Technical Report #5-32560
Contract Number NAS8-36955
Delivery Order No. 110

FNAS Materials Processing and Characterization

(5-32560)

Final Technical Report for the Period
January 12, 1991 through July 17, 1991

Principal Investigator

Dr. John P. Golben

Research Institute
The University of Alabama in Huntsville
Huntsville, AL 35899

Prepared for:

NASA Marshall Space Flight Center
Huntsville, AL 35812

ATTN: Eugene Urban
ES-63

5

NASA
National Aeronautical and Space Agency

Report Document Page

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
5-32560		

4. Titile and Subtitle

"FNAS Materials Processing and Characterization"

5. Report Due

07/17/91

6. Performing Organization Code

Research Institute, UAH

7. Aurthor(s)

John P. Golben

8. Performing Organization Report No.

5-32560

9. Performing Organization Name and Address

UAH Research Institute
RI E-47
Huntsville, AL 35899

10. Work Unit No.

11. Contract or Grant No.

NAS8-36955, D.O. 110

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Washington, D.C. 20546-001
Marshall Space Flight Center, AL 35812

13. Type of report and Period covered

Final Report

14. Sponsoring Agency Code

15. Supplementary Notes

16.Abstract

Research on melt-sintered high temperature superconducting materials is reported upon.

10 16

17. Key Words (Suggested by Aurthors(s))	18. Distnbution Statement		
High temperature superconductors, application of superconductors			
19. Security Class. (of this report)	**20. Security Class. (of this page)**	**21. No. of pages**	**22. Price**
Unclassified	Unclassified	16	TBA

NASA FORM 1626 OCT 86

PREFACE

This technical report was prepared by the staff of the Research Institute, The University of Alabamba in Huntsville. This report is to serve as documentation of technical work performed under contract number NAS8-36955, Delivery Order 110. Dr. John P. Golben was Principal Investigator. Dr. Eugene W. Urban, Chief of the Infrared & Cryogenic Physics Branch, Astrophysics Division, Space Sciences Laboratory, Science and Engineering, MSFC/NASA, provided technical coordination.

The views, opinions, and/or findings contained in this report are those of the author and should not be construed as an official MSFC/NASA position, policy, or decision unless so designated by other official documentation.

Except as otherwise provided by the contract, the distribution of any contract report in any stage of development or completion is prohibited without the approval of the Contracting Officer.

Prepared for MSFC
Marshall Space Flight Center, AL 35812

Principal Investigator

Approval:

Research Institute

TABLE OF CONTENTS

LIST OF FIGURES

INTRODUCTION

The research performed during the course of this delivery order was mainly involved with the preparation and characterization of melt-sintered high temperature superconductors. The PAR vibrating sample magnetometer was optimized to provide some of this characterization.

Melt-sintered samples include those prepared in-house, those samples received from Catholic University, and a sample received from Nippon Steel in Japan. In addition, other in-house samples were subjected to melt-quenching conditions in zero gravity. The preparation and characterization of these samples is discussed.

SUPERCONDUCTOR MATERIAL INVESTIGATIONS

Princeton Applied Research Vibrating Sample Magnetometer Set Up

A significant portion of the work in the present research was involved with measurements taken on the PAR vibrating sample magnetometer. Under the present contract, the system was set up and optimized. This involved efforts to isolate the system from mechanical interference (floor vibrations, pump connections, etc.), electrical interference (fields as a result of computers, power supplies, wires etc.), and atmospheric interference (water in the cooling lines). The insulating dewar required a higher vacuum than first expected. If this vacuum was not obtained then temperature stability could not be obtained. As we were normally using liquid nitrogen as the coolant in a dewar designed for liquid helium, we could not use the small heater that was present in the dewar set up. Hence, temperature stability by other methods was crucial.

It was desired to obtain as low a temperature as possible below the boiling point of liquid nitrogen so as to avoid temperature instability near that temperature. It was found that the dewar could obtain temperatures down to 58K. This ultimately was a problem in itself as nitrogen freezes at a temperature of 64K. At temperatures below 64K, a few scans could be obtained before the cooling lines froze. Nevertheless, the capability of the system to measure a sample below 60K provides a large range over which high temperature superconductors can be studied, since most of these superconductors have transitions above 90K. Of course lower temperatures can be obtained depending upon the availability of liquid helium.

With the magnetometer, important information concerning superconductors can be gathered without actually making contact with the sample. The magnetic susceptibility can be measured, and a good estimate of the superconducting volume fraction of the sample can be made. The transition temperature can also be measured (Figure 1 is an example of a sample with Tc=83K). An estimate of the degree of flux trapping can be surmized: propensity towards the "suspension" effect can be observed. An estimate of the critical current present in grains of the sample can be obtained using Bean's law. This data is probably superior to transport measurements since the latter involves contact resistance with the sample that might influence the data.

Melt-Sintering of Bismuth-based Superconductors

In a previous study, it was found that Sb substitution into the Bi-based superconductor system enhanced the formation of oriented thick films on the surfaces of the samples. The extent of this effect was later found to be sample dependent, i.e. there were other processing factors involved. It became clear that the

standing position. This was to minimize the contact of the samples with the crucible, and hence minimize any external reaction. This technique also served to maximize oxygen access to the sample, a result that is no longer desired as detailed above. For samples of the size needed, this technique would also result in slight curvatures and bending. A flat surface of alumina could be employed to avoid this problem; allowing crucible interaction with one side of the sample, but keeping the other side flat and interaction-free.

