

RESISTANCE MEASUREMENTS OF HIGH  $T_c$  SUPERCONDUCTORS  
 USING A NOVEL "BATHYSphere" CRYOSTAT†  
 John Moreland, Y. Li†, R. M. Folsom and T. E. Capobianco  
 Electromagnetic Technology Division  
 National Bureau of Standards  
 Boulder, CO 80303

### Abstract

We have developed a novel cryostat for variable-temperature testing of high temperature superconductors. The cryostat is a bathysphere consisting of an overturned stainless steel Dewar suspended in liquid helium. A sample-heater-thermometer assembly is located at the top of the encapsulated (and thermally insulated) vapor space inside of the Dewar. The sample can be rapidly cycled from 300 K to 4 K at an average rate of 1 K/min with a thermal hysteresis of less than 0.1 K. Helium vapor flows through a plug in the bottom of the bathysphere so that pressure of the vapor is roughly ambient. This provides ample heat transfer to and from the sample to maintain thermal equilibrium in the vapor space. Results for resistance versus temperature of some high temperature superconductors in a magnetic field are presented. Also, various definitions for thermodynamic and practical  $T_c$ 's derived from transport resistance measurements are suggested and discussed. These definitions are based on  $T_c$  midpoint, various relative resistance criteria, or absolute resistivity criteria.

### Introduction

A bathysphere is a sealed container designed for observation of deep sea phenomena. It isolates the observer from surrounding sea water in a regulated environmental chamber. This simple concept can be adapted to physical measurements that require variable temperature environments. In particular, a bathysphere cryostat can be used to thermally insulate an environmental chamber from surrounding cryogenic fluids such as liquid He or liquid  $N_2$ . Vapor exchange between the cryogenic fluid and the inner experimental space allows for the formation of a dry, ambient pressure, thermal exchange gas in the experimental space.

In this paper, we describe a bathysphere cryostat for resistance-versus-temperature (R-T) measurements of the recently discovered high temperature superconductors<sup>1-3</sup> in the temperature range from 300 K to 4.0 K. We also report data including the R-T curves for sintered  $YBa_2Cu_3O_x$  powder in magnetic fields of 0 T, 1 T, 5 T, and 8 T. Finally we address the issue of the role of transport resistance in the definition of thermodynamic and practical  $T_c$ 's for high temperature superconductors.

### Apparatus

The apparatus is described in detail in ref. 4. The essential feature is an overturned stainless steel Dewar that thermally insulates an experimental space from the surrounding cryogenic environment as shown in fig 1. A plug fits snugly into the mouth of the Dewar preventing excessive convection between the inner vapor and the surrounding outer fluid. The sample and thermometer are suspended in the vapor by a circuit board holder. The circuit board is mounted on a copper thermal anchor that is supported by the Dewar plug. A heater wrapped around the thermal anchor can be used to regulate temperature. Typically, however, the data are taken in a drift mode from high temperature to low temperature without the use of a heater. The average temperature drift rate is 1.6 K/min in liquid He and about 3.7 K/min in liquid  $N_2$ . The natural temperature drift is slow enough that the thermal lag between the

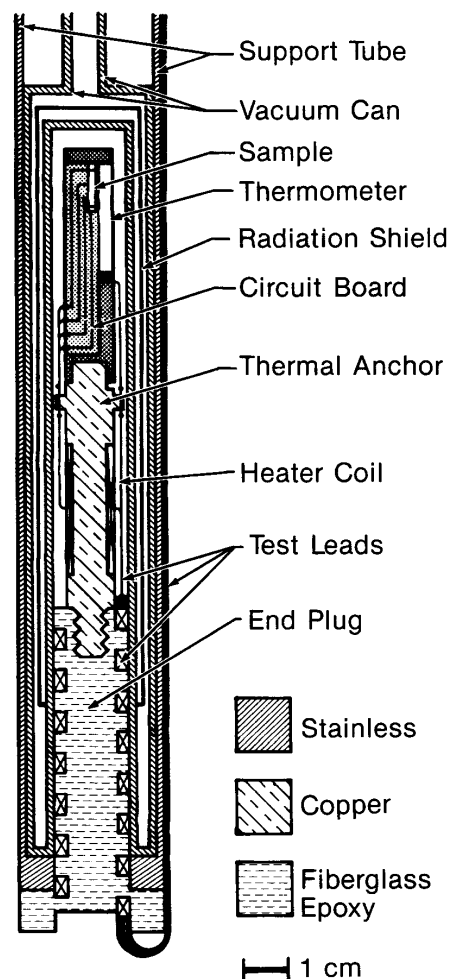
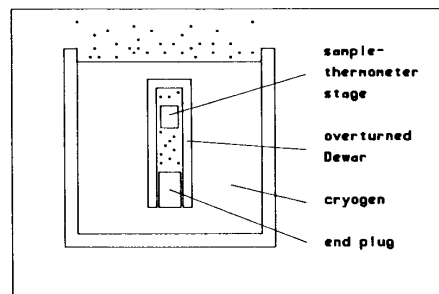


