EXPERIMENTS ON THE RF SURFACE RESISTANCE OF THE PEROVSKITE SUPERCONDUCTORS AT 3 GHZ

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I. INTRODUCTION

Since the discovery of the perovskite superconductors many experiments to explore their physical properties have been performed and various potential applications have been considered. The high critical temperature of more than 90 K obtained with $Y_1Ba_2Cu_3O_{7-\delta}$ (Y may be substituted by other rare earth elements) makes these superconductors interesting for applications in microwave technology. This has focused our interest on the investigation of their rf properties. Due to the sensitivity of the rf surface resistance to surface impurities and remaining non superconducting phases rf measurements are a good means to provide useful informations about the quality of sample preparation and about physical properties of the superconductor itself.

This contribution reports on the experimental determination of the rf surface resistance of $Y_1Ba_2Cu_3O_{7-\delta}$ and $Eu_1Ba_2Cu_3O_{7-\delta}$ in the normal and superconducting state at 3 GHz. In the first chapter the preparation of the ceramic samples and initial dc experiments are described. The main part of the paper describes the rf measurements which are performed in a superconducting niobium "host cavity" . The obtained results for both the surface resistance and the high field performance are discussed with respect to the preparation of the samples and regarding possible applications.

II. SAMPLE PREPARATION AND INITIAL EXPERIMENTS

Stoichiometric mixtures of high purity powders ($\geq$99,99%) of Y_2O_3 and Eu_2O_3 respectively, $BaCO_3$ and CuO were ball milled using agate devices. In the case of our first sample W3-T2 manual grinding was applied. After a heat treatment in air at 930^oC and a final ball milling pellets with 13 mm diameter and 1,6 mm thickness were pressed with a pressure of 7 kbar. The pellets were annealed in a pure oxygen atmosphere at 930^oC for at least 6 hours and then slowly cooled down to room temperature. For each experiment several samples are prepared under identical conditions. First some measurements are performed to obtain an initial quality assurance. The diamagnetic behaviour is tested by placing the superconducting pellet underneath a permanent magnet which rests on the tray of a sensitive scale . The weight reduction of this "calibration magnet" is used as a relative measure of the bulk susceptibility of a pellet (table 1) .

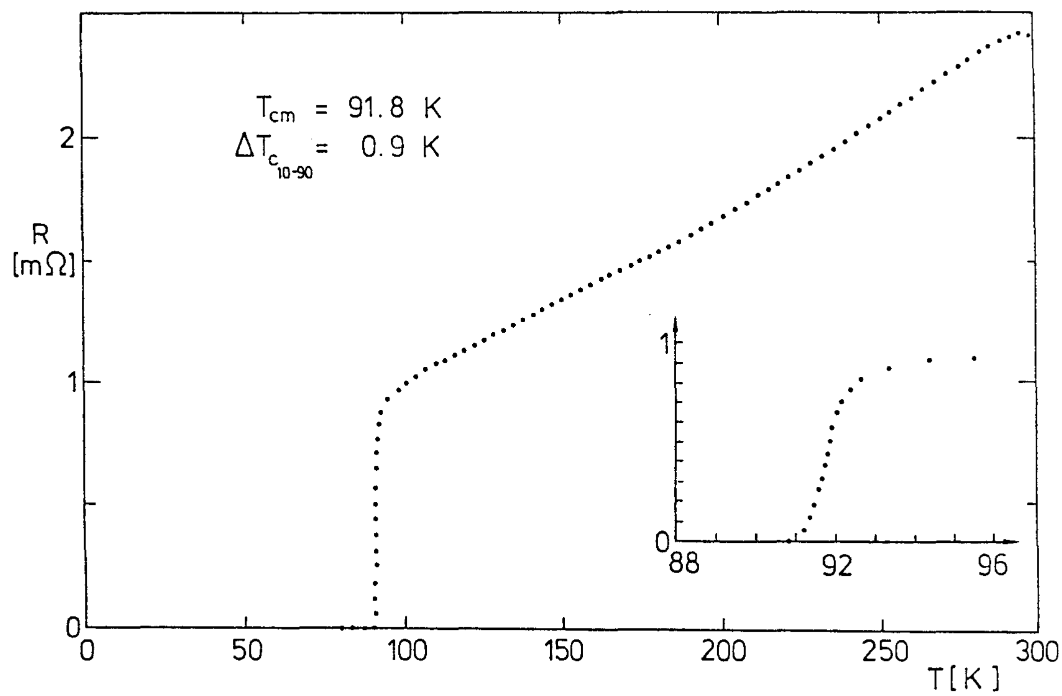


Fig.1: Temperature dependence of the dc resistance of sample W1-E2 measured by a four point technique with a midpoint of T_{CM} = 91.8 K and a transition width (10 - 90%) of 0.9 K.