A major processing problem of these large samples that needs to be addressed is that of binding. Normally the size of samples processed are relatively small so that a very large pressure (35000 psi) can be applied to insure that the sample remains intact prior to the sintering step. Using the same equipment available under maximum conditions, the equivalent of only about one tenth of this pressure could be applied to the new larger samples. The temporary solution to this problem was simply to employ extreme care in the handling of the pre-sintered samples. Even with this care, more than 90% of the samples would not make it to the sintering step and had to be repressed. A suitable binder would help, but it was desired to avoid organic compounds since carbon would likely reside after the compounds were burned away. (Carbon has been shown to degrade superconducting properties.)

A possible solution to some of the above problems is to mix a small percentage of silver powder with the sample to facilitate mechanical bonding. While it is not clear that this would help in the binding of the pre-sintered sample, it clearly would help in the mechanical binding of the post-sintered sample. A few test samples with up to 15% Ag by weight, were very hard and well-bonded after heat treatments above 900C. Transition temperatures were not harmed by the presence of the Ag as evidenced by Figure 2 which demonstrates a sharp 90K transition for an Ytterbium 123/Ag composite. Normal state resistance can also be improved as well as the magnetic flux pinning if a suitable amount of Ag is employed.

KC-135 Results

Initial characterization of the Yttrium 123 samples melt-sintered in both the zero-gravity state and under 1g, demonstrated no particular advantage of the former state over the latter. However a microstructure study (SEM) needs to be performed to be more conclusive on this point. X-ray diffraction of the as-melted portion of the sample prepared in both states, demonstrated very little of the 123 phase present after melt-processing. Figure 3a demonstrates this point for the zero gravity sample. While the major peaks of the 123 phase can be discerned near 2theta=32 , the dominant phase is the Yttrium 211 "green" phase whose major peaks reside near 2theta=30 . The predominant phase here is the Yttrium 211 or "green" non-superconducting phase. Subsequent annealing/sintering at 927C

under oxygen re-formed the 123 phase in more than 90% of the sample (Figure 3b). In the scans shown the annealed zero-gravity sample (Figure 3b) appears slightly more oriented than the annealed ground-processed sample (Figure 3c), but this orientation is likely due to unequal grinding times employed for the powder diffraction samples. Inherently there is no major difference between the two groups of samples.

Magnetization measurements performed on both samples also showed no clear difference between the two groups of samples. A sample magnetization plot is shown (Figure 4). This scan is reminiscent of ordinary sintered samples and does not not exhibit the more symetric curves characterisitic of melt-sintered samples with enhanced flux pinning (to be shown later in this report). Hence, since these samples were not adequately melt-sintered, a true comparison of the zero-gravity state to the ground-processed state for this melt-sintering process cannot be made with these samples.

There were no specific expectations for the melt-sintering results from the KC-135 flights. The conditions that would be applied to the samples would be unique to any conditions applied in our own laboratory. The samples themselves were unique, as detailed above. For instance, it is clear that melt-sintering effects can be very sample dependent, especially as a function of sample size. For completeness, the samples that would be flown under the micro-gravity conditions were also be subjected to the same melt-sintering conditions on the ground, i.e. under 1g. But most likely these conditions would not be the most ideal for these particular samples. Or maybe more appropriately, the samples would not be the most ideal for the melt-sintering conditions prescribed. Since these samples were to be included in an already ongoing study of melt-quenching effects, the samples were subjected to conditions that had been optimized for other workers' samples. Still, the knowledge gained from this experience was very valuable. More insight into melt-sintering factors was obtained.

In conclusion, much was learned as to the proper sample preparation for these studies. The samples should be processed using oxide constituent powders. The heat treatments should be conducted in air at elevated temperatures. The samples should be quenched from these temperatures to avoid oxygen uptake. A small amount of silver binder may be added to improve the mechanical properties. If these microgravity experiments are continued, these and other techniques will be employed.

Bulk Melt-Processed Yttrium 123

In addition to studies of melt-sintered samples that are processed in-house, we also conducted characterization studies on samples given to us from other workers in the field. Details of the actual sample preparation of these latter samples are not specifically known. Inference from published papers indicates that the samples are processed at extremely high temperatures

(approaching 1400C) and that sometimes off-nominal stoichiometries are used. Samples from Catholic University (USA) and Nippon Steel (Japan) have been studied.

Several batches of samples from Catholic University were sent to us. The surface of a sample from Lot#231 demonstrated only slight orientation in the (00L) peaks (Figure 5a). Nevertheless this sample showed a pronounced orientation effect in the magnetization (Figure 6). The area encompassed by this latter curve was reduced by a factor of about three. Hence, magnetically these melt-sintered samples have a magnetic anisotropic effect, where the magnitude of the magnetization is three times greater perpendicular to the ab plane than parallel to this plane. The positive magnetization (1st quadrant) is characteristic of the propensity to exhibit the suspension effect. Indeed, lab demonstrations of this sample have shown it to suspend a magnetic weight of considerable size. Calculations involving Bean's formula would put the value of the critical current for these samples above 1000 Amps/sq.cm. Data from another Catholic University sample is also shown in Figure 7. A similar orientation effect to the first sample is observed as well as a similar range of values for the flux contained and the critical current calculated. The other samples received from Catholic University are not as good as the ones shown. These samples exhibit more of the Yttrium 211 "green" phase. Evidently, different attempts by this particular group to optimize the melt-sintering process involved broad changes in the amount of Yttrium 211 phase present in the nominal composition.

The range of critical currents observed for the Catholic University samples is an order of magnitude higher than the transport critical currents measured on our in-house samples. To be sure, the magnetic method would in general estimate critical current values far above values obtained from transport measurements since the former method reflects inter-grain interaction while the latter requires a percolating path (or intra-grain interaction) through the sample. Still, the higher processing temperatures available in other labs probably allow for a more pronounced melt-sintering effect.

