Specific Resistance Measurement of a Single Grain Boundary in Pure Niobium

H. Safa, M. Boloré, Y. Boudigou, S. Jaidane, R. Keller, P. Nardin, G. Szegedi,
CEA Saclay, DSM/DAPNIA/SEA, 91191 Gif-sur-Yvette, France

Abstract

Grain boundary is a key issue for RF performance of superconducting cavities as the electromagnetic field is forced to cross through. A special apparatus has been developed at Saclay that is able to measure the specific resistance of a each grain boundary of a sample. The results obtained on ultrapure niobium samples confirm experimentally the non-uniformity of the local resistance and the important contribution of the grain boundary. The average value of the specific resistance of a grain boundary in niobium is measured to be 2.10^{-13} Ω.m2.

1 - INTRODUCTION

It has been previously established that grain boundaries may give rise to a non linear increase in the surface resistance of superconductors [**1**]. The grain boundary, considered as a weak link with a lower critical current density J_c than the bulk, will suffer transition in the normal state above a given magnetic field. This is particularly true in the case of a radiofrequency (RF) regime where the electromagnetic field is forced to flow through the grain boundary. Therefore, a measurement of the specific resistance of a grain boundary was necessary to confirm this theory. In order to separate the contribution of the grain boundary from the grain itself, very high RRR niobium is required. Using a purification process [**2**], extremely pure bulk niobium can be obtained with overall RRR values exceeding 2000. In this high temperature treatment, while reducing light impurities contents inside the grains, segregation of impurities might occur at the grain boundary [**3**].

2 - PRINCIPLE OF MEASUREMENT

The idea is a simple extension of the RRR measurement on samples done on a grain size scale (from 500 µm to 2 mm). A static current I is forced to flow along a thin sample (the thickness t should be smaller or of the same order than the grain size).

The measured voltage drop between two pins simply is

$$(1) \qquad (V_2 - V_1) = R\,I$$

The residual resistance R_0 is calculated from measurements done above the critical temperature (T_c = 9.25 K for Nb) and extrapolated at T = 0 K using the simplified law [**2**]

$$(2) \qquad R_0 = R - \alpha R_{295\,K}\, T^3$$

The coefficient α is equal to 5.10^{-7} K^{-3} for niobium.

The residual resistance will be the sum of the grain and the grain boundary contribution

$$(3) \qquad R_0 = \rho_1 \frac{l_1}{S} + \rho_2 \frac{l_2}{S} + \frac{G}{S}$$

where G is the specific resistance of the grain boundary (in $\Omega.m^2$). If the two pins hit the same grain, the contribution of the grain boundary vanishes and the measure gives directly the real residual resistance of the grain. Assuming that the residual resistivity of the grains is known (or measured), the specific resistance G of the grain boundary is then deduced from the above relation.

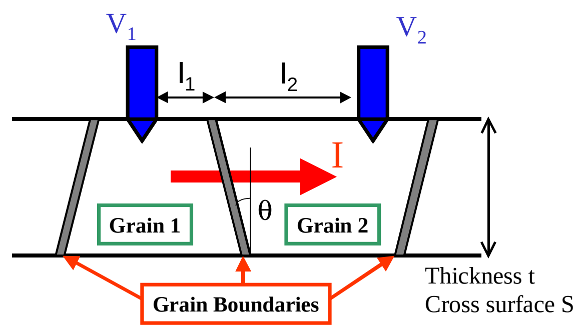

Figure 1 - Principle of grain boundary measurement.

In fact, the resistance is measured at room temperature (T = 295 K) giving the normalization for the length and cross surface. At room temperature, the phonon resistivity dominates all other contributions, and the resistance is reduced to the standard relation

$$(4) \qquad R_{295\,K} = \rho_{295\,K} \frac{l_1 + l_2}{S}$$

with $\rho_{295\,K}$ = $1.45.10^{-7}$ Ω.m for niobium.

The RRR value will be defined as*

$$(5) \qquad RRR = \frac{R_{295\,K}}{R_0}$$

* Actually, the usual definition is generally taken at the liquid helium temperature 4.2 K. But this definition only depends on the intrinsic properties as there is still some contribution of the phonons even at 4.2 K.

3 - EXPERIMENTAL SET-UP

Figure 2 show a picture of the experimental set-up. The niobium sample is milled then etched by a buffered chemical polishing (acid mixture). The sample is about 60 mm long, 2 mm wide and 0.5 mm thick.

The measured voltages are in the nanovolt scale and special care has to be taken to suppress thermoelectric effects and reduce all noise to a few nanovolts.