The dc resistance is measured using a standard four lead and lock in amplifier technique . In fig. 1 the temperature dependence of one of our samples is presented. The transition width from 10 to 90 % of the normal conducting resistance just above the critical temperature is less than 1 K. Values of both the transition width ΔT_C and the critical temperature T_{CM} measured at the midpoint of the transition are summarized in table 1.

III. RF MEASUREMENTS

a) Surface resistance

The rf surface resistance of $Y_1Ba_2Cu_3O_{7-\delta}$ ($Eu_1Ba_2Cu_3O_{7-\delta}$) samples was measured by exposing them to the rf field of a niobium cavity at 3 GHz in a temperature range from 4.2 to 300 K. The pellet is located in the high magnetic field region of the cavity (fig. 2) which is cooled in liquid helium. At 4.2 K the host cavity is superconducting and the rf residual losses of the pellet can be measured[1]. The sample is just laid on the cavity surface. In order to avoid contact currents between the sample and the niobium surface the cavity was covered with a highly insulting layer of Nb_2O_5 (thickness: 600 Å) by anodizing. The cooling of the pellet is provided by helium gas at a pressure of 20 mbar inside the cavity.

During the slow warming up of the cavity the difference between the lower and the upper resistor thermometers was less than 2 K. The surface resistance $R_s = G/Q_o$ of the sample has been derived from the difference of the inverse Q_o values with and without a sample (fig. 3a)[2]. The geometry factor G of 6800 Ω ± 10% was determined by calibration measurements with samples of well known resistivity (stainless steel and bismuth). Fig. 3b shows the temperature dependence of the rf surface resistance R_s of sample W7-T6 . The residual surface resistance of the sample was measured at 4.2 K (dashed line) when the host cavity is superconducting. The metallic behaviour of the sample is well demonstrated by the surface resistance above 100 K. Using the normal skin effect formula R_s(300 K) corresponds to a resistivity ρ(300K) of 400 μΩcm. This value agrees well with the 600 ± 150 μΩ cm found in the dc measurements[2], especially if one takes into account the porosity of the sample which is about 25%.

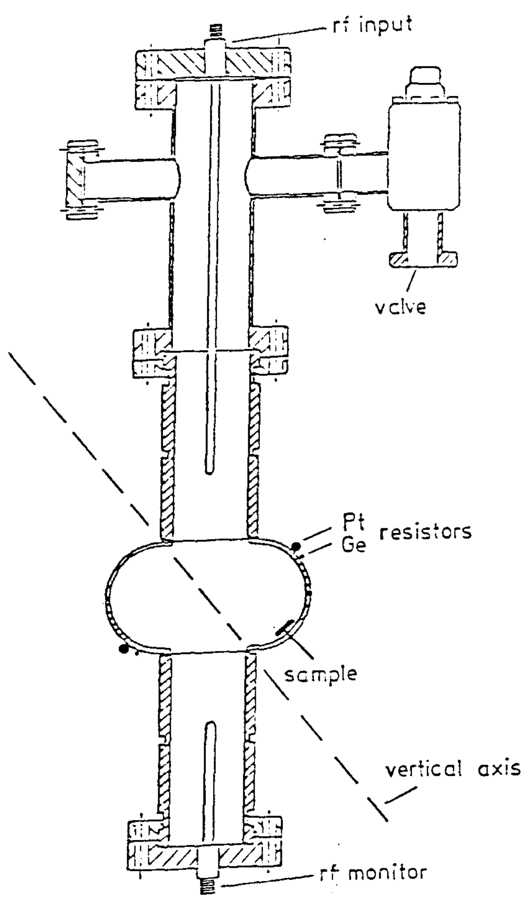


Fig. 2: Experimental setup for measuring the rf losses of superconducting pellets.

