Superconductivity of Rhodium at Ultralow Temperatures

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Superconductivity has been discovered in polycrystalline rhodium with $T_c = 325\ \mu K$ and $B_c(T=0) = 49$ mG. The investigated samples exhibit full Meissner effect and show behavior typical of a type-I superconductor. The influence of sample purity has been studied, and the possible influence of spin fluctuations is discussed.

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Ever since the discovery of superconductivity, efforts have been made to investigate whether the superconducting state is the universal low-temperature phase of nonmagnetic metals. Indeed, as refrigeration techniques have improved, a superconducting transition has been detected in most nonmagnetic metallic elements, the most recent being W,[1] with a superconducting transition at 15.4 mK.[2] There remain only two areas in the periodic system where the metals that are neither superconducting nor magnetic are concentrated: some alkali or alkaline-earth metals and the noble (Cu, Ag, and Au) and Pt metals (Rh, Pd, and Pt). No superconductivity has been observed in Cu, Ag, and Au, presumably because the electron-phonon interaction is weak and the electronic density of states is low.

A completely different situation is found in Pd, Pt, and Rh: The electronic density of states is much higher and the mass enhancement is rather strong.[3,4] All three elements show strongly exchange-enhanced paramagnetism. The associated spin-density fluctuations contribute to the electronic mass enhancement and are supposed to be detrimental for singlet superconductivity.[5] Several unsuccessful searches for superconductivity in these elements have been reported,[3,6,7] the most recent reaching a minimum temperature of 1.7 mK.[7] In our laboratory, the accessible temperature regime for such experiments has been extended significantly and we have reported on an investigation of superconductivity of Au alloys down to 50 μK.[8]

In this Letter we report on the observation of superconductivity in several Rh samples at ultralow temperatures. The cleanest of them displays $T_c = 325\ \mu K$ and a critical field $B_c(0) = 49$ mG. By this discovery, Rh has become the lowest-T_c element, with a critical temperature 3 orders of magnitude below that of the neighboring elements Ru and Ir. In addition, this is the first observation of superconductivity in a metallic element where spin fluctuations probably depress T_c by orders of magnitude.

Our result, $T_c = 325\ \mu K$, verifies the extrapolations of Andres and Jensen[3] [T_c(Rh) < 1 mK] from a study of Ir-Rh alloys at $T > 15$ mK, and of Mota *et al.*[6] [T_c(Rh) ~ 0.2 mK] from a study of Ir-Rh and Os-Rh alloys at $T > 5$ mK.

The experiments were performed in the Jülich two-stage nuclear demagnetization refrigerator.[9,10] One end of each sample was screwed by a 1-mm Cu screw to a Cu cold finger mounted on the Cu nuclear stage.[8] Its temperature was measured by pulsed NMR on Pt wires. The error in absolute temperature is estimated to be ± 5%.[9] Details of the magnetic field shielding to approximately 1 mG at the samples and of the SQUID ac susceptibility and dc magnetization measurement system have been published before.[8] All measurements are done on the free ends of the samples, which are not influenced by the screw joints. All signal sizes were estimated and checked by comparison to an installed reference sample of $Au_{98}In_2$.[8] Some further improvement was achieved by installing two separate SQUID systems and three additional primary coils to determine unambiguously the susceptibility of six samples simultaneously. The susceptibilities were measured by applying fields of 12 μG_{rms} at 1 or 11 Hz, resulting in a negligible eddy-current heating of below 10^{-19} W in the samples.

All data were taken at constant temperatures while very slowly sweeping the applied dc field. For increased thermal conductivity, all samples were kept normal conducting by application of a magnetic field whenever the temperature was changed. Some samples displayed a surprisingly long thermal relaxation time of many hours which became evident as a change of the measured critical field with time. Therefore at the minimum temperatures a holding time of 48 h was used. At these temperatures we also observed the influence of a time-dependent heat leak of unknown origin with a decay time of about three weeks.[10] This is probably responsible for the fact that we

TABLE I. Detected impurities and observations on measured samples.

