



RRR-Measurement Technique on High Purity Niobium

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Contents

1 Introduction.....	3
1.1 Superconductivity.....	3
1.2 The Meissner effect.....	4
1.3 Types of superconductors.....	6
2 Niobium – material for SRF cavities.....	7
2.1 The purity of niobium.....	7
3 Residual Resistivity Ratio RRR.....	8
4 Non-destructive RRR eddy current (AC) measurement system.....	11
4.1 Eddy current in metal.....	11
4.2 Specially-designed sensor probe structure.....	12
4.3 Calculated value of RRR.....	13
4.4 Accuracy estimation.....	15
5. Experimental results.....	16
References.....	18

1. Introduction

The most common application of superconducting RF is in particle accelerators. Accelerators typically use resonant RF cavities formed from or coated with superconducting materials. Electromagnetic fields are excited in the cavity by coupling in an RF source with an antenna. When the RF frequency fed by the antenna is the same as that of a cavity mode, the resonant fields build to high amplitudes. Charged particles passing through apertures in the cavity are then accelerated by the electric fields and deflected by the magnetic fields. The resonant frequency driven in SRF cavities typically ranges from 200 MHz to 3 GHz, depending on the particle species to be accelerated. The most common fabrication technology for such SRF cavities is to form thin walled (1–3 mm) shell components from high purity niobium sheets by stamping. These shell components are then welded together to form cavities.

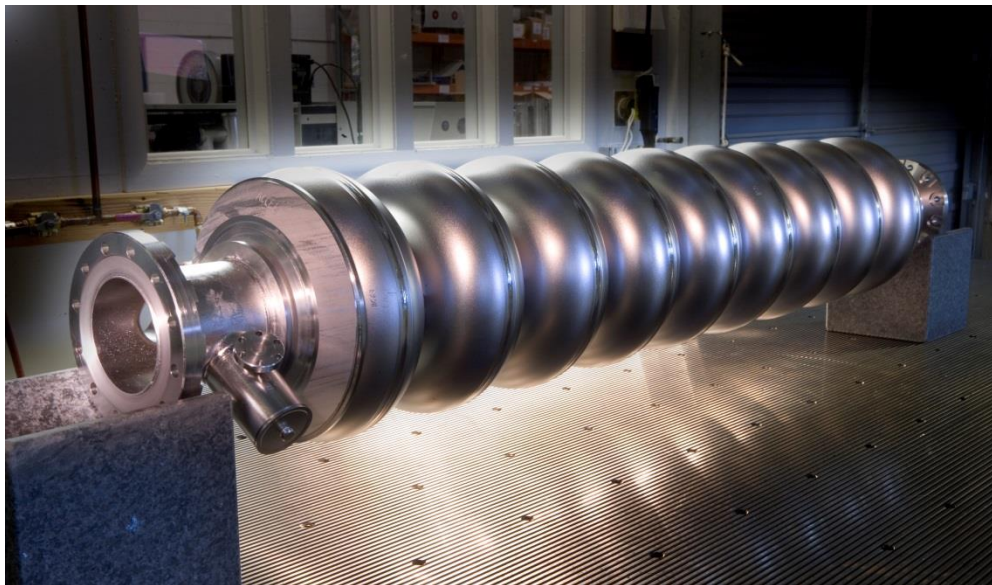


Figure 1 – SRF 9-cell cavity

1.1. Superconductivity

Superconductivity is a phenomenon of exactly zero electrical resistance and expulsion of magnetic fields occurring in certain materials when cooled below a characteristic critical temperature. It was discovered by Dutch physicist Heike Kamerlingh Onnes on April 8, 1911 in Leiden. Superconductivity is characterized by the Meissner effect, the complete ejection of magnetic field lines from the interior of the superconductor as it transitions into the superconducting state. The occurrence of the Meissner effect indicates that

superconductivity cannot be understood simply as the idealization of perfect conductivity in classical physics.

The electrical resistivity of a metallic conductor decreases gradually as temperature is lowered. The thermal vibrations of the atoms decrease with fall in temperature, and the conduction electron are less frequently scattered. The decrease in resistance falls less rapidly as the temperature falls (figure 2). Even near absolute zero, a real sample of a normal conductor shows some resistance [1].

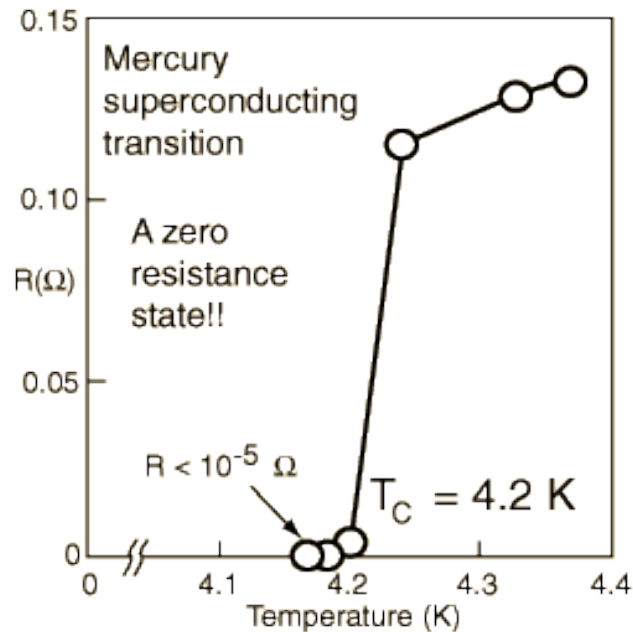


Figure 2 – Superconducting transition of resistance of mercury

1.2. The Meissner effect

The superconducting state is characterized not only by zero resistance, but by the Meissner effect. The Meissner effect is the expulsion of a magnetic field from a superconductor during its transition to the superconducting state. The exclusion of the magnetic field from a superconductor takes place regardless of whether the sample becomes superconducting before or after the external magnetic field is applied. In the steady state, the external magnetic field is cancelled in the interior of the superconductor by opposing magnetic fields produced by a steady screening current that flows on the surface of the superconductor. Consider first the behavior of a perfect conductor.

