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HIGH-TEMPERATURE CERAMIC SUPERCONDUCTORS

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GENERAL ATOMICS

1. INTRODUCTION

This is the second quarterly progress report on the work performed in the period from October 1, 1988 through December 31, 1988 on ONR Contract N00014-88-C-0714, entitled "High-Temperature Ceramic Superconductors." The principal objectives of this program are (1) to demonstrate fabrication of high-temperature ceramic superconductors that can operate at or above 90 K with appropriate current density, J_c, in forms useful for application in resonant cavities, magnets, motors, sensors, computers, and other devices; and (2) to fabricate and demonstrate selected components made of these materials, including microwave cavities and magnetic shields.

1.1 PROJECT OUTLINE

This program has been divided into six tasks: (1) metal alkoxide synthesis and processing, (2) microstructural evaluation and property measurement, (3) electrical and magnetic property measurement, (4) superconductor ceramic processing, (5) component fabrication and demonstration, and (6) reporting.

Task 1 is to synthesize a homogeneous alkoxides solution that contains all the constituent elements which can be easily made to powders, thin film, or drawn into fiber form. Ideally, this solution should possess precise stoichiometry, adequate stability, polymerizability, adherence, and spinnability. Also, the polymeric materials formed from this solution should be thermosetting, be able to be dissolved in organic solvents and contain as little as possible low-temperature pyrolyzable organics with high char yield.

Task 2 is to study the microstructure as a function of processing parameters. The study includes: density, pore size and pore size distribution, phase identification, chemical composition and purity, environmental stability, effects of heat treatment, residual strain, seeding, annealing in magnetic fields, and epitaxy on grain growth and orientation.

Task 3 is to study the electrical and magnetic properties of the $YBa_2Cu_3O_7$ (1,2,3) high T_c ceramic superconductors. It will include both the ac electrical resistance (R_{ac}) and the ac magnetic susceptibility (χ_{ac}) magnetic properties.

Task 4 is an investigation of superconductor ceramic processing. Most of the important applications of superconductors require material in the form of fiber or films. Magnets, conductors, motors, and generators are examples of applications employing fiber; while detectors, microwave cavities, and microcircuitry require superconducting material in the form of films. The sol-gel process is ideally suited to producing materials in these forms; in fact, it is used commercially to produce antireflection and mirror coatings, and to produce continuous ceramic fibers, for structural reinforcement in composite materials, and for thermal insulation.

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Task 5 is to demonstrate component fabrication. GA will design and build a high Q, high T_c superconducting cavity using its unique sol-gel coating process capabilities. This task would proceed after some initial coating tests verified dc superconductivity and questions of adhesiveness, surface preparation, and processing procedures are answered. As the fabrication process and the materials quality are improved throughout the three-year program, two additional cavities will be constructed and tested. Coupling would be through a waveguide inductive iris into an end wall with a logarithmic decrement technique of Q measurement being considered most appropriate for the high Q anticipated. An X-band (10 GHz) frequency choice allows for convenient dimensions of 4.3 cm diameter by 2.8 cm height.

This report will focus mostly on the first task and briefly on tasks 2, 3 and 4.

2.0 PROGRESS

2.1 TASK 1 - METAL ALKOXIDE SYNTHESIS AND PROCESSING

2.1.1 SYNTHESIS

As mentioned in the previous report, in order to obtain precursors with the proper chemical stoichiometry to give the 123 compound, it is advantageous to use homogeneous liquid solutions of the metallic components. Synthesis using the required ions and an organic acid (ref. 1), the hyponitrites (ref 2), yttrium and barium alkoxides with different coordination compounds of copper (ref's. 3 - 6) have been reported.

We are attempting to determine which one of these syntheses will yield superconducting films and fibers capable of carrying high currents at critical temperatures approaching 90K. During this report period, we have successfully prepared the 123 compound by combining certain aspects from syntheses reported by Payne (ref 3) and Mecartney (ref 4).

Homogeneous 123 precursor solutions were prepared in 2-ethoxyethanol using $Y(OR)_3$, $Ba(OR)_2$, and the soluble copper II mixed-ligand species $(C_5H_7O_2)_2Cu_2(\mu\text{-}OR)_2$, where $R=CH_2CH_2OCH_2CH_3$ and $C_5H_7O_2$=2,4 pentanedionate. The 2-ethoxyethoxo compounds were chosen instead of the 2-methoxyethoxo compounds used by Payne in order to increase the solubility.

2.1.2 EXPERIMENTAL

$(C_5H_7O_2)_2Cu_2(u\text{-}OCH_2CH_2OCH_2CH_3)_2$(I) was obtained as a turquoise blue solid by alcohol exchange from Di-u-methoxo-bis(2,4-pentanedionato)-dicopper (II). The latter compound (II) was synthesized using the procedure of Bertrand and Kaplan (ref 7). 3.316 g (0.0086) mole of II was placed in an dry 125 ml standard-taper ehrlenmeyer flask along with 15 ml of dry 2-ethoxyethanol. The exit of the flask was protected from moisture with a Drierite tube. The mixture was stirred with a magnetic stirrer and heated in an oil bath at 115°C. After one hour the Drierite tube was removed and a dry nitrogen purge was established over the solution. The solvent evaporated in 15 minutes and an additional 6 ml of hot, dry

2-ethoxyethanol was added to dissolve the product. After cooling, a turquoise blue solid crystallized from the blue solution. The solid was recrystallized from hot 2-ethoxyethanol giving 4.056 g (.0081 mole, 94% yield).

A 0.534 M stock solution of $Y(OCH_2OCH_2CH_3)_3$ was prepared by alcohol exchange of Y(III)isopropoxide. In an oven-dried 100 ml round bottom flask was placed 30 ml of dry 2-ethoxyethanol and 6.814 g (0.0256 mole) of $Y(OC_3H_7)_3$ (prepared by reaction of yttrium with dry isopropyl alcohol). The flask was fitted with a dry Claisen head and water condenser. All exits were protected from moisture ingress with Drierite tubes. The solution was heated in an oil bath at 100C for 1.5 hours and then the bath temperature was increased to 155C. The solution was refluxed for 45 minutes and the distillate boiling between 85-90C was removed. The remaining yellow solution was cooled and transferred to a storage container while under a dry nitrogen atmosphere. The volume was adjusted to 50 ml with dry 2-ethoxyethanol. The concentration of $Y(OCH_2CH_2OCH_2CH_3)_3$ was determined gravimetrically after hydrolyzing a known volume with water and calcining at 900°C.

Typically, homogeneous solutions containing the 123 compounds were prepared by reacting 0.033g (0.00024 mole) of barium granules (Alfa Products) with 0.225 ml of the stock yttrium alkoxide (0.00012 mole) and 0.275 ml dry 2-ethoxyethanol. The barium reacted completely in about 2 hours at room temperature. To this solution was added 0.0914 g (0.00036 mole Cu) of the Cu(II) compound, which dissolved readily. After stirring at room temperature for 20 minutes, 1 to 10 equivalents of water per mole of alkoxy ligand were added. After a 1 to 4 hour reaction time, the solvent was removed under vacuum at 56°C giving a black powder.

Figure 1 shows the decomposition behavior of a precursor powder when heated in oxygen at 1 C/min. Three regions of rapid weight loss are observed: 150-200C, 550-600C, and 775-825 C. The total weight loss for this sample approaches 50 wt%. The 25 % loss at temperatures less than 200 C is thought to be bound solvent and water since a sample dried in a vacuum oven at 135 C lost only about 5 wt% up to 200 C. Furthermore, the latter sample lost only a total of 28 wt%. We are currently attempting to use gas chromatography to determine what species are evolved during the several regions of weight loss.

Based on figure 1, a sample of 123 powder was prepared by calcining in oxygen according to the following schedule:

1) heat at 60°C/hr to 900 C
2) hold 5 hr at 900°C
3) cool at 300°C/hr to 500°C
4) hold 5 hr at 500°C
5) cool to room temperature

Figure 2 shows the x-ray diffraction pattern for material prepared as described above using 3.6 equivalents of water per mole of alkoxide ligand. The diffraction data indicate that the 123 compound is clean, with undetectable amounts of barium carbonate, copper oxide, or barium cuprate which have been found as contaminates in other syntheses.

Current work is concentrating on understanding the decomposition process for the 123 precursor. In addition to determining the gases evolved during the decomposition, differential thermal analysis (DTA) is being used to determine the temperature of phase changes or decomposition reactions.

3.0 HIGH T_c CERAMIC SUPERCONDUCTOR FIBER

3.1 REQUIREMENT

Again as reported in the first quarterly report, the sol-gel derived ceramic fiber with the required electromagnetic properties must have the right stoichiometry and reproducibility; good flexibility at green state; retain flexibility after heat treatment; adequate strength and modulus; and above all acceptable superconductivity with appropriate current density.

3.2 PREPARATION OF SOLUTION WITH FIBER FORMING ABILITIES

The stock solution containing all the necessary elements as described previously was concentrated by using a rotovaporator to remove isopropanol instead of by distillation. This gives rise to a greenish viscous solution as contrast to a brownish-green solution obtained by distillation.

The dried mass was dissolved in benzene and was further concentrated in a vacuum oven. Filaments of 20-30 cm long and 1/2 - 1 mm (sample 9997.S28) in diameter can be hand-drawn (Figure 3). Fibers of diameter ranging from 20-200 microns can also be obtained by adjusting the amount of benzene in the viscous solution.

