Effect of heat treatment of pure and carbon-polluted rhodium samples on the low-temperature resistivity

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We present a systematic investigation of conditions for heat treatment of Rh with the aim of increasing the residual resistivity ratio (RRR). The maximal value of RRR for a 25 μm thick foil was found to be 1050 and the optimal treatment conditions were high temperatures, above 1400°C, and a low pressure of pure oxygen, around 1 μbar. Another batch of foils, containing less magnetic impurities, showed an RRR of only 600. A 0.4 mm thick single crystal was heat treated to an RRR value of 740. Our findings are discussed in the light of a model with magnetic and non-magnetic impurities in Rh, where the latter is found to have an important contribution for this unusual metal. Especially carbon impurities were found to be quite detrimental for the resistivity, and the recovery of the RRR after a carbon contamination is extremely slow in subsequent heat treatments. © *2001 Kluwer Academic Publishers*

1. Introduction
1.1. Heat treatment of Rh
Heat treatment is often used to improve the transport properties of a metal, as it may either remove or neutralize impurities, thereby increasing the electronic mean free path. For many low temperature applications, good thermal conductivity is crucial, and heat treatment of copper and silver is routinely performed. The platinum-group metal rhodium (Rh) has been used as a sample in a few low-temperature experiments [1–5], but little is known about the optimal heat treatment procedure of this metal. The purpose of this study was to investigate the effect of heat treatment on Rh in order to prepare a sample for a nuclear ordering experiment [6, 7].

The thermal resistivity ρ_{th} at low temperatures is most easily estimated from the electrical resistivity ρ_e, using the Wiedemann-Franz relation $\rho_e/\rho_{th} = L_0 T$, where $L_0 = (\pi k_B)^2/(3e^2) = 24.5$ nWΩ/K^2. The low-temperature electrical resistivity may in turn be found from the residual resistivity ratio, here defined as RRR $= \rho_e(295 \text{ K})/\rho_e(4.2 \text{ K})$, since at room temperature the electrical resistivity is almost solely determined by the phonon contribution and is thus independent of sample quality.

The highest RRR value reported for Rh is 2200 [8]. This was achieved in a rod prepared from zone melting of very pure powder, followed by annealing in air at temperatures up to 1500°C. The samples in which superconductivity of Rh were first observed [1] had RRR values of up to 450, the best value obtained by treatment at 1750°C in air. The foil samples used in the unsuccessful search for nuclear ordering in Rh had RRR values of 250 and 530, respectively. These samples were treated at 1300°C in 0.4 μbar of O_2 for 16 h, while higher treatment temperatures were found to reduce the RRR [5]. For a planned renewed search for the

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nuclear ordering transition, we have aimed for an RRR of 800–1000, based on cooling requirements evaluated by numerical simulations [9].

1.2. Sources of resistivity in Rh and similar metals

It is commonly agreed that heat treatment of the noble and Pt-group metals in a low oxygen pressure neutralized the impurities by selective oxidation and precipitation, besides annealing the crystal structure [10–12]. Precipitation reduces the number of scattering centers, and the oxidization of magnetic impurities reduces the conduction electron scattering cross section considerably. Impurities like N and C, on the other hand, are expected to be mobile and to be able to evaporate from the sample (in the forms of N_2 and CO_2, respectively).

In Cu, O_2 is rather soluble and easily diffuses as atomic O into the lattice, oxidizing the magnetic Fe ions to form magnetically ordered Fe_3O_4 clusters of $r >$ 200 Å [11, 13], after which the RRR may exceed 10000 [14]. A treatment in vacuum, on the other hand, gives less favorable results [11]. In Ag, the best value for RRR is 10000, achieved by heat treatment at 900°C at 0.2 μbar of pure O_2 [12]. Other related studies of heat treatment include Ta [15] and Au [16]. A theoretical description of the oxidization kinetics of impurities in a metal sample is given in [12]. All results suggest that the optimal conditions for heat treatment are a thin O_2 atmosphere and high temperatures.