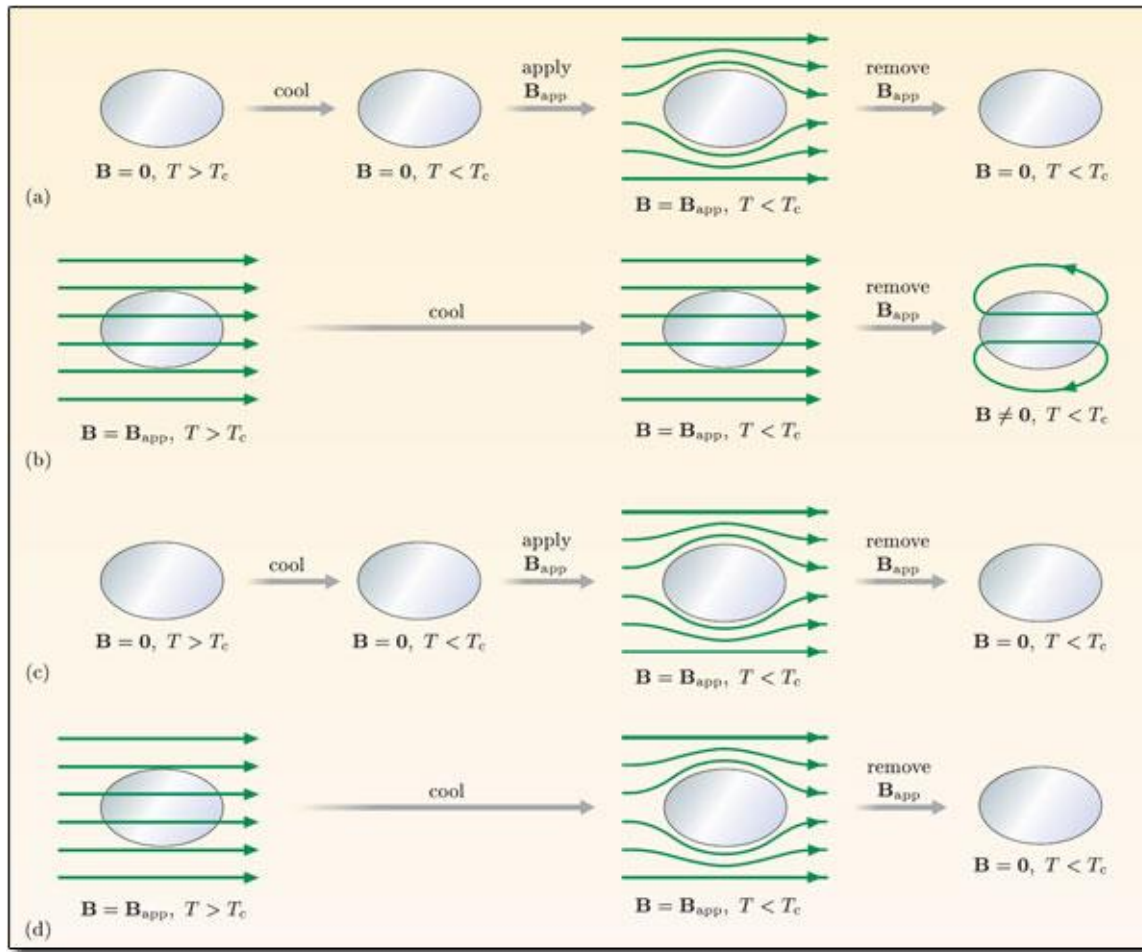


Figure 3 – A comparison of the response of a perfect conductor, (a) and (b), and a superconductor, (c) and (d), to an applied magnetic field

In part (a) of this figure, a perfect conductor is cooled in zero magnetic field to below the temperature at which its resistance becomes zero. When a magnetic field is applied, screening currents are induced in the surface to maintain the field at zero within the material, and when the field is removed, the field within the material stays at zero. In contrast, part (b) shows that cooling a perfect conductor to below its critical temperature in a uniform magnetic field leads to a situation where the uniform field is maintained within the material. If the applied field is then removed, the field within the conductor remains uniform, and continuity of magnetic field lines means there is a field in the region around the perfect conductor. Clearly, the magnetisation state of the perfect conductor depends not just on temperature and magnetic field, but also on the previous history of the material.

Contrast this with the behaviour of a superconductor, shown in Figure 10 parts (c) and (d). Whether a material is cooled below its superconducting critical temperature in zero field, (c), or in a finite field, (d), the magnetic field within a superconducting material is always zero. The magnetic field is always expelled

from a superconductor. This is achieved spontaneously by producing currents on the surface of the superconductor. The direction of the currents is such as to create a magnetic field that exactly cancels the applied field in the superconductor. It is this active exclusion of magnetic field – the Meissner effect – that distinguishes a superconductor from a perfect conductor, a material that merely has zero resistance. Thus we can regard zero resistance and zero magnetic field as the two key characteristics of superconductivity [2].