As a first try, the fibers were subjected to 897°C, 3 hours heat treatment in air to determine the crystal phase in the fibers. The x-ray diffraction shows the phase in the fibers is almost pure orthorhombic $YBa_2Cu_3O_{7-x}$ with only very small amount of Y_2BaCuO_5 phase (Figure 4). These filaments were further annealed in a furnace with flowing oxygen, first at 700°C for 1 hour, then 450°C for 2 hours for optimizing oxygen stoichiometry. The resistance- temperature curve (sample 9997.S28-H1) shows the transition at 89.5 K and $T_{R=0} = 70$ K (Figure 5). However, the resistance-temperature can be quite different by different heat treatment schedule (Figure 6). This indicates that suitable heat treatment schedule for optimal electrical properties should be further investigated.

Four additional batches of solution (samples 9997.S29 - 9997.S32v5) have been prepared to examine the reproducibility of this method. From all of these solutions, fibers have been successfuly drawn (Figure 7). Fibers prepared from these solutions and heat treated at 875°C-920°C all exhibit nearly single phase $YBa_2Cu_3O_{7-x}$ with only very small amounts of Y_2BaCuO_5 indicating "123" compound can be reproducibly prepared by this method (Figure 8). Subsequent experiments indicated that single phase orthorhombic $YBa_2Cu_3O_{7-x}$ can be obtained by calcining these fibers at 900°C for 4 hrs in flowing O_2 (Figure 9).

3.2.1. HEAT TREATMENT SCHEDULE STUDY

The heat treatment schedule must be optimized not only for better electrical properties but also for good mechanical properties. At present time, the first goal is to find a heat treatment schedule that will result in fibers with a reasonable length (e.g. 5-10 cm) and, at the same time, without any blisters or microcracks. Additionally, the fibers should also be straight and not wavy. Also the fiber should be relatively strong and capable of being bent without fracture.

To obtain fiber which does not break into small pieces and remains straight, the determining factor is to find a heat treatment schedule which controls the organic removal rate and minimizes the shrinkage stress at relatively low temperature to avoid microcracks which translate to adequate mechanical strength. Additionally the fiber should have a desirable microstructure (no porosity, small grain size and smooth surface). This critical heat treatment temperature for controlling the microstructure most likely is in the range of 400-1000°C.

From TGA study, weight loss occurs at 200-300°C (Figure 10). Another weight loss starts from 800°C probably due to decomposition of carbonate. this indicates that the heat treatment at 200-450°C region will be critical for the fiber to remain intact and straight. Also, the formation of barium carbonate should be suppressed by further tailoring the solution chemistry or by modifying the heat treatment schedule. From DTA, the exothermic peaks are from 200-450°C (Figure 11). More detailed studies of DTA and TGA traces are needed to understand the meaning of these exothermic peaks to find the favorable low temperature heat treatment schedule. Presently, high temperature heat treatment of the fibers is arbitrarily chosen at 875°C-950°C as the starting condition for examining the microstructure development. Again, the fibers show different morphology using different heat treatment schedules. Sometimes, flat fibers with a dense crust and porous interior were obtained (Figure 12). Relatively dense and circular cross- sectioned fibers have also been obtained (Figure 13). Also, fibers with uniform submicron grain size have been formed at 875°C, for 10 hours and at 925°C for only 1 minute (Figure 14).

Fibers as long as 8 cm long (limited by the present size of furnace) were obtained after 875°C - 920°C heat treatment. It is noted that the fibers are relatively strong but they are usually slightly wavy. However, they are flexible and can be bent into small radius (Figure 15).

The experimental result obtained to-date indicates that the drifting of the solution from desired stoichiometry has been overcome and the heat treatment schedule for relatively strong mechanical properties of the fiber needed has been established. Searching for heat treatment schedule for better electrical properties is still in progress. Whenever optimized heating and processing conditions are found, improved electromagnetic properties are anticipated.

4. ELECTRICAL AND MAGNETIC PROPERTY DETERMINATION

4.1 In this section, the measurements made on $Y_1Ba_2Cu_3O_{7-\delta}$ powders and some of the first $YBa_2Cu_3O_{7-\delta}$ fibers are reported. Powders prepared by the sol-gel technique were pressed into pellet form, annealed in O_2 at 973°C for 14 h, and cooled in O_2 over a 12 h period. X-ray diffraction scans of the powders and reground pellets were identical and consistent with a high-T_c perovskite structure with less than 5 volume percent of impurity phases. Rectangular specimens were cut from the pellets with a diamond wheel saw. Figure 16 shows the resistivity of an O_2-treated specimen as a function of decreasing temperature T in zero applied magnetic field. We define T_n as the temperature at which the resistivity drops to the fraction n of the extrapolated normal-state value. The critical temperature $T_c = T_{0.5}$ has a value of 91 K with a transition width $\delta T = T_{0.9} - T_{0.1}$ of less than 2 K. These values are in good agreement with published values for samples prepared by solid-state reaction.

Resistivity measurements were also carried out in applied magnetic fields H up to 10 T. The transitions broadened with increasing H, suggesting some inhomogeneity and/or magnetic field anisotropy. Figure 17 shows upper critical fields H_n at which the resistivity drops to the fraction n of the extrapolated normal-state value at the field. Ignoring the curvature of H_{c2} vs. T in low fields, the initial upper critical field slope $(dH_{c2}/dT)T_c = -2.75$ T/K for n = 0.5. These results are also in agreement with data reported for samples prepared by solid-state reaction (Ref. 8).

Magnetic susceptibility data were taken by first cooling in zero field; then a field of H = 25 Oe was applied and the susceptibility was measured for increasing temperatures. Subsequently, the Meissner signal was measured by cooling in the applied field, and are shown in Figure 18. The onset of superconductivity occurs below 89 K. The strength of the diamagnetic signal was greater than the Meissner signal by a factor of 3.9.

The magnetization M was also measured as a function of magnetic field. After cooling the sample in zero applied field, the magnetic field was increased to 50 kOe and decreased back to zero at a fixed temperature of 5 K. These results shown in Figure 19 can be used to estimate the critical current density using Bean's critical state model (Ref. 9). In this model, the current density is assumed to be uniform over the volume of the sample, and is given by

$$J_c(\mathrm{A/cm^2}) = F\Delta M(\mathrm{emu/cm^3})d/(\mathrm{cm}),$$

where F is a geometrical factor such that $F \cong 34$ for a sphere of diameter d (Ref. 10), and $F \cong 30$ for a long cylinder of diameter d with H parallel to the cylindrical axis (Ref. 11). The estimated critical current density as a function of the applied field is shown in Figure 20, where the values of F = 30 and d = 0.0075 cm (the pellet thickness) were used. At 5 K, the critical current density has values of $J_c \cong 4.1\times10^4$ a/cm² at 3 kOe and $J_c \cong 1.0\times10^4$ A/cm² at 50 kOe. These estimates are consistent with published values for polycrystalline bulk samples (Ref. 12).

The magnetic susceptibility for some of the first $Y_1Ba_2Cu_3O_{7-\delta}$ sol-gel fibers have also been measured. For a sample annealed in air at 850-900°C for 6 h and at 500°C for 3 h shown in Figure 21, it was found that the onset of superconductivity is at approximately 86 K. Although the magnetic transition was broad, we believe that it can be narrowed in samples prepared under more carefully controlled annealing conditions and with continuing refinements in the future sample preparation techniques.

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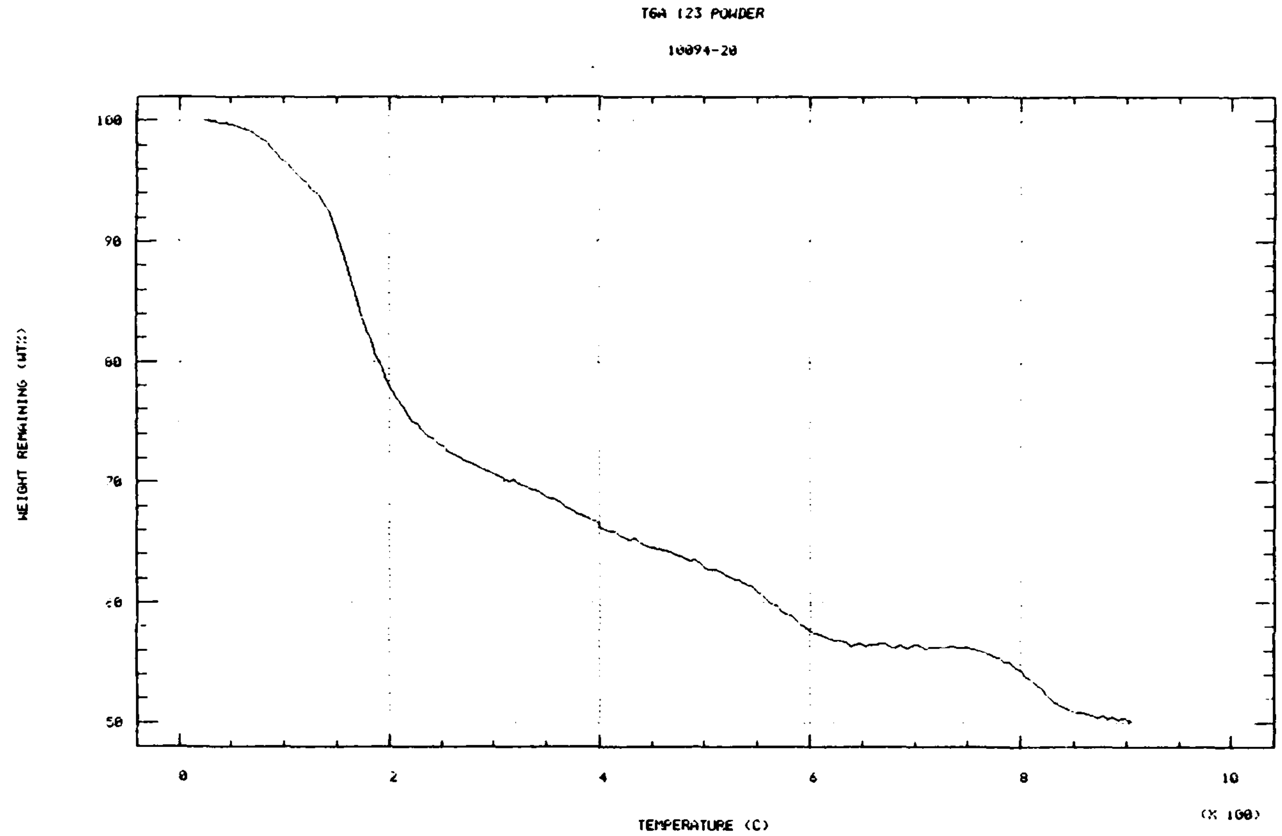

Figure 1. Weight loss as a function of temperature during calcining of 123 precursor in O2 at 1C/min.