Even the Catholic University samples are outdone by the sample sent to us by Nippon Steel in Japan. This latter sample exhibited large grain formation on the surface. X-ray diffraction analysis demonstrated this grain formation to be highly c-axis oriented, i.e. the ab plane lies along the plane of the surface (Figure 5a). Such orientation is similar to melt-sintered samples produced in-house (Figure 5c) and to single crystals produced in-house (Figure 5d). The single crystal pattern can in-effect be used as a standard.

Magnetization measurements on the Nippon Steel sample demonstrate a pronounced change in the magnitude of the magnetization (up to a factor of 4) with orientation, while the flux encompassed changes by a lesser factor (Figure 8). The total area of the magnetization curve is 2 orders of magnitude larger than the area of the Catholic University samples. Hence

the critical current of this sample is more in the range of 100000 amps/sq.cm., which is only about 1 order of magnitude less than that observed for thin films or single crystals. This sample demonstrates that the bulk processing is beginning to approach the success of thin films and crystals.

FIGURE 1

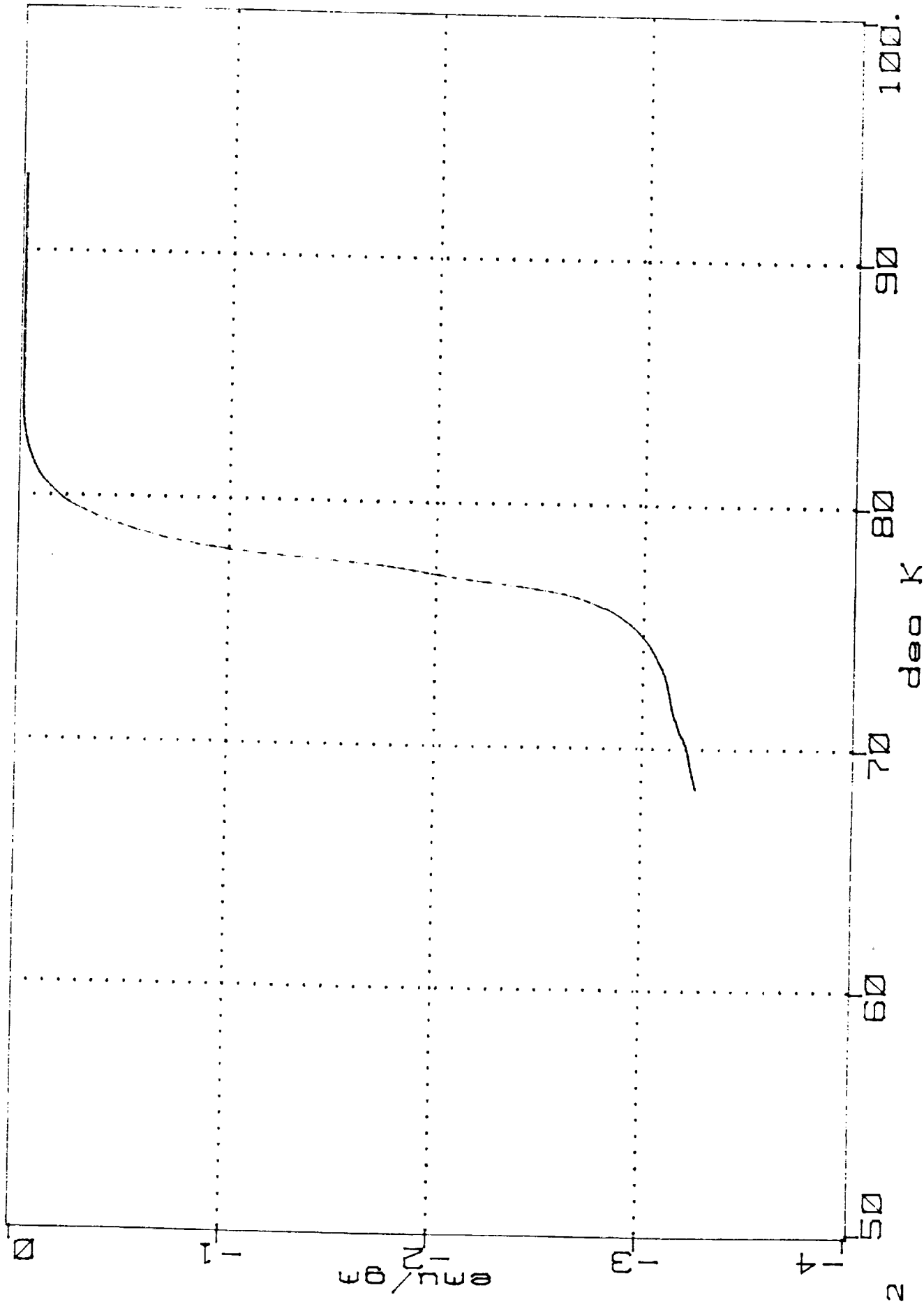


FIGURE 2

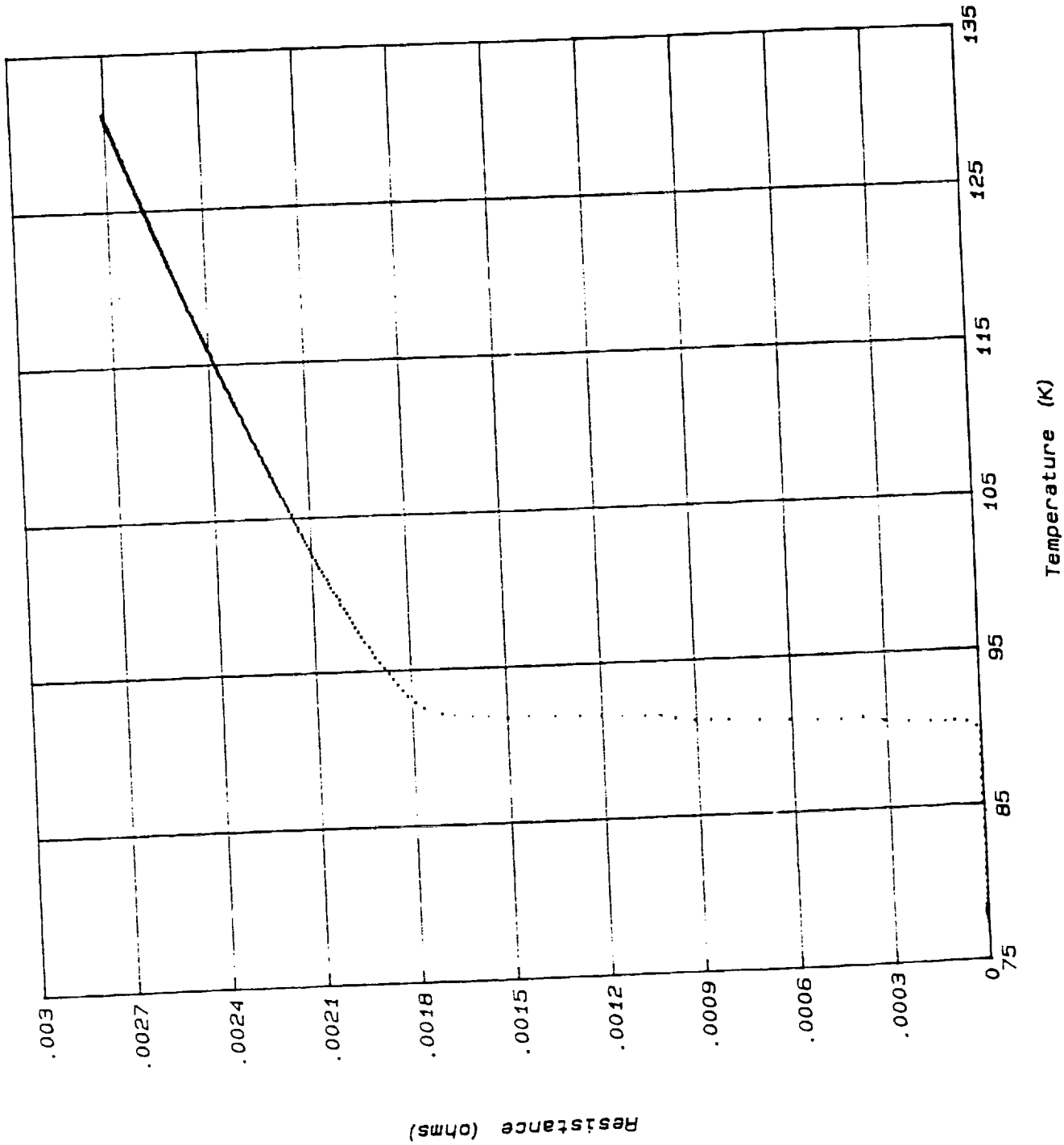

.003
.0027
.0024
.0021
.0018
.0015
.0012
.0009
.0006
.0003
0
Resistance (ohms)
75
85
95
105
115
125
135
Temperature (K)

