PARAMETRISATION OF THE NIOBIUM THERMAL CONDUCTIVITY IN THE SUPERCONDUCTING STATE

F.Koechlin, and B.Bonin

DSM/DAPNIA/SEA Centre d'Etudes de Saclay, 91191 Gif sur Yvette, France

Abstract

Thermal conductivity measurements of niobium sheets manufactured for deep-drawing of superconducting cavities have been gathered. Due to various histories of the niobium samples and a wide range of metal purities (35<RRR<1750) the data offer a large scatter of thermal conductivities. An attempt is made to obtain an analytical expression with realistic parameters for the thermal conductivity between 1.8 K and 9.25 K. The set of parameters deduced from a least square fit of experimental data is not very different from those yielded by the theory of superconducting metals, taken as a starting point. This should make possible to obtain a reasonable guess of the thermal conductivity of niobium in this temperature range, once the RRR and the past history of the metal samples have been determined.

I. Introduction

In the recent years, industrial suppliers of niobium have made an important effort to produce very pure niobium. The main motivation was the increasing use of superconducting RF cavities in particle accelerators.The thermal conductivity of the metal is an important criterion, which determines the thermal stability of the superconductor. Consequently, several laboratories - as well as manufacturers - have studied the improvement of niobium purity by various processes, including vacuum melting by electron bombardment, and post-purification by solid-state gettering.The authors of this paper have gathered a large experimental database of niobium thermal conductivity at cryogenic temperatures, and tried to compare these results with a theoretical model.

Then, it has been tried to adjust a semi-empirical parametrisation of the thermal conductivity profile. The aim of this work is to demonstrate that the thermal conductivity of niobium can be estimated rather precisely from two basic informations, namely the material residual resistivity ratio (RRR) and the knowledge of the material history (annealings, cold working,...). We believe that the resulting parametrisation can be useful for thermal model calculations describing the behaviour of various superconducting niobium devices, including RF cavities for accelerators.

II Theoretical model for niobium thermal conductivity

The thermal conductivity of pure niobium at temperatures lower than 9.25 K is given by the theory of metals, modified in order to take into account the superconducting state. The thermal conductivity of a metal is dominated by that of the electron "gas", but the lattice heat conductivity, due to the propagation of phonons has to be added. This writes :

$$K = K_e + K_{lattice}$$

1) Electron heat conductivity

-normal state

The dominant term in the thermal conductivity is usually that due to electron conduction, given for the normal state by [MAK]:

$$K_{en} = 1 / W_{en} = \left[\rho / L_0 T + a \cdot T^2 \right]^{-1}$$

where W_{en} is the electron thermal resistance term, ρ the residual resistivity, measured at 4.2 K $\rho = \rho_{295K} /$ RRR, RRR the residual resistivity ratio, L_0 the Lorentz constant ,

($L_0 \sim 2.45 \cdot 10^{-8}$ W.K^{-2}), and a is the coefficient of momentum exchange with the lattice vibrations. The first term in thermal resistance is due to the scattering of electrons by impurities and lattice defects, the second term describes the scattering of electrons by phonons.

-superconducting state

The electron heat conduction in the superconducting state is reduced because the electrons which have condensed into Cooper pairs do not contribute any more to any disorder or entropy transport. This decrease in electron heat conduction has been calculated by Bardeen, Rickaysen and Tewordt [BRT] using the BCS theory. It amounts to a factor :

$$K_{es} / K_{en} = R(y) \qquad\qquad R(y) \leq 1$$

$$y = \Delta(T) / k_B T = \Delta(T) / k_B T_c \cdot (T_c / T)$$

The approximation $\quad y \cong \alpha . T_c / T \quad$ is valid if $\quad T / T_c \leq 0.6$

Here T_c is the superconductor critical temperature, $\Delta(T)$ the superconductor energy gap, k_B the Boltzmann constant, and $\alpha = 1.76$ in the BCS theory, but may take values in the range $1.5 \leq \alpha \leq 2$ according to experiments carried out with metals.

2) lattice thermal conductivity

The lattice thermal conductivity is well known in the case of insulators - as it is the only one to exist. In the case of metals, it is usually negligible as compared to the electron contribution. However, in the superconducting state, due to the quasi vanishing electron heat conduction at temperatures below $T/T_c = 0.3$, the lattice heat conduction obviously plays a role and is observed experimentally. The lattice thermal conductivity could be limited by two phenomena :

(i) **scattering of phonons by the electrons** :
In a normal metal, the thermal resistance W_{gen} due to interaction with electrons has a T^{-2} dependence [MAK]. In the superconducting state, its contribution is strongly modified, due to electron decoupling resulting from the condensation into Cooper pairs. As T decreases, the normal electron density falls like $\exp(-\Delta/k_B T) = \exp(-y)$. The lattice thermal conductivity thus writes :

$$K_{ges} = \exp(y) . H(y) . D . T^2$$

as calculated by Bardeen et al.[BRT].
y has already been defined ; H(y) has a flat maximum at 1 in the range $0 < T/T_c < 1$;

(ii) the second resistance to heat transport is the **scattering by grain boundaries,** lattice dislocations, and sample boundaries in the case of a monocrystal. In a general way, this implies a mean free path for phonons, and a T^{-3} dependence with temperature [LYN]. This term was calculated by Casimir [CAS] in the case of scattering by crystal boundaries as :

$$K_{gb} = B . l . T^3$$

where l is the phonon mean free path, and B a constant depending on the mechanism of scattering and the metal.