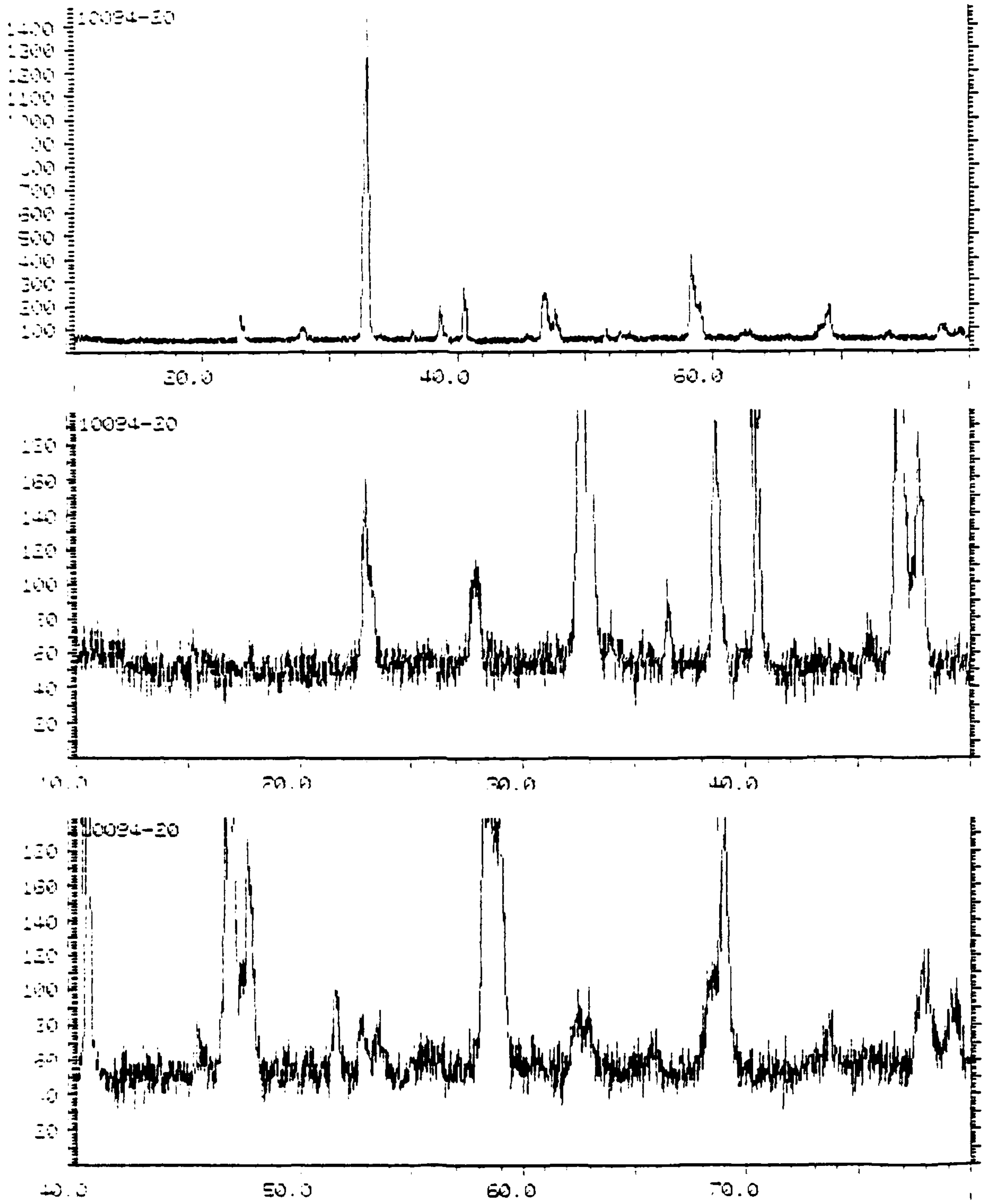

Figure 2. X-ray diffraction pattern for powder obtained by hydrolysis of 123 Y:Ba:Cu solutions with 3.6 equivalents of water per mole alkoxide.

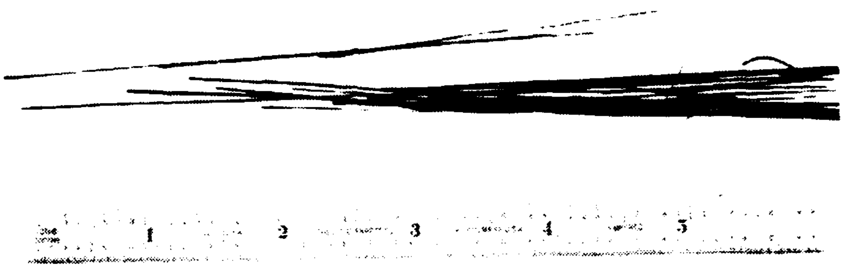

Figure 3. Hand-drawn pre-ceramic superconducting fibers, (sample 9997.S28).

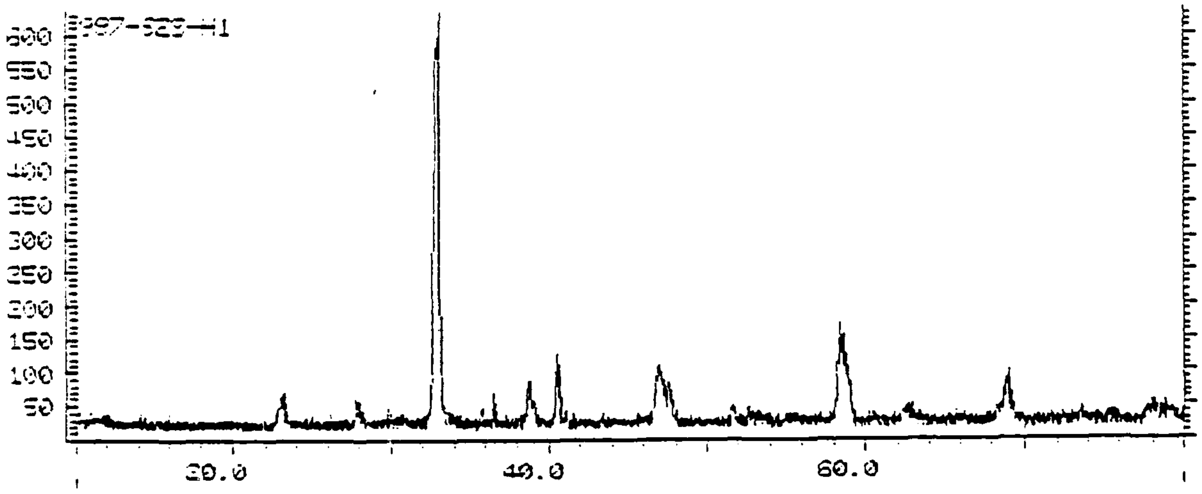

Figure 4. X-ray diffraction pattern of the fiber after 897°C, 3 hours heat treatment.

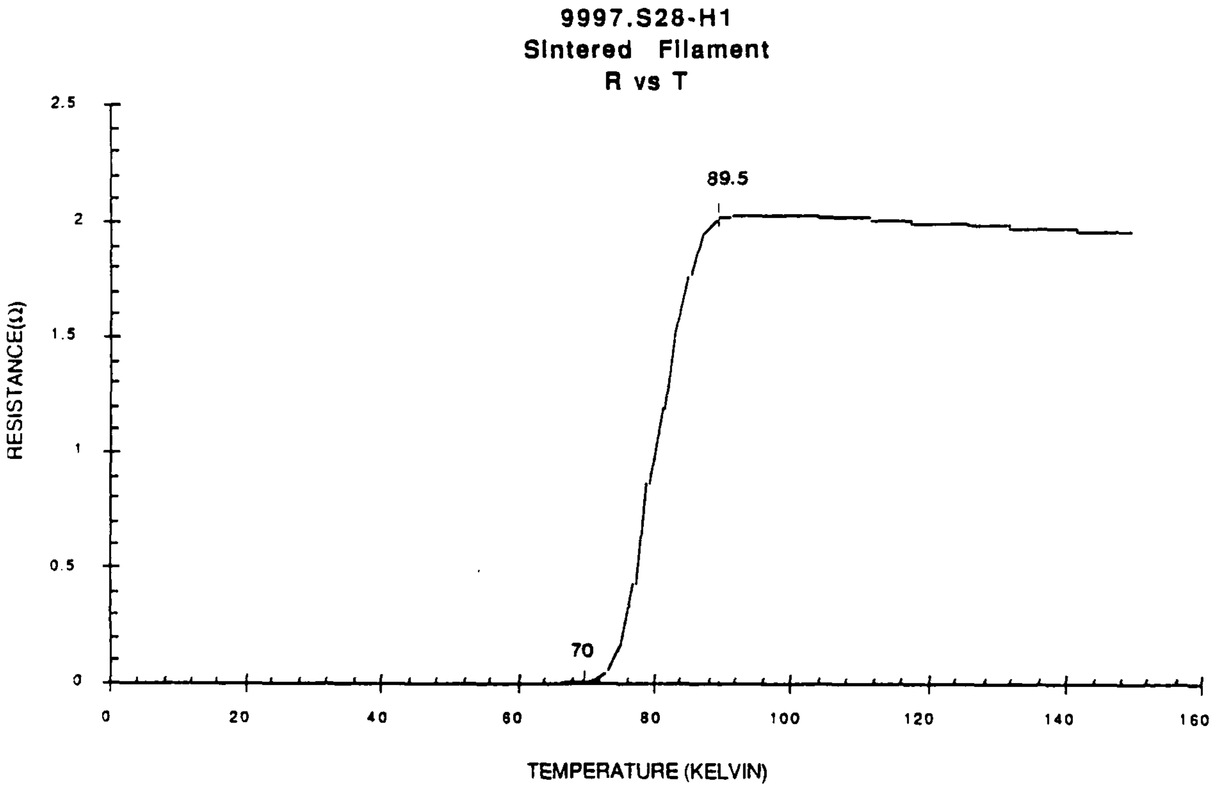

Figure 5. Sample 9997.S28-H1 resistance-temperature plot.