1.3. Types of superconductors

The difference between type I and type II superconductors can be found in their magnetic behavior (figure 4).

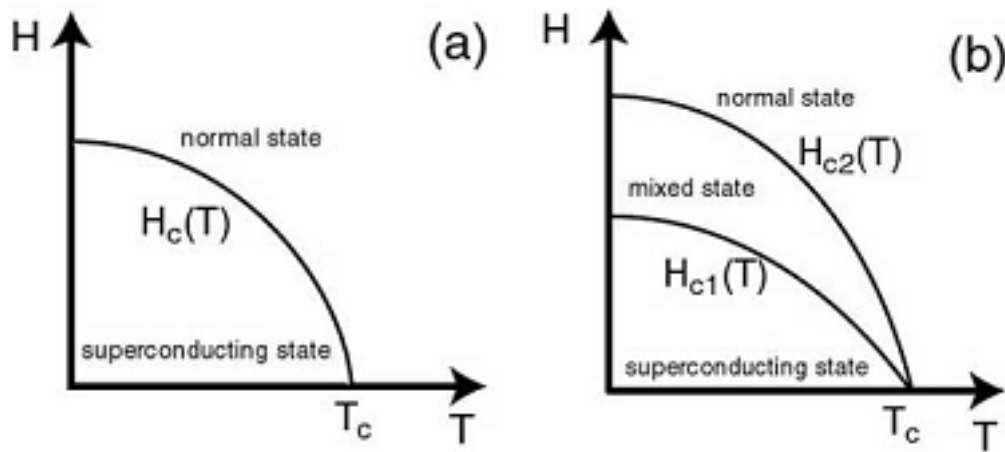


Figure 4 – Critical magnetic field as a function of temperature for (a) type I superconductors and (b) type II superconductors

A type I superconductor keeps out the whole magnetic field until a critical applied field H_c is reached. Above that field a type I superconductor is no longer in its superconducting state.

A type II superconductor will only keep the whole magnetic field out until a first critical field H_{c1} is reached. Then vortices start to appear. A vortex is a magnetic flux quantum that penetrates the superconductor. Where the vortex appears the superconducting order parameter drops to zero. In this region the metal is no longer a superconductor. Around the vortex a current starts to circulate. Even though the vortices have formed, the rest of the metal stays superconducting. If the field is increased to the second critical field H_{c2} the metal stops to be superconducting. H_{c2} is usually a lot bigger than H_c that's why type II superconductors are typically used for superconducting magnets [3].

2. Niobium – material for SRF cavities

At present, the de facto choice for SRF material is still pure niobium. Niobium, having the highest critical temperature and critical magnetic field of all pure metals (critical temperature 9.3K; superheating field of ~ 240 mT) has for many years now been the preferred metal for the fabrication of superconducting RF cavities. This is because niobium is chemically inert (at room temperature, the surface is covered by a protecting pentoxide layer), it can easily be machined and deep drawn, and it is available on the market, in the required amounts, in bulk and sheet material form. In the past three decades, improvements of Electron-Beam Melting (EBM) and purification techniques have made good progress. The purity of industrially produced niobium has steadily increased due to the reduction of concentrations of metallic impurities such as tantalum (Ta) and tungsten (W) and of the interstitially dissolved elements carbon, oxygen, and nitrogen. The application of ultra-high-vacuum technology additionally increases purity. Several companies worldwide are currently in a position to produce tonnes of niobium for high-gradient cavities [4].

2.1. The purity of niobium

During cavity fabrication Nb goes through multiple stages of treatments (annealing, chemical and electrochemical polishing, electron beam welding, centrifugal barrel polishing etc.). At each stage the purity of the Nb can be significantly diminished.

Important metrics of SRF cavity technology are the quality factor Q_0 and the maximum electric field E_{acc} to which high values of Q_0 can be sustained. There are many phenomena that can occur in an SRF cavity to degrade its Q_0 vs E_{acc} performance, such as impurities in the niobium, hydrogen contamination due to aggressive chemical etching during the cavity preparation, and a rough surface finish. At higher fields, typically, electron field emission or thermal breakdown due to particles causes problems. After a couple decades of development, a necessary prescription for successful SRF cavity production is emerging. This includes:

- eddy-current scanning for impurities of the raw niobium sheets used for cavity production;
- good quality control of electron beam welding parameters used for cavity production;

- chemically etching the surface of the cavity to remove layers that were damaged during production. Maintaining a low acid temperature to avoid contaminating the niobium with hydrogen;
- electropolishing of the cavity interior to achieve a very smooth surface;
- baking the cavity in a vacuum furnace between 600 °C and 900 °C to remove hydrogen that has been dissolved in the niobium;
- high pressure rinsing (HPR) of the cavity interior in a clean room with filtered water to remove particulate contamination that otherwise can cause field emission and thermal breakdown;
- carefully assembling of the cavity to other vacuum apparatus in a class 100 or better clean room with clean practices;
- vacuum baking the cavity at 120 °C for about 48 hours.