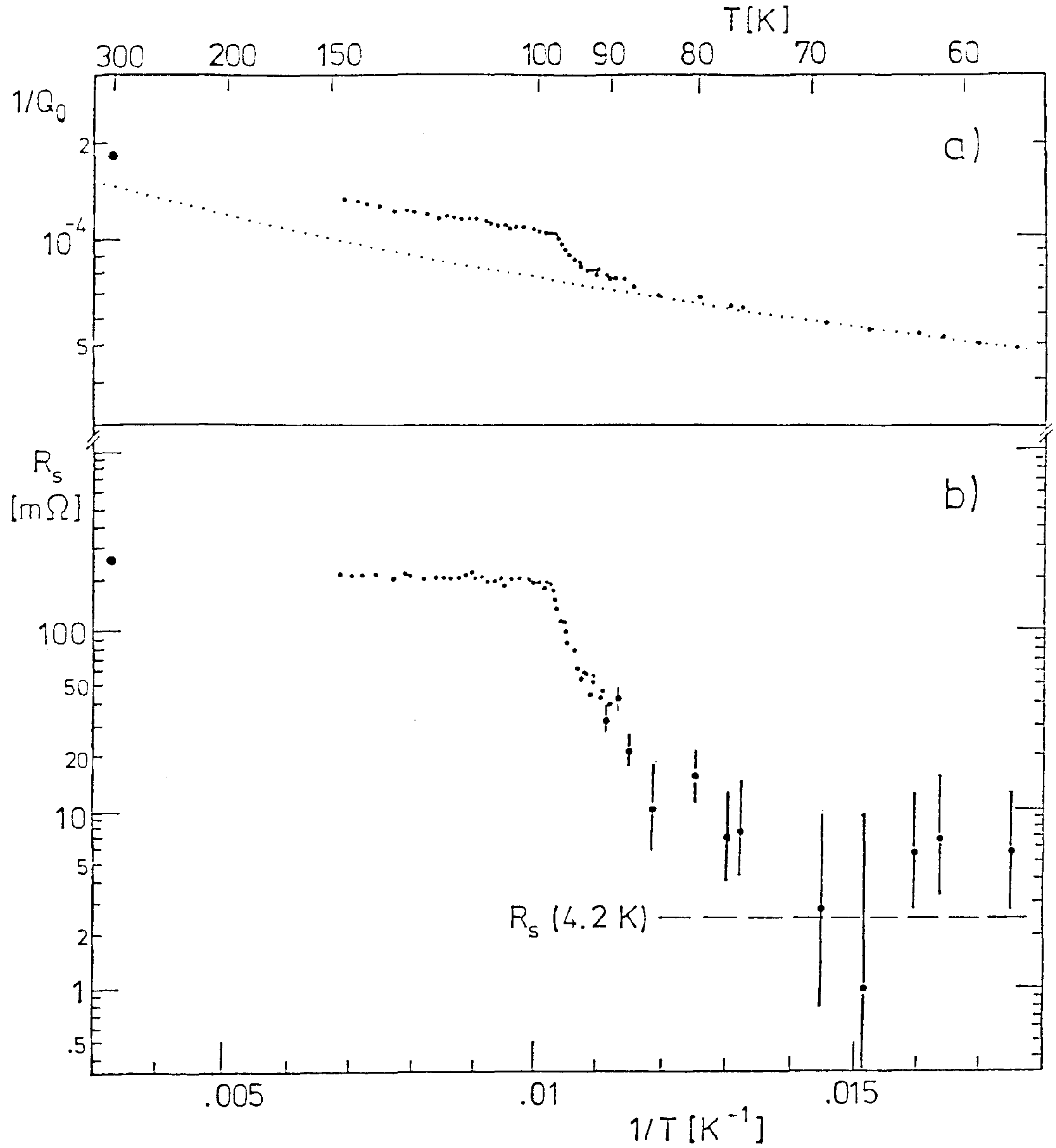


Fig.3: a) Temperature dependence of the inverse quality factor measured with sample W7-T6. The decrease of the rf losses ($\sim Q_0^{-1}$) at about 90 K shows rf superconductivity of $Y_1Ba_2Cu_3O_{7-\delta}$. At lower temperatures the Joule losses of the normal conducting niobium cavity (dotted line) dominate.

b) Surface resistance R_s derived from fig. 3a.

In table 1 the preparation parameters , the results of both the dc and rf measurements of all our samples are summarized. For the majority of the samples values for the residual surface resistance R_S (4.2K) of less than 1 mΩ were obtained.

Even the lowest R_{res} value achieved of 0.16 mΩ is very high compared to the nanoohms obtained with superconducting niobium. We attribute this result to an imperfect microscopic stoichiometry of our ceramic samples. The first significant improvement of R_{res} was achieved when the manual grinding of the powders (W3T2) was replaced by a ball milling procedure (W7T6). The stoichiometry of the metal compounds within single grains was measured using energy dispersive X-ray analysis with a scanning electron microscope. In sample W3T2 local deviations of the stoichiometry from the nominal composition and even unreacted particles of CuO were found (fig. 4a).

