Rhodium Sets New Standards

SUPERCONDUCTIVITY NEAR ABSOLUTE ZERO

By Ch. Buchal and J.-M. Welter

Institut für Festkörperforschung, Kernforschungsanlage Jülich, West Germany

What does the ground state of conduction electrons of metals look like, if the temperature is lowered further and further? This question has been fascinating low temperature physicists for a long time. Nowadays we know that most metallic elements become superconducting at sufficiently low temperatures. In 1964 the superconductivity of tungsten was discovered by lowering the temperature to 15 mK above absolute zero. After a long pause due to the limits of refrigeration, a new superconducting element has now been discovered: rhodium. Various samples fabricated with rhodium sponge were installed in a special set-up in the world's most powerful refrigerator at the Kernforschungsanlage Jülich. Temperatures down to 50 μK were used to investigate the superconductive properties of rhodium, which shows a superconductive transition at 325 μK.

What will be the behaviour of the mobile conduction electrons in metallic elements if they are cooled closer and closer to absolute zero? At the beginning of this century Kamerlingh-Onnes expected that most probably the conduction electrons would "freeze onto the atoms they belong to" and that the metal would turn into an insulator. But in 1911 he observed in his pioneering experiment that below a critical temperature T_c the opposite situation occurred: the metal changed into a new state in which the electronic current flowed completely without loss. This was unexpected and could not be understood at the time. It took nearly 50 years until Bardeen, Cooper and Schrieffer could explain in 1957 the phenomenon of superconductivity (1): the clue was the formation of a superconductive condensate consisting of paired conduction electrons (Cooper pairs). The striking features of such a pair are: the pair stabilising interaction between two electrons is mediated by lattice vibrations (phonons) and the two electrons have opposite spin directions.

In this situation two interesting questions arise for low temperature solid state physics:

1. When looking at the Periodic Table of the elements one sees that most non-magnetic metals become superconducting, Fig. 1. Magnetic metals have to be excluded because magnetism destroys superconductivity. What will happen if the temperature is lowered further with those few metals which until now are not known as either magnetic or superconducting?
2. For all known superconductors the electron-phonon interaction seems to be responsible for the pairing of the electrons. But does nature provide another interaction which possibly could also stabilise Cooper pairs and hence superconductivity?

Both questions are a consequence of Cooper's calculations. He could show that every system of particles obeying Fermi's statistics (for example, electrons) will become unstable for any attractive interaction existing between the fermions and that it would undergo a transition into the superconductive state. For a long time the existence of another attractive interaction seemed unlikely. But the discovery of the superfluidity of the Fermi liquid ^{3}He around 3 mK (which is stabilised by a paramagnon

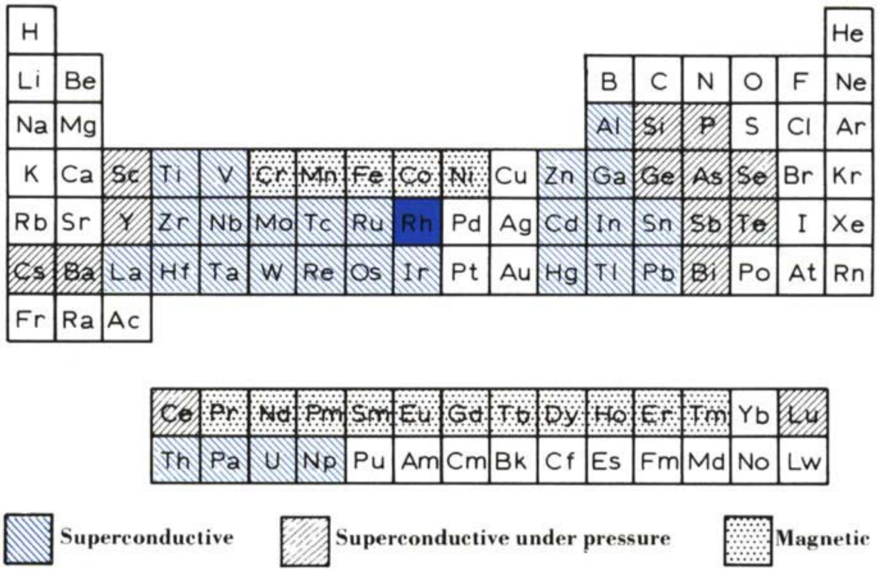

Fig. 1 The Periodie Table of the elements, showing their low temperature behaviour

feedback) stimulated much theoretical work on superconductivity in metals induced by paramagnons. The central idea is that in certain paramagnetic metals electron spins prefer to align in the same direction, which could lead to Cooper pairs stabilised by a magnetic interaction.

It turns out that rhodium plays an important part in providing answers to these questions.

