A New Approach for RRR Determination of Niobium Single Crystal Based on AC Magnetic Susceptibility

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Abstract. Residual resistivity ratio RRR is an important integral characteristic of material purity. It was proposed to determine the RRR on base of the AC susceptibility. AC susceptibility of a number of single crystal niobium samples of different orientations types (<100>, <011>,<111>) and differently treated(BCP 70, 150 µm, annealing 800ºC/2h) was measured. The RRR value was determined on base of these results using a relation between the imaginary part of χ'' of AC magnetic susceptibility at low frequency, AC magnetic field and resistivity ρ of the sample.

Keywords: Niobium single crystal, electrical resistivity, residual resistivity ratio, AC susceptibility.
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INTRODUCTION

Among the different techniques to determinate the Residual Resistivity Ratio (RRR) value of superconducting materials the AC susceptibility has an additional advantage to search for and study the critical parameters such as critical magnetic fields. Application of AC magnetic fields by changing of its amplitude and frequency allows determining the residual resistivity ratio value as an integral characteristic of the purity of material supplementary to DC RRR data. The SQUID based AC susceptibility technique allows a rather precise investigation of superconducting single crystal material.

The aim of this paper is to analyze the method for determination of RRR value of niobium single crystal based on AC susceptibility and compare with other methods.

EXPERIMENTAL

From part of niobium ingot provided by W. C. Heraeus 3 samples (raw cylinders of 1.3-2 mm height; 3-4.5 mm diameter) were cut by EDM (electrical discharge machining).The first sample (N1) was marked as received. The chemical etching (BCP) in a mixture 1:1:2 HNO_3 (60%), HF (40%), H_3PO_4 (85%) and annealing at 800ºC for 2 hours have been applied to another two samples (N2, N3).The orientation of the samples was established by the company Mathek. The base crystallographic plane of each sample was oriented along plane (011). The measurements of the AC magnetic susceptibility were done by using the measurement device MPMS-5XL from Quantum Design [1] in the temperature range from 2 to 300K in a permanent magnetic field up to 5 T and AC magnetic field with maximal amplitude of 4 Oe and a frequency up to 1 kHz. The measurement system MPMS-5XL reveals itself a sensitive tool for measuring the magnetization of the materials as a function of temperature and magnetic field. The system based on Superconducting Quantum Interference Device (SQUID) technology gives the high measurement sensitivity and dynamic range. The principle on the system is based on the positioning of the sample inside the measuring contour including the couple of compensating and pick-up coils. The output signal is proportional to the magnetic flux in the pickup coil which gives the minimal variation of sensitivity over the entire frequency range: sensitivity - 5 x 10^{-8} emu.

In all measurements the magnetic fields (DC & AC) were applied along the main crystallographic directions<100> or<011> or<111>. The measurement of the residual resistivity ratio by the standard DC 4-point method was done using the high precision multimeter Keithley 2001 with a preamplifier in the nanovolt range.

MAIN PRINCIPLES OF RRR DETERMINATION

The AC susceptibility is caused by eddy currents induced form an external alternative magnetic field $h = h_0 exp(-i2\pi f)$ h_0 = const, f - frequency. Generally the AC susceptibility can be expressed as

$$\chi_{AC} = \chi' + i\chi'' \tag{1}$$

where $\chi'$is a real part of susceptibility and χ''- the imaginary part that describes the absorption in material. In case of spherical samples with radius a and skin depth $\delta = 1/(\pi\mu_0\mu\sigma f)^{0.5} = (\rho/(\pi\mu_0\mu f)^{0.5}$ where $\mu_0 = 4\pi\times10^{-7}$ H/m, μ - the relative permeability, ρ – resistivity. The AC components can be expressed [2] as:

$$\chi' = \frac{9}{4}\left(\frac{\delta}{a}\right)\frac{[\sinh(2a/\delta) - \sin(2a/\delta)]}{[\cosh(2a/\delta) - \cos(2a/\delta)]} - \frac{3}{2} \tag{2}$$

$$\chi'' = \frac{9}{4}\left(\frac{\delta}{a}\right)\frac{[\sinh(2a/\delta) + \sin(2a/\delta)]}{[\cosh(2a/\delta) - \cos(2a/\delta)]} - \frac{9}{4}\left(\frac{\delta}{a}\right)^2 \tag{3}$$