Sample[a]	Major Impurities (at ppm)	RRR	T_c (μK)	B_c (mG)
#1, annealed 1750°C	Si 30; S 4; Cu 500 Ir 25; Ru 15; Cr 1; Fe 15; Ni 2	450	325	49
#2, no annealing	Si 20; S 100 Cu 200; Ir 5; Ru 2; Cr 3; Fe 7.5; Ni 1.5	130	325	47
#3, cut from cast block	Si 50; S 150; Cu 400; Cr 2; Mn 1; Fe 15; Ni 2; Zn 50; Zr 80; Ru 3; W 70; Ir 4	50	200	34
#4, 80 ppm Zr added to #1	Si 20; S 30; Cu 200; Cr 2; Fe 15; Ni 4; Zr 80; Ru 10; Ir 30	55	290	35
#5, approx. 200 ppm Fe added to #1	Si 70; S 120; Cu 100; Cr 2; Fe 100; Ni 6; Zr 3; Ru 30; Ir 30	40	not s.c. at T > 65 μK	

[a] From various batches of Rh from Johnson-Matthey, Ltd.

measured somewhat lower critical fields during the first weeks after cooldown.

Various polycrystalline samples from different batches of starting material were investigated. They all had approximately the same size of $10 \times 4 \times 2$ mm^3. Most were inductively melted in a cold Cu crucible and thereafter analyzed by spark mass spectrometry. Table I summarizes characteristics and observations.

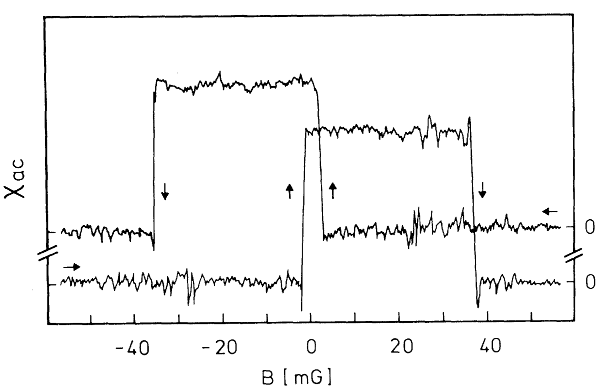

FIG. 1. Susceptibility of sample No. 1 as a function of applied field at 160 μK. The vertical axis shows two shifted traces of the pickup signal amplitude in arbitrary units: The upper trace is a slow sweep (10 mG/min) from 60 to -60 mG, and the lower one runs in the reverse direction. The ac drive field had an amplitude of 12 μG rms at 11 Hz. Note the strong supercooling and the sharp transitions.

We will first discuss the observation made on sample 1, which had the largest residual resistivity ratio (RRR = 450) and displayed the "cleanest" superconductive signals with fully developed Meissner effect, and whose behavior, we believe, most closely approaches that of ideally pure Rh. This sample shows a very sharp superconducting transition with strong supercooling (Fig. 1). We were able to measure $B_c(T)$ in the temperature range from 65 to 265 μK (Fig. 2). Closer to T_c, the small residual field in the setup exceeded the supercooling field and no transition could be detected; but by allowing the temperature to drift slowly upwards we could observe the superconductive signal up to 305 μK.

The measured critical field can be fitted well by $B_c/B_c(0) = 1 - T^2/T_c^2$ with $B_c(0) = 49 \pm 2$ mG and $T_c = 325 \pm 10$ μK. The supercooling field B_{sc} at all temperatures remained below 2 mG.

The very low T_c is reflected in a long characteristic time $\tau = \hbar/1.76\pi k_B T_c \simeq 4 \times 10^{-9}$ sec and a very long BCS coherence length $\xi_0 = v_F \tau \simeq 1$ mm. From our resisitivity measurements we estimate the transport lifetime $\tau_{tr} \approx 10^{-11}$ sec and the mean free path $l \sim 3$ μm. Hence we observe type-I superconductivity in the dirty limit and estimate $\xi = 0.85(\xi_0 l)^{1/2} = 0.06$ mm, which is obtained from measured quantities only by using $v_F l = \pi^2 k_B^2 \sigma / e^2 \gamma = 1.2$ m^2/sec. We find a Ginzburg-Landau parameter $\kappa = 0.72\lambda/l = 6 \times 10^{-3}$ and $B_{sc}(0) = 2.4\kappa B_c(0) = 0.7$ mG in good agreement with the observation.