FIGURE 3

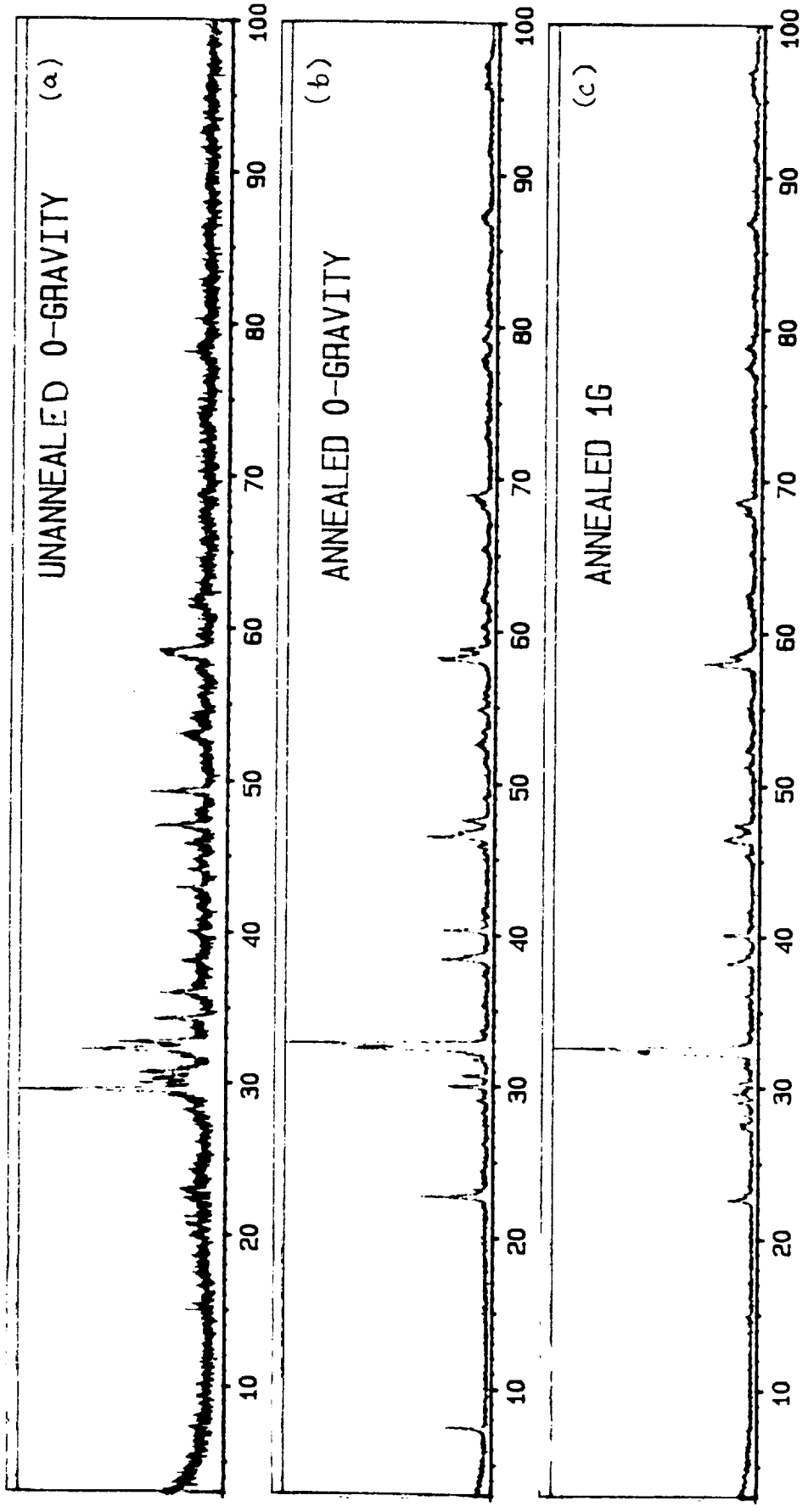

UNANNEALED 0-GRAVITY
(a)
ANNEALED 0-GRAVITY