3. Residual Resistivity Ratio

The value of residual resistivity ratio RRR is an indication of the purity and the low-temperature thermal conductivity of the niobium, and is often used as a material specification in commerce. The interstitial impurities oxygen (O), nitrogen (N), carbon (C) and hydrogen (H) have major influence on the thermal conductivity of niobium. By rising of the thermal conductivity the thermal breakdown happens at higher field level. The RRR gives information about the total impurity content and the thermal conductivity of superconducting niobium.

As well-known from the electron theory of metals, in general cases the electrical resistivity of metals (Mathiessen's rule) at low temperature can be described as

$$\rho = \rho_{res} + \rho_{ph}(T) \quad (1)$$

where the first term is the residual resistivity at $T \sim 0K$ caused mainly by electron-impurity scattering and scattering on lattice defects ($\rho_{res} = \rho_{imp} + \rho_{def}$); the second term in equation 1 represents the temperature dependent electron-phonon scattering.

Scattering of conduction electrons on the lattice (phonon scattering) is absent at $T=0K$ due to the zero kinetic thermal energy. For recrystallized niobium the ρ_{def} contribution is small. In this case the total resistivity described by equation 1 and consists only of electron-impurity scattering and electron-phonon scattering contributions.

The residual resistivity is dependent on impurities and other lattice defects of the metal, whereby the concentration of impurity atoms contributes linearly to the residual resistivity

$$\rho_{res} = \sum_i \frac{\Delta\rho_i}{\Delta C_i} C_i \quad (2)$$

The resistance coefficients $\Delta\rho_i/\Delta C_i$ are given in table 1.

Table 1 - Residual Resistance Coefficients of different atoms as found by K. K. Schulze

Impurity atoms	O	H	N	C	Ta	Zr
$\Delta\rho_i/\Delta C_i, 10^{-10}$ ohm-cm/at.-ppm	4,5	0,8	5,2	4,3	0,25	0,6-1,4

As the total resistivity of technically pure niobium at 4.2 K is dominated by the residual resistivity, RRR is very suitable as an integral value for estimation of the impurities contains.

In absolutely pure metals having a lattice without structural defects at temperatures close to 0 K, resistivity tends to be zero (as shown in figure 5). The RRR is defined as the ratio:

$$RRR = \frac{\rho(295K)}{\rho(4.2K)} \quad (3)$$

where $\rho(300\text{ K})$ and $\rho(4.2\text{ K})$ are the resistivity of metals at room and liquid helium temperatures, respectively, at standard atmospheric pressure. With the superconducting behavior of Nb (below $T_C=9.3\text{ K}$), $\rho(4.2\text{ K})=0$ has to be taken into account for RRR determination [5].

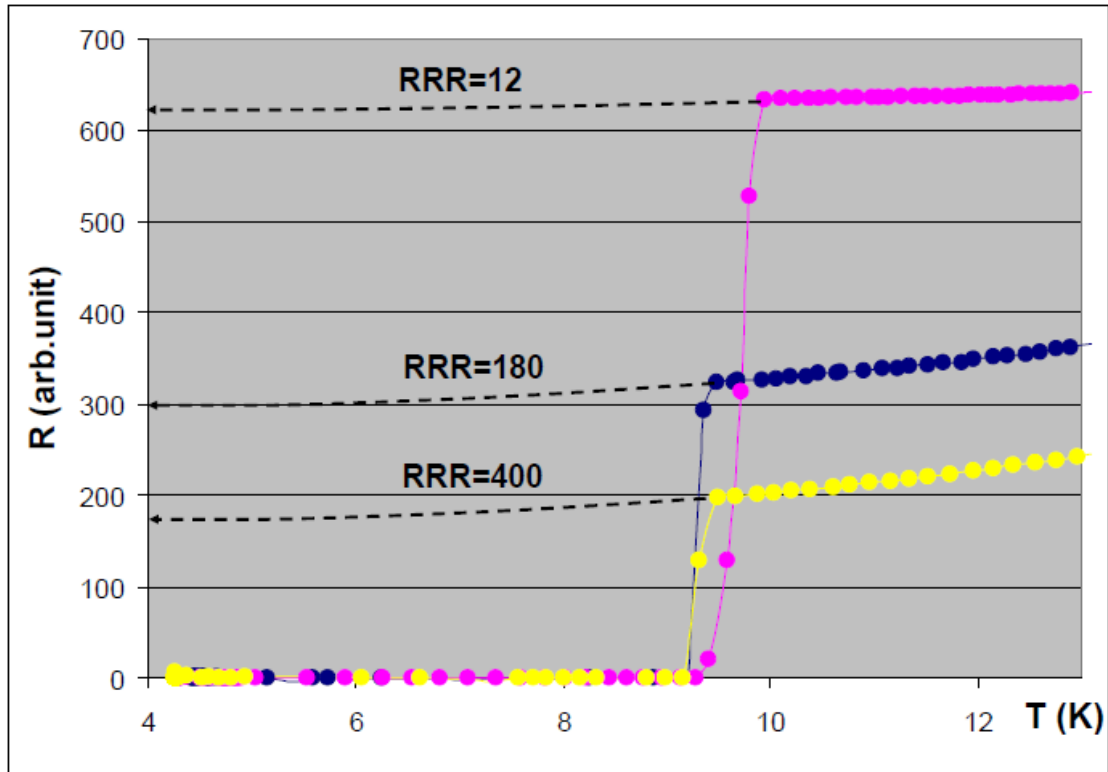


Figure 5 - Typical $\rho(T)$ curves for Nb samples of different purity [4]

Electrical resistivity is frequently measured using 4-terminal-potentiometric AC or DC methods. These methods all involve the connection of two current leads and two potential leads to the specimen.