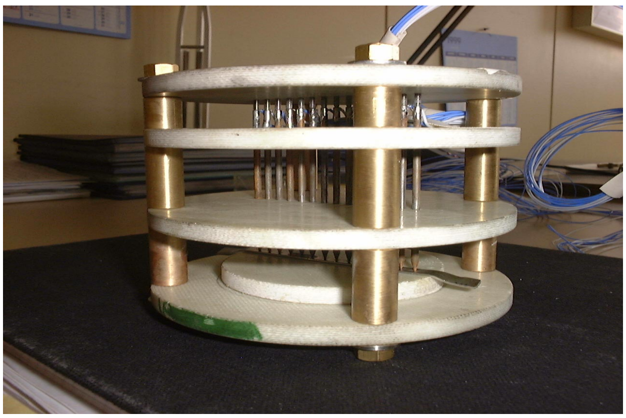

Figure 2 - Experimental set-up showing the needle pins pressed over a niobium sample. The current leads (not shown) are connected on each end.

4 - EXPERIMENT PROCEDURE

The sample is measured at room temperature in order to check all connections and to evaluate precisely the distances between pins. This gives the reference value as stated in equation (4). The resistance is linear with the length and the slight departure from absolute linearity observed in figure 3 is only due to a non equal distance between pins, as checked by the microscopic pictures shown later.

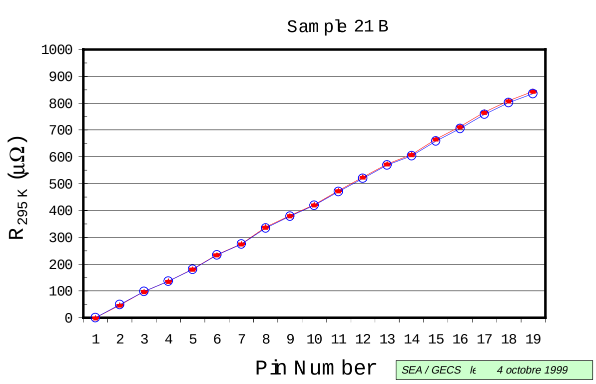

Figure 3 - Room Temperature Measurements. As expected, the resistance is linear with distance.

When the set-up is cold inside the cryostat, the measurement is done at different temperatures above T_c, typically between 10 K and 15 K. The residual resistance is then extrapolated to T = 0 K using equation (2).

5 - RESULTS

One example of the residual resistance obtained is shown in the next figure. One may immediately notice that, in contrast with the room temperature value, very important differences are measured depending on the area explored. This broken line type of the resistance along the sample denotes a non linear behaviour of the residual resistance. Therefore, one can immediately deduce that the RRR *is not* uniform along the sample.

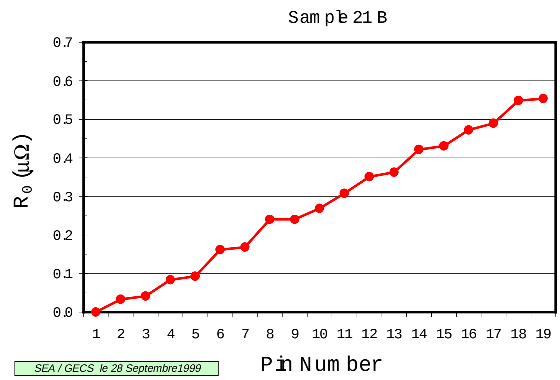

Figure 4 - Integrated residual resistance measured on a niobium sample. The result clearly shows a non uniform RRR.

Figure 5 is derived from figure 4 and gives the local residual resistance in between two following pins. Although the difference value will have higher error bars (the differences are in the nanoOhms scale), it definitely indicates that the residual resistance is strongly localised. Some measures may exceed 50 nΩ, while some others are lower than 10 nΩ, the average value being 30.8 nΩ, giving an average overall RRR of 1500 for this sample.

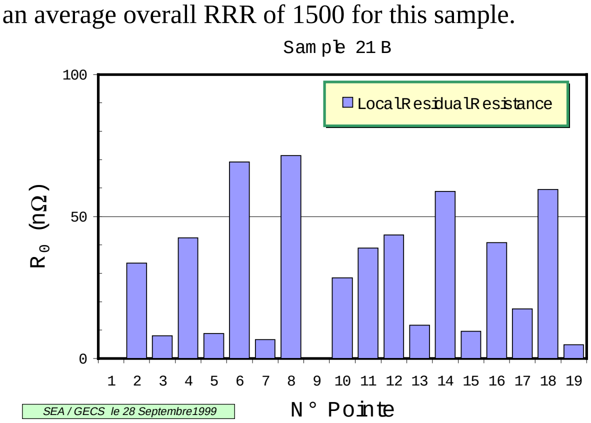

Figure 5 - Local measured residual resistance. Note that the value may vary by more than one order of magnitude from one place to another.