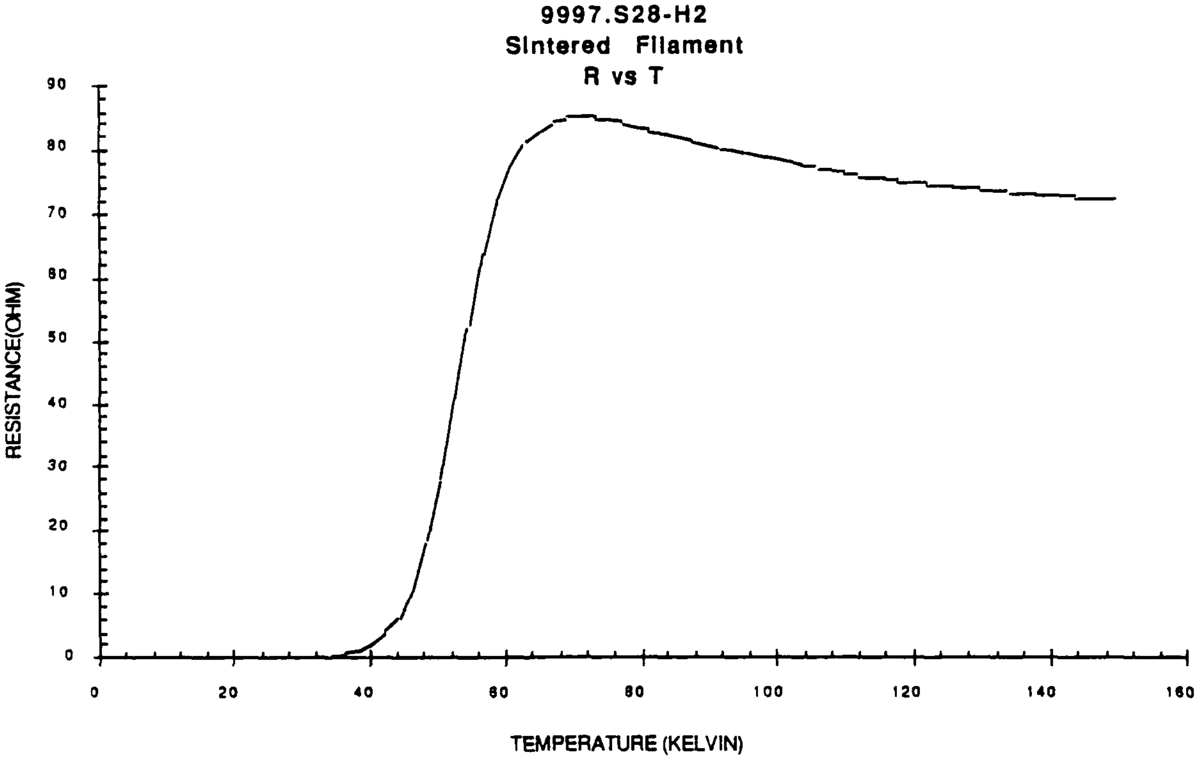

Figure 6. Sample 9997.S28-H2 resistance-temperature plot.

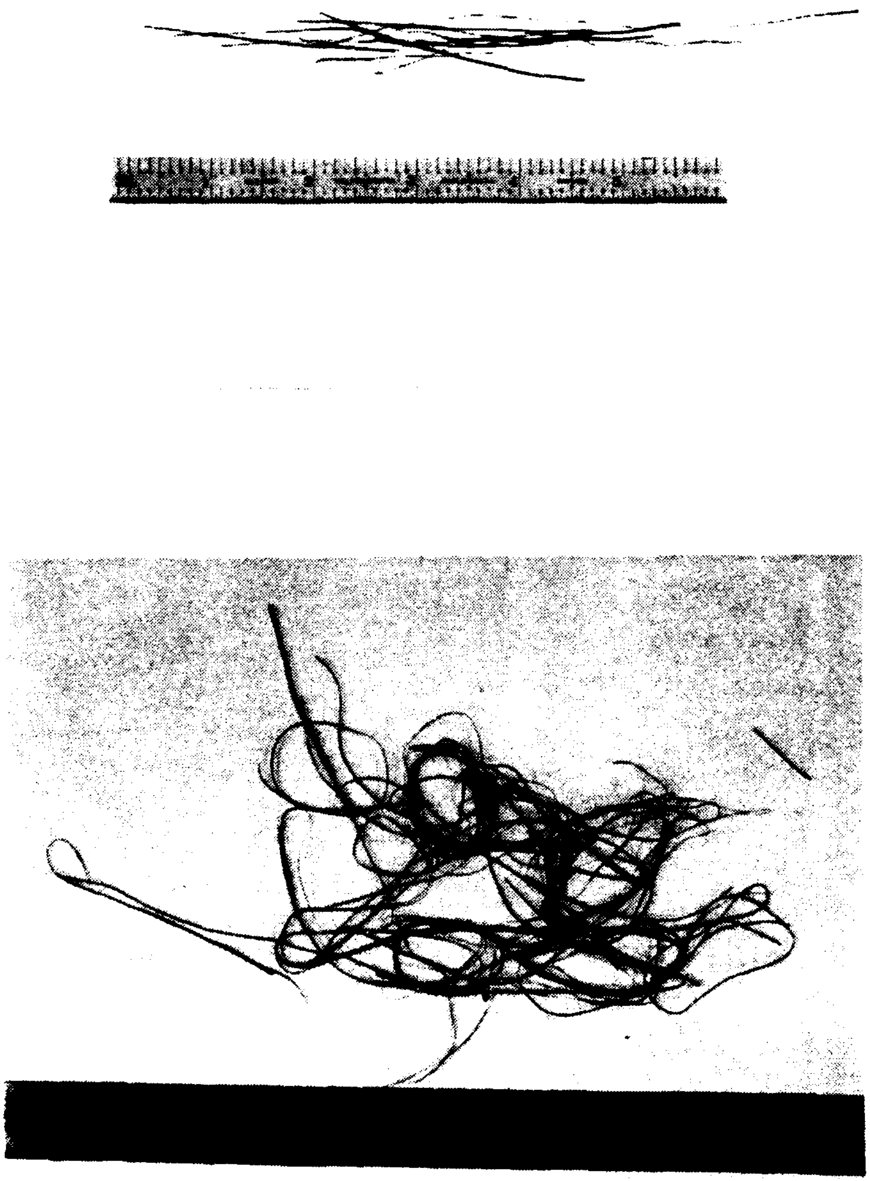

Figure 7. Pre-ceramic fiber batches (sample 9997.S29 and 9997.S30).

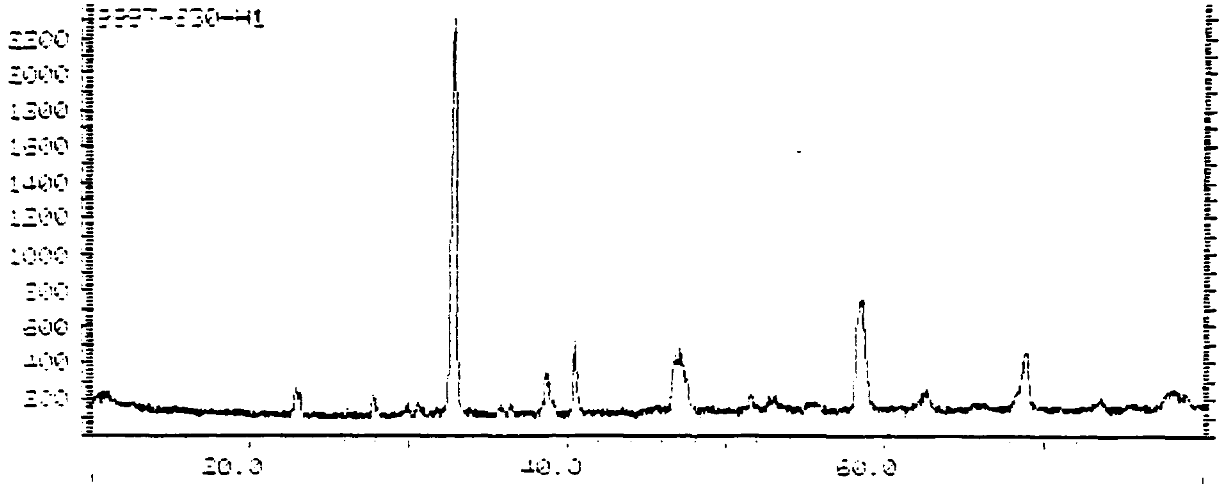

Figure 8. X-ray diffraction pattern of sample 9997.S30-H1
(897°C, 3 hours).