In contrast to most other metals, Rh does not display a Kondo effect upon introduction of magnetic impurities [17]. The resistance of this "Coles alloy" may be understood in terms of impurity spin fluctuations, in a model very similar to that used to describe the Kondo effect [18]. The important difference of the role of spin fluctuations in the two cases is that in the Kondo alloys, the conduction electrons are s-like, whereas in the Coles alloys, the conduction electrons are d-like just as the impurity spin orbitals. A careful explanation of this theory is given in [19]. The measured resistivities of dilute RhFe alloys vs. temperature are monotonic, entering a linear regime below 10 K in agreement with theory. This feature has made the material well suited for resistance thermometry down to very low temperatures [14].

The resistivity of RhFe has earlier been measured as a function of temperature and Fe content [20], and was found to match the predictions of the spin fluctuation theory for Fe concentrations up to 0.35 at%. We replotted some of these data as a function of Fe concentration for two temperatures, 1 K and 4.2 K, see Fig. 1. For both temperatures, the resistivity is almost linear in the Fe concentration, as expected in the dilute limit [19], but with an offset at zero concentration, corresponding to contributions from other types of impurities. The Fe-impurity contribution to the specific resistivity at 4.2 K is found to be 7.1×10^{-5} $\mu\Omega$cm/(ppm Fe), which is much lower than e.g. the corresponding value for Cu, 1.6×10^{-3} $\mu\Omega$cm/(ppm Fe).

The slope of the $\rho(T)$ curve, calculated from the data of Ref. [20], is linear in impurity concentration and extrapolates to zero at zero concentration, see Fig. 1. This
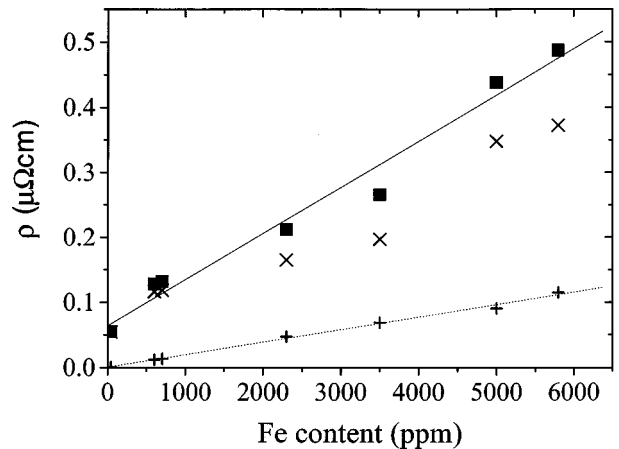

Figure 1 Resistivity of RhFe samples vs. Fe content. The three symbols show data at 4.2 K (■), data at 1.0 K (×), and the difference between those two (+). The solid line is a linear fit to the 4.2 K data, while the dotted line is a linear fit to the 4.2 K–1.0 K difference. All data are taken from [20].

suggests that the change in resistivity across that temperature regime in their sample is caused exclusively by the Fe impurities, and that the slope of the $\rho(T)$ curve can be used for determining the Fe content. The impurity contribution to the temperature slope of the specific resistivity is 6.0×10^{-6} $\mu\Omega$cm/(ppm Fe K). We expect other 3d magnetic impurities to contribute in a similar way, although possibly with a different strength, so that the magnetic impurity content may be described simply by the equivalent amount of Fe.

Since significant contributions to the residual resistivity of Rh may come from both magnetic and non-magnetic impurities, it is not possible just from the RRR to determine the effective concentration of Fe impurities. This may be done by measuring the temperature slope of the resistivity. This view disagrees with that of the previous Helsinki work on Rh [3–5].

2. Experimental details

The samples consist of 25 μm thick foils from three batches, of which two were used in the earlier nuclear ordering experiment [4, 5], of one 75 μm thick foil, and of two single crystals of thickness 0.4 mm. One batch of foils was supplied by Reactor Experiments[†] (in the following denoted RX) and two batches by Goodfellows[‡] (in the following both denoted GF, as they in all respects behaved similarly). The two 0.4 mm thick, slab shaped single crystals (A and B) were supplied by MaTecK[§] (denoted MT). The impurity contents of the foils and the single crystals, as listed by the manufacturers, are presented in Table I. We did not perform independent analyses of the impurity contents.