For low frequency f - $\delta/a >> 1$

$\chi' \approx -k_{a1} f^2/\rho^4$ and $\chi'' \approx k_{a2} f/\rho$

For infinite length cylinder with diameter d:

For low frequency f - $\delta/d >> 1$

$\chi' \approx \chi^0(f = 0) - k_{1d} f^2/\rho^2$ and $\chi'' \approx k_{2d} f/\rho$

where k_{ij} - coefficients defined by size of the sample - *a*, *d*. The peak of the imaginary part of the AC susceptibility reveals itself as a compromise between the increase of the local absorbed power density (~ ½ σE^2 ~ ½ ρJ^2) and the decrease of the field penetration depth into the material in dependence of its electrical conductivity. It is necessary to emphasize that in case of low shielding ($a/\delta<<1$), both the χ'' and χ' values can be obtained by a direct measurement of the electrical resistivity ρ:

$$\chi' \approx \chi^0(f=0) + k_1 \bullet f^2/\rho; \chi'' \approx k_2 \bullet f/\rho \quad (4)$$

Based on this consideration the residual resistivity ratio can be calculated using the standard equation:

$$RRR = \frac{\rho_{300K}}{\rho_{4.2K}} \quad (5)$$

The experiments on polycrystalline samples allow to suggest that contactless AC-susceptibility method can be applied for studying the single crystals.

AC SUSCEPTIBILITY – FREQUENCY (TEMPERATURE) EXTRAPOLATION METHOD

For determination of RRR value the experiments in low temperature range at $T<T_c$ and high magnetic fields sufficient for destroying the superconducting state were carried out. In Figure 1 the isotherms M(H) for samples N1 and N2 are shown. In the Fig. 2 the same data in coordinates M/H(H) are shown.

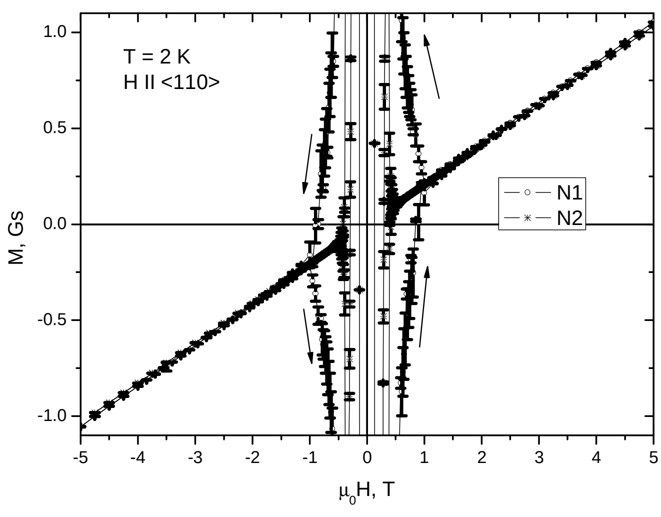

FIGURE 1. The isotherms M(H) for sample N1, N2, B||<110>.

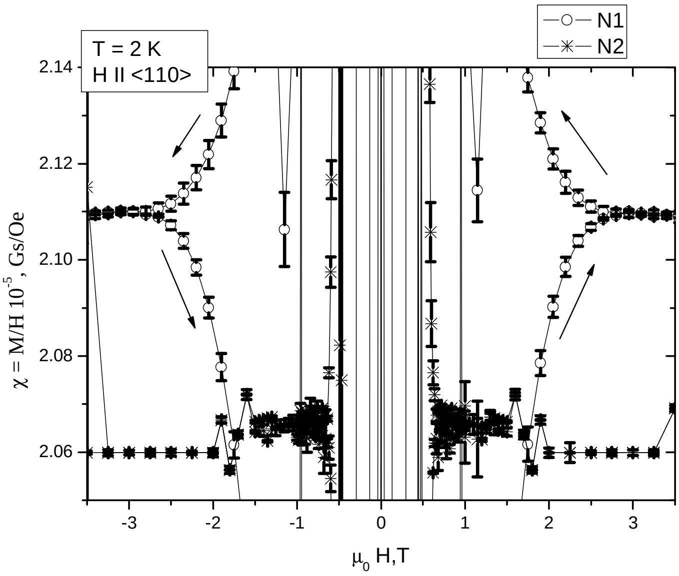

FIGURE 2. The isotherms M/H(H) for samples N1, N2, B||<110>.

