Superconductivity of the Platinum Metals and Their Alloys

A REVIEW SUMMARISING THE PUBLISHED SCIENTIFIC DATA

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Continuing investigation of superconductivity, particularly of platinum metal compounds, has resulted in a growing understanding of the phenomenon. Accumulating data contain some remarkable experimental results which in time must surely find both theoretical explanation and industrial application.

The electrical and magnetic behaviour of the platinum metals and their compounds has fascinated solid state chemists and physicists for many years. Together with iron, cobalt and nickel the platinum metals belong to Group VIII of the Periodic Table, and one of the earliest problems was to consider why they did not show any magnetic ordering, in contrast to iron, cobalt and nickel. On the other hand, when in the form of solid solutions or compounds they exhibited very interesting magnetic behaviour, for example localised moments and spin glass behaviour. The magnetic strengths of cobalt-platinum alloys even found industrial application.

With the discovery of “superconductivity” by Kammerlingh-Onnes and the hypothesis of B. T. Matthias and others that superconductivity—that is the loss of any electrical resistance below a critical temperature, $T_c$—and ferromagnetism exclude each other even though they are based on similar phenomena, the investigation of the low temperature electrical and magnetic behaviour of the platinum metals and their compounds became of special interest.

In the course of this research many new and unexpected phenomena were discovered in platinum metal alloys, namely superconductivity of hydrides, and superconductivity/ferro- or antiferromagnetism in ternary compounds, topics which subsequently developed into specialised research areas of their own. Even now it is impossible to predict the $T_c$ or $T_m$ ($T_m =$ magnetic ordering temperature) of an alloy. Indirectly this work has led to new approaches in other areas, for example the growth and study of single crystals.

Up to now superconductivity has found only limited application in high technology areas for example in magnets for fusion and atomic research at CERN and Culham, and for electrical motors and generators. However, one can expect that the platinum metal compounds discussed here, with their unique properties, will in time find applications which cannot be envisaged at present, perhaps especially for solid state devices.

It has been known for some time that three of the six platinum group metals in high purity...
form become superconducting, these being ruthenium, osmium and iridium. In addition, many years ago, it was predicted from investigations made of rhodium alloy systems that the element rhodium might also become a superconductor at a temperature around 0.2 mK (1), and this has recently been established (2, 3). The superconductivity of the individual metals will now be considered.

Ruthenium

The superconducting transition temperature of ruthenium has been placed between 0.40 and 0.50 ± 0.002 K (4, 5, 6). The generally accepted values for its superconducting properties are: transition temperature \( T_c = 0.49 \pm 0.015 \) K, critical field \( H_c = 69 \pm 2 \) Oe, Debye temperature \( \theta_D = 580 \) K, and the coefficient of low temperature specific heat \( \gamma = 2.8 \) mJ/mol/K (7). The dependence of critical temperature on its atomic mass \( M \) (isotope effect) is relatively small. For powdered and arc furnace melted samples of \( \text{Ru}_{99} \) and \( \text{Ru}_{104} \) it was reported that the critical temperature coincides within the accuracy of measurements (8) and similar results were obtained later (9, 10). Measurements made on samples with an average atomic mass \( \mu \) of 99.2, 101.1 and 103.9 in magnetic fields up to 70 Oe gave the dependence: \( T_c - M^{-1/4} \). At pressures up to 30,000 atmospheres the critical temperature is not affected by the applied pressure (11), while its volume dependence \( \frac{\delta \ln(T_c/\theta_D)}{\delta \ln V} = -16 \) (12).

Osmium

The critical temperature of osmium as given in the literature ranges from 0.4 to 0.71 K (13). An arc furnace melted sample of 99.9 per cent purity had a resistance ratio of \( \rho_0/\rho_{273} = 0.4 \) and \( T_c = 0.71 \) K, at a width of transition of 0.02 K (14). Today generally accepted values for the superconducting properties are \( T_c = 0.66 \pm 0.03 \) K, \( H_c = 70 \) Oe, \( \theta_D = 500 \) K and \( \gamma = 2.35 \) mJ/mol/K (7). Isotope effect measurements do not agree, even when apparently identical samples are checked (10, 15). According to Geballe and Matthias (10) osmium has no isotope effect, while Hein and Gibson (15) found \( T_c \propto M^{-0.2} \). The critical field is 80.9 Oe when \( M = 187.4 \), and 80.2 Oe when \( M = 192.0 \) (15). At a pressure of 30,000 atm the critical temperature of osmium is reduced by 0.05 K (11). In a review paper considering the influence of the purity of samples on their critical temperature it was shown that the sample with the highest resistance ratio, which was \( \rho_{273}/\rho_0 = 500 \), had \( T_c = 0.638 \) K (16).