In comparison in sample W7T6 no unreacted particles were found and the stoichiometry measured from grain to grain was found to deviate from the nominal compositon only within errors (fig.4b) .

Fig. 5 exhibits a definite correlation between the residual surface resistance and the duration of the heat treatment $t_1 + t_2$. This supports our assumption that the residual losses of our samples are partially caused by a poor microscopic stoichiometry.

Sample No.	comp. 1)	preparation 2) t_1 [h]	t_2 [h]	ρ [g/cm^3]	T_{CM} [K]	ΔT_C 3) [K]	Δm 4) / m	R_S [mΩ] 300 K	77 K	4.2 K	H_{max} [A/m]	H_{S0} [A/m]	β 5)
W3-T2	YBaCuO	16	6		90.0	5.5		370±50	≤25	1.80±0.50	340±20	3.5	0.73
W7-T6	YBaCuO	20	20		92.0	1.0	0.081	250±30	31±10	0.62±0.47	690±43	13.8	0.67
W9-T5	YBaCuO	67	24	5.6	92.5	1.2	0.275	210±30	≤15	0.42±0.14	440±55		
W12-T6	YBaCuO	98	152	4.7			0.417	200±40	≤15	0.16±0.03	402±26	11	0.79
W13-T1	YBaCuO	62	65	5.1				160±30	≤10	0.29±0.04	563±65	37	1.09
W18-T2	YBaCuO	64	30	6.0				181±31	≤10	0.30±0.04	463±31	0.45	
W19-T1	YBaCuO	20	20	5.7				142±26	≤10	0.55±0.10	540±72		
WE1-T1	EuBaCuO	68	70		93.0	1.9	0.116	170±30	≤10	0.2±0.1	547±36		
W1 -E2	YBaCuO				91.8	0.9		360±60	≤15	0.56±0.08	171±20		0.65
OFHC	- copper							13.7	5.3	2.5			

Table 1: Comparison of the preparation parameters, the dc measurements and the characteristic rf superconductivity parameters at 3 GHz of different samples. Further details concerning the preparation are given in the text.

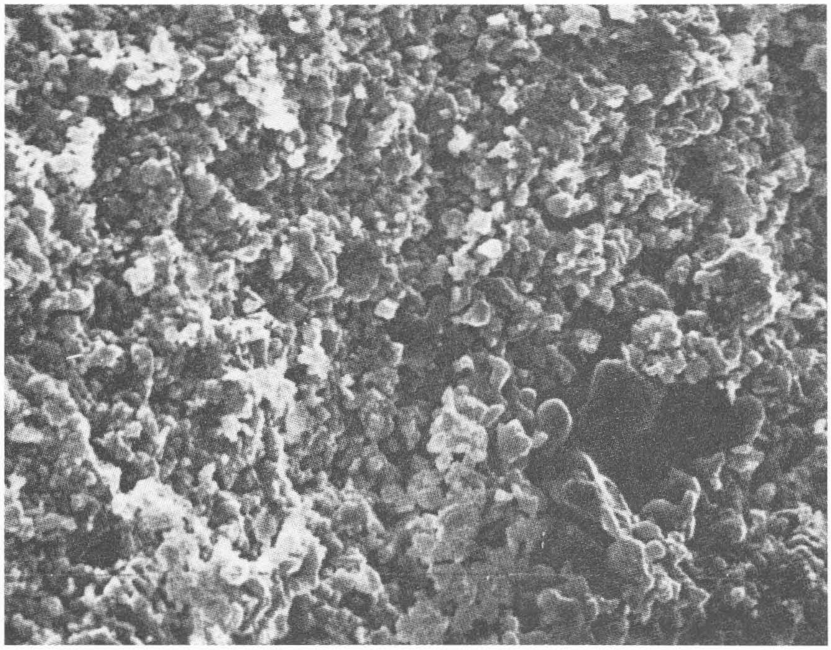
1) YBaCuO: $Y_1Ba_2Cu_3O_{7-\delta}$ EuBaCuO: $Eu_1Ba_2Cu_3O_{7-\delta}$

2) t_1 : duration of powder annealing in air at 930 C. t_2 : duration of final annealing of the pressed pellet at 930 ^{o} C in pure oxygen.