In the sample N1 the superconducting state remains in magnetic field up to ~ 25- 28 kOe, in the sample N2 - up to 15-20 kOe. In the current paper we do not consider the reasons of such a high magnetic field. In the paramagnetic state in a whole temperature range the isotherms of magnetization appear to be a linear function of H: M = χH (χ = M/H) and temperature dependence χ(T); H=const have no signs of Curie-Weis law. Magnitude of AC susceptibility is close to $2*10^{-5}$ and its relative change with magnetic field is not more than 4%. Hence in this case we are deal with Pauli susceptibility and the data obtained indicate the high purity of the material without ferromagnetic inclusions.

The frequency dependency of the imaginary part of the AC susceptibility for frequencies up to 50 Hz for the as received sample (magnetic field applied along <111>) for various magnetic field values can be seen in Fig. 3. The red lines show the linear extrapolation to zero frequency of fitted curve. In relatively low magnetic fields scattering of the measured values at frequencies lower than 15 Hz in an applied magnetic field of 2T has been observed. Also a change of the curve slope at magnetic fields higher than 2 T was monitored (Figure 3).

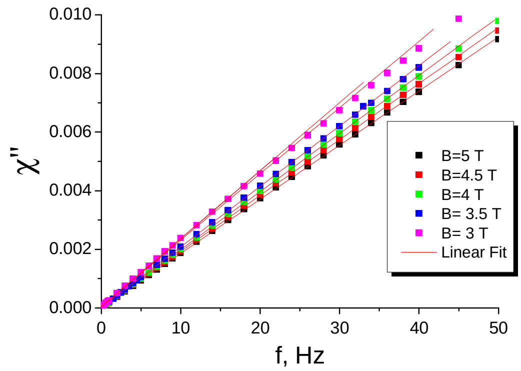

FIGURE 3. Frequency dependencies of the imaginary part of AC-susceptibility of sample N1 (as

received, B || <111>) for different values of the applied magnetic field at T=2K.

The Eq. 4 can be expressed in another way: the imaginary part of AC-susceptibility as a linear function of the frequency $\chi'' = A2 * f$, so one can write: $1/A2 = \rho / k$, where $1/A2$ is a slope of the curve. The coefficient *1/A2* can be expressed in dependency on frequency or temperature making two types of extrapolations possible: frequency or temperature extrapolations. In case of the frequency extrapolation, the resulting slopes are determined at a fixed temperature. Taking Eq. 4 into account and using the data extrapolated to zero frequency at the various magnetic fields measured (Figure 3), a dependency can be deduced, which reflects the change of 1/A2 on the magnetic field (Figure 4).

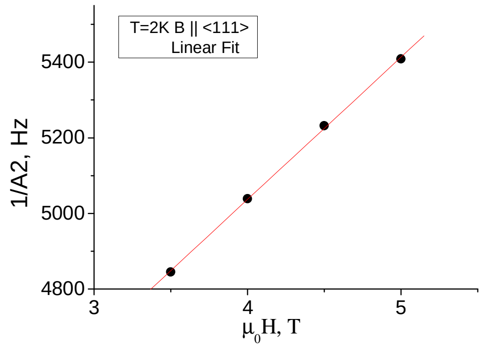

FIGURE 4. Magnetic field dependence of coefficient 1/A2. B||<111>, sample N1 'as received'

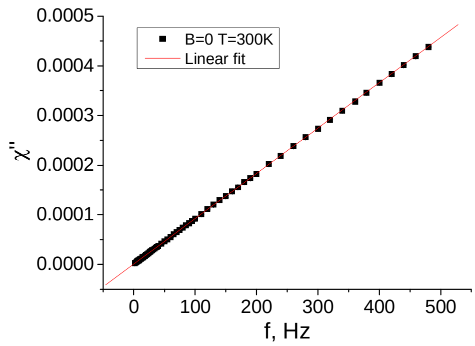

FIGURE 5. Imaginary part of AC susc. versus f. B||<111>, sample N1 'as received'

At fields higher than 3T the Kapitza linear law [3] (Figure 4) is fulfilled (linear increasing of the electrical resistivity by applying of high magnetic field). Using the frequency extrapolation at T=300K, obtained from the measured curve shown in Figure 5, one can calculate the residual resistivity ratio RRR:

$$RRR = \frac{1/A2_{300K}}{1/A2_{2K}} \tag{6}$$

TABLE 1. Residual resistivity ratio values obtained by the AC-susceptibility method for samples 'as received' in different orientations of the applied magnetic field.

