A MULTI-SAMPLE RESIDUAL RESISTIVITY RATIO SYSTEM FOR HIGH QUALITY SUPERCONDUCTOR MEASUREMENTS*

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Abstract

For developing accelerator cavity materials, superconducting transition temperature (T_C), transition width (ΔT_C), and residual resistivity ratio (RRR), are useful parameters to correlate with SRF performance and fabrication processes of bulk, thin film, and novel materials. The RRR gauges the purity and structure of the superconductor based on the temperature dependence of electron scattering in the normal conducting state. Combining a four point probe delta pulse setup with a switch allows multiplexing of the electrical measurements to 32 samples per cooldown cycle. The samples are measured inside of an isothermal setup in a liquid helium (LHe) dewar. The isothermal setup is required for a quasistatic warmup of the samples through T_C. This contribution details the current setup for collecting RRR and T_C data, the current standard of throughput, measurement quality of the setup, and the improvements underway to increase the system's resolution and ease of use.

INTRODUCTION

Superconducting materials have two convenient DC figures of merit associated with superconducting RF performance, the transition temperature and the residual resistivity ratio. The transition temperature marks the onset of the superconducting state. T_c and ΔT_c, are the parameters used to characterize the phenomena. RRR is a comprehensive gauge of the quality of the material. The conduction of electrons includes several scattering mechanisms with one mechanism usually dominating at a given temperature [1]. The RRR for Nb is determined according to equation 1 by dividing the averaged measured values of resistivity at 300 +/- 0.1 K and at 10 +/- 0.1 K to create a unitless figure of merit [2,3].

$$RRR = \frac{R_{300K}}{R_{10K}} = \frac{V_{MEASURED\,300K}/I_{DRIVE}}{V_{MEASURED\,10K}/I_{DRIVE}} = \frac{V_{300K}}{V_{10K}} \qquad (1)$$

Jefferson Lab Superconducting Radio Frequency Process and Materials Group has developed a residual resistivity ratio system capable of measuring up to 32 samples per cooldown cycle with a temperature resolution of less than 50 mK through Nb T_c range. The samples are measured inside of an isothermal setup in a liquid helium

dewar in the JLab vertical test area [4]. Systematic quick feedback on superconducting character is instrumental in process development of thin films and novel materials.

MEASUREMENT SYSTEM

The RRR system is capable of measuring bulk and thin film samples of various shapes and sizes. The high throughput RRR system is capable of meeting the demands of a multitude of projects in the lab and the sample volumes associated with concurrent research programs. The sample's resistivity is measured in a four point probe setup as a function of temperature. This method eliminates sources of error that are intrinsic to two wire measurements, such as thermal EMF and line resistances. Figure 1 depicts the four point probe setup, and equation 1 details how RRR is calculated from the resistivity data.
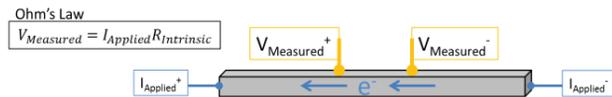
Figure 1: Four point probe measurement scheme.

There have been numerous methods developed for determining RRR, adopting a simple unambiguous method is essential to reproducibility, technique equivalency for different materials, and rapid communication of results [5]. A slight discrepancy is presented where NIST has chosen the room temperature resistance at 273 K, while the accelerator community had previously chosen the room temperature resistance at 300 K.

A calculation of a sample's expected voltage is based on the sample's geometry, RRR seat design, and the material's resistivity. For novel materials, such as MgB_2, NbTiN, and Nb_3Sn, the resistivity is selected slightly above the literature value for pure specimens. An expected sample RRR projects the low temperature voltage that will be measured and then is compared to the systems noise floor to anticipate the low temperature signal quality. If the voltage is too low, the sample's voltage will not be observable above the noise floor of the system, making the data set unusable.