The samples were heat treated in an Al_2O_3 boat within an Al_2O_3 vacuum tube, which was radiation heated in an oven at temperatures up to 1560°C. The atmosphere was set by a constant flow of pure O_2 into

TABLE I Representative impurity levels of the samples (in ppm) as given by the suppliers. A "-" indicates that this element was not specified. The values for foil samples from Goodfellows (GF) and Reactor Experiment (RX) are adopted from [5]. MT denotes the single crystals from MaTeck

	Fe	Cu	Mg	Cr	Ni	Ti	Co	Mn
GF	10	1	<1	3	2	<1	<1	<1
RX	100	4	4	-	-	-	-	-
MT	<10	-	-	-	<3	-	<8	-

	B	Si	Ca	Al	Ir	Pt	Pd	Ru	Ag
GF	-	1	1	3	200	70	20	10	<1
RX	200	10	4	-	30	20	1	-	1
MT	-	-	-	-	<60	<60	<20	<10	-

Figure 2 Measured RRR *vs.* oxygen pressure, P, after repeated heat treatments of two different 25 μm foils at 1530°C. Triangles represent the RX foils, while circles represent the GF foils.

Figure 3 Measured RRR *vs.* heat treatment temperature, T. The open symbols denote 25 μm foil samples treated in vacuum, while the closed symbols represent similar samples treated in an oxygen atmosphere of 0.4 μbar. Triangles represent the RX foils, while circles represent the GF foils.

one end of the tube, which was pumped from the other end by a turbo-molecular pump. The O_2 pressure at the sample was varied from 0.02 μbar to 10 μbar, while the air leak contributed less than 1 nbar. Prior to each heat treatment, the sample surface was cleaned in concentrated *aqua regia*, which does not affect pure Rh [21], and washed in turn in distilled water, pure ethanol, and acetone. The Al_2O_3 surfaces were frequently cleaned in HNO_3 and washed as the sample. We always treated more than just one sample at a time to be able to identify possible errors in the heat treatment procedure.

Two series of four-wire measurements, one at room temperature and one at 4.2 K in a He dewar, were used to determine the RRR. The voltage were measured by an HP digital nano-volmeter 34420A. The untreated foils had RRR values of 30 (GF) and 40 (RX), and the single crystals 80 (A) and 250 (B). The resistance of single crystal B was measured to be 4.8 $\mu\Omega$cm at room temperature (295 K), which matches the tabulated value of 4.3 $\mu\Omega$cm at 273 K [22], when the temperature difference is taken into account.

We performed a few measurements of the resistivity between 1 K and 4.2 K, using four-wire measurements in a pumped ^{3}He cryostat. Due to lack of sensitivity, the data quality is very poor (not shown), but a general increase of resistivity with temperature is seen, as expected (se the discussion in Section 2). These measurements are not discussed further.

3. Heat treatment results
3.1. Foil samples
Initially, we studied the time dependence of the heat treatment. The RRR for 25 μm foils treated in 1300°C and 0.4 μbar O_2 was seen to have almost saturated after 3 hours and to be completely saturated after 11 hours of treatment (data not shown). To ensure saturation, all later heat treatments were performed for 22 ± 2 hours. A long heat treatment at high temperatures evaporates the material; one 25 μm foil vanished during a heat treatment of 163 hours at 1530°C. No degradation of the RRR with treatment time was observed, in contrast to earlier reports on Au and Rh [16, 23].

The influence of oxygen pressure was studied for both foils at a temperature of 1530°C. In Fig. 2, the resulting RRR is initially seen to increase with increasing pressure, but above 0.4 μbar no further improvement