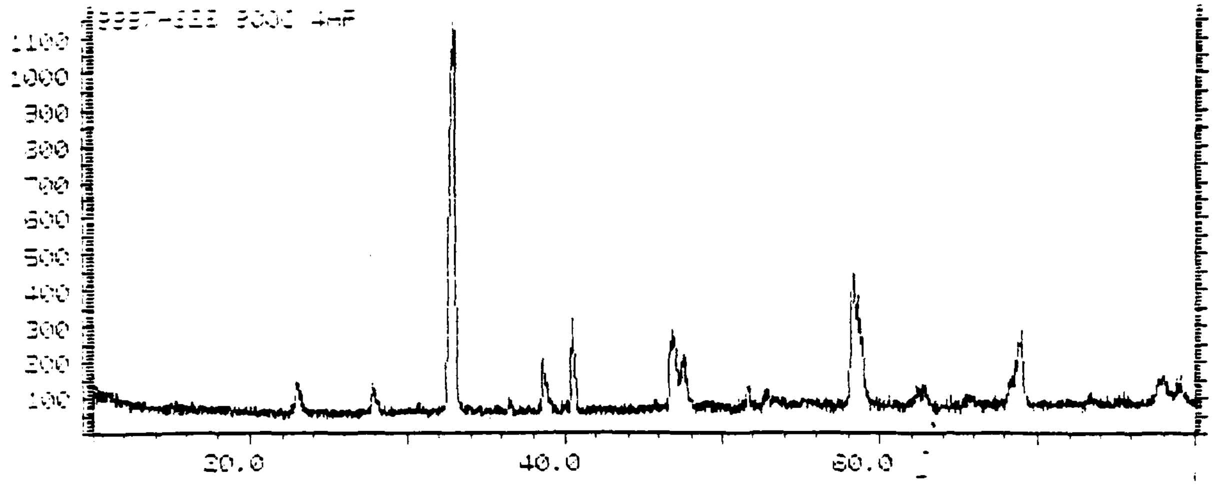

Figure 9. X-ray diffraction of sample 9997.S28 heat treated at 900°C. 4 hr in flowing oxygen.

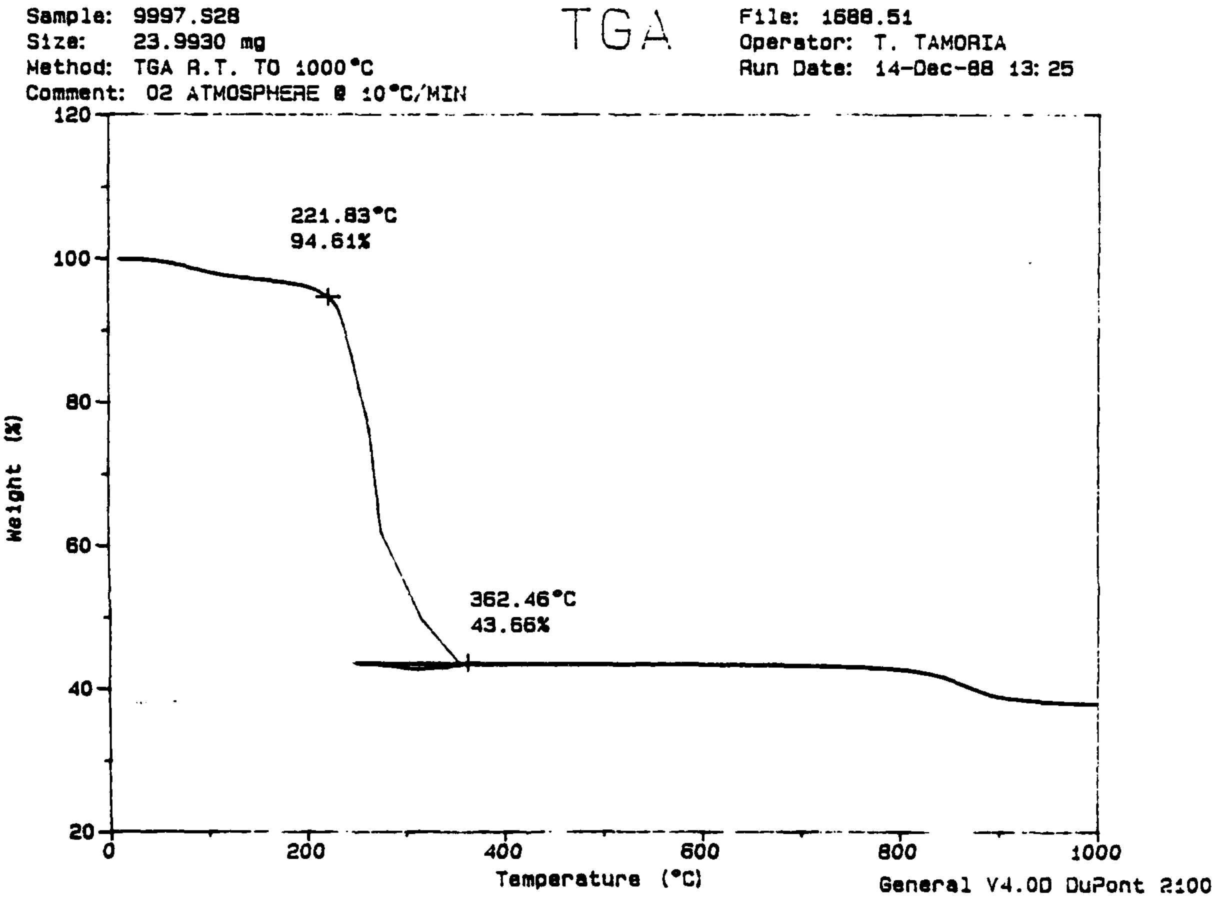

Figure 10. TGA of pre-ceramic superconducting fiber (sample 9997.S28).

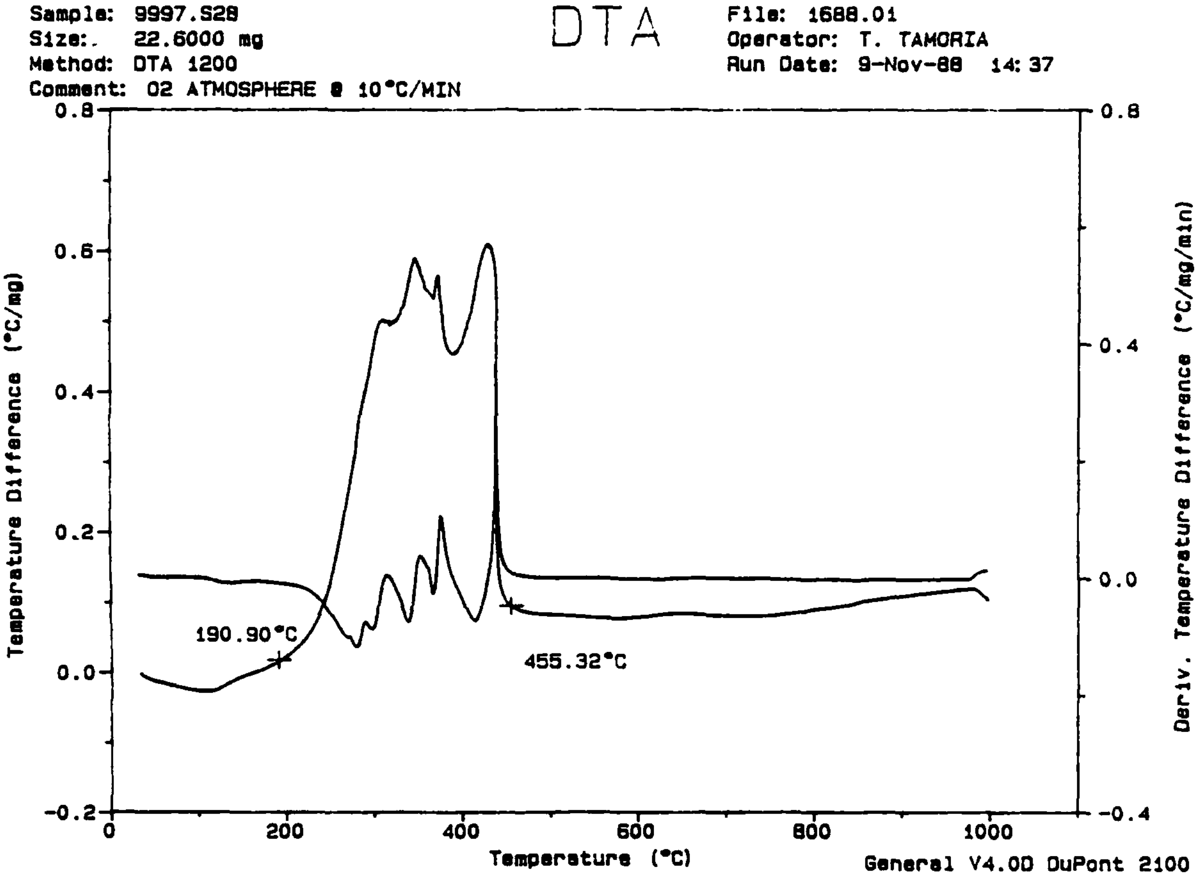

Figure 11. DTA of pre-ceramic superconducting fiber (sample 9997.S28).

Figure 12. SEM micrograph of sample 9997.S28-H4 (875°C, 10 hours, 925°C, 1 minute).