3) $\Delta m/m$: weight loss of a calibration magnet due to diamagnetic shielding (measured at 77 K), proportional to the magnetic bulk susceptibility

4) transition width from 10 to 90% of the resistance in the n.c. state just above T_C . T_{CM} is the mid-point transition temperature.

5) At field levels below H_0 the Q_0 value decreases weakly with growing H_S , at higher field levels Q_0 decreases according to $Q_0\,(H_S) = H_S^{-\beta}$.



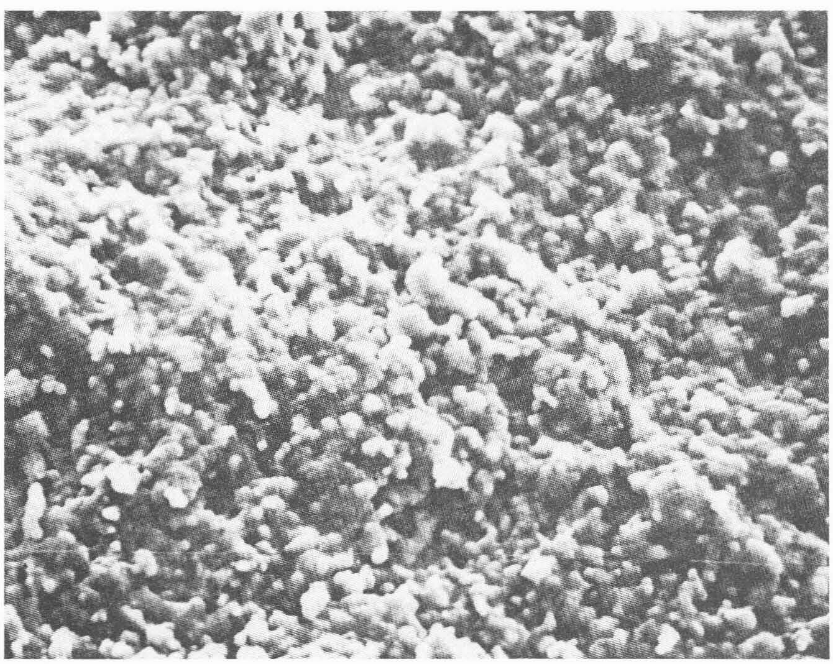


Fig.4: Electron micrographs of $Y_1Ba_2Cu_3O_{7-\delta}$ samples (x 1250)
a) W3T2 (upper) b) W7T6

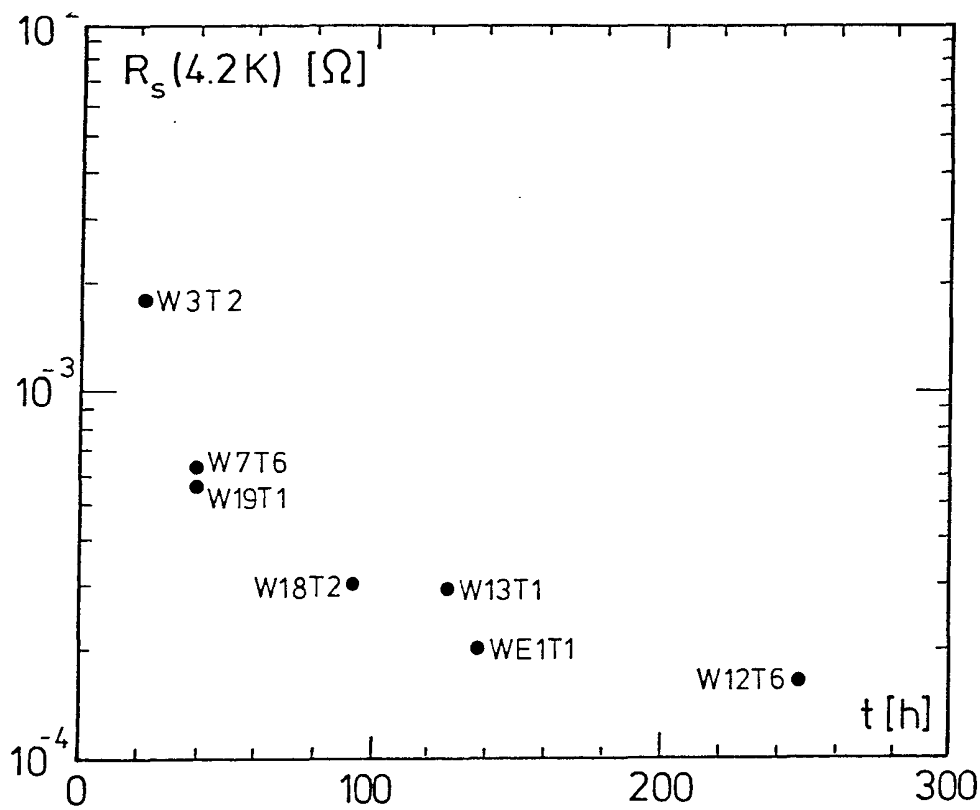


Fig. 5: Dependence of the residual surface resistance $R_S(4.2\ K)$ from the annealing time $t=t_1+t_2$. The corresponding values for $R_S(4.2\ K)$, t_1 and t_2 are given in table 1.