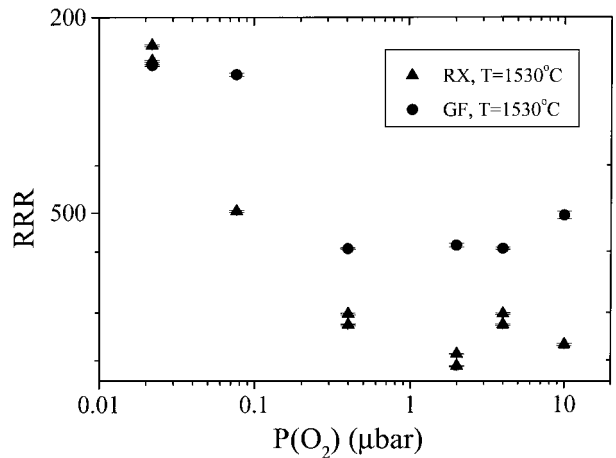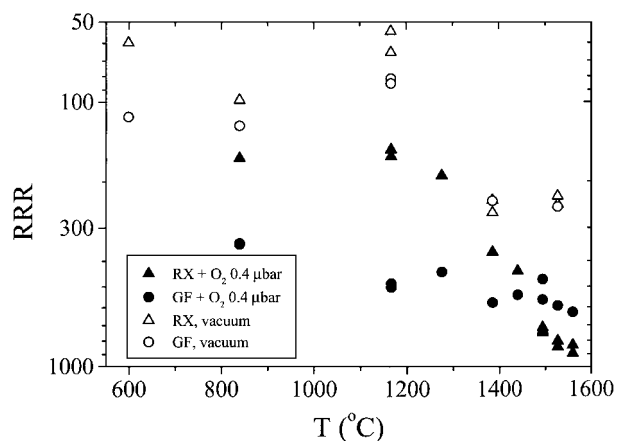is seen. We used a pressure of 0.4 μbar in most of the treatments presented in the following. No significant difference in RRR was observed between virgin samples and multiply treated samples. The RRR depended only on the O_2 pressure of the last treatment, in accordance with earlier findings in Cu [10].

The dependence of the RRR on the treatment temperature was studied both in vacuum (approx. 1 nbar air leak) and in 0.4 μbar of O_2 for two foils, one of each type. The results are displayed in Fig. 3. For both types of foils treated in vacuum, an improvement in RRR by a factor of 2–3 is seen at $T > 1400$°C compared to treatments at $T < 1400$°C. This temperature coincides with the onset of crystallite growth in Rh [21]. The grain sizes of our Rh foils were clearly visible both before and after the heat treatments. The grains were of a rather irregular shapes. Their typical size grew from 50–100 μm before heat treatment to 100–150 μm after treatment at the highest temperatures. We did not perform a systematic investigation of the temperature dependence of grain growth.

Foils treated in O_2 display a more intricate temperature dependence. The lowest temperature used was 830°C, since at the applied pressures, Rh will oxidize

below 800°C. At 830°C, the GF foils show a remarkable improvement over the untreated foils, while the RX foils remain at a much lower level. At temperatures up to 1270°C, the behavior is almost unchanged and consistent with the results obtained earlier [5]. Around 1400–1500°C, however, the RX foils undergo a drastic improvement of RRR, while the GF foils only display a minor improvement. This is in contrast to what was reported in [5]. During one treatment in 1170°C, a thin, black layer formed at the surface of the Rh samples, whence the results for this temperature must be viewed with some caution. This did not happen at any other treatment temperature, and we did not investigate it further.

Another observation is that foils treated in similar O_2 pressures more than once display an RRR value consistent with the highest treatment temperature. If, however, a sample was re-treated in vacuum, the effect of the first treatment seemed to be erased. This observation is consistent with a picture of impurity oxidization/reduction where the impurity atoms stay within the material. In a vacuum treatment, the impurity-oxides may be reduced and the impurities diffuse away, increasing the resistivity [10].

3.2. Oil pollution of foils and of a single crystal

In the first few heat treatments, an oil diffusion pump was used instead of the turbomolecular pump to evacuate the vacuum system. Accidentally, the pump overheated and polluted the vacuum system with oil during a treatment of the single crystal A, while the furnace temperature was 1400°C. This had a detrimental effect on the electrical conductivity of the crystal. The RRR dropped below its initial value, and subsequent heat treatments (after surface cleaning) did not seem to improve the RRR.