The measurement of the residual resistivity is problematic due to the superconductivity of niobium below temperatures of $T_c = 9.3$ K. Two methods can be employed to overcome this problem. The first method suppresses superconductivity by exposing the sample to an external magnetic field of field strength $H \geq H_c$. The second method avoids this problem by measuring the specimen's resistivity at a temperature above T_c but very close to it. Another disadvantage is that the 4 point method needs rather long samples of definite geometry.

One of the important tasks of cavity production is to control the RRR during different production steps, from the «as delivered» niobium sheet till ready cavities. Very desirable is to do it without destroying the material. The four point method is not suitable for this task. Eddy current inspection is a very accurate method for measuring electrical resistivity (and resistivity ratios). Besides it has the advantage that no electrical connections to the specimen are needed. So eddy current inspection is non-destructive.

4. Non-destructive RRR eddy current (AC) measurement system

4.1. Eddy current in metal

For the control of purity at such stages a non-destructive RRR eddy current (AC) measurement system is used at DESY. It is designed for controlling RRR directly on the surface of the superconducting resonators.

When a normal conducting metal placed in an AC magnetic field with the frequency f , an eddy current will be induced in the metal (figure 6). Eddy currents concentrate near to the surface adjacent to an excitation coil and their strength decreases with distance from the coil i.e. Eddy Current density decreases exponentially with the penetration depth δ .

$$\delta = 1/\sqrt{\pi\mu\sigma f} \quad (4)$$

where σ -conductivity, μ -permeability. The feature of this method is that eddy currents are measured the RRR of a small area with a penetration depth in a sample.

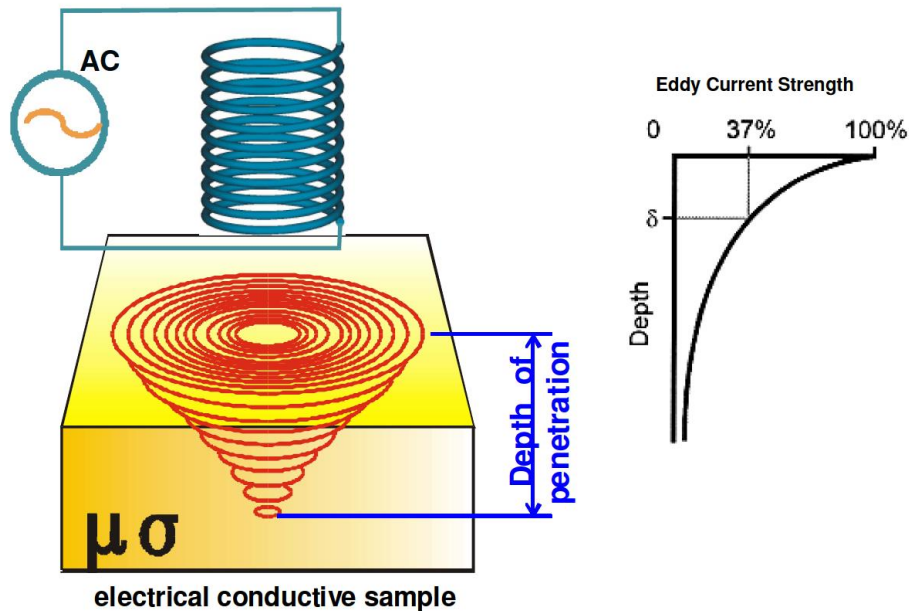


Figure 6 – The induced eddy current with a depth in the metal under AC magnetic field

The detection and measurement of the magnetic fields allow for obtaining contact-less information about the conductive properties of materials.

4.2. Specially-designed sensor probe structure

The measurement probe consists of a primary coil for establishing the AC magnetic field, a pick up coil for detecting the eddy current, and a compensation coil for compensation of the signal induced by the primary coil. Figure 7 shows its structure.

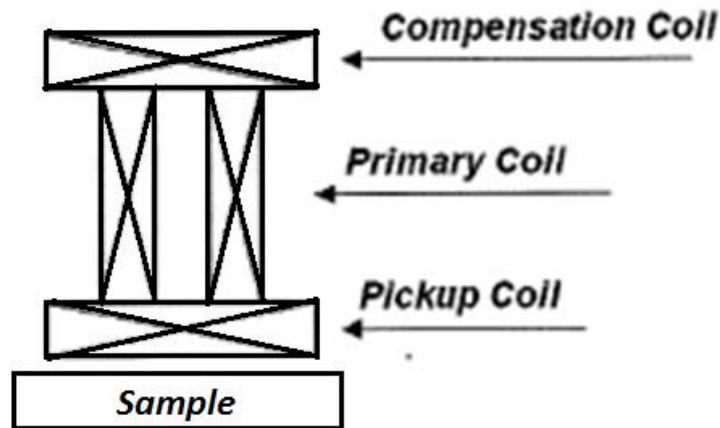


Figure 7 – Probe structure for eddy current RRR measurement

The primary coil is a small solenoid magnet with 50 turns' coils. The pickup coil is a one-layer pancake coil (figure 7). The cancel coil should be the same shape as pickup coil but with opposite induced voltage direction. It is used for eliminating the signal of pickup coil induced by primary coil, which is much bigger than that induced by eddy current in the metal.