Iridium

By suitable heat treatment in an arc melting furnace it has been possible to remove from iridium samples, by evaporation, ferromagnetic impurities such as iron, when a \( T_c = 0.14 \) K is obtained for the iridium (17). However, for samples containing 50 ppm of iron \( T_c = 0.10-0.11 \) K (18). Iridium purified by electron beam melting until the total impurity content is below 10 ppm has a critical temperature curve with a mid point at 0.1125 ± 0.005 K.

Furthermore its transition curve is characterised by an uncommon hysteresis; the transition from the normal to the superconducting state occurs discontinuously but from the superconducting to the normal state it is continuous. Additionally, it is influenced by the applied magnetic field. The coherence length is \( 4.4 \times 10^{-3} \) cm, and the penetration depth \( 3.9 \times 10^{-6} \) cm. Small impurity concentrations reduce the critical temperature of iridium and make it a superconductor of the second kind. Accepted values are now: \( T_c = 0.1125 \pm 0.001 \) K, \( H_c(T = 0) = 16 \pm 0.05 \) Oe, \( \theta_D = 425 \) K and \( \gamma = 3.19 \) mJ/mol/K (13); the pressure dependence of \( T_c \) is \(-5.1 \pm 0.9 \) x \( 10^{-4} \) K/atm (19).

Rhodium

In the purities generally available commercially, rhodium is not superconducting at 0.086 K (13) nor at 0.003 K (1). On solid solution samples of the alloy systems rhodium-osmium and rhodium-iridium the superconductivity was measured at compositions of up to 80 atomic per cent rhodium and an estimate then made of the behaviour of
rhodium as an element (1). X-ray analysis suggested the samples were homogeneous, but microprobe investigations of the rhodium-iridium alloys showed some slight coring, but for the rhodium-osmium alloys the concentration varied by up to 20 atomic per cent. In order to avoid the introduction of impurities and segregation, the alloys had not been heat treated and therefore showed relatively broad transitions. The superconducting transitions for the rhodium-iridium alloys were spread over a width of 1 mK while for the rhodium-osmium alloys, at the higher temperatures, the spread was very wide and sometimes incomplete. However, as mentioned earlier, it was deduced from these results that rhodium would become a superconductor at a temperature of \(0.2 \times 10^{-3}\) K, a temperature predicted to be “at least a decade away” (1). With significantly improved refrigeration facilities it has recently been established that polycrystalline rhodium is in fact superconducting at a critical temperature of 325 \(\mu\)K (2, 3).

**Palladium and Platinum**

Even extra purified palladium and platinum are not superconducting. The lowest test temperature published is 0.1 K (7, 13, 20) but according to a private communication from A. C. Mota neither palladium nor platinum are superconducting, even if checked at temperatures as low as \(10 \times 10^{-3}\) K.