In fig. 6 the temperature dependence of the surface resistance for W12-T6 is compared with niobium, Nb_3Sn and OFHC copper. The residual surface resistance of the $Y_1Ba_2Cu_3O_{7-\delta}$ sample is more that one order of magnitude lower than the corresponding value of OFHC copper but still three orders of magnitude higher than the corresponding values of niobium and Nb_3Sn respectively. At liquid nitrogen temperatures, however, the quality factor of a cavity consisting of pure $Y_1Ba_2Cu_3O_{7-\delta}$ is at least as high as for a cavity consisting of any known material and most likely a factor of 10 higher. This uncertainty results from our present inability to measure the surface resistance at 77 K with a good enough accuracy.

b) high field performance

The high field performance of each sample was measured at a temperature of 4.2 K. In order to minimize rf heating of the whole sample pulsed rf operation (pulse length: 100 µsec, duty cyle: 10^{-3}) was applied. A typical measurement

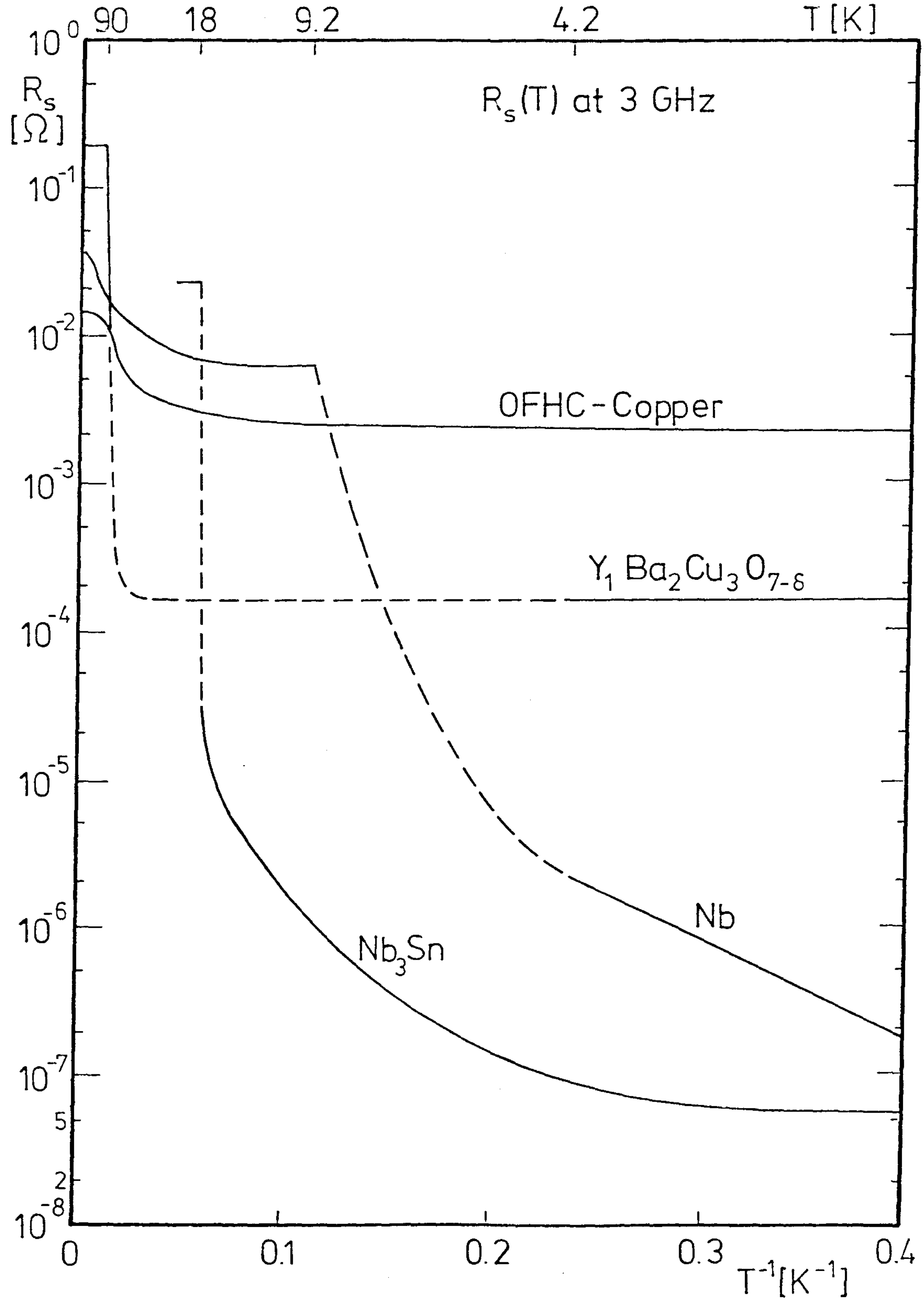


Fig. 6: Comparison of the temperature dependence of the surface resistance R_S of $Y_1 Ba_2 Cu_3 O_{7-\delta}$, niobium[3], Nb_3Sn [4] and OFHC-copper. The dashed lines were extrapolated. The values for OFHC copper values were scaled from ref. 5 using a $f^{2/3}$ frequency dependence predicted by anomalous skin effect theory. The values for niobium above T_C were calculated using normal skin effect theory.

