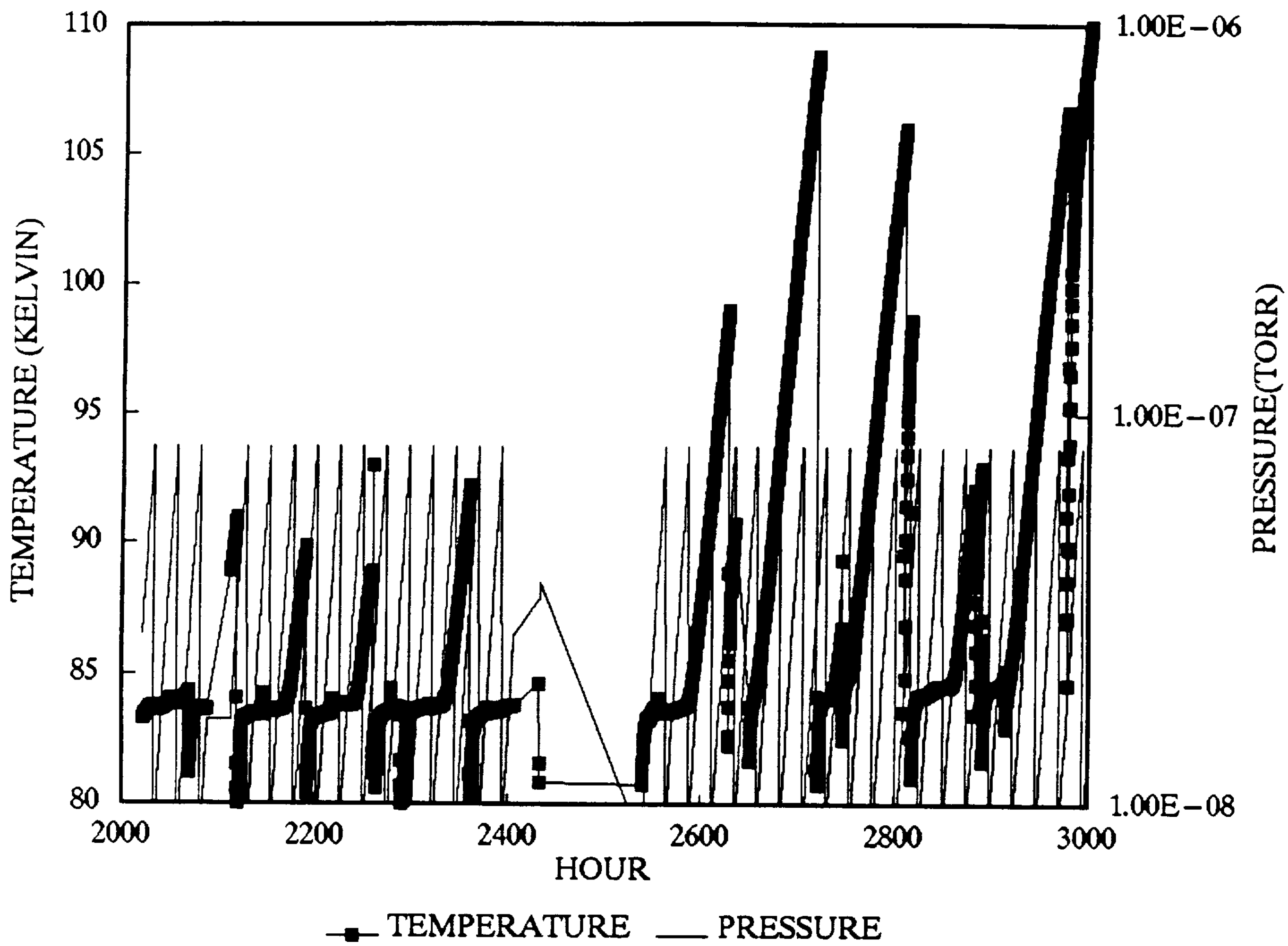


FIGURE 19 TEMPERATURE AND SYSTEM PRESSURE VS. HOURS
2000-3000 HOURS