**Alloys of Platinum Group Metals: with Hydrogen**

The discovery of superconductivity in palladium-hydrogen samples, loaded electrolytically up to H:Pd ratios >0.8, started an intensive investigation of binary and ternary palladium-hydrogen alloys with regard to superconductivity (21). By using ion-implantation techniques and low temperature electrolysis, H:Pd ratios >1.0 were obtained with critical temperatures of 8.8 K for palladium-hydrogen and \(\sim 10.7\) K for palladium-deuterium samples (22). Ternary palladium-copper-hydrogen samples exhibited a maximum critical temperature at H:Pd, Cu,\(\approx 0.8\) of about 17 K. The values in the system palladium-silver-hydrogen are: H:Pd\(_{16}\)Ag\(_{10}\) \(\approx 0.8\) and \(T_c = 16\) K and in the system palladium-gold-hydrogen they are: H:Pd\(_{16}\)Au\(_{16}\) \(\approx 0.9\) and \(T_c = 13.6\) K (23). In these alloys the maximum critical temperature shows up at lower H:Pd ratios and this effect is explained by the reduction of the critical temperature lessening “spin” fluctuations (24). Apparently the disappearance of the strong paramagnetism of palladium is a prerequisite for the occurrence of superconductivity, as has been shown earlier for palladium-molybdemen and palladium-tungsten solid solutions (24). Ion-implantation experiments on Pd\(_{1-x}\)Al\(_x\), and Pd\(_{1-x}\)Ti\(_x\) alloys (H:Pd \(\leq 0.15\)) showed a reduction in the maximum critical temperature with increasing aluminium and titanium concentration (25, p. 236). Palladium with ion-implanted lithium, boron, carbon or nitrogen showed superconductivity only for the palladium-boron-hydrogen and palladium-carbon-hydrogen alloys at 3.8 and 1.3 K. The lithium and nitrogen containing samples were not superconducting above 0.2 K (25, p. 237). The effect of replacing part of the palladium by nickel, platinum or rhodium and silver in ion-implanted and pressure loaded palladium-hydrogen and palladium-deuterium alloys has been considered (25, p. 243; 26, 27, 28). Up to 10 atomic per cent nickel suppresses the critical temperature rather strongly, but platinum has little influence on critical temperature at concentrations up to 25 atomic per cent (25, p. 253).

There is no relationship between critical temperature, susceptibility and the coefficient of the low temperature specific heat for the rhodium-palladium-silver and nickel-palladium-platinum alloys investigated (25, p. 254).

The pressure coefficient of palladium-hydrogen alloys \(\delta\ln T_c/\delta P\) is \(-0.01\) K/bar (25, p. 253).

For samples containing identical hydrogen and deuterium concentrations, the isotope effect results in a \(T_{cH}/T_{cD}\) in the range 1 to 2.2 (29). In thin palladium films it was observed that the behaviour corresponds to that of bulk
palladium at thicknesses above 2000 Å. Films with thicknesses of 320 Å exhibit no superconductivity at up to 1 K (30). In very fine palladium-hydrogen powder samples, produced by electrolytic co-deposition at −30°C, which X-rays showed to be amorphous, no superconductivity was observed above 1.9 K even if the palladium:hydrogen ratio was varied (29), confirming observations by Raub and Loebich (31).

Alkaline Metals

None of the alloys of the platinum metals with lithium, sodium or potassium is superconducting above 2 K. This is valid for the solid solutions, as well as for the compounds at present known (7, 13, 32). Electrolytically loading palladium-lithium solid solution samples with hydrogen did not produce superconductivity above 1.9 K (33).

Copper, Gold and Silver

None of the alloys of the platinum metals with copper, gold or silver is superconducting above 2 K. Rhodium-copper samples, in the solid solution range, are not superconducting down to 0.3 K (33). The ternary phase Ag₃Pd₁₋₂S, A₁₃-type, a = 7.235 Å, has Tₘ = 1.1 K (34).

Group II Elements

Barium, Beryllium, Calcium, Magnesium, and Strontium

Beryllium forms superconducting phases with four of the platinum metals but not with palladium and platinum; however sometimes it is unclear to which phases superconductivity must be attributed (7, 13, 35). Be₁₁Ru and Be₂Ru show critical temperatures of 1.3 and 1.35 K, respectively (35). Of the many beryllium-rhodium compounds only Be₂Rh is superconducting at 1.37 K (35). The transition temperatures of the beryllium compounds increase with beryllium content: for Be₂Os Tₘ = 9.2 K, for Be₂Os₂ Tₘ = 3.07 K and for Be₄Os₄O₂₀₃ Tₘ = 0.57 K (7, 35). Among the beryllium phases with iodide only Be₁₁Ir is superconducting, with Tₘ = 1.5 K (35). The transition temperatures of the calcium compounds with C₁₅-type Laves phase structure are for CaRh₁₂ Tₘ = 6.4 and for CaIr₁₂ Tₘ = 4 to 6.15 K; for the corresponding strontium and barium phases SrRh₁₂ Tₘ = 6.2, SrIr₁₂ Tₘ = 5.7, SrPt₁₂ Tₘ = 0.7, and BaRh₁₂ Tₘ = 6.0 K (36, 37).