As superconductivity is normally favoured by a high density of electronic states at the Fermi level, rhodium, platinum and palladium should be superconductors. Furthermore these three elements are not magnetic. Nevertheless one notices that their paramagnetic susceptibility is much stronger than one could expect from their density of electronic states. This increase of susceptibility (Stoner enhancement) is most probably due to a correlation effect in the high density gas of the conduction electrons. In such a system parallel spin alignment is favoured. Therefore superconductivity which is carried by Cooper pairs with antiparallel spin alignment might be suppressed. Within the spin fluctuation theory the origin of this situation has been explained by assuming that strongly damped magnetic waves (paramagnons) exist in the non-magnetic (that is paramagnetic) electron gas. But together with the insight into the negative influence of the paramagnons on the normal superconductivity (s-wave superconductivity) the hope grew that they possibly might stabilise another type of superconductivity, now being carried by Cooper pairs with parallel spin (p-wave superconductivity). This would be an entirely new phase of matter like p-wave superfluidity, which, as was already mentioned, exists in ^{3}He. Put crudely the question is: does nature allow only hetero- or also homo-erotic superconductive liaisons?

In 1979/80 new experimental possibilities were opened when samples could be cooled below 50 μK in the Jülich two-stage nuclear demagnetisation refrigerator. When searching for the possible superconductivity of rhodium the Jülich low temperature team discovered in a sample with a residual resistivity ratio (RRR) of 50 a weak diamagnetic signal around 20 mK. It increased slowly with decreasing temperature and reached the full superconductive value around 200 μK. RRR is the ratio of the

Optical Emission[(a)] and Mass[(b)] Spectrometry Analysis of Two Rhodium Samples

Sample	RRR = 50		RRR = 450	
Analysis[(c)] Number	Optical emission 1	Mass 2	Optical emission 3	Mass 4
Element	Impurity level,[(d)] atomic parts per million			
C		~1000		~1000
N		4		7
O		20		~30
Na		1		1.5
Mg	< 4	1	< 4	
Al	< 4	4		4
Si	4	~43	< 4	24
P				2
S		121		~100
K				2
Ca	< 2.5	0.5	8	1
Ti		2		
V		0.5		1.5
Cr	2	2	< 2	1.5
Mn		0.8	< 2	0.5
Fe	2	13	< 2	12
Co		0.5		0.4
Ni		2		2.5
Cu	12	250	< 1.5	200
Zn		5		
Zr		~20		0.5
Ru		1.5		~11
Ce		~ 6		~ 2
W		64		
Ir		1.5	1	21
Pt		1.5		1
Pb	< 0.5			

(a) Data from Johnson Matthey Chemicals Limited. (b) Data from Dr. H. Beske, ZCH, KFA Jülich.
(c) Analysis 1, 2 and 4 were made on the final sample, analysis 3 on the starting sponge.
(d) The limit of detection for mass spectrometry are 0.5 at ppm., for optical spectrography in general 1 wt.ppm (osmium, ruthenium: 10 wt.ppm and tungsten: 100 wt.ppm).

resistivities at 300 K and 4.2 K and is a good measure of the overall (electrical) purity of the sample. A rule of thumb states that the higher RRR the purer the material. This first sample was prepared by Johnson Matthey Chemicals by arc melting Grade 1 sponge with a tungsten electrode in a beryllium-copper mould. The mass spectrometry analysis, given in the Table, reveals clearly the tungsten and copper contamination. The optical emission analysis made by the producer gives also a high copper value but no result for tungsten since the limit of detection is approximately 60 atomic ppm.

The amazing results obtained with this sample could not be interpreted and caused exciting discussions. Very soon the need for better samples became clear and various batches of the purest possible rhodium sponge from Johnson Matthey Chemicals were purchased. In particular the level of magnetic impurities like iron had to be low. The sponge was consolidated by r.f. induction melting in a water cooled boat crucible made from copper. Eventually one sample was annealed for 15 hours at 2020 K in ultra-high vacuum (10^{-10} mbar). With this sample we obtained the highest RRR of 450. Its mass spectrometry analysis as well as the optical emission analysis of the starting sponge are given in the Table. Now sharp signals were obtained and could be attributed unambiguously to the volume superconductivity of rhodium.

The results of this work have been published recently (2) and the details will not be repeated here. But let us summarise what rhodium has taught us about the physics of conduction electrons near absolute zero:

(A) As can be seen from the scale of observed superconductive transition temperatures, shown in Figure 2, the transition in rhodium occurs at extremely low temperatures: the transition temperature of 325 μK is approximately three orders of magnitude below those of the neighbouring elements iridium (0.1 K) and ruthenium (0.49 K).