The BCS theory relates the ratio $B_c(0)/T_c$ to the electronic specific-heat coefficient γ in the normal conducting state, $B_c(0)/T_c = (5.95\gamma/V_M)^{1/2}$. With the measured $\gamma = 4.65$ mJ/mol K^2 we obtain

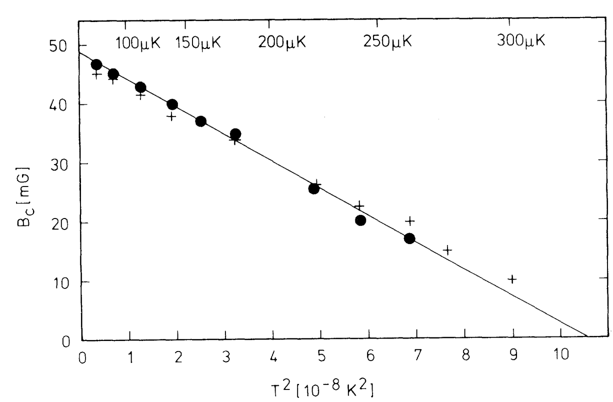

FIG. 2. Critical magnetic field data for samples No. 1 (dots) and No. 2 (crosses). The straight line is given by $B_c(T)/B_c(0) = 1 - T^2/T_c^2$ with $B_c(0) = 49$ mG and $T_c = 325$ μK.

$B_c(0)/T_c = 182$ G/K. This ratio is unusually large because of the high electronic density of states. The observed value is 151 G/K. It is known that some 3*d* impurities may not form a local moment in Rh.[11] Otherwise the detected impurities might suppress superconductivity completely, unless they undergo a transition into a spin-glass state,[12] which interferes only weakly with superconductivity. Possibly a "perfectly clean" sample might display superconductivity at 0.5 mK already.[8]

By applying the BCS formula, $T_c = \theta_D \exp(-1/NV)$, we obtain $T_c/\theta_D = 6\times10^{-7}$ and $NV = 0.070$. It is obvious that the interaction parameter NV is extremely small although N is rather high.

A suitable model for further analysis of our observations may be provided by spin-fluctuation theory.[3,5] It follows from Andersen's band-structure calculation that the specific-heat coefficient γ is enhanced by $\gamma/\gamma_{\rm band} = 1 + \lambda = 1.44$.[4] If the total enhancement λ is divided up into an electron-phonon part $\lambda_{\rm ep}$ and a spin-fluctuation contribution $\lambda_{\rm sf}$, one obtains $\lambda_{\rm ep} + \lambda_{\rm sf} = 0.44$. As spin fluctuations weaken the pairing, we follow a suggestion of Jensen and Andres to account for this effect by modifying McMillan's T_c formula[3]:

$$T_c \simeq \theta_D \exp\{-(1+\lambda_{\rm ep}+\lambda_{\rm sf})/(\lambda_{\rm ep}-\lambda_{\rm sf}-\mu^*)\}.$$

From this analysis we obtain $\lambda_{\rm ep} = 0.34$ and $\lambda_{\rm sf} = 0.10$, using $\mu^* = 0.13$. It implies that spin fluctuations contribute 25% to the observed mass enhancement and strongly reduce T_c. Rh would probably be a superconductor with $T_c \sim 0.5$ K if the spin fluctuations could be supressed, provided this model is correct. A similar argument holds for Pd, where no superconductivity is found for $T > 150$ μK.[13] Furthermore, the same analysis applied to Ir gives $\lambda_{\rm ep} = 0.34$ but only $\lambda_{\rm sf} = 0.03$, allowing $T_c = 0.1$ K.

We now want to report the results for the other investigated samples (see Table I). Sample No. 2 was prepared exactly as was sample No. 1, but from a different batch, and it was not annealed. It had a lower conductivity (RRR = 130). This sample also shows very sharp superconductive transitions but very little supercooling was observed. As can be seen from Fig. 2, the critical-field data deviate only slightly from those of sample No. 1. In addition, we noticed a small diamagnetic signal (~10%) already at 1 mK.