of the quality factor Q_0 of the cavity versus the magnetic field H_S at the location of the pellet is shown in fig 7. Up to a field level H_{S0} the Q_0 value decreases slowly with growing H_S. At higher field levels the Q_0 value decreases according to $Q_0(H_S) \approx H_S^{-\beta}$. At a field level H_{Smax} quenching of the cavity field occured.

The Q_0 value just below H_{Smax} was more than one order of magnitude higher than the corresponding value of the normal conducting sample indicating that most of the sample is still superconducting. Therefore a current density of about H_{Smax}/λ_L exists at the surface of the new superconductor. Measurements of the London penetration depth λ_L of $Y_1Ba_2Cu_3O_{7-\delta}$ using muon spin rotation[6] give a value of 0.14 µm at 4.2K. Using this value the maximum obtained field of 690 A/m (table 1) leads to a surface current density of $4.9 \cdot 10^5$ A/cm^2. For an accelerating cavity consisting of pure $Y_1Ba_2Cu_3O_{7-\delta}$ this maximum field level corresponds to an accelerating field of 0.2 MV/m. Due to a field enhancement at some parts of the surface of the sample these values give lower bounds. Due to the poor cooling conditions of the samples thermal effects are likely to be responsible for the strong decrease of the Q_0 values with growing magnetic field (table 1).