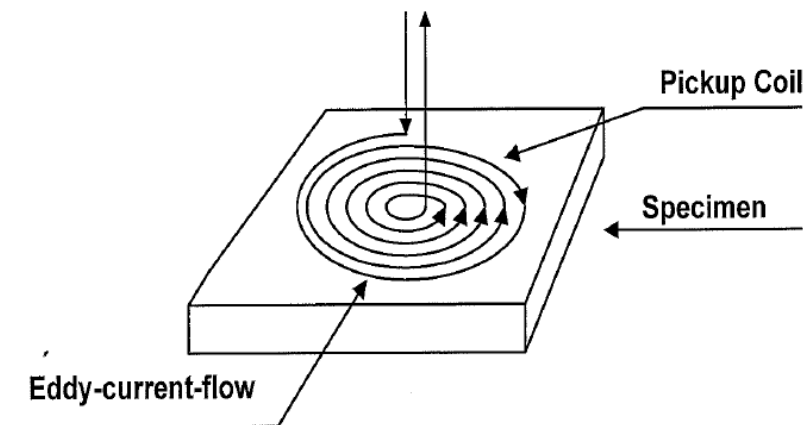


Figure 8 – One-layer pancake-shape coil

Support for fixing probes on the cavity wall shown in figure 9.

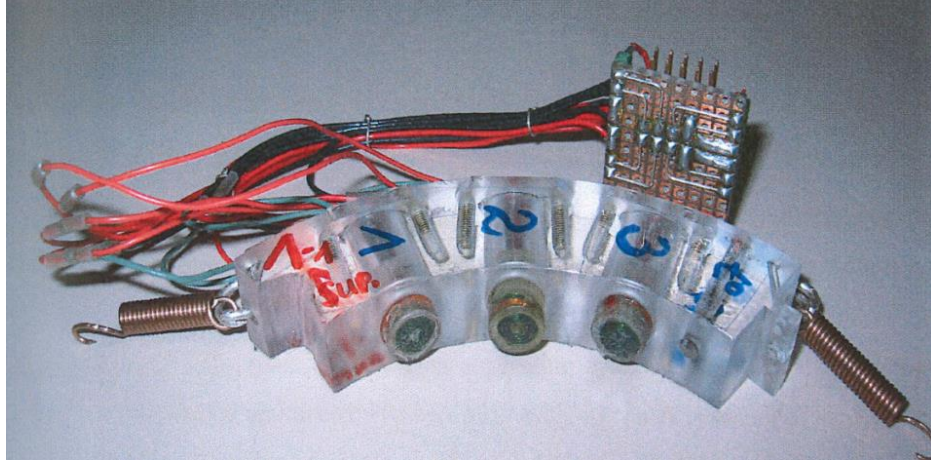


Figure 9 – Support for fixing probes on the cavity wall

Each probe is pressed by a spring for keeping a good contact between the probe and cavity wall. The support fixed on the cavity wall with two springs on both ends of the support. Figure 10 shows how the supports are assembled on the cavity wall [7].

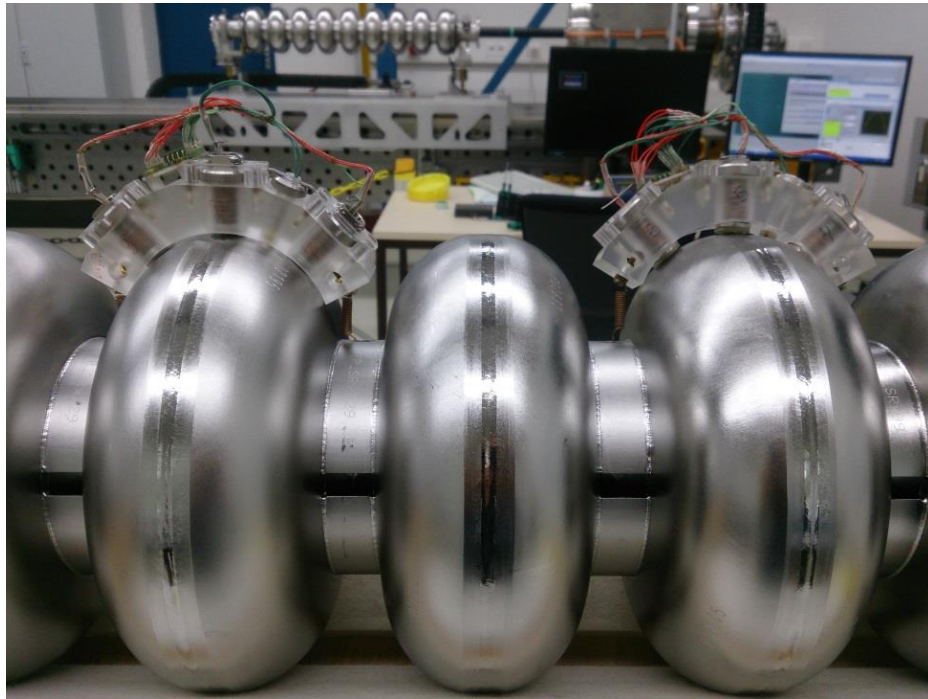


Figure 10 – Photo of probes supports on cavity wall

4.3. Calculated value of RRR

It is not so easy to express quantitatively the relationship between the eddy current and the sample resistivity since this depends on the probe structure, the sample shape, the distance between coil and sample etc. A relative method based on the relationship between pick-up voltage jump at T_c and RRR is

applied. For the samples with different RRRs, the superconducting jumps U_j will be different. The samples with higher RRRs will produce smaller superconducting jumps. In principle, if we can create the same coils with the same parameters and keep the good contact between probe and cavity wall, the superconducting jump U_j can be used for evaluating RRR. One measures the temperature dependence of the pick-up voltage (figure 11).