(b)
ANNEALED 1G
(c)
10
20
30
40
50
60
70
80
90
100

FIGURE 4

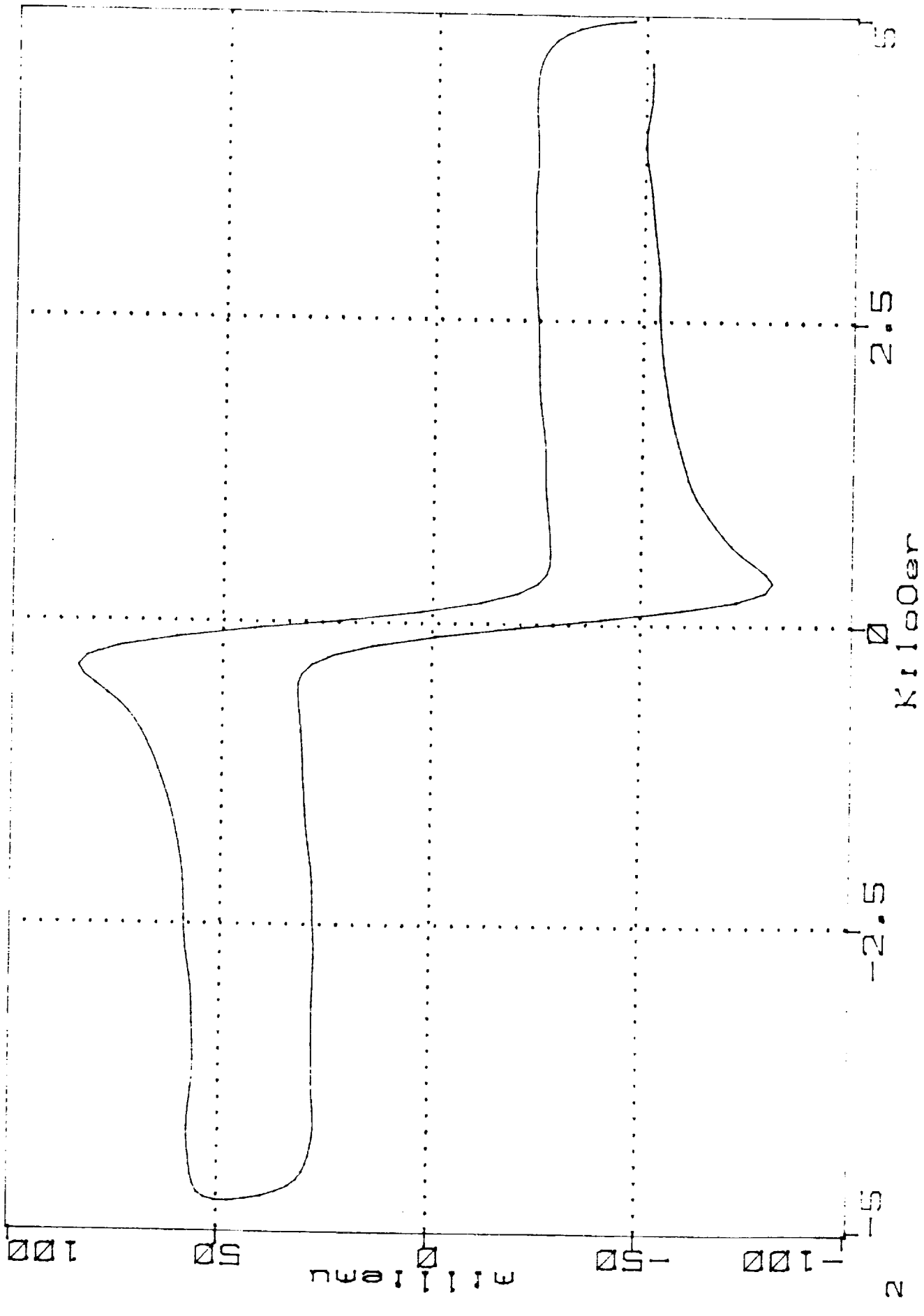