In order to investigate contamination by oil, we performed a similar "oil treatment" on a 75 μm GF foil, which displayed an RRR decrease from 587 to 45. After cleaning the foil in *aqua regia*, we performed several successive heat treatments of this foil in 0.4 μbar of O_2. The results of these treatments are shown in Fig. 4. After 4 days of treatment at 1370°C, the increase of RRR seemed to have leveled off, and the temperature was raised to 1500°C. After 10 more days in the oven, the initial RRR value of 587 was almost recovered. Assuming a model where the resistivity consists of a constant term (corresponding to an RRR value of 587) plus an exponential decay, the last treatment series yields a characteristic recovery time of 2.5 ± 0.5 days. The slight decrease of RRR during the third treatment was also seen in a reference foil. This was probably caused by (observed) air leaks in the system.

A similar "cleaning" strategy was tried with the polluted crystal A. Again, the oxygen pressure was 0.4 μbar, and now the initial temperature of 1370°C was increased to 1560°C after 5 days. The outcome of these treatments is shown in Fig. 5. It can be seen that after more than 18 days of treatment, the RRR has only improved marginally. The recovery time constant is estimated to be 56 ± 20 days, using the model above with
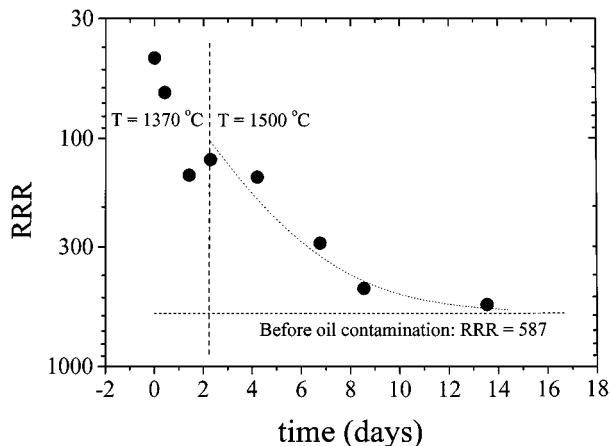

Figure 4 RRR *vs.* duration of heat treatment after oil contamination of a 75 μm foil sample. The oxygen pressure was 0.4 μbar, and the temperature was 1370°C initially, later 1500°C. The dotted line is a tentative fit to an exponential recovery behavior, as explained in the text.
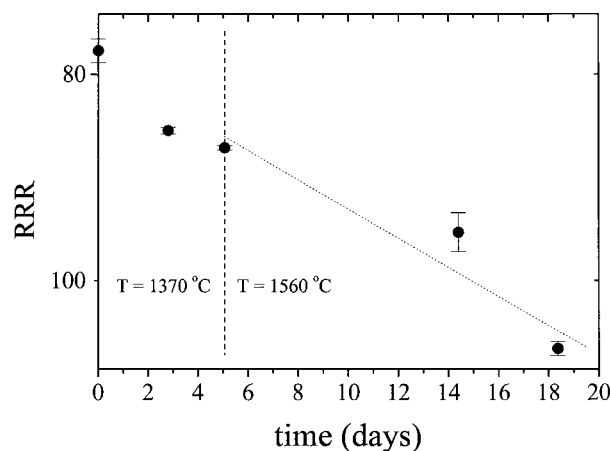

Figure 5 RRR *vs.* duration of heat treatment after oil contamination of the single crystal A. The treatment was performed at 0.4 μbar of O_2, initially at 1370°C, later at 1560°C. The dotted line is a tentative fit to an exponential recovery behavior, as explained in the text.

a guess of the unpolluted RRR of 800. The treatments were always done together with an unpolluted reference foil. The reference foils all showed a decrease in RRR after treatment with crystal A. This suggests that the contamination is caused by diffusing impurities, most probably carbon from decomposed pump oil. For a slab sample, the diffusion is essentially one-dimensional, whence the diffusion time will be proportional to d^2, d being the sample thickness. The ratio of the recovery times should thus correspond to a thickness ratio of 4.7 ± 1.0, which is consistent with the actual ratio of 5.3.