Orientation	RRR (B=0)	RRR (B=3T)
<111>	310	
<110>	280-300	270
[100]	280-300	260

To confirm the obtained results we measured the RRR value for single crystal samples using the standard 4-point DC method in zero magnetic fields. In this case the RRR-value was determined by extrapolating the slope of the temperature-dependent resistivity in the low temperature region to T = 0.The samples were cut out from the same material. The current through the sample was applied in 2 directions: [110], [111]. The measurement results are shown in Table 2.

TABLE 2. RRR values obtained by the standard 4-point DC method for 'as received' samples in zero magnetic field.

Orientation	RRR (B=0)
[110]	269
[111]	280

Comparing Table 1 and Table 2 it can be concluded that the results obtained by the DC method are in good correlation with RRR-values measured by means of the AC magnetic susceptibility.

For the sample N2 the frequency dependency of χ'' for a magnetic field oriented along direction [100] is shown in Figure 6A, B.

The different slopes for B=0 and B=3T (T=300K) are caused by a small magnetoresistivity (Fig. 6A).

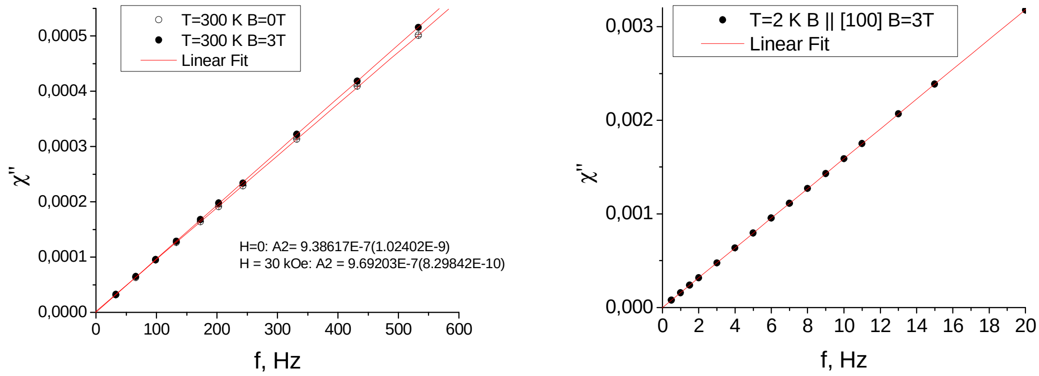

FIGURE 6A, B. Frequency dependencies of imaginary part of susceptibility at B=0; 3T (T=2K; 300K) for sample N2 (etched 80μm, 800°C/2h annealing).

From the extrapolation of each curve to zero frequency the RRR value can be determined (Eq. 6). The RRR values obtained on this sample for different orientation of magnetic fields are given in Table3.

TABLE 3. Residual resistivity ratio values obtained by the AC-susceptibility method for sample N2 for different orientations of the applied magnetic field.

Orientation	RRR (B=0)	RRR (B=3T)
<111>	not measured	226
<110>	not measured	198
[100]	207	169

The temperature dependence of the coefficient A2 was determined for the sample N2 along [100] at a fixed frequency f=33Hz in a magnetic field with B=3T (see Fig. 7). From this curve a linear dependency of the reciprocal of A2 with T^3 has been deduced as shown in Fig. 8. The values extrapolated to T=0 (Fig. 8) and at T=300K yield RRR=166. This value is in good correlation with the RRR value obtained by the frequency extrapolation method (RRR=169).

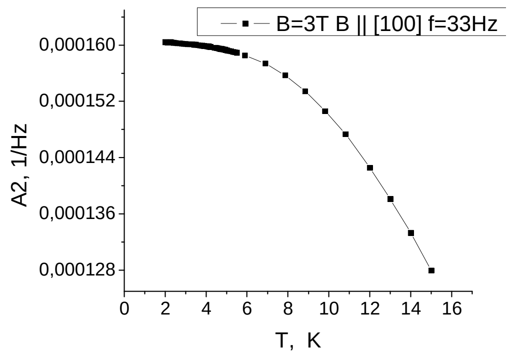

FIGURE 7. Temperature dependence of coefficient A2 of sample N2 in magnetic field B=3T along axis [100] at f=33Hz

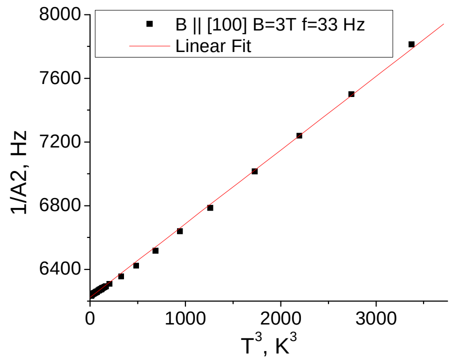

FIGURE 8. Dependence of coefficient 1/A2 vs T^3 for sample N2 in magnetic field B=3T along axis [100] at f=33Hz.