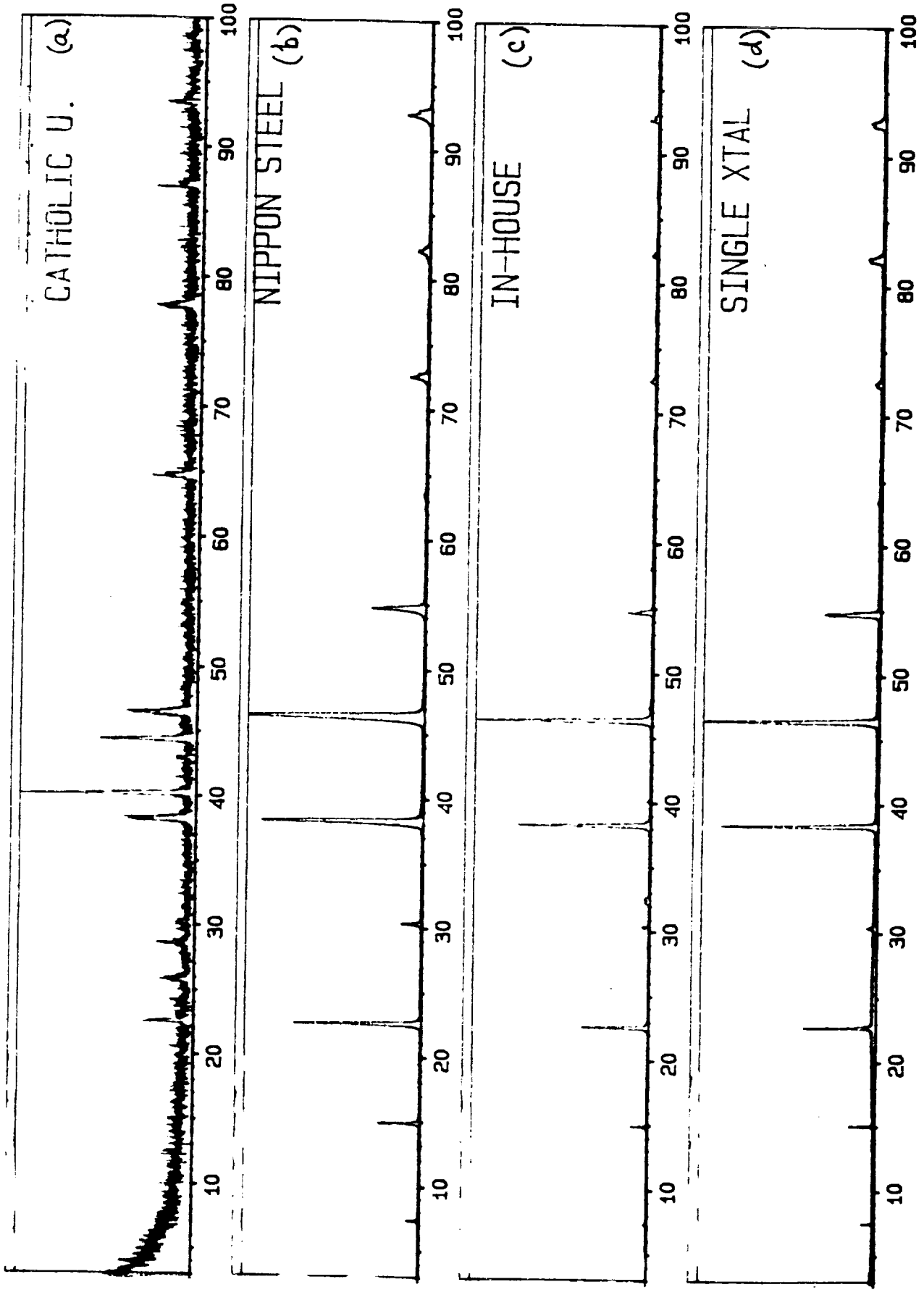
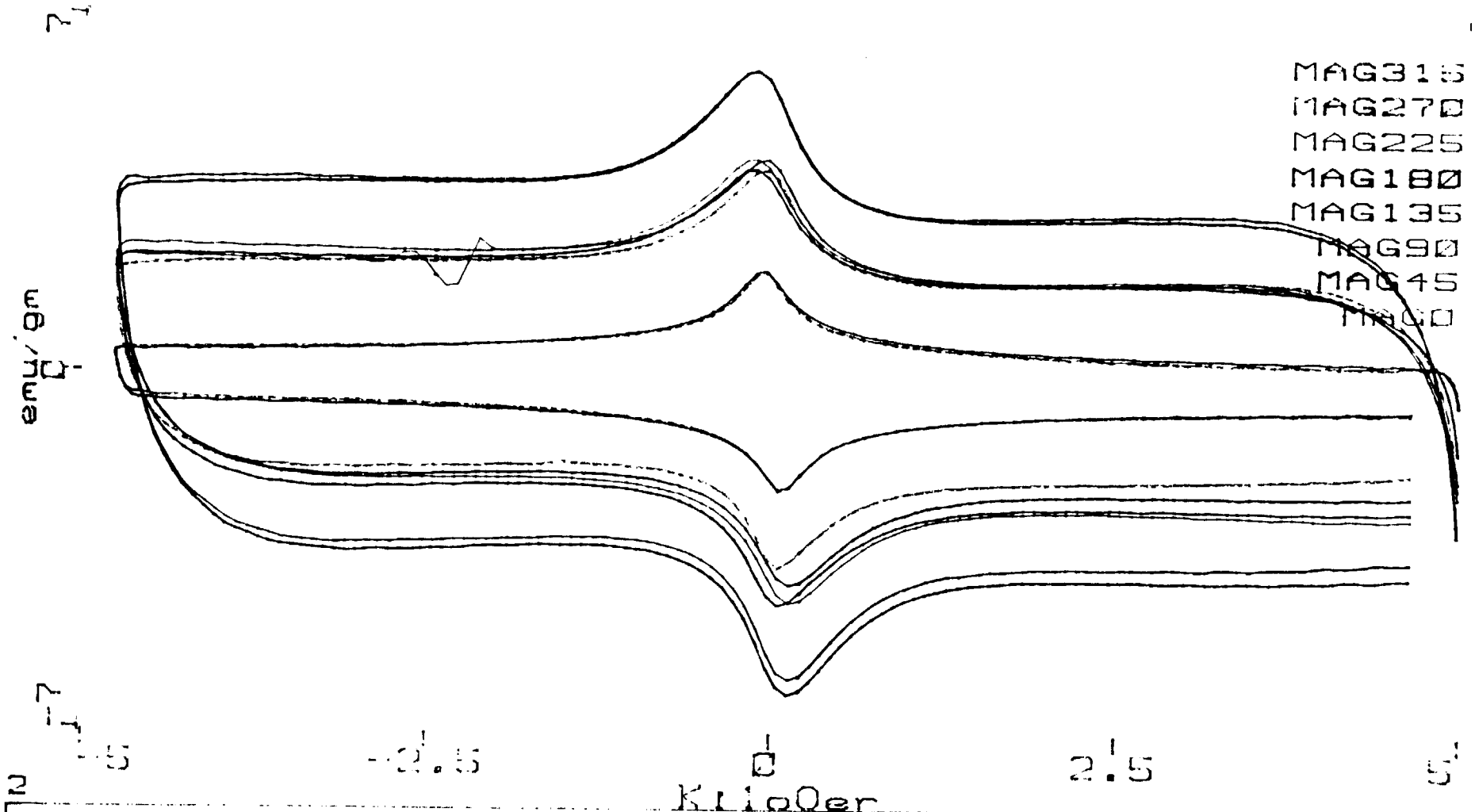