3) total thermal conductivity

The total heat conductivity of the superconducting metal is obtained by adding the electron term $K_{es}(T)$ and the lattice term $K_{gs}(T)$. This of course is valid for temperatures T lower than the critical temperature, because $y = \Delta(T) / k_B T$ is defined only in this domain.

$$K_s(T) = R(y) . \left[\frac{\rho_{295K}}{L . RRR . T} + a . T^2 \right]^{-1} + \left[\frac{1}{D . \exp(y) . T^2} + \frac{1}{B . l . T^3} \right]^{-1}$$

In order to obtain $K_s(T)$ by using this model, it is necessary to give experimental values to three variables : temperature **T**, residual resistivity ratio **RRR**, and phonon mean free path **l**. On the other hand the following five theoretical parameters should be defined : **a, L, α, B, D**. In section IV these parameters were adjusted by a fit procedure, taking as initial values the theoretical estimates deduced in the first part of this paper.

Taking into account the experimental data for niobium (ρ_{295K}=14.5 10^{-8} Ohm.m ; $\Theta_D \cong 275$ K ; a_0=2.6 Å ; K_{295K} =54 W/m.K), these parameters are easily calculated :

L=2.45 10^{-8} W/K^2	a=2.30 10^{-5} m/W.K	α=1.76
1/D=300 m.K^3/W	B=7.0 10^3 W/m^2K^4	

III. Experimental data base

1) Summary

Measurements of the thermal conductivity of the niobium sheets prepared for the fabrication of superconducting high frequency cavities have been carried out at Desy laboratory [SCH] and at Saclay [DOK,KOD].

16 experimental curves K=ƒ(T) have been obtained in a large range of residual resistivity ratios, namely RRR values varying from 35 to 1750. Among these :

-3 curves have been measured at Desy (RRR=244, 379, 1071);

-13 curves have been measured at Saclay, with 13 different samples, including :

2 samples of high purity russian niobium [ELI] (RRR=1750, 830);

1 sample of american (Wah-Chang) niobium post-purified (1350°C, 20 h.) at Wuppertal laboratory (RRR=560).

(these three samples were sent from Wuppertal to Saclay in order to be characterized).

The experimental set-up used at Saclay has been described elsewhere [DOK,KOD].

The total number of experimental points included in these curves was 322.

2) Experimental results

A part of these results are shown in figure 1, for samples of niobium sheets kept "as received" from the manufacturer. The continous lines between the experimental points are sketched here only for a better understanding of the picture.

As can be seen in figure 1 ("as received" niobium), the curves for RRR=40 and 265 show a pronouced bump in thermal conductivity between 1.5 and 3 or 4 K. This unusual feature, as compared to the other curves, could be due to the lattice thermal conductivity. However, the correlation between high temperature annealing, producing larger grain sizes, and the existence of a bump on the curves due to enhanced lattice thermal conductivity, is not perfectly established. This might be due to our poor knowledge of the past history of the "as received" samples.

On the other hand, the value of the total heat conductivity at 4.2 K is roughly equal to RRR/4, as was stated several years ago by Padamsee [PAD]. This can easily be explained by using the theoretical equation given in this paper for the electron heat conductivity K_{en}, and the ratio R(y) for the temperature of 4.2 K (with α=1.76, R(y)=0.309).
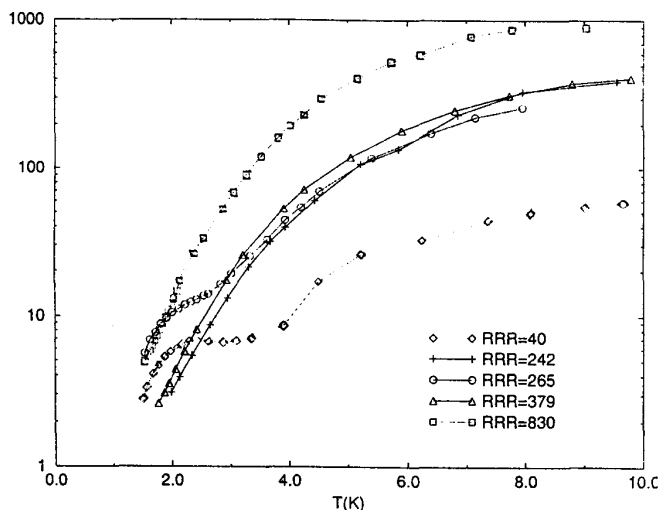
"AS SUPPLIED" NIOBIUM