The dependence of 1/A2 on the magnetic field obtained for the sample N3 (150 µm BCP, 800°C/2h, B || [100]) applying the frequency extrapolation method detailed above is plotted in Fig. 9. The curve shows a pronounced discontinuity at a magnetic field around B=1.5 T. Again this behavior can be associated with a transition from a partially disordered superconducting state to the normal conducting state, while the electrical resistivity above this transition level obeys the Kapitza law.

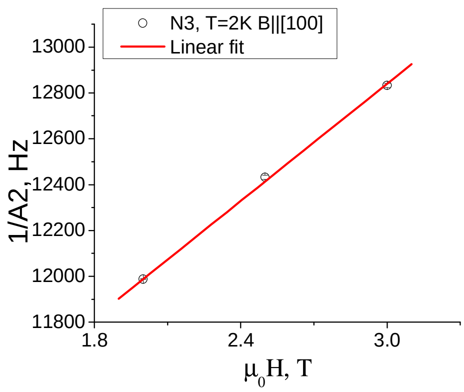

FIGURE 9. Magnetic field dependence of coefficient 1/A2 of sample N3. At B≥1.5 T curve follows the Kapitza law: R=K*f(B)

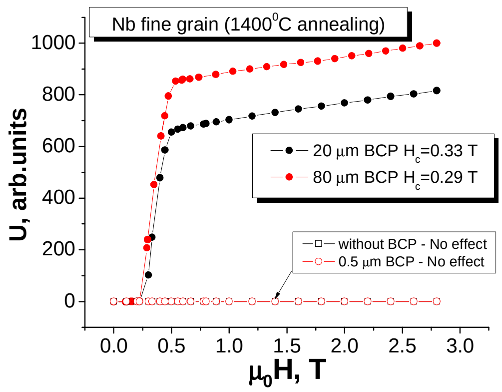

FIGURE 10. Magnetic field dependence of electrical resistivity for Nb fine grain samples with different etching rate.

In the same manner as described above, the RRR values for sample N3 at B||[100] have been determined, i.e. RRR (B=0)=205 and RRR (B=3T)=181 respectively.

A similar behavior was observed for the magnetic field dependencies of the electrical resistivity for Nb fine grain samples annealed at1400C [4]. The curves of electrical resistivity measured with the standard DC method, shown in Fig. 10, reveal that the normal to superconducting state transitions occur at magnetic fields close to 0.3 T for etched samples (20µm, 80µm BCP). For unetched samples and samples with a not completely removed surface damage layer the magnetic field doesn't influence the electrical resistivity and the sample remains in its superconducting state for magnetic fields up to 3T. This behavior can be connected with surface effects in Nb described, for example, in [5].

SUMMARY

A method for measuring the residual resistivity ratio RRR of Nb single crystals was proposed and examined. This method is based on measurements of the imaginary part of the AC-magnetic susceptibility. The RRR values of a number of Nb single crystal samples were obtained. The measurements of the AC-magnetic susceptibility were performed on Nb single crystals oriented along the main crystallographic directions for various different surface treatments. The dependency of the imaginary part of AC magnetic susceptibility demonstrates a typical transition from the superconducting state to the normal conducting state at different critical magnetic field levels. The behavior of samples in magnetic fields above the critical transition obey the Kapitza law taking into account the dependence of imaginary part of the AC-susceptibility on electrical resistivity. The RRR values obtained by the AC-magnetic susceptibility method are in good correlation with values obtained by standard 4-point DC-method.

The proposed method has the advantage to measure simultaneously the different magnetic and electrical properties even in case of very small values of magnetization and electrical resistivity. For measurements the anisotropy of resistivity on the single crystal samples the AC-susceptibility method also can be used more reliably in comparison with normal DC method. The determination of the resistivity can be carried out by taking into account the size and the shape of the samples.

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