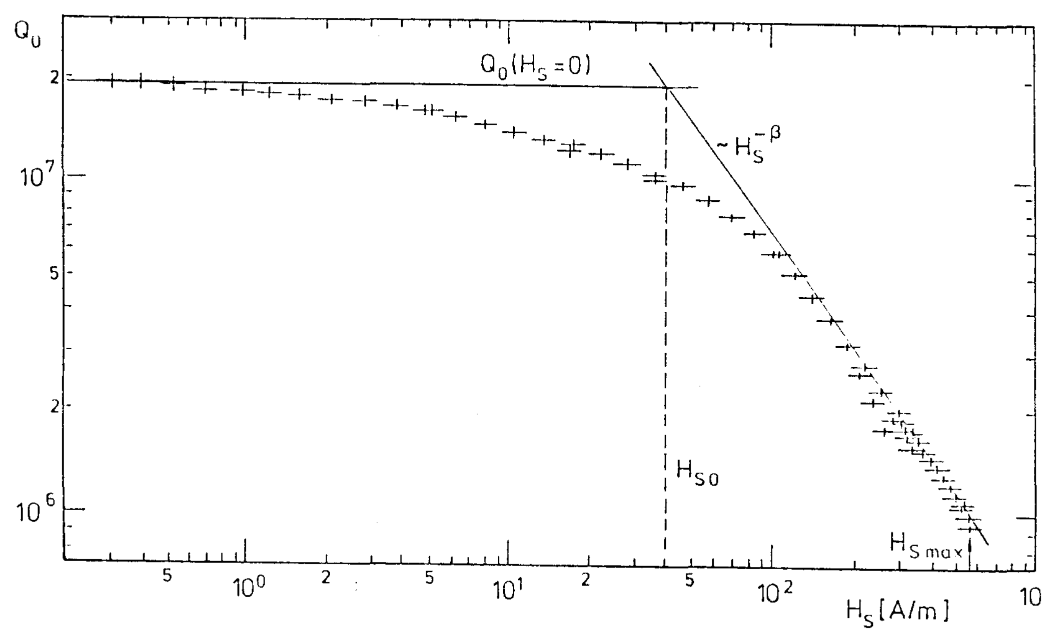


Fig.7: Q_0 degradation of the superconducting niobium cavity due to the Joule losses in a $Y_1Ba_2Cu_3O_{7-\delta}$ sample (W13-T1) as a function of the magnetic field at the surface of the sample.

In order to improve the cooling conditions and to exclude field enhancement further experiments will be performed using the samples as endplates of TE011 cavities. Then the obtained results can be compared with model calculations of the thermal field breakdown. The low value for the thermal conductivty of 0.02 W/mK (ref.7) for $Y_1Ba_2Cu_3O_{7-\delta}$ indicates that for an application in accelerating cavities surface layers of the new superconductors are required. One possibility to obtain such layers would be to work with emulsions of $Y_1Ba_2Cu_3O_{7-\delta}$ prepared from reacted and then powdered (ball milled) $Y_1Ba_2Cu_3O_{7-\delta}$. It is therefore important to find out if $Y_1Ba_2Cu_3O_{7-\delta}$ is still superconducting after the ball milling process during which the micron sized particles are exposed to high pressure and temperatures. If superconductivity in such powders is destroyed it is valuable to know the annealing temperature at which the superconducting transport properties are restored. To obtain these informations we ball milled four of our tested samples, pressed them into pellets again and annealed them at different temperatures. After each of these steps their surface resistance was measured at 300 and 77K. The results are summarized in table 2.

sample	initial R_S [mΩ] 300 K	initial R_S [mΩ] 77 K	reground R_S [mΩ] 300 K	reground R_S [mΩ] 77 K	reannealed T [°C]	reannealed R_S [mΩ] 300 K	reannealed R_S [mΩ] 77 K
W13-T1	170±30	≤ 10	374±58	176±28	650	614±93	860±128
W18-T1	378±59	37±10	1240±190	382±58	750	428±66	315±48
W18-T3	315±50	37±10	602±91	221±34	850	253±41	39±10
W7–T6	250±30	31±10	2300±300	900±100	925	170±30	22±11

Table 2: Performance of superconducting $Y_1Ba_2Cu_3O_{7-\delta}$ pellets (first column) after an additional ball milling and pressing (second column) and after a subsequent annealing in the temperature range from 650 to 925°C.

It is observed that the superconducting transport properties are completely lost after the ball milling procedure. This although a diminished Meißner effect could still be found. We interprete this result by assuming that the superconducting properties of a thin surface layer of the powder grains are destroyed, whereas the interior of the grains is undisturbed. A restauration of this damage layer and a contacting of the individual grains to a superconducting ceramic pellet was achieved at temperatures between 850 and 925°C under pure oxygen. After a heat treatment at 750 °C the sample remained normalconducting at 77K but exhibits a metal like behaviour. In the case of a heat treatment at 650°C the surface resistance increases with decreasing temperature indicating a semiconductor like behaviour which was confirmed by a dc resistance measurement.

IV. CONCLUSIONS

In this contribution first rf surface resistance measurements at 3 GHz with the new perovskite superconductors are discussed. A minimum surface resistance of 0.16 mΩ has been achieved for a $Y_1Ba_2Cu_3O_7$ sample at 4.2K and low field level. This is more than one order of magnitude lower than the surface resistance of high purity copper but about three orders of magnitude higher than the surface resistance of niobium and Nb_3Sn at the same temperature.
At a surface magnetic field of 690 A/m parts of one sample are still superconducting. For an accelerating cavity consisting of pure $Y_1Ba_2Cu_3O_{7-\delta}$ this field corresponds to an accelerating field of 0.2 MV/m . The high field performance of the samples are probably limited by the bad cooling conditions .
It was observed that after a new grinding and pressing of samples rf superconductivity was completely lost. A recovery of the sample was achieved by a further heat treatment at temperatures above 850°C in a pure oxygen atmosphere . The initial values of the surface resistance were reproduced.
Further experiments will be performed using perovskite samples as endplates of a TE011 cavity. Besides these activities further work will be concentrated on the preparation and rf measurements of surface layers of the new material.

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