The system collects the useful values of pickup coils at three temperature points:

1. at room temperature, all values of the pickup signals produced by the unequal signals between pickup coil and the compensation coil (U_x^0, U_y^0) are collected as zero points, which will be subtracted from the measured signal;
2. at about 9.3K, before superconducting jump, the cavity is still in normal conducting state (U_x^n, U_y^n);
3. at the temperature lower than 9.3K, when the cavity becomes superconducting (U_x^s, U_y^s) [7].

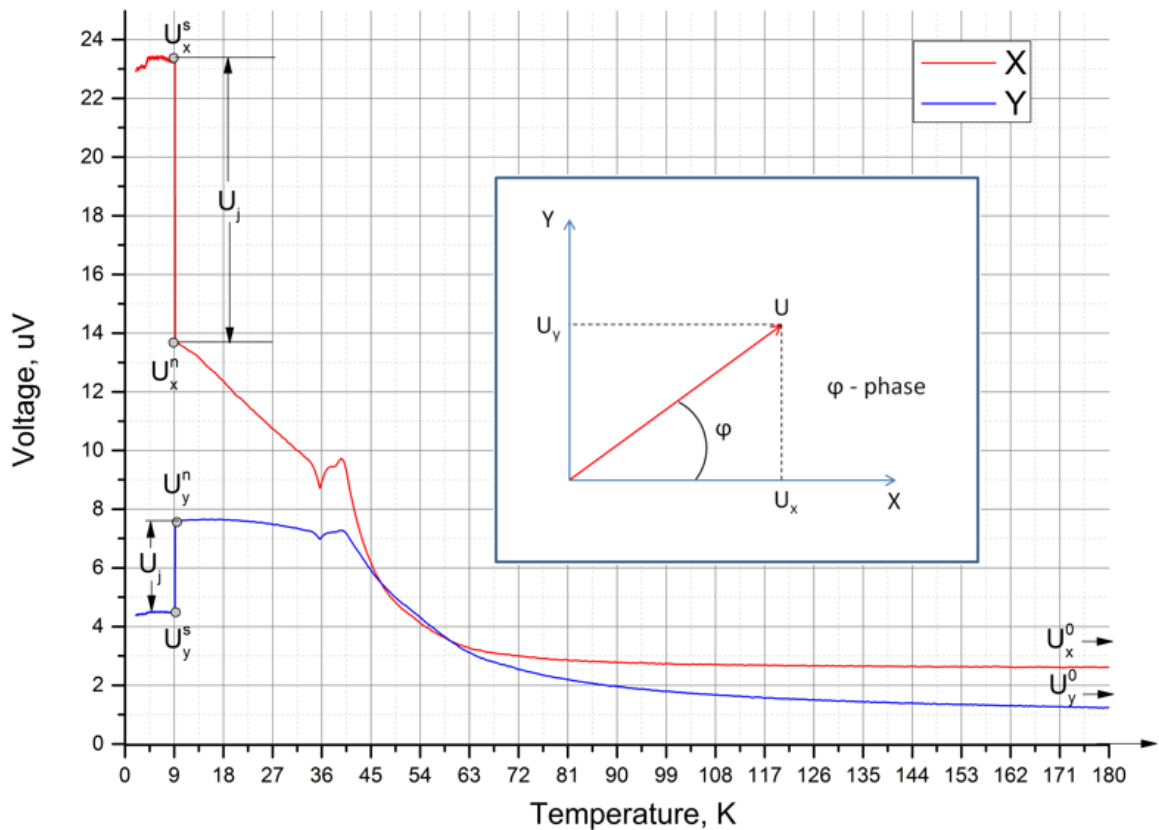


Figure 11 - Values of pickup coils one of the probes

The value of U_j/U_s is calculated by the formula:

$$\frac{U_j}{U_s} = \frac{\sqrt{(U_x^s - U_x^n)^2 + (U_y^s - U_y^n)^2}}{\sqrt{(U_x^s - U_x^0)^2 + (U_y^s - U_y^0)^2}}, \quad (5)$$

and then RRR is calculated by the formula:

$$RRR = e^{\left(-\frac{U_j/U_s - a}{b}\right)}, \quad (6)$$

where a and b is the calibration data for each probes.

4.4. Accuracy estimation

Two main factors influence the measurement accuracy. One is the contact quality. The measured RRR dependence on the distance between probe and the niobium sample (figure 12). It can be seen that the deviation of RRR can be within 5% for a distance deviation between probe and cavity wall smaller than 0.2 mm.