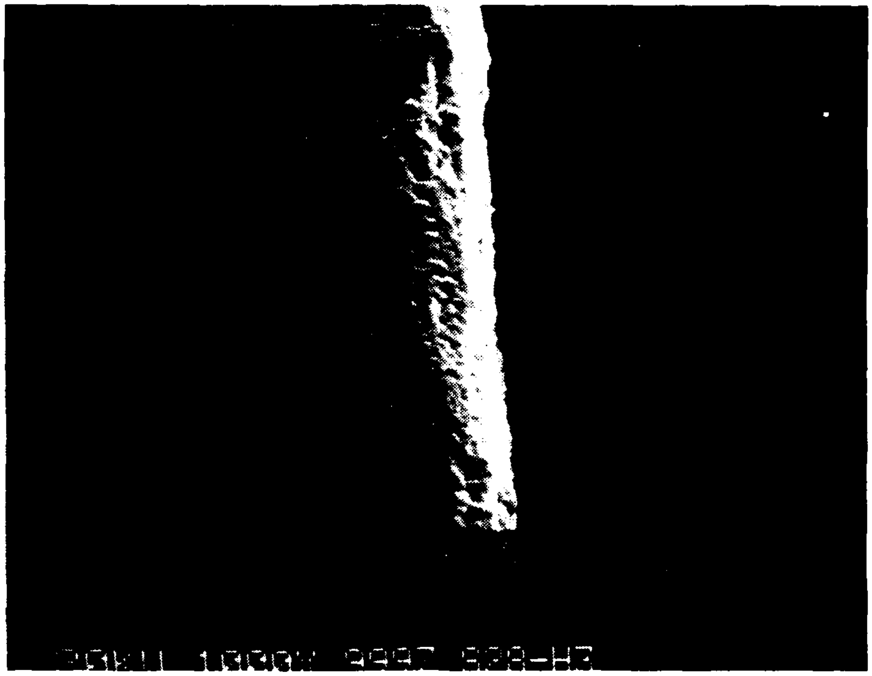

Figure 13. SEM micrograph of sample 9997.S28-H3 (900°C, 1 hour; 950°C, 1 minute).

Figure 14. SEM micrograph of sample 9997.S28-H4 (875°C, 10 hours, 925°C, 1 minute, slower heating rate).

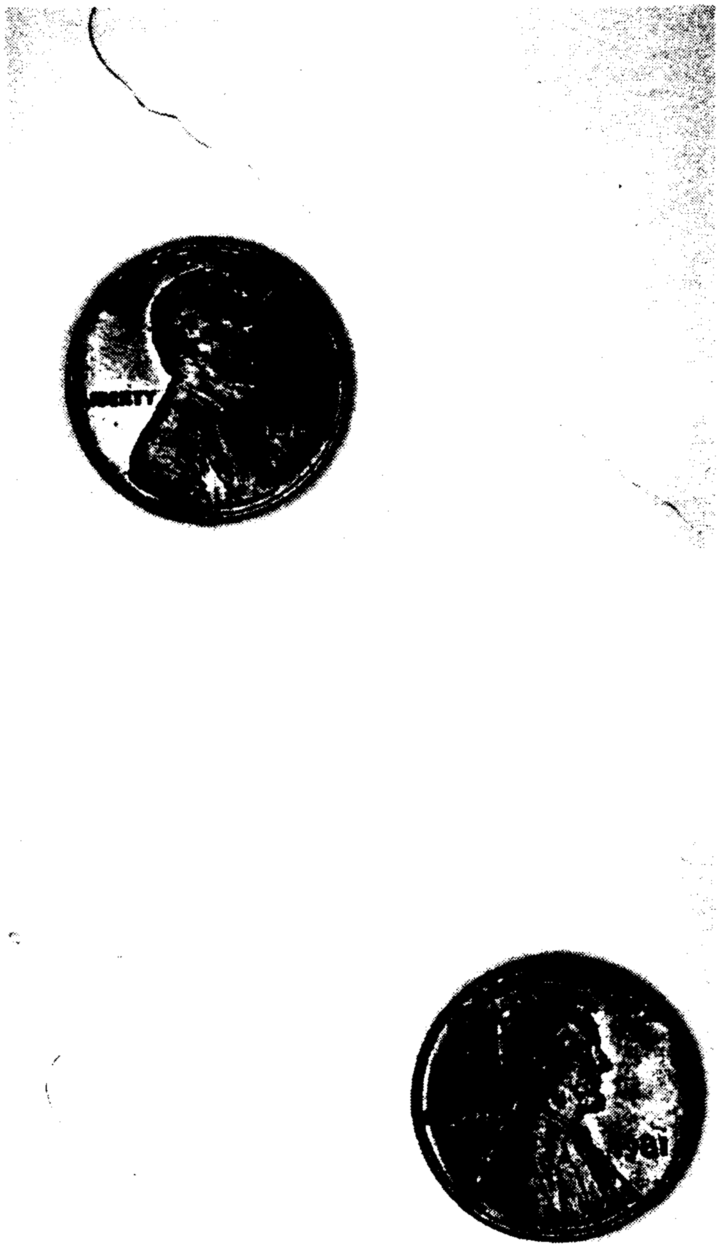

Figure 15. Fiber can be bent into small radius after heat treatment (sample 9997.S28-H2).

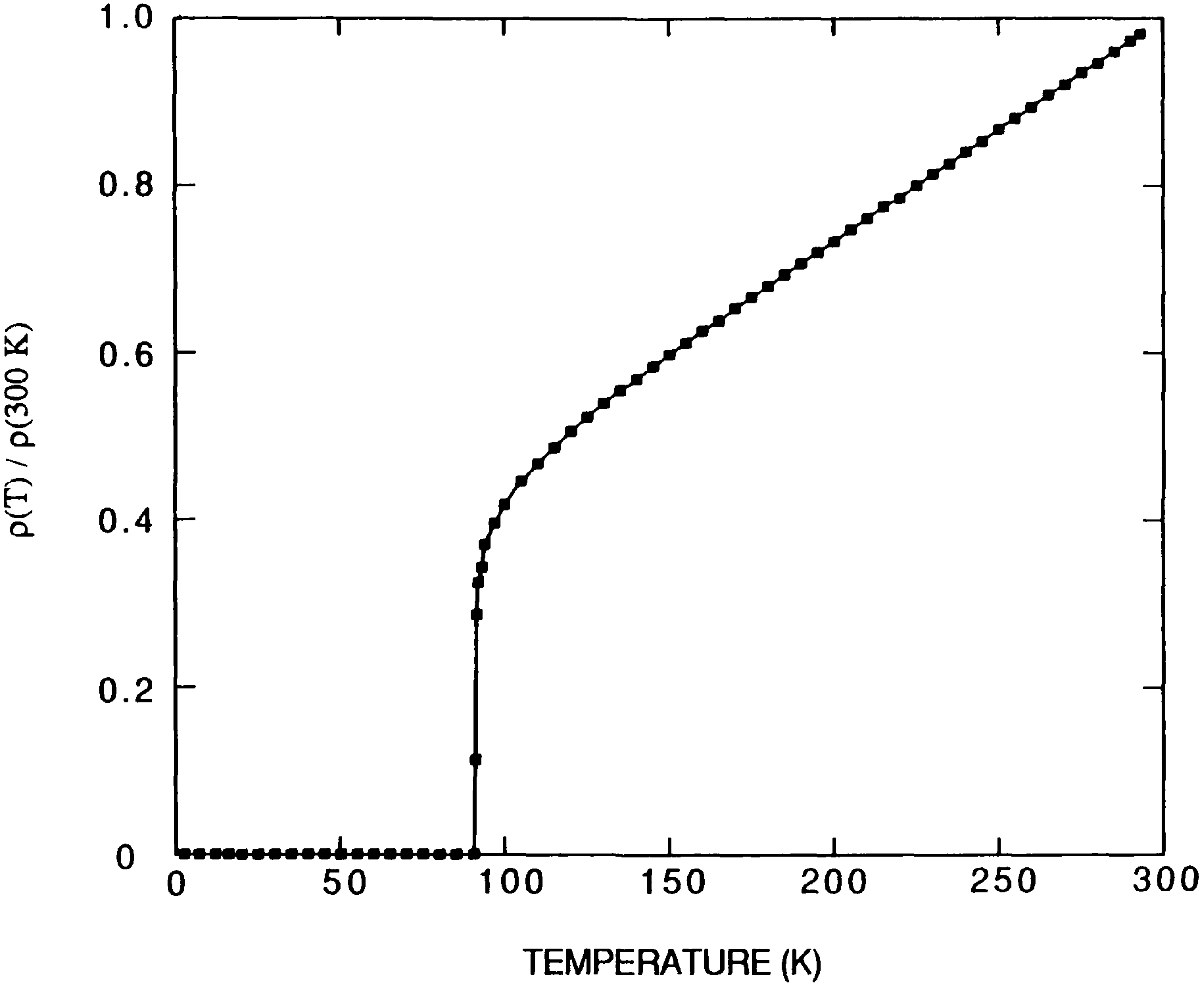

Figure 16 **Resistivity, normalized to the value at 300 K, as a function of decreasing temperature for $Y_1Ba_2Cu_3O_{7-\delta}$ powder prepared by the sol-gel method.**