Cadmium, Mercury and Zine

None of these three are known to form superconducting phases with the platinum metals, which is at least partially explained by the problems concerned with the formation of superconducting shields and the experimental difficulties due to the wide range of vapour pressures among the components (37).

Group III Elements

Aluminium, Boron, Gallium, Indium and Thallium

The compound Bi₂Ru is superconducting at 2.58 K and Bi₂Ru at 1.6 K (38, 39). None of the binary borides of platinum or palladium shows superconductivity above 1.2 K (32, 39). Superconducting ternary palladium-hydrogen-boron alloys can be prepared by ion-implantation techniques (25). OsB₂ has a critical temperature of about 2 K (39), but superconducting binary iridium borides are unknown. Ternary iridium-boron phases having an orthorhombic structure are B₁₁IrMo₂ with Tₘ = 1.25, B₁₁Ir₁₂V₁₈ Tₘ = 1.25 and B₁₁IrV₂ Tₘ = 1.12 K. The corresponding ruthenium compounds are B₁₁RuMo₂ with Tₘ = 2.48 to 2.57, B₁₁RuW₁₅ Tₘ = 2.83 to 3.28, B₁₁RuW₂ Tₘ = 3.32 to 3.42 K (39). The hexagonal phases Ba₀₆Pt₁₃B₂, Sr₀₆Pt₁₃B₂ and Ca₀₆Pt₁₃B₂ are superconductors below 5.6, 2.7 and 1.57 K, respectively (40).

Among osmium-aluminium phases OsAl and Os₄Al₁₁ become superconducting at 0.9 and 3.3 K, respectively (32, 41). The critical temperature of 5.9 K for Os₄Al₁₁ is probably the same for Os₄Al₁₁ (41, 42).

Lanthanum, Scandium, Yttrium and the Rare Earth Metals

With the exception of palladium and platinum, the platinum metals together with lanthanum, scandium, yttrium and the rare earth elements form many superconductors (7,
It was first shown by V. B. Compton and B. T. Matthias (48) that the C14- and C15-type Laves phases of the platinum metals and the rare earths, and the Group III metals without free 4f electrons, exhibit superconductivity, while those with free 4f electrons, that is the elements from praseodymium to ytterbium exhibit ferromagnetism, an exception being CeRu2 (C15-type) for which $T_c = 4.9\,\text{K}$ (32, 48).

Among the C15 phases of the noble metals with Group III elements, CeRu2 and LaOs2 exhibit the highest critical temperature, this being 6.5 K. Among C14-type phases they are YOs2 and LuOs2 with $T_c = 4.7$ and 3.49 K, respectively. Among the Os2-rare earth compounds the Curie temperature is highest at OsGd2 (80 K). It drops down evenly to near 0 K at OsLu2 (46). The magnetic moments show two maxima at Ru$_3$Pr and Ru$_3$Dy and a minimum for europium compounds. This behaviour is equalled by that of the iridium and osmium rare earth C15-type phases (52).

In the system iridium-yttrium a maximum critical temperature of 0.5 K is found at about 50 atomic per cent. Most likely this is caused by shields of Ir$_3$Y or Ir$_2$Y. Ir$_2$Y is superconducting at 1.61 K and Ir$_3$Y is superconducting in its homogeneity range, from 0.88 to 2.18 K. The composition of the superconducting phase richest in iridium is near Ir$_5$Y (53). Nevertheless the behaviour is still somewhat unclear.

Scandium-rich rhodium alloys show superconductivity beginning (partial superconductivity) near 0.9 K (53).

In the systems consisting of platinum metals with yttrium, scandium and lanthanum superconductivity is explained by T. H. Geballe...
as most likely being of a filamentary nature (54). In the lanthanum-rhodium system approximately 1 per cent lanthanum in the melt is enough to make the solidified alloy appear fully superconducting. Even 0.1 per cent lanthanum gave a smeared transition (54).