For high quality data, it is essential for the setup to have a reliable representation of the samples' temperature with a thermal measurement device. Temperature uniformity in a vertical dewar is challenged by the stratification of the helium gas within the dewar. The thermal latency of the setup in the LHe dewar dictates the temperature rise of the system which is compounded by the number of samples and the amount of time it takes to

collect a data point. These factors define the temperature resolution of the transition. The necessity of a near isothermal state requires a quasistatic warmup and low thermal slew rate of the samples for resistivity measurements near the transition temperature.

The RRR system utilizes mass, insulation, and thermal shields to create an isothermal environment for the samples. The samples are mounted on 23 cm^2 Cu boards inside of a $61 \times 24 \times 23$ cm closed copper box. The only openings in the Cu box are penetrations in the back of the box for four card edge connectors. The card edge connectors pass electrical connections to the sample boards for the four point probe and Cernox temperature sensors. Figure 2 is an image of the test fixture used to create an isothermal environment for collecting the RRR data.

Figure 2: RRR test stand Cu sample measurement box with Al shield and super insulation open exposing with front panel removed.

The Cu box is wrapped in superinsulation, surrounded by an Al shield assembly that is sealed with vinyl tape, and then wrapped in heavy Al foil. The samples are mounted on four Cu board assemblies that are held inside the Cu box with rails. The four boards are physically separated by 15 cm on each level. The top and bottom board are about 46 cm apart. The Cu board assemblies holding the samples have a circuit board that mates into the card edge connector. The card edge connector provides heat stationing outside of the Cu box for the ribbon cable and Cernox wires from the test stand lid. The card edge connectors also thermally station any heating from the drive current to preserve the best isothermal setup for the sample's measurement inside the box. The card edge connectors are 40 pins each. In each card edge connector, 32 pins are for 8 four point probe measurements and 8 pins for two four-wire calibrated copper bobbin Cernox™ sensors (1050-CU-HT-1.4L). The circuit board terminates the four point probe leads to 8 polarized latching connectors. The connectors can be attached to a variety of seat geometries creating a modular

design around the card edge connecting circuit boards. The Cu sample boards have an array of tapped holes for seat posts or Cernox mounting. The standard seats have poker pins epoxied into G10 plate held above the sample with springs around threaded rods. The poker pins are lowered into contact with finger nuts that tension the springs into the G10 plate. The double spring mechanism provides some control over how much force the pins exert on the samples. The seat springs' force constant is chosen slightly above the poker pins' force constant so that when the seat retracts from the sample the extended the pins easily clear the samples. In operation under 10 K , typical thermal spread between the top and bottom board in the setup is 0.1 K. Figure 3 shows the sample boards installed in the Cu box.

Figure 3: Four small sample boards installed in the Cu box.

The electrical signals are passed into the LHe dewar using a custom feedthrough that has four DB-37 connectors on the atmosphere side and four 40 pin IDC rectangular connectors on the dewar side. The Cernox leads are passed into the dewar through a 32 pin round feedthrough and spliced into the 40 pin ribbon cable in the dewar.

The temperature of the samples is measured with a Lakeshore model 218 controller. The resistivity is measured using the delta pulse technique with a Keithley model 6221 current source and a model 2181A nanovolt meter. The nanovolt meter is a slave to the current source for the delta pulse measurements. The signals are routed through a Keithley model 7002 switch using four model 7053 high current relay cards and four model 7168 nanovolt scanner cards to multiplex the delta pulse measurements to up to 32 samples. The instruments are controlled by LabView™ on a standard desktop PC using a USB to GPIB interface. The speed of data acquisition is highly dependent on the acquisition computer's overhead and the GPIB interface limitations. Figure 4 depicts the RRR setup showing the hardware, electronics, and cabling.
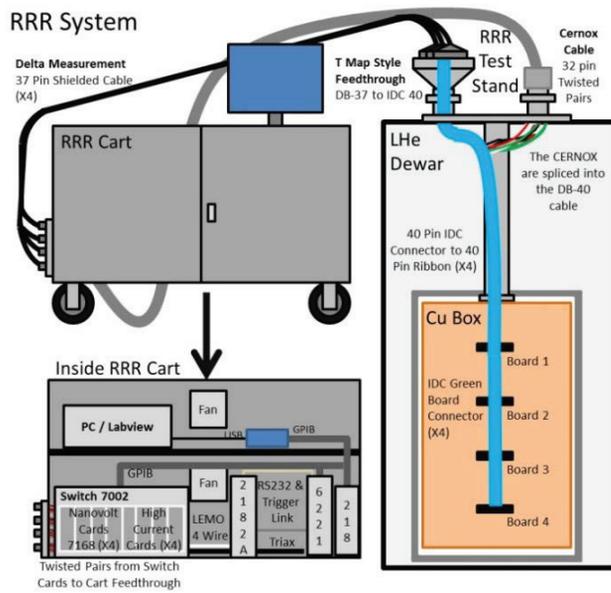
Figure 4: RRR setup electronics and dewar details.