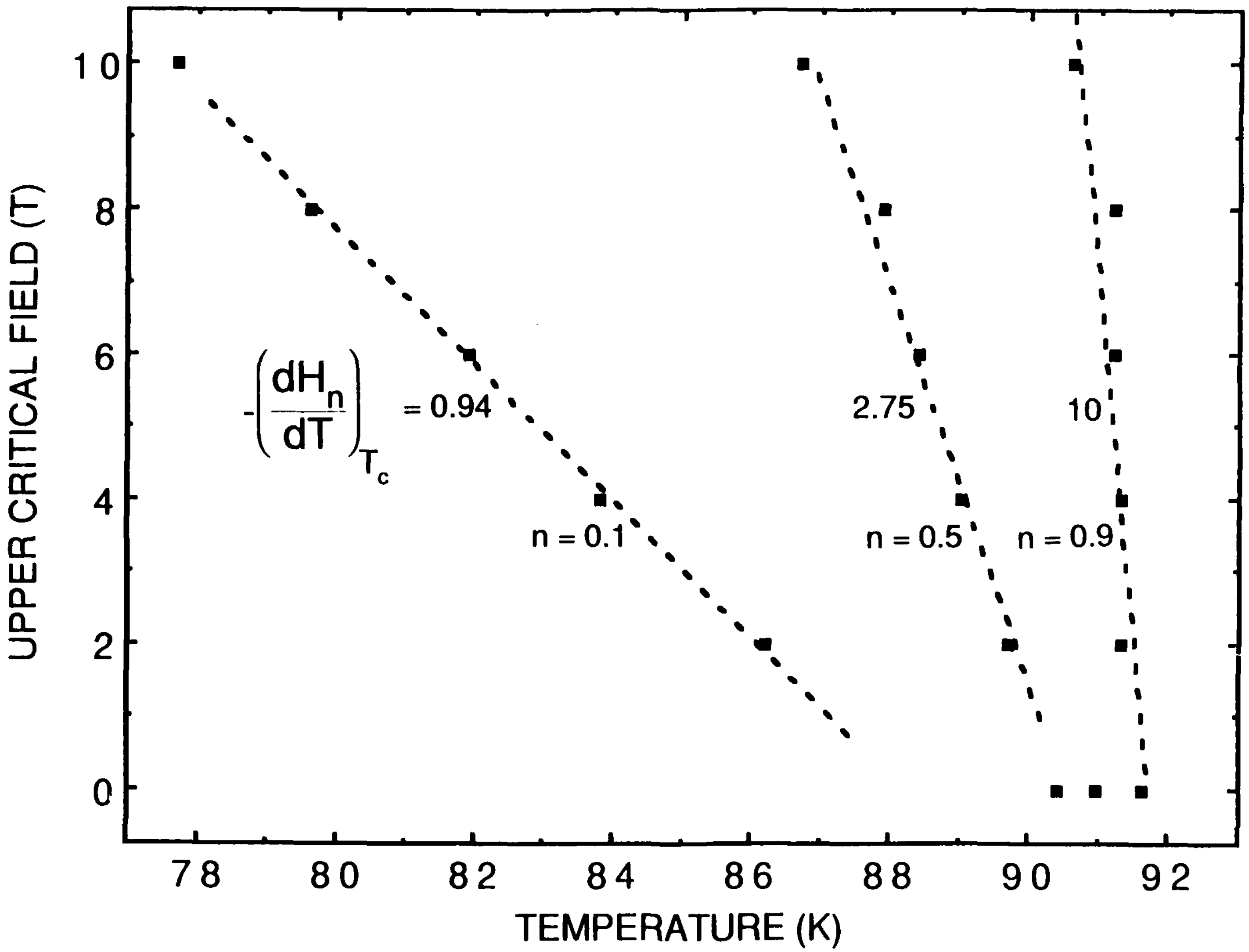

Figure 17. Upper critical filed Hn as a function of temperature for $Y_1 Ba_2 Cu_3 O_{7-\delta}$ powder. Hn is the field at which the resistivity drops to a fraction n of its extrapolated normal-state value at the field. Values are shown for n = 0.1, 0.5, and 0.9.

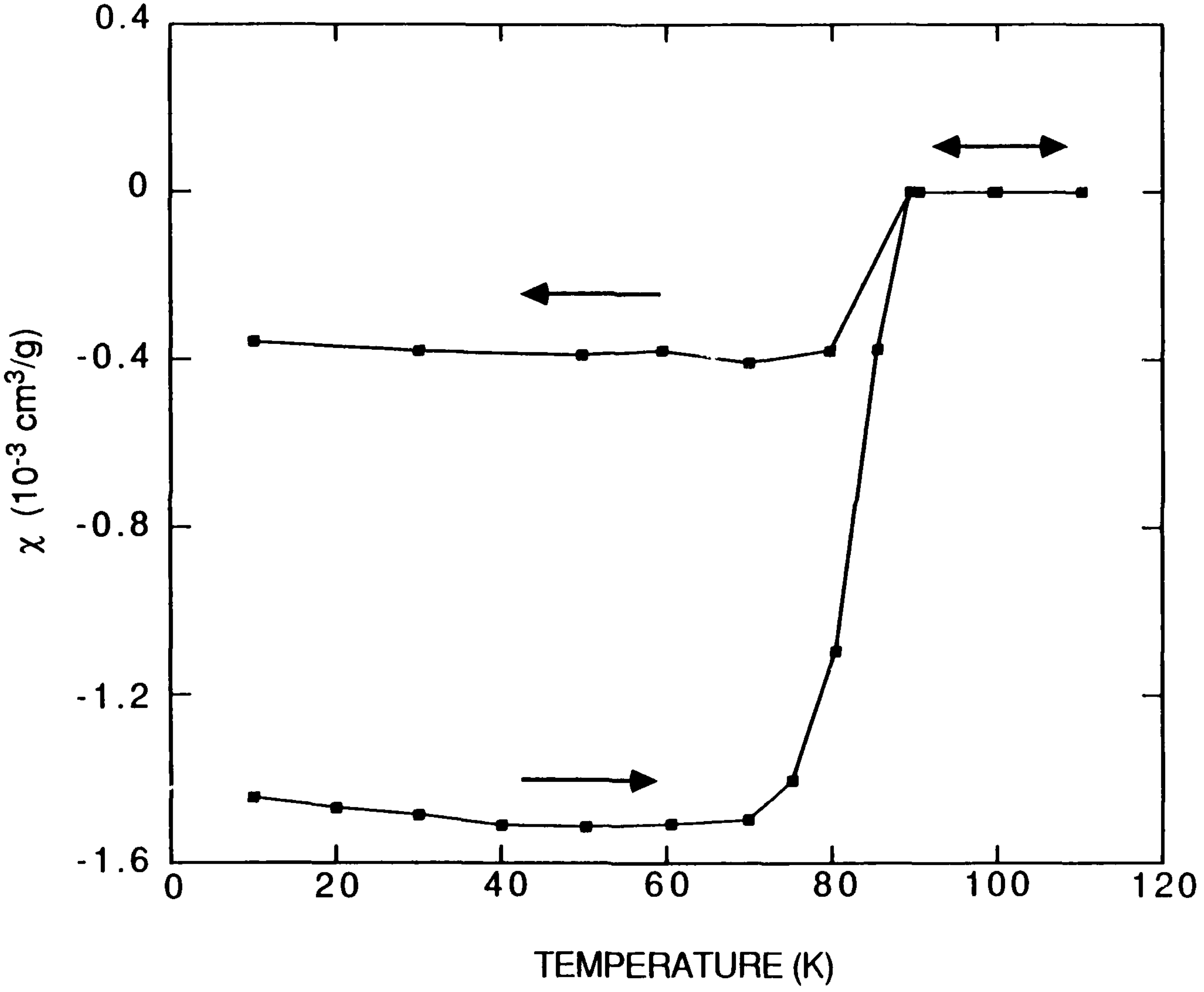

Figure 18. **Magnetic susceptibility as a function of temperature for $Y_1Ba_2Cu_3O_{7-\delta}$ powder. A magnetic field of 25 Oe was applied after the sample was cooled in zero field. The sample was then warmed through its superconducting transition and subsequently cooled again.**