Sample No. 3 was cut by a diamond saw from a block which had been prepared by the supplier. It contained many metallic impurities and had a RRR of only 50. At 60 μK the full sample volume was superconductive at fields below 27 mG; at 200 μK the 100%-volume signal disappeared. At fields exceeding a "critical" field, the superconductive signal decreased rather slowly. Even at 60 μK the measured magnetization curves are broadened, showing a *continuous* decrease of superconductive volume in the field range from 27 to 58 mG. Nevertheless, there was noticeable supercooling observed in all measurements at temperatures below 200 μK. Above 200 μK a strong superconductive "precursor" (~ 50% of full volume) remained whose size decreased with $\log T$ over nearly two decades in temperature (!), until at 25 mK it finally vanished. This "precursor" appears as a diamagnetic peak in susceptibility as a function of field with a width of only about 10 mG. Surprisingly this field value drops slightly with falling temperatures; furthermore it is much smaller than expected from a corresponding transition temperature.

Since there are various superconductive Rh alloys known,[6] we decided to investigate whether the high Zr content of sample No. 3 is responsible for the high-temperature precursor. We prepared sample No. 4 by alloying 80-ppm Zr with our high-purity Rh. However, this new sample displayed very sharp supercooled transitions at *lower* temperatures than the cleaner samples and no precursor was seen. Because of long thermal relaxation times in sample No. 4, T_c and $B_c(0)$ can only be estimated to 290 ± 20 μK and 35 ± 5 mG.

It is known that *Rh*Fe exhibits unusual resistivity and susceptibility anomalies.[11] Therefore sample No. 5 was prepared to study the influence of iron impurities on the superconducting properties of Rh. This sample did not display any superconductive signal at $T > 65$ μK.

We would like to summarize: Bulk superconductivity with complete Meissner effect has been observed in various Rh samples at ultralow temperatures. The cleanest samples display $T_c = 325$ μK and $B_c(0) = 49$ mG. The $B_c(0)/T_c$ ratio is 17% below the BCS value. Analyzing T_c with spin-fluctuation theory suggests that spin fluctuations depress T_c by about 3 orders of magnitude. These results evoke analogies to the discovery of superconductivity in irradiated Pd films at 3 K which is attributed to a reduced susceptibility.[14] In two samples a "high-temperature" precursor is observed. This might be interpreted as a filamentary "impurity alloy" with a local reduction of spin fluctuations.

Rhodium has been regarded as a possible candidate for paramagnon-induced p-wave superconductivity; however, the short transport lifetime calculated from the electrical resistivity makes it unlikely that we are observing triplet superconductivity as it is discussed in the literature.

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Floating of the Modulation Wave and Phase Pinning in Incommensurate Rb_2ZnBr_4

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Nuclear-magnetic-resonance measurements in incommensurate Rb_2ZnBr_4 show the existence of regions where the modulation wave is floating. The floating regions coexist with other regions where the modulation wave is static. Impurity phase pinning and a roughening of the modulation wave at higher temperatures is proposed to account for these effects.

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The possible existence of a "floating" incommensurate phase[1-4] has recently attracted a great deal of attention. The continuum theory of structurally incommensurate (I) phases[2,3] predicts the existence of a gapless sliding mode in the I phase. This is the Goldstone mode which recovers the broken continuous phase symmetry[2] of the incommensurate phase. The occurrence of such a gapless phason mode in structurally incommensurate systems would lead to the existence of a liquid-like "floating" phase where the modulation wave would be moving freely[3,4] with respect to the underlying lattice. Discrete lattice effects[3] and impurity pinning of phase solitons[1] lead to a gap in the phason spectrum and to a locking of the modulation wave to the underlying lattice. Above some finite temperature thermal fluctuations should become large enough to overcome the pinning energy which continuously decreases as the incommensurate-paraelectric transition temperature T_I is approached. The energy gap in the phason spectrum should abruptly disappear and the truly incommensurate floating phase should be restored.[3]

In spite of many investigations, no experimental evidence has been found so far for the exis-