The system has the flexibility to be configured for high quality measurements or high sample throughput. For high resolution temperature measurements, all of the Cernox and delta measurements are devoted to a single sample with data taken about every 0.65 seconds. In high throughput mode, the measurement loop for 32 samples takes about 20 seconds.

The delta pulse wave form is generally 10 pulses at 500 Hz and a 50% duty cycle. An average of the last five pulse values is used to calculate the sample's voltage. The 6221 can deliver up to 105 mA at 102 V, and in this setup the nanovolt meter can read down to 10's of nA. The combination of high drive currents and low noise floor provides for a dynamic range for determining RRR in excess of 10^5. The system flexibility allows for mixing material types, sample geometries, etc. in a single run. In addition to acquiring the data and performing the calculations, the LabView™ program writes the data and results to a text file and displays plots of the resistivity as a function of temperature. A MATLAB™ program has been written to analyse the resistivity data.

SYSTEM PERFORMANCE

The RRR system is a versatile measurement setup that provides feedback for numerous projects across the lab. Several projects have used the system to characterize the thermal conductivity of Cu based on the resistivity curves. Qualification of Nb stock for cavity fabrication has been performed on numerous shapes and sources of stock. Table 1 presents the RRR measurement data for a sample that was fabricated from ingot Nb material [6].

The bulk Nb sample was cut with wire EDM, BCP etched, and then baked with an 800 °C heat treatment exactly as a cavity would be treated. The resistivity data collected from the ingot was self-consistent, with both Cernox sensors providing essentially the same values for

T_c and ΔT_c, even though they were physically separated from the sample by different distances. The resistivity

Table 1: T_c and RRR Data for an Ingot Nb Bar Comparing the two Cernox Temperature Sensors on the Measurement Assembly

	Cernox 4	Cernox 8			
Transition Temperature (K)	9.265	9.260	RRR	100.26	
Transition Width (K)	3.60E-02	3.60E-02			

			Range - Low (K)		Range - High (K)	
	Ave (V)	Std Dev (V)	Ave [Cernox 4]	Ave [Cernox 8]	Ave [Cernox 4]	Ave [Cernox 8]
Noise Floor	8.75E-09	1.18E-08	4.84	4.84	9.306	9.24
Low Temperature - 10K +/-0.1K	1.86E-07	5.26E-09	9.99	9.99	NA	NA
Room Temperature - 300K +/- 0.1K	1.87E-05	1.52E-08	NA	NA	300.0	300.0

measured in the normal state just above the transition was an order of magnitude higher than the noise floor when the sample was in the superconducting state. This signal to noise ration provides confidence in the calculated RRR. In addition, the voltages associated with the calculation of the RRR had very low standard deviations. The four point probe setup RRR is within the level of measurement uncertainty compared to values determined from thermal conductivity measurements on samples fabricated from the same ingot sheet [6]. Bulk samples' measurements benefit from a longer seat and smaller cross sections which raises the measured voltage at low temperatures, allowing high drive currents to be avoided. If significant heat is developed in the sample, or in leads to the sample, depression of sensed T_c and broadening of ΔT_c will occur. An advantage of the delta pulse measurement technique is very low average power delivered to the sample.