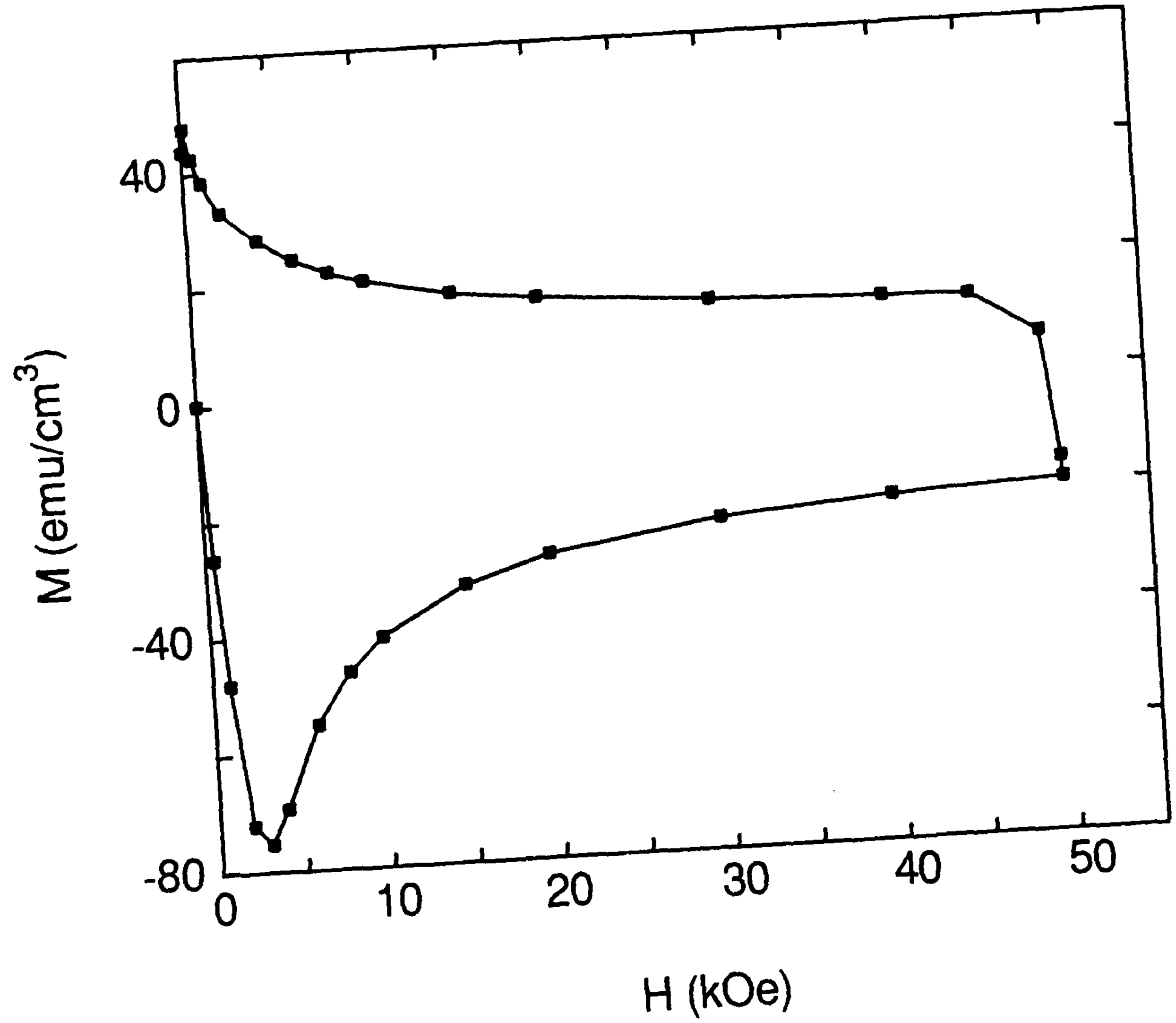

Figure 19. Magnetization as a function of magnetic field after cooling the sample in zero applied field.

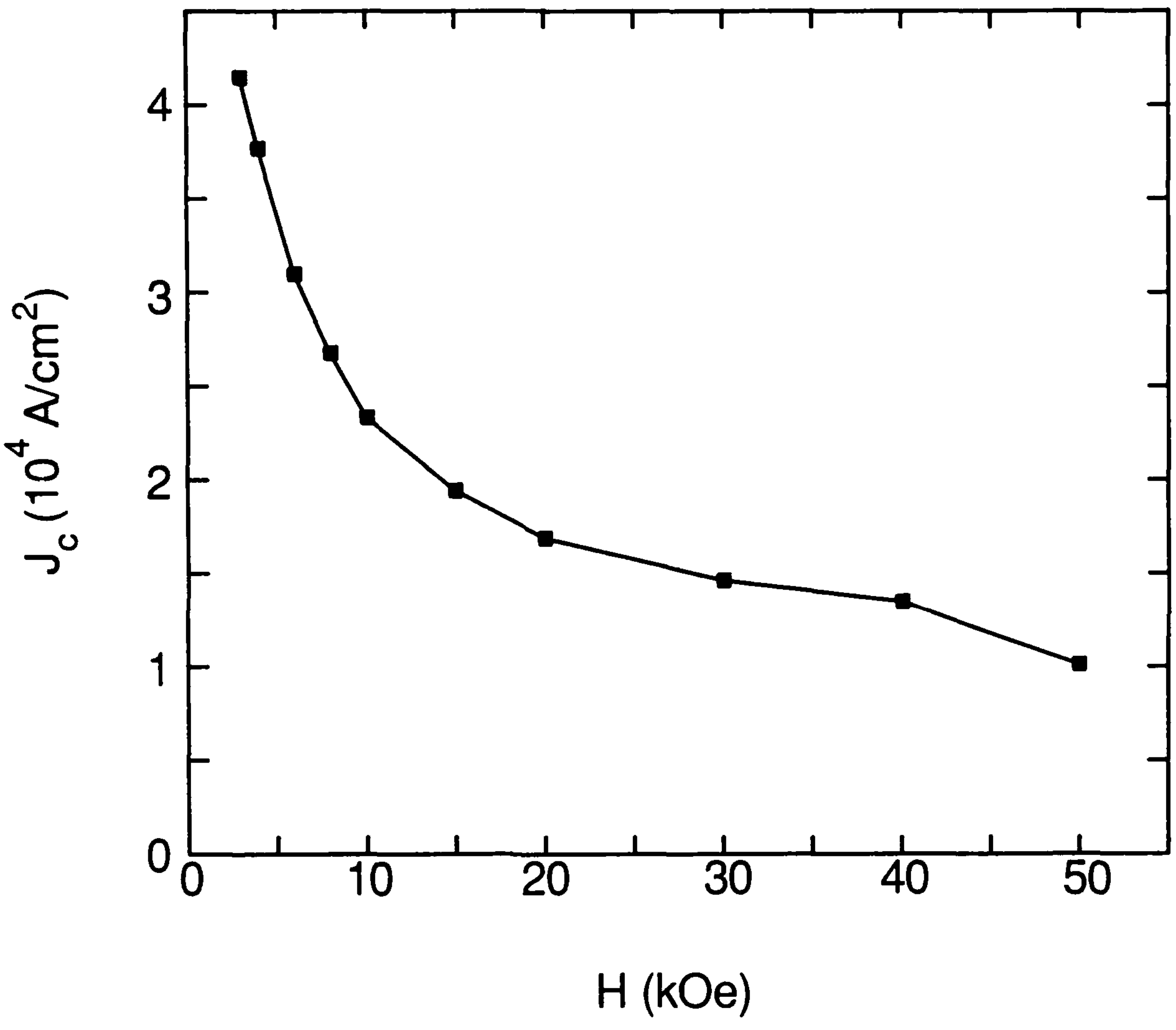

Figure 20. Estimated critical current density as a function of the applied field at 50KOe at 5K.

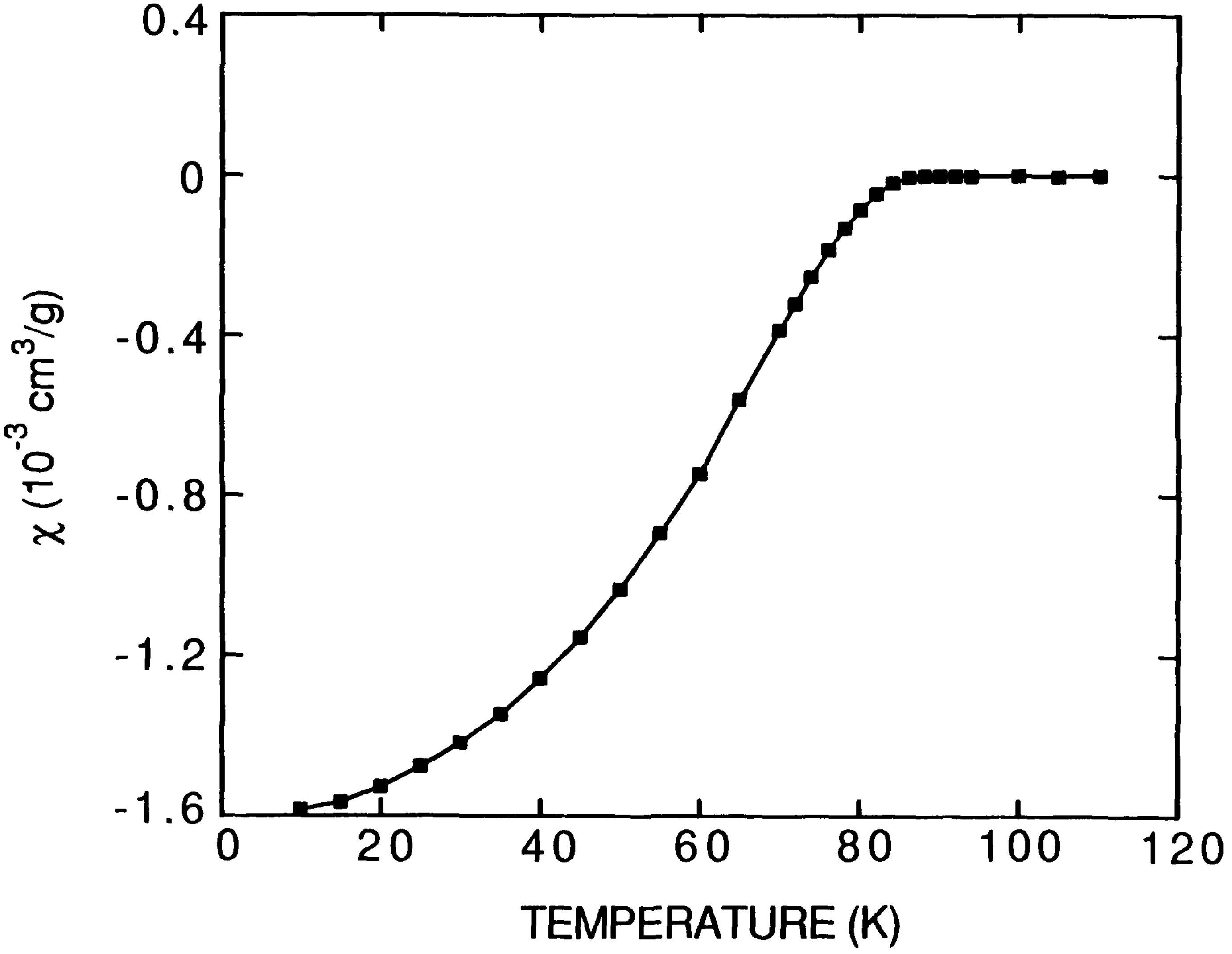

Figure 21. Magnetic susceptibility for the sol-gel derived 123 fiber.