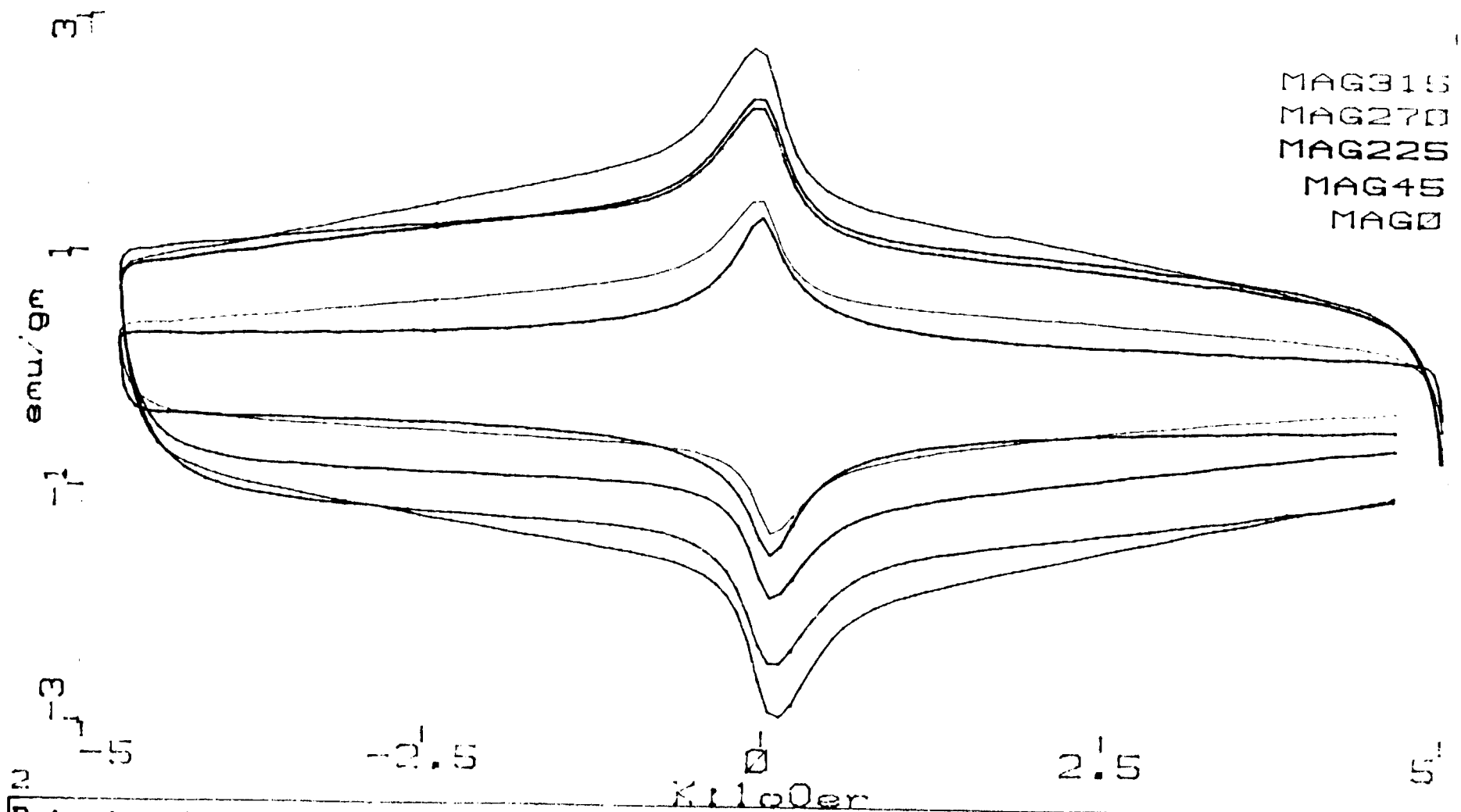
FIGURE 5


CATHOLIC U. (a)
NIPPON STEEL (b)
IN-HOUSE (c)
SINGLE XTAL (d)
10
20
30
40
50
60
70
80
90
100



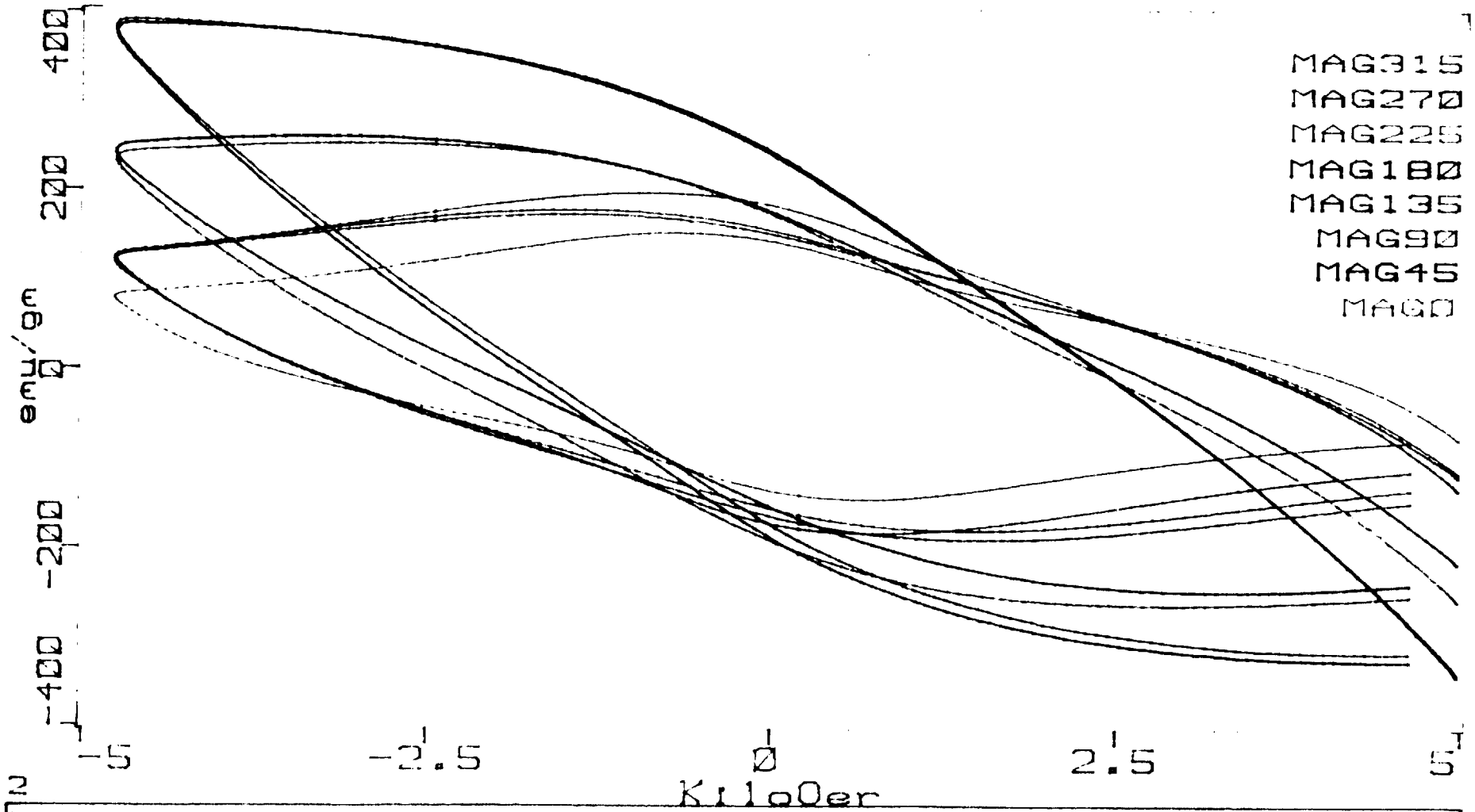
Retentivity 3.785 EMU/gm	Mass 0.0275 gm	Date 04/24/91	Operator ID J.P. Golben
Sample ID Cath.U. Lot#230	Magnetization 3.993 EMU/gm	Squarness Ratio 0.948 EMU/Oer	Coercivity 2328 Oer
Sweep Time 30 Min	Time Constant 1 sec	Filename mag233.dat	Total Area 4.101e+004 ergs/gm

FIGURE 6



Retentivity 1.298 EMU/gm	Mass 0.06 gm	Date 04/24/91	Operator ID J.P. Golben
Sample ID Cath. U. Lot#231	Magnetization 1.502 EMU/gm	Squarness Ratio 0.8644 EMU/Oer	Coercivity 0 Oer
Sweep Time 30 Min	Time Constant 1 sec	Filename mag234.dat	Total Area 1.139e+004 ergs/gm

FIGURE 7



Retentivity 182 EMU/gm	Mass 0.0179 gm	Date 05/31/91	Operator ID J.P. Golben
Sample ID Nippon Steel YBCO	Magnetization 264.2 EMU/gm	Squarness Ratio 0.6889 EMU/Oer	Coercivity 2429 Oer
Sweep Time 30 Min	Time Constant 1 sec	Filename mag334.dat	Total Area 2.316e+006 ergs/gm

FIGURE 8

CONCLUSIONS

The vibrating sample magnetometer has now become a valuable and common characterization tool for our study of high temperature superconductors. Important information regarding the superconducting properties of a sample can be obtained without actually making contact with the sample itself.

A step toward microgravity processing of high temperature superconductors has been taken. In the future, the samples need to be optimized prior to this processing of the samples before the specific effects of the microgravity environment can be isolated. Much has been learned about what optimization needs to take place. The adaptation to larger bulk superconductor samples is also being performed.

A series of melt-sintered samples from Catholic University, Nippon Steel, and those synthesized in-house, demonstrate that bulk processing of high temperature superconductors is getting better. Particularly, the success of the Nippon Steel sample suggests that higher temperatures during processing is essential.