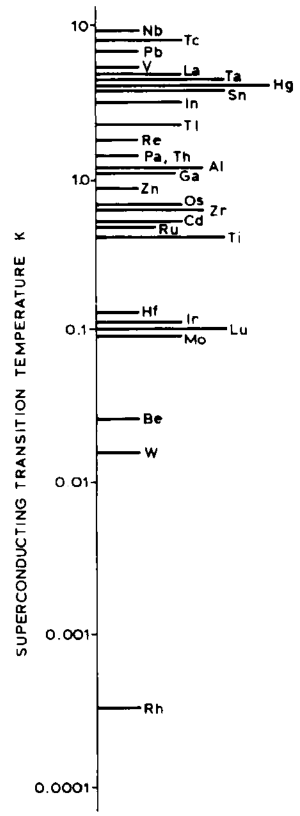

Fig. 2 Superconducting transition temperatures, plotted here on a logarithmic scale, show that the transition in rhodium occurs approximately three orders of magnitude below those of iridium and ruthenium

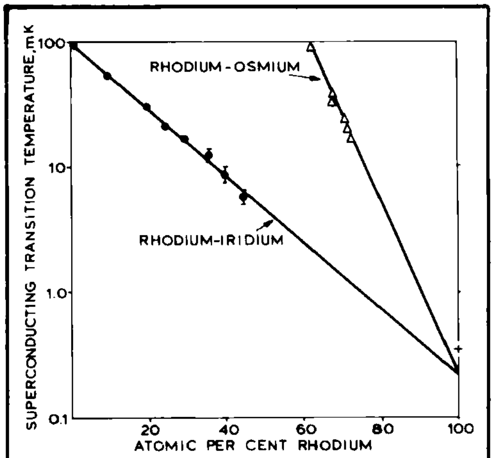

Fig. 3 Superconducting transition temperatures of rhodium-osmium and rhodium-iridium alloys, after (4), and of pure rhodium (+). There is quite good agreement between the earlier extrapolations and the results of the present work

(B) The Jülich measurements have demonstrated that the critical field curve of rhodium follows well the theoretical description given by Bardeen, Cooper and Schrieffer. This implies that the superconductive state itself follows the known laws, although the pair binding interaction seems to be very weak.

(C) There is a quite good agreement between the early extrapolations of the superconductive transition temperatures of rhodium-iridium and rhodium-osmium alloys occurring at far higher temperatures and our results for pure rhodium, see Figure 3. This indicates clearly (3, 4) the smooth change of the pairing interaction with concentration. In other words, it is almost certain that rhodium is unfortunately an electron-phonon coupled superconductor.

(D) Nevertheless, the above mentioned proximity to magnetism and the pair weakening influence of the enhanced paramagnetism lowers T_c drastically. If this "magnetism" could be switched off, T_c probably would go up to approximately 1 K.

As a conclusion we would like to remark that improved experimental techniques, better sample preparative methods together with the intrinsic properties of rhodium permitted us to gain new insights into the world of superconductivity near absolute zero.

References

1 J. Bardeen, L. N. Cooper and J. R. Schrieffer, *Phys. Rev.*, 1957, **108**, 1175

2 Ch. Buchal, F. Pobell, R. M. Mueller, M. Kubota and J. R. Owers-Bradley, *Phys. Rev. Lett.*, 1983, **50**, (1), 64

3 K. Andres and M. A. Jensen, *Phys. Rev.*, 1968, **165**, 533

4 A. C. Mota, W. C. Black, P. M. Brewster, A. C. Lawson, R. W. Fitzgerald and J. H. Bishop, *Phys. Lett.*, 1971, **34A**, (3), 160

Improved Platinum Investment Castings

The interest in platinum as a jewellery material that was regenerated in the United Kingdom by the introduction of the Hallmarking Act of 1973 stimulated efforts by investment casters to improve the quality of their products by the use of modern technology. Early work by Johnson Matthey to develop the most suitable platinum alloys has been reported here previously (G. Ainsley, A. A. Bourne and R. W. E. Rushforth, *Platinum Metals Rev.*, 1978, **22**, (3), 78–87). Depending on the application, two alloys are recommended, 4.5 per cent cobalt-platinum with an as-cast hardness of 135 Hv, and where a soft alloy is required 4.5 per cent palladium-platinum (as-cast Hv = 65).

Of course, the high melting point of platinum imposes severe conditions on all materials involved in the investment casting process, so more recently alternative refractory materials and plant have been evaluated. Careful utilisation of the most suitable refractories has produced an investment which is resistant to the high temperatures involved and also a crucible with an extended working life. As a result it is now normal practice to produce investment trees containing up to 60 ring shanks or 150 settings and weighing up to 1 kg, a ten-fold increase on previous capabilities. Simultaneously the use of the improved investment material has led to a dramatic improvement in the surface quality of the castings, and so the task of the manufacturing jeweller producing the finished article has been made significantly easier.

The tree illustrated here consists of a small selection of the many patterns that are cast in platinum for the manufacturing jeweller. These include fine and delicate settings weighing under 1 gram, complicated dress rings and signet rings weighing over 30 grams. Now, within the limiting parameters of the investment casting process, any item of jewellery or allied products can be cast successfully in platinum. G. A.