The system has been routinely used to characterize thin films from the Nb electron cyclotron resonance (ECR) plasma deposition system on a variety of substrates [7]. Sapphire is one of the most stable and best lattice matched substrates commercially available for Nb depositions allowing for better discernment of process conditions by blocking for substrate variability. Eight Nb samples deposited with different biases in a single deposition on a-plane and r-plane sapphire were used to characterize the reproducibility of the RRR data by measuring the same 16 samples in four different RRR runs without removing the samples from the Cu plates. Table 2 details the measured RRR, T_c, and ΔT_c for the 16 samples with a 10 mA drive 1 ms pulse for three RRR runs.

Table 2: Comparison of Calculated RRR, T_c, and ΔTc using a 10 mA Drive Current

ECR-136 a-Al₂O₃		Seat 1	Seat 2	Seat 3	Seat 4	Seat 5	Seat 6	Seat 7	Seat 8
Average Values	RRR	40.1	23.7	41.2	39.0	47.3	22.1	26.2	31.4
	Tc (K)	9.29	9.25	9.25	9.24	9.25	9.17	9.20	9.21
	ΔTc(K)	0.08	0.07	0.06	0.07	0.06	0.07	0.13	0.09
Standard Error	RRR	0.15%	0.18%	0.17%	0.01%	0.09%	0.02%	0.02%	0.22%
	Tc (K)	0.10%	0.12%	0.05%	0.05%	0.05%	0.05%	0.05%	0.00%
	ΔTc(K)	29.3%	33.3%	15.7%	16.7%	11.1%	9.5%	15.4%	33.3%
ECR-136 r-Al₂O₃		Seat 1	Seat 2	Seat 3	Seat 4	Seat 5	Seat 6	Seat 7	Seat 8
Average Values	RRR	117.1	75.5	102.2	107.2	110.6	91.6	39.2	96.3
	Tc (K)	9.29	9.28	9.28	9.27	9.28	9.26	9.26	9.27
	ΔTc(K)	0.06	0.06	0.06	0.06	0.05	0.06	0.08	0.07
Standard Error	RRR	0.27%	0.20%	0.27%	0.18%	0.18%	0.12%	0.26%	0.26%
	Tc (K)	0.07%	0.05%	0.05%	0.14%	0.05%	0.12%	0.12%	0.17%
	ΔTc(K)	14.0%	11.1%	7.8%	17.5%	38.1%	45.6%	5.3%	16.7%

After the first 10 mA RRR run, the samples were measured with a 102 mA drive current to determine if there were any observable self-heating effects that would lead to poor data quality in measured thin films on insulating substrates. Repeating the 10 mA drive current after the higher drive current would also expose any detriment to the samples. Table 3 presents the measured RRR, T_c, and ΔT_c data for the same 16 ECR Nb/Al$_2$O$_3$ samples comparing the of 102 mA data to the average values for the 10 mA data in the standard error rows.

Table 3: Comparison of Calculated RRR, T_c , and ΔT_c Between 10 mA and 102 mA Drive Currents

ECR-136 a-Al$_2$O$_3$		Seat 1	Seat 2	Seat 3	Seat 4	Seat 5	Seat 6	Seat 7	Seat 8
Average Values	RRR	40.2	23.6	41.1	39.1	47.4	22.2	26.2	31.6
	Tc (K)	9.18	9.21	9.11	9.21	9.22	9.09	9.13	9.16
	ΔT$_c$(K)	0.13	0.06	0.15	0.18	0.17	0.19	0.15	0.20
Standard Error	RRR	0.26%	-0.15%	-0.22%	0.23%	0.18%	0.17%	0.13%	0.61%
	Tc (K)	-1.22%	-0.47%	-1.48%	-0.36%	-0.29%	-0.91%	-0.80%	-0.54%
	ΔT$_c$(K)	56.0%	-18.2%	164.7%	170.0%	183.3%	171.4%	15.4%	130.8%
ECR-136 r-Al$_2$O$_3$		Seat 1	Seat 2	Seat 3	Seat 4	Seat 5	Seat 6	Seat 7	Seat 8
Average Values	RRR	117.0	75.5	101.6	107.1	110.6	92.6	39.2	96.7
	Tc (K)	9.23	9.18	9.21	9.22	9.22	9.02	8.93	9.23
	ΔT$_c$(K)	0.13	0.17	0.11	0.09	0.08	0.26	0.19	0.15
Standard Error	RRR	-0.05%	0.00%	-0.56%	-0.08%	-0.01%	1.00%	0.13%	0.40%
	Tc (K)	-0.65%	-1.11%	-0.79%	-0.54%	-0.68%	-2.63%	-3.60%	-0.47%
	ΔT$_c$(K)	105.3%	183.3%	94.1%	42.1%	71.4%	310.5%	128.0%	125.0%