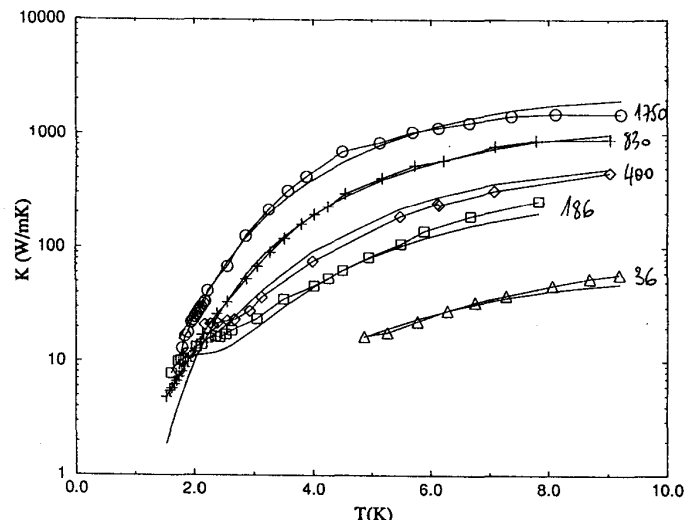Figure 1 : Experimental data : thermal conductivity for "as supplied" niobium samples

Figure 2 : Comparison of calculated curves K(T) with the best fitted parameters (full line), with experimental plots (line joining symbols), for typical RRR values.

3) **Data associated with experimental profiles :**

322 experimental points, each being a separate measurement, were recorded. The information which had to be included in the data base for each point was the following :

the temperature **T**;

the thermal conductivity **K**;

the **RRR** of the sample (measured separately);

the information : "**HT annealed**" or "**as received**".

This seemed sufficient to give a crude estimation of the phonon mean free path **l**, which was itself assumed to be comparable to the average grain size (AGS). The purchased niobium sheets all had an AGS corresponding to the ASTM index 5.5 to 7.5, i.e. approximately 50 μm. On the other hand, niobium annealed during several hours at 1100 to 1300°C (with or without titanium getter), showed AGS of 0.3 to 1.5 mm. In order to simplify, we assumed that l was equal to 50 μm in the case of "as received" and to 500 μm in the case of "annealed" niobium.

IV. Fit calculations and results

1) **Method**

A computer code was written in order to calculate the thermal conductivity of niobium with the equations given in this paper, using the theoretical values for the five parameters **L, a, α, B, D**. The computed heat conductivity was compared with experimental results (plot of K versus T). Quantitative agreement was good at 4 K, but the slope of the theoretical curve was steeper than the experimental profile.

In order to improve the fit, free variation of the parameters **L, a, α, B, D** was allowed. A Monte-Carlo least-square fit procedure in five dimensions space was used. The starting point was the set of theoretical values already given at the end of part II. The criterion was the minimisation of the quantity :

$$Q^2 = \sum_{1}^{322} \left[\frac{K_{exp} - K_{cal}}{K_{exp} + K_{cal}} \right]^2$$

where K_{exp}=measured K(T,RRR,l)

K_{cal}=computed K(T,RRR,l,$\{L,a,\alpha,B,D\}$)

2) **Results**

The results of the fit calculation are shown in table I as regard to the best values obtained for the five parameters which were allowed to vary freely. Moreover, the comparison of the curves K=f(T) calculated with these best values (solid lines) and the experimental curves (lines joining the experimental points), is shown in figure 2, for typical values of the RRR.

Table I

Parameter	Initial value (theory)	Best fit value	Unit
L	2.45 10^{-8}	2.05 10^{-8}	W/K^2
a	2.30 10^{-5}	7.52 10^{-7}	m/WK
α	1.76	1.53	
B	7.00 10^3	4.34 10^3	W/m^{2}K^4
1/D	3.00 10^2	2.34 10^2	mK^3/W

3) **Discussion :**

L : the best fit value is slightly lower than the theoretical value L$_0$. This was expected.

a : the value given by the fit is 10 times smaller than the experimental one, and 30 times smaller than the theoretical one.

α : a value lower than given by theory is unusual [TWS], but it can be explained by the need of a reduced slope for the plot of K versus T, as found when comparing theory with experiment.

B : the fitted value is not far from the estimated one (60%), if one takes into account the uncertainties surrounding the definition of the phonon mean free path.

D : the discrepancy between the two values (20%), is unexpectedly small.

4) **Quality of the fit**

With the 322 measured points, the minimum reached by Q^2 is equal to 9.8. The resulting uncertainty on K_{cal} is :

$$\left\langle (\Delta K / K)^2 \right\rangle^{1/2} \cong 35\%$$

This relatively large error bar can be appreciated in figure 2, where it can also be noticed that the shape of the experimental plot is hardly reproduced in the range of temperatures lower than 2 K. On the contrary, for the temperatures higher than 2 K and up to 9 K, the approximation of the thermal conductivity by the best fit is quite satisfactory.

V. Conclusion

The resulting parametrisation reproduces the experimental data reasonably well in a wide temperature range and for a variety of niobium samples. The parametrisation is less valid for temperatures below 2 K. In this range, the thermal conductivity is influenced by the lattice contribution which depends strongly on the past metallurgical history of the material. Nevertheless, the overall precision of the parametrisation (35 %) is sufficient for most thermal model calculations. We hope it will be a valuable tool for future applications of superconductivity.

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