In order to correlate the measured residual resistance to the grain boundaries, a microscopic picture of the sample after cryogenic test is taken. From figure 6, there is a clear correlation between a measured high residual resistance and the presence of one (or sometimes) two grain boundaries in between the corresponding pins. This confirms that the grain boundaries are significantly contributing to the overall residual resistance and cannot be neglected. As a matter of fact, all the high residual resistance are associated to grain boundaries crossing, while all the lowest residual resistance measured are localized when the pins hit the same grain. On some point where two pins strike the same grain (see the detail of figure 7), the residual resistance is so small that the measure gives zero within the error bars. This indicates that the local RRR value inside a given grain can be extremely high (it is evaluated to exceed 20000 in this case !). This has been confirmed on other samples.

Figure 6 - Microscopic picture of the sample showing the impact of the pins and the grain boundaries.

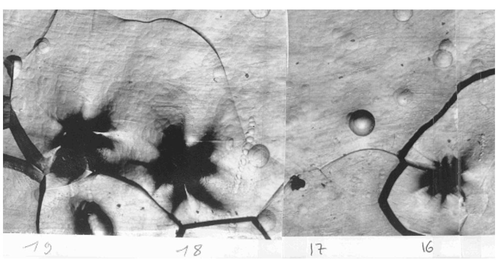

Figure 7 - Detail of the impact of two pins striking the same grain. The corresponding residual resistance is measured to be extremely small.

6 - DISCUSSION

From the above measurements, one may deduce using equation (3) and assuming that all the grains have the same residual resistance a value for the specific grain boundary. The deduced values are shown in the next figure. The specific resistance value is measured to be between 1.10^{-13} $\Omega.m^2$ and 3.10^{-13} $\Omega.m^2$ for the ten grain boundaries examined. The average value being

$$(6) \qquad \overline{G} = 2.10^{-13} \quad \Omega.m^2$$

This value is about 1000 times higher than what is commonly taken for pure bulk niobium [**4**] which is consistent with the well known theoretical relation [**5**]

$$(7) \qquad G = \frac{\Delta}{e.\,J_c}$$

(Δ/e) is the superconducting gap expressed in eV.
The assumption that all the grains offer the same residual resistivity is probably not quite true, as even when hitting the same grain, the measured residual resistance have some discrepancy. But these are of the order of the error measurement, which is evaluated for the time being to be about 20 nΩ. In the near future, improvements are planned to reduce this error to less than 5 nΩ, which should give more accurate results.

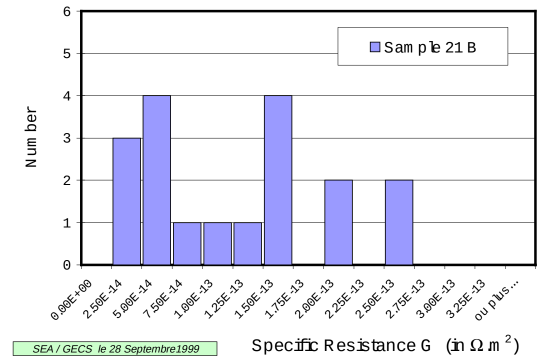

Figure 8 - Histogram of the specific resistance of grain boundaries in one sample.

All the above results shown are typical of more than twenty tests done on five different niobium samples, having different RRR values ranging from 30 to 2000. On low RRR samples where the grain size is rather small (50 to 100µm), the measure gives only an average value which is still compatible with the above results.

7 - CONCLUSION

In conclusion, a simple device has been fabricated to measure the specific resistance of grain boundaries. The experimental results indicate that :
1) The residual resistance is not uniform along the sample showing an important variation of the local RRR.
2) The contribution of grain boundaries to the residual resistance is far from negligible. It is even the major contribution in high RRR samples.
3) The average specific resistance of a grain boundary in pure niobium has been measured to be G = 2.10^{-13} $\Omega.m^2$.

8 - REFERENCES

1 B. Bonin & H. Safa, "Power Dissipation at high fields in granular RF superconductivity ", Superconductor Science & Technology, 4, p. 257, [1991]

2 H. Safa, D. Moffat, B. Bonin, F. Koechlin, "Advances in the purification of niobium by solid-state gettering with titanium ", Journal of Alloys and Compounds, 232, p. 281-288, [1996]

3 C.Z. Antoine & al., "Evidence of preferential diffusion of impurities along grain boundaries in very pure niobium used for radiofrequency cavities", J. of Applied Physics **81** (4) p. 1677, [1997]

4 K. Schulze, "Extractive metallurgy of refractory metals", Chicago Conf. [1981]

5 V. Ambegaokar & A. Baratoff, Phys. Rev. Letters, 10, p. 479 [1963]