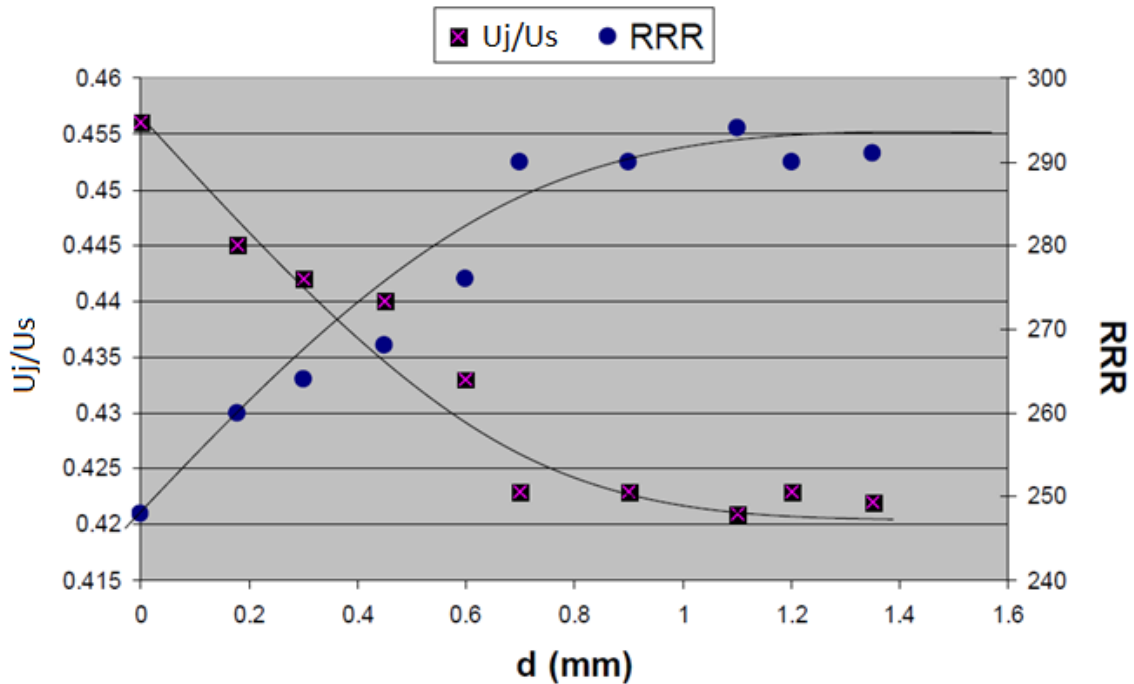


Figure 12 - Influence of distance between probe and sample surface on RRR measurement [5]

The other important factor is the temperature homogeneity of the cavity close to TC, needed for a clearly expressed superconducting jump. The temperature deviation during cool-down should not exceed 0.1K. The superconducting jump is sufficiently expressed for temperature identification

with an error less than 0.2K. Therefore, the error for a RRR value around 300 due to cool-down or warm-up can be well controlled within 3%. The systematic error coming from instruments and current sources can be controlled within 1%. The pickup cables have to be twisted for minimizing parasitic noise.

Considering all the mentioned aspects, received value of the RRR has an error within 9% [7].

5. Experimental results

I did the RRR measurement for EXFEL cavity CAV00705, which was annealed at the temperature of 1100 degrees Celsius and has contaminations from the furnace. There were two measurements: during cooling and during heating. The results are shown in tables 2 (cooling) and 3 (warming up).

Table 2 - Cooling of the cavity

Channel	Support NO.	Probe SP_No.	Calibration data		U_j/U_s	RRR
			a	b		
1	1	32	1,3805	0,17054	0,600938324	165,0
2	2	2	1,4615	0,1797	0,596263528	210,5
3	3	25	1,3835	0,16953	0,599603622	174,0
4	22	43	1,3556	0,16847	0,548308216	205,7
5	23	42	1,4232	0,17575	0,600807881	183,8
6	24	44	1,3387	0,16573	0,5569209	190,9
7	25	11	1,3528	0,16373	0,479808207	353,8

Table 3 – Warming up of the cavity

Channel	Support NO.	Probe SP_No.	Calibration data		U_j/U_s	RRR
			a	b		
1	1	32	1,3805	0,17054	0,596686018	162,5
2	2	2	1,4615	0,1797	0,586957497	213,0
3	3	25	1,3835	0,16953	0,587393873	179,6
4	22	43	1,3556	0,16847	0,562659596	181,5
5	23	42	1,4232	0,17575	0,61057836	167,1
6	24	44	1,3387	0,16573	0,538459326	205,1
7	25	11	1,3528	0,16373	0,473284098	353,2

As can be seen from the tables, the value RRR of the cavity 1.5-2 times less than the value of the standard sample (number 7 in the tables) and is out of the EXFEL specifications (>300).

Non-destructive RRR eddy current (AC) measurement method performed directly on the cavity surface makes it possible to estimate the RRR value on a definite location of the cavity or average RRR value of the complete cavity as delivered by the cavity producer or after different stages of cavity preparation.

References

- [1] Neeraj, Mehta. *Applied Physics for Engineers*. PHI Learning Private Ltd, pages 930–931, 2011.
- [2] Web-page «<http://www.open.edu/openlearn/science-maths-technology/engineering-and-technology/engineering/superconductivity/>», The Open University.
- [3] A. Orthacker, *Superconductivity*
- [4] W. Singer, *SRF Cavity Fabrication and Materials*, DESY, 2015.
- [5] W. Singer, A. Ermakov, and X. Singer, *RRR-measurement techniques on high purity niobium*, TTC Report 2010 (http://flash.desy.de/reports_publications/tesla_reports/ttc_reports_2010).
- [6] A. Bosotti, D. Corti, M. Fusetti, G. Varisco, *RRR Measurement with eddy currents method*. National Institute for Nuclear Physics (INFN), pages 1-2.
- [7] H. Wen, *TTF Cavity RRR Measurement System*, MPL, DESY, 2005.