3.3. Proper treatments of a single crystal sample

The (unpolluted) single crystal B was heat treated in 0.4 μbar O_2 at 1300°C and 1530°C in several steps. The results of these treatments are shown in Fig. 6. The exponential time constant for the highest temperature was 3.5 ± 0.2 days, while the treatment at lower temperatures seems to saturate faster. After a total of 16 days of treatment, the RRR still had not saturated completely, but evaporation of the material forced us to
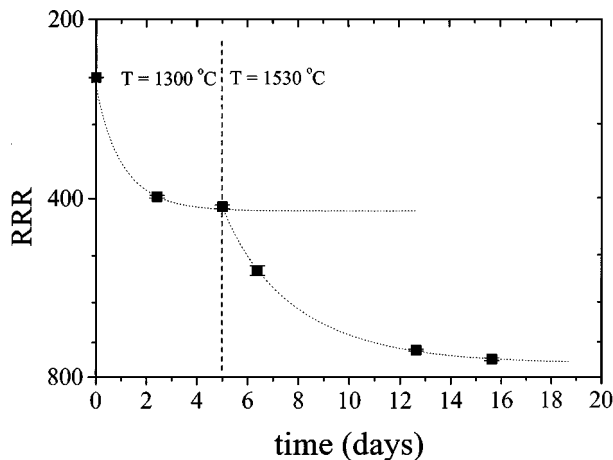
Figure 6 RRR *vs.* duration of heat treatment of the single crystal B at 0.2 μbar of O_2 at two temperatures, 1300°C and 1530°C. The dotted lines are tentative fits to exponential treatment behavior, as described in the text.

refrain from further treatments; the sample mass was reduced from 570 mg to 487 mg. The resulting RRR was 740.

4. Discussion

The heat treatment of the foils clearly showed that the presence of oxygen was an important factor in lowering the sample resistance. Also the resistance increase after a (reducing) vacuum treatment verifies that oxidization of impurities plays a role. This oxidization must take place in the bulk, otherwise the acid treatment would have removed the impurity oxides before the vacuum treatment. We expect that heat treatment in an air atmosphere may give worse results than in a pure O_2 atmosphere due to the resistivity of interstitial nitrogen. This is would explain our observation in experiments with accidental air leaks, although we did not test this assumption further.

The difference in the behavior of the RRR *vs.* treatment temperature in the two samples shows that there is more than one significant contribution to the low temperature resistivity in Rh. Assuming one of these to come from Fe (or similar magnetic $3d$) impurities, the sharp increase of RRR at $T > 1400°C$ for the RX foils could be interpreted as being caused by clustering of the Fe impurities as oxides, probably Fe_3O_4 [11]. This clustering could very well be related to the onset of crystallite growth of the Rh host at that temperature [21]. The smaller maximum values of RRR in the GF foils must then be due to the higher amount of other impurities, in particular the Rh-like elements (Ir, Pt, Pd, Ru), which are present here in fairly large quantities (total 200–300 ppm). Not much is known about the behavior of these elements as impurities in Rh, but we assume that they (as in Ag and Cu) will not oxidize, but rather be dissolved in the host matrix as single scattering centers (or small clusters, see below). The contribution of various impurities to the resistivity of Cu is given in [14]. In particular, an unoxidized Fe impurity contributes more than 100 times as much as an Ag impurity to the resistívity. As discussed earlier, this ratio is almost certainly much smaller in Rh because of the absence of the Kondo effect. Hence, non-magnetic impurities must as well be considered as important sources of resistivity.

An additional reason for the resistivity decrease in treatments above 1400 °C could be the formation of high-temperature crystal forms; one could imagine non-magnetic Rh-Feoxide combinations. Those crystals forms might not be able to return to the low-temperature forms during the sample cooling, which was relatively fast above 1000 °C. We do not, however, have any clear indications to support this hypothesis.

The measured reduction of the resistivity by treatments at $T < 1400°C$, compared to the resistivity of untreated Rh, is in absolute numbers much larger than the additional decrease in the high-temperature treatments. A major part of this reduction is also seen in the vacuum treatments, indicating annealing of structural defects. Possibly, this effect is enhanced by diffusion of some of the non-magnetic impurities to form small clusters, perhaps located on the grain boundaries. Adding oxygen to the heat treatments at intermediate temperatures changes the resistivity by the same amount for the two types of foils (by 1.0% of the room temperature value). This implies that the oxygen must have some effect also on other impurities than Fe. This effect cannot be explained by the model above, containing oxidization and clustering of magnetic impurities, possible clustering of non-magnetic impurities, and structural annealing.