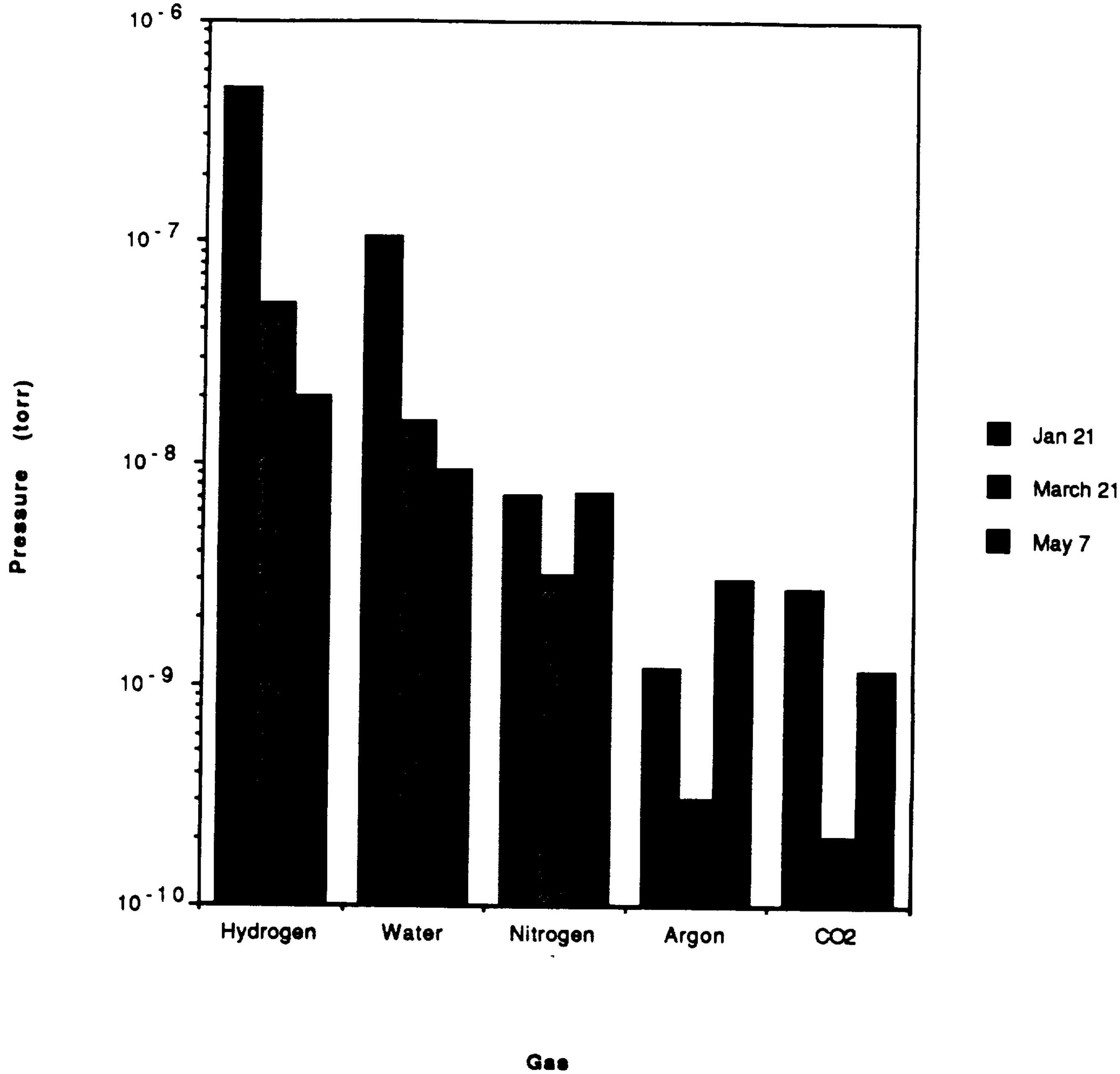


FIGURE 20 THE PARTIAL PRESSURES OF VARIOUS GASES PRESENT IN THE VACUUM SYSTEM AND THEIR CHANGE WITH TIME