Figure 1. Section of the variable temperature bathysphere apparatus configured for resistance measurements. The inset is a conceptual diagram demonstrating the idea of an overturned Dewar for insulating trapped vapor from a surrounding cryogenic fluid. (from ref. 4)

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sample and the thermometer is less than the 0.1 K precision of the thermometer.

The sample resistance is measured using an in-line four-terminal probe configuration. A lock-in amplifier is used to measure the voltage drop along the surface of the sample between contacts in response to a constant 10  $\mu$ A ac current flow ( $f = 177$  Hz).

The temperature is measured using a silicon diode sensor. The sensor precision and accuracy are better than 0.1 K and 1 K respectively over the range from 300 K to 4 K at zero field. At 8 T we found that the temperature accuracy of the sensor is within 5% above 60 K and within 1% above 70 K.

The end of the bathysphere probe fits into the bore of a superconducting  $\text{Nb}_3\text{Sn}$  tape magnet. R-T curves at various magnetic fields are taken in the following way. First, the magnet is ramped to the desired field. Second, the magnet is put into persistent mode. Third, the bathysphere is lowered into the bore of the magnet. Finally, data acquisition begins. Data are always taken during drift cooling of the sample.

#### Samples

The samples are prepared from  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$  powders (99.9% purity). The powders are ground and mixed in a hand mortar and reacted at 930°C for 10 h. The product is then ground, pelletized, and annealed at 930°C in 1 atm of flowing  $\text{O}_2$  for 10 h followed by a temperature ramp down to 450°C at a rate of 2.4°C/min. Rectangular bars are then dry cut from the annealed pellet using a diamond wheel. Current and voltage contacts to the sample are made by ultrasonic soldering InAg(2% Ag) contacts directly to the sample. The contact resistance of the InAg pads ranges from 0.1 to 1.0  $\Omega$  with corresponding surface resistivities (contact area-resistance product) of 0.001 to 0.01  $\Omega\text{-cm}^2$ . Typically samples are  $1 \times 1 \times 10$  mm<sup>3</sup> with voltage taps separated about 5 mm apart along one face of the sample. The critical current of these bars is about 1 A in the earth's magnetic field.

#### Results

Figure 2 shows the R-T curves of the  $\text{YBa}_2\text{Cu}_3\text{O}_x$  samples in magnetic fields as high as 8 T. Notice the general shifting of the resistance transition toward lower temperatures with increasing fields. Let us define  $T_c$  to be the temperature at which the resistance of the sample falls to one half of the normal state value,  $R_N$ , assuming a linear normal state resistance (" $T_c$  midpoint"). Then,  $B_{c2}(T) = 1.3 \times (89.5 - T)$  (in SI units). This is in good agreement with the results obtained by Orlando et al.<sup>5</sup>