In the higher drive current data, breakdown of the superconducting state is induced at lower temperatures than for the 10 mA drive. Thermal breakdown of the superconductor is driven by heat generated in the sample / electrical leads. The removal of heat from the Nb thin film is limited to convective transfer to the He gas due to the relatively low thermal conductivity of the Al$_2$O$_3$ impeding cooling through the Cu plate. Differential conductivity measurements will be used in the future to systematically probe where self-heating becomes evident in shifts to the T_c and broadening of the transition.

This RRR setup can reliably differentiate high quality thin film samples in large part due to the limited thickness of the films. With the thickness limited to microns, the voltage developed in the films is quite large even for 1 cm^2 samples. Figure 5 demonstrates one of the outputs from the MATLAB code used to systematically analyse the RRR data.
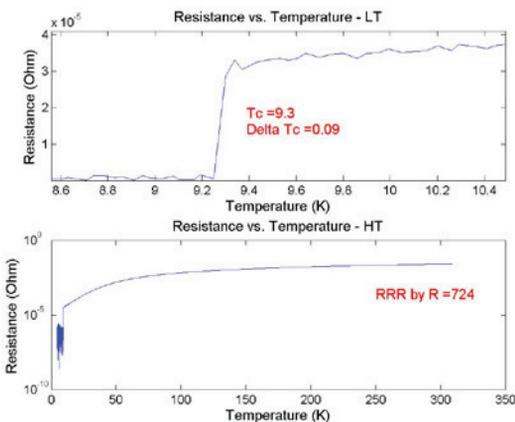
Figure 5: RRR plots from MATLAB program demonstrating the RRR system's dynamic range and low temperature resolution for an ECR deposited Nb thin film.

The RRR system described in this work provides vital feedback for the novel and high T_c materials projects at JLab [8]. These materials are being developed to extend the operating range of SRF cavities and to lower the operating cost by reducing the cryogenic heat load for a given gradient. Determining the deposition conditions for the high T_c materials requires unambiguous data to gauge and guide the process.

Commercial MgO is one of the witness samples used to determine the properties of the reactively sputtered ternary high T_c superconductor NbTiN at JLab. Figure 6 presents the RRR results for 2 samples of high purity NbTiN on MgO.
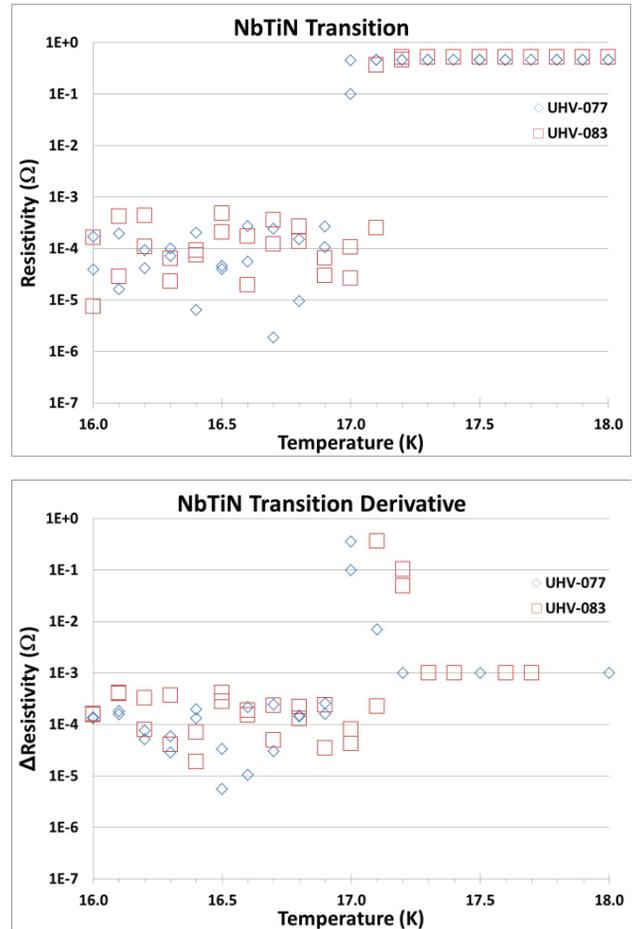
Figure 6: NbTiN transition plot (upper) and derivative of the resistivity (lower).