Unfortunately, we were not able to raise the temperature above 1560°C to approach the melting point of Rh at 1966°C. However, with our present understanding of the heat treatment process, no dramatic increase of the RRR should take place upon increasing the treatment temperature.

We may estimate the contribution from the finite sample size to the foil resistivity. The limiting factor is clearly the sample thickness $d = 25$ μm, since this is much smaller than the observed grain sizes of 100–150 μm. We use the relation $\rho/\rho_0 = 1 + 3l/(8d)$, where ρ is the measured resistivity, ρ_0 is the resistivity of the bulk material, and l is the mean free path of the conduction electrons [24]. The formula is valid for $l \ll d$. Using the Rh chemical valence, $Z = 3$, to determine the density of conduction electrons, the (free electron) mean free path at room temperature is 7.3 nm. An bulk RRR value of 1000 would give a low-temperature mean free path of $l = 7.3$ μm, leading to a measured RRR of 900. The "real" RRR values are thus up to 10% higher than shown in our figures. We have, however, chosen to work with the uncorrected data, since the small corrections would not affect our conclusions.

The long time constants for heat treatment of the single crystal B support the assumption of oxidization of impurities by oxygen diffusing into the sample. The 16 days diffusion time in the 0.4 mm thick single crystal B would then correspond to 1.5 hours for the 25 μm foils. This is in good agreement with the short saturation times found for the foils, although these could not be measured very accurately due to the warm-up and cool-down times of the oven, totaling 2–3 hours. The asymptotic values for the RRR *vs.* time curves of the single crystal B changes almost a factor of two from the 1300°C treatment to the 1530°C treatment. This

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suggests that the general RRR *vs. T* behavior for the single crystal B is like that of the (Fe-poor) GF foils. This is reasonable since also the single crystals are supposed to have a low Fe content.

It seems that pump oil has a detrimental effect on the Rh resistivity. This cannot be a mere surface effect, since the strong acid would here have etched away all but pure Rh. The source of the contamination must be atomic carbon from decomposed pump oil [16]. The severeness of the oil pollution was unexpected, especially as C contamination in Ag is supposed to be unimportant [12], although it was reported to cause problems in Ta [15]. The faster recovery for the foil than for the crystal supports that C diffuses inside the material and most probably disappears at the surface as CO_2. The discrepancies between our findings and that reported earlier (decrease of RRR with higher treatment temperatures or longer treatment times) may very well be explained by carbon pollution in their experiments.

5. Conclusion

We have investigated the dependence of the RRR in Rh foils and in a few single crystals with impurity content, treatment time and material thickness. Our results suggest that at low temperatures, the RRR is lowered by structural annealing (and possibly clustering of non-magnetic impurities), while at high temperatures there is an additional effect of oxygen diffusion into the material followed by selective oxidization of magnetic impurities. This is further supported by the observation of reversibility in the process. The observed difference in heat treatment results with and without oxygen at intermediate temperatures suggest that besides structural annealing, at least two different oxidization processes take place inside the Rh sample: (a) Neutralization of some impurities below 1400 °C, and (b) Specific neutralization of Fe (and other magnetic $3d$) impurities above 1400 °C; the detailed mechanism in (a) is not understood. This behavior is much more complex what is seen in e.g. Cu, Ag, and Pt, making Rh an exception among the noble and Pt-goup metals from the heat treatment point of view.

Pump oil was found to be very poisonous to the Rh conductance, most probably due to the effects of atomic carbon impurities within the crystal. Recovery of carbon pollution by further heat treatment was found to be possible, although the recovery times were extremely long.

Our results suggest the following optimal conditions for heat treatments of Rh in order to obtain the lowest residual resistivity: High temperature, $T > 1400°C$ and a thin oxygen atmosphere, $P = 0.1$–$10\,\mu$bar. Using

these conditions, we reached a final RRR of the single crystal B of 740, which is still significantly less than the best foil value (1050). However, the corresponding thermal conductance is judged to be sufficient for the planned investigation of nuclear ordering in Rh.

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