Also notice the presence of a foot in the R-T curves. Practical limits on high current superconducting materials, based on an electric field criterion of 1  $\mu\text{V/cm}$ , require that the resistivity of the material fall below  $10^{-11}$  to  $10^{-12}$   $\Omega\text{-cm}$ .<sup>6</sup> The lock-in measurement is capable of detecting  $10^{-6}$   $\Omega\text{-cm}$  resistivities with the sample configuration mentioned above. The primary resistivity sensitivity limitation is that the current used for the measurement should be limited to low levels in order to minimize heating effects at the current contacts of the sample. We noticed heating when the rms current exceeded 10 mA. With this in mind, we can safely say that the sample is not superconducting, practically speaking, at temperatures well below  $T_c$  midpoint based on an arbitrary  $R/R_N$  criterion of 0.001 (corresponding to a resistivity criterion of about  $10^{-6}$   $\Omega\text{-cm}$ ). The shape of the resistance foot and the location of the upper bound on  $T_c(R = 0)$  are field dependent, as is apparent in the figure. The cause of

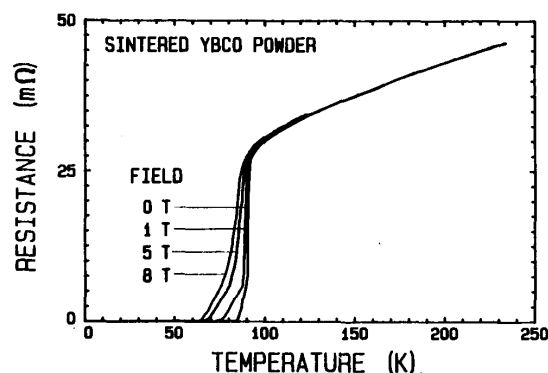


Figure 2. Resistance versus temperature for sintered powder  $\text{YBa}_2\text{Cu}_3\text{O}_x$  samples at various magnetic fields. The field is perpendicular to the current flowing in the sample.

the resistance foot below  $T_c$  midpoint is unresolved. It may be caused by the existence of a lower  $T_c$  phase at grain boundaries that may give rise to a SNS proximity Josephson matrix within the sample. Preliminary results for our samples, after being subjected to a second  $\text{O}_2$  anneal, indicate that the foot was nearly eliminated. However, our upper bound on  $T_c(R = 0)$  still shifts down to 70 K at a field of 8 T compared to 65 K for the samples that had undergone only one anneal.

#### Some Definitions of $T_c$

Traditionally, resistive transitions have been characterized using the  $T_c$  midpoint construction and the 25-75% (or alternatively the 10-90%) normal state resistance criterion as illustrated in Fig. 3.<sup>7</sup> This construction method is sufficient for superconductors with narrow transition widths,  $\Delta T$ , giving a reasonably accurate estimate of the thermodynamic  $T_c$ . However, for high temperature superconductors,  $\Delta T$  can be several kelvins wide, especially at high fields. Under these circumstances the thermodynamic  $T_c$  is probably close to  $T_c$  midpoint. But, one might ask, How well  $T_c$  midpoint for high  $T_c$  materials with resistivities (at temperatures well below  $T_c$  midpoint) greater than that of copper at room temperature, corresponds to the practical definition of a high current superconductor? Our measurements indicate that under moderate fields ( $< 8$  T), practically speaking, the samples are not superconducting above 70 K, whereas  $T_c$  midpoint is substantially higher, above 80 K.

An alternative construction method for determining  $T_c$  is shown in Fig. 4. This method is similar to that shown in Fig. 3 in that  $T_c$  midpoint is defined to be the thermodynamic  $T_c$ . It differs from the previous method, however, in that  $\Delta T$  is defined as the temperature difference between  $T(R = 0)$  (established using a resistivity criterion and not a resistance criterion) and the onset temperature where the normal state resistance intersects a line projected from the steepest ascent of the R-T curve. Presently, we feel that the main limitation on resistivity sensitivity and a  $T_c$  resistivity criterion of either a dc measurement using nanovoltmeters or an ac measurement that uses a lock-in amplifier, is the contact resistance of the sample-current contacts. Ekin, et al. developed a method that minimizes the surface resistivity of contacts to  $\text{YBa}_2\text{Cu}_3\text{O}_x$  to levels below  $10^{-10}$   $\Omega\text{-cm}^2$ .<sup>8</sup> Low surface resistivity contacts, make it possible to increase the excitation current level to improve the

resistivity sensitivity of a given measurement. Other limitations on the maximum excitation current level include possible self-field effects and the high intrinsic normal state resistivity of high temperature superconductors.