The graph above presents nearly ideal transitions for NbTiN. The figure also demonstrates how the MATLAB code determines where the transition occurs. The derivative of the resistance curve peaks at the temperature at which the transition occurs. The MATLAB program identifies this point then calculates the noise floor average voltage and the normal state average voltage. The transition width is calculated as the temperature difference between the first value which is ≤ 10% above the noise floor and ≥ 90% of the normal state values. The transition temperature is calculated as the mean of the transition width temperatures.

FURTHER IMPROVEMENT PLANS

The RRR system has been evolving for over half a decade with the goals of improving the resolution of data, the accuracy of the measurements, and increasing sample throughput. The system's isotherm method is cumbersome and can be improved. Figure 7 details a new test stand design that implements a consolidated copper box that is welded on five sides with built-in lift plates.

Figure 7: The new test stand test fixture with one of the sides of the shroud and Cu box rendered transparent.

The Cu box is thermally isolated with a G10 adapter from the supporting 2 ¾" conflat tube that connects to the test stand lid. The dewar buffering and isolation is implemented with a welded stainless steel clamshell shroud that is thermally isolated from the Cu box with G10 spacers. The measurement and thermometry cabling will come into the top of box through the 2 ¾" conflat that supports the box from the top plate. The cabling in the dewar will have polyolefin insulation that should withstand thermal cycling better than the currently used PVC flat ribbon cable. The resistivity and thermometry signals will be consolidated into a single shielded twisted pairs cable per Cu plate throughout the setup, which should minimize unbalanced noise. Reconfiguring the current and voltage pin assignments in the ribbon cable from the switch to the sample seats will reduce cross-talk noise. The new test stand design will simplify the isothermal methodology in the dewar, reducing the cryogens, consumables, and labor per run. The proposed RRR system will have better temperature uniformity, better T_c resolution, and a lower resistivity noise floor. The new design will improve the measurement of difficult samples that have high dynamic ranges, sharp transitions, or have diluted resistivity responses due to sample geometry. We anticipate implementation of this system upgrade in the coming year.

REFERENCES

[1] G. W. Webb, "Low-Temperature Electrical Resistivity of Pure Niobium", Phys. Rev. **181**(3), 1127 (1969).

[2] E. Bemporad et al., "Superconducting and microstructural studies on sputtered niobium thin films for accelerating cavity applications", Supercond. Sci. Technol. **21**, 125026 (2008).

[3] C. Reece et al., "A Closed Cycle Cryogenic System for Testing Superconducting RF Cavities", Proc. PAC1991, p. 2325.

[4] W. Singer et al., "RRR Measurement Techniques on High Purity Niobium", TTC-Report 2010-02.

[5] J. D. Splett et al., "A Comparison of Methods for computing the Residual Resistivity Ratio of High-Purity Niobium", J. Res. Natl. Inst. Stand. Technol. **116**, 489 (2011).

[6] G. Ciovati et al., "RF Performance of Ingot Niobium Cavities of Medium-Low Purity", Proc. SRF2015, MOPB001, Whistler, Canada (2015).

[7] A.-M. Valente-Feliciano et al., "SRF performance and material quality of Nb films grown on Cu via ECR plasma energetic condensation", Proc. SRF2015, TUPB029, Whistler, Canada (2015).

[8] A.-M. Valente-Feliciano, PhD Thesis, Orsay 2014.