Ternary Compounds of the Type RERh₄B₄

The ternary borides of the rare earth metals belong to a group of new superconducting compounds, which was discovered by B. T. Matthias and collaborators in 1977 (55). The compounds are tetragonal in structure, of the CeCo₄B₄ type (55, 56). As with the binary C₁₅ phases of the rare earths, elements with an unfilled 4f shell, namely neodymium, samarium, erbium, thulium and lutetium, show superconductivity; those with the filled shell, that is gadolinium, terbium, dysprosium and holmium are ferromagnetic (57). Up to now, it is impossible to prepare compounds with lanthanum, cerium, europium and ytterbium. All superconducting phases exhibit long range magnetic ordering at a temperature Tₙ which is below the superconducting transition temperature Tₙ. The superconducting transition temperatures and the ferromagnetic Curie temperatures of the RERh₄B₄ compounds are shown in Figure 1 (55).

A wide range of pseudo-binary compounds of these phases was investigated for the interaction between superconductivity, magnetic ordering and “crystalline field splitting”, for example Er,Gd,Rh₄B₄ (58) and Sm₁₋ₓ Erₓ Rh₄B₄ (55). Rhodium can be replaced at least partially by ruthenium (59) or iridium (60). For the phase Ho(Ir₀₋ₓ Rhₓ)₄B₄ co-existence between superconductivity and antiferromagnetism was observed, the Néel temperature being higher than the critical temperature (60). Crystallographic, magnetic and superconducting properties of the system YRh₄B₄-LuRh₄B₄-ThRh₄B₄ lead the authors to conclude that the lattice volume has relatively little influence on the electronic density of states.

Several reviews of the numerous investigations carried out on ternary borides have already been presented (59–64). The structure of RERh₄B₄ is shown in Figure 2 (64).

Group IV Elements

Germanium, Lead, Silicon and Tin

Among these compounds the only superconductors are PdSi, where Tₙ = 0.93 K; PtSi, Tₙ = 0.8 K; Rh₅Ge₃, Tₙ = 2.12 K (7, 13, 32); together with RhGe, Tₙ = 0.96 K (65); IrGe, Tₙ = 4.7 K (66); PtGe, Tₙ = 0.4 K (32); and RhSn₂, Tₙ = 0.60 K (67). Ternary superconductors are the ruthenium and osmium germanides Y₁Ru₄Ge₁₃ and Y₁Os₄Ge₁₃, having a Yb₁Rh₄Sn₁₃ type structure, see Tables I and II (68, 69, 70). Ternary silicides and germanides with ruthenium, rhodium and osmium and the rare earths, of the Sc₃CO₄Si₁₀ type of structure, show a similar behaviour (68, 69, 70). The superconducting transition temperatures of the RE₅T₅Ge₁₃ phases are shown in Table I and the magnetic ordering temperatures in Table II (68, 69, 70).

<table>
<thead>
<tr>
<th>Osmium compounds</th>
<th>Tₙ ± 0.1 K</th>
<th>Ruthenium compounds</th>
<th>Tₙ ± 0.1 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce₅Os₅Ge₁₃</td>
<td>6.1</td>
<td>Ce₅Ru₄Ge₁₃</td>
<td>6.7</td>
</tr>
<tr>
<td>Pr₅Os₅Ge₁₃</td>
<td>16.0</td>
<td>Pr₅Ru₄Ge₁₃</td>
<td>14.2</td>
</tr>
<tr>
<td>Nd₅Os₅Ge₁₃</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu₅Os₅Ge₁₃</td>
<td>10.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb₅Os₅Ge₁₃</td>
<td>14.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dy₅Os₅Ge₁₃</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er₅Os₅Ge₁₃</td>
<td>1.9</td>
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</tbody>
</table>