### Summary and Discussion

We have constructed and tested a novel variable temperature cryostat. The cryostat serves as a cryogenic bathysphere insulating a sample vapor space from surrounding cryogenic fluid. The advantages of this type of variable temperature apparatus are several-fold. The system is compact enough to fit into the bore of a high field superconducting solenoid without the use of a reentrant Dewar. Thermal contact between sample and thermometer provided by ambient pressure exchange gas is sufficient to maintain thermal equilibrium within 0.1 K while the temperature changes as fast as 3 K/min. The sample remains in the dry vapor of the cryogen during the cooling and warming process preventing moisture contamination. Finally, the cryostat has no moving parts and is inexpensive to construct.

The apparatus has been used to measure the R-T curves of sintered  $\text{YBa}_2\text{Cu}_3\text{O}_x$  powder in the presence of a magnetic field. Our results indicate that the resistivity of the samples is much larger than the resistivity criterion usually associated with high current conventional superconductors below  $T_c$  midpoint. As field is applied to the sample, the discrepancy between our upper bound on  $T_c(R=0)$  and  $T_c$  midpoint becomes larger. As discussed by Orlando et al., an optimistic interpretation of the data, based on  $T_c$  midpoint only, would lead to predictions of critical fields at  $T=0$  of better than 80 T. Since our measurements used an extremely low current level (10  $\mu\text{A}$  rms) corresponding to a current density of 1  $\text{mA}/\text{cm}^2$ , we think that the relatively high resistance of that sample below  $T_c$  midpoint is intrinsic and not a measurement artifact. We therefore suggest that a conservative estimate of  $\Delta T$  be based on a practicable resistivity criterion to determine  $T_c(R=0)$ . In this way,  $\Delta T$  will become a more useful indicator of the potential superconductor performance at lower temperature and higher current and field. The issue of practicable criteria for high temperature superconductors is yet unresolved. Reasonable criteria must allow for ease and repeatability of measurement as well as an acceptable level of sensitivity. Until a standard is developed, we suggest that, when reporting an upper bound on  $T_c(R=0)$ , the resistivity and current density at that temperature should also be noted. The onset temperature, on the other hand, can be considerably more difficult to characterize, since typically,

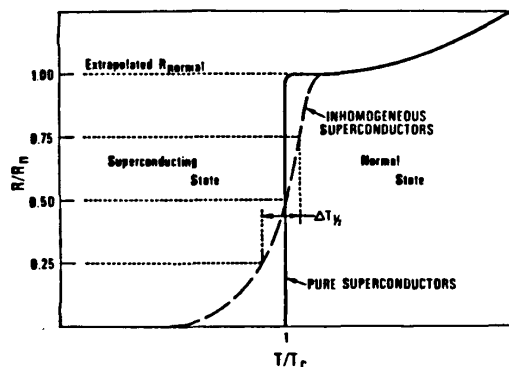


Figure 3. Definition of  $T_c$  midpoint and  $\Delta T$  based on arbitrary relative resistance limits.

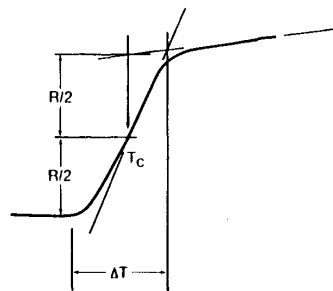


Figure 4. Definition of  $\Delta T$  based on a resistivity criterion for  $T_c(R=0)$  and the intersection of the normal state resistance and the projected steepest ascent of the R-T curve.

high temperature superconductors show rounding in the R-T curves above  $T_c$  midpoint. Arbitrary criterion such as the 75% or 90% normal state resistance criteria or the method shown in Fig. 3 may be useful, but cannot fully describe the rounding phenomenon. Another possible method is to plot  $dR/dT$  versus  $T$  to accurately locate features in the R-T curve. This method may be particularly helpful for characterizing the onsets of resistive transitions in the R-T data but may be misleading when determining  $T_c(R=0)$ .

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‡ Visiting scientist from Institute of Physics, Chinese Academy of Science, Beijing, China.