Table II

Magnetic Ordering Temperatures (Tₙ) for Some RE₅T₅Ge₁₃ Compounds
Table III
Superconducting Transition Temperatures (T_c) and Magnetic Ordering Temperatures (T_m) of Sc_{x}Co_{y}Si_{10} Type Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>T_c(K)</th>
<th>T_m(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc_{x}Co_{y}Si_{10}</td>
<td>5.0 - 4.8</td>
<td></td>
</tr>
<tr>
<td>Sc_{x}Rh_{y}Si_{10}</td>
<td>8.54 - 8.45</td>
<td></td>
</tr>
<tr>
<td>Sc_{x}Ir_{y}Si_{10}</td>
<td>8.46 - 8.38</td>
<td></td>
</tr>
<tr>
<td>Y_{x}Ir_{y}Si_{10}</td>
<td>3.0 - 2.3</td>
<td></td>
</tr>
<tr>
<td>Lu_{x}Ir_{y}Si_{10}</td>
<td>3.76 - 3.72</td>
<td></td>
</tr>
<tr>
<td>Tm_{x}Ir_{y}Si_{10}</td>
<td>2.62 - 2.58</td>
<td>1.0</td>
</tr>
<tr>
<td>Er_{x}Ir_{y}Si_{10}</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>Ho_{x}Ir_{y}Si_{10}</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Dy_{x}Ir_{y}Si_{10}</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Y_{x}Ir_{y}Si_{10}</td>
<td>2.62 - 2.58</td>
<td>1.0</td>
</tr>
<tr>
<td>Y_{x}Os_{y}Ge_{10}</td>
<td>8.68 - 8.41</td>
<td></td>
</tr>
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</table>

The superconducting transition and magnetic ordering temperatures of Sc_{x}Co_{y}Si_{10} type phases, having a primitive tetragonal lattice of a new structure type, are listed in Table III (68, 69, 70).

Similar superconductivity/magnetic ordering behaviour is shown by ternary stannides RERh_{1.5}Sn_{3.5} and REOs_{3}Sn_{9}, respectively (71-81). Both ErOs_{3}Sn_{9} and ErRh_{1.5}Sn_{3.5} for example show re-entrant superconductivity (72-81). The phases in the system Me-tin show at least four different structures: I, I', II, and III depending on the kind of Me (80). Phase I compounds are cubic, space group Pm3n with a lattice constant a = 9.7 Å; I' compounds are distorted cubic; II are tetragonal with a_{II} = 13.75 and c_{II} = 27.4 Å while III are cubic with a_{III} = 13.7 Å (80). Phases I and II with Me being rare earth elements from the series lanthanum to gadolinium, and ytterbium, calcium, strontium and thorium are superconducting between 8.7 and 1.9 K. Phase II of the erbium compound exhibits re-entrant superconductivity (where T_c = 0.97 K and T_m = 0.57 K). Phase II of yttrium and scandium are superconducting at 3.2 and 4.5 K, respectively (80).

Ternary compounds of the MnCu_{2}Al (Heusler) type YPd_{3}M (where M is tin, lead, indium and antimony) are superconducting. Superconducting transition temperatures are YPd_{3}Sn 3.72 YPd_{3}Pb 4.76 and YPd_{3}In 0.85 K (82).

The phases RhPb_{2} and PdPb_{2}, being C16- or CuAl_{2}-type are superconducting at 2.66 and 2.95 K, respectively (83).

Titanium, Zirconium, Hafnium and Thorium

Many alloys of titanium, zirconium and hafnium with even fairly small additions of other transition elements show a big increase in the transition temperature of their hexagonal close-packed a-phase (43, 84), see Figure 3. Most of these effects are caused by superconducting filaments or shields of the β-phase or a/β transition intermediate phases, as was at first assumed (85) and recently discussed (85). In these systems, a very careful definition of the state of the sample is necessary in order to obtain reliable results on their superconductivity. For example oxygen impurities may play a role which is shown by the superconductivity of the ternary EO_{3}-type

| Table IV
Superconducting Transition Temperatures and Structures of Binary Phosphides and Arsenides of Rhodium and Palladium |
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Compound</td>
<td>T_c(K)</td>
<td>Structure</td>
</tr>
<tr>
<td>Rh_{x}P</td>
<td>1.3</td>
<td>cubic (CaF_{2})</td>
</tr>
<tr>
<td>Rh_{x}P_{3}</td>
<td>2.5</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>RhAs</td>
<td>0.58</td>
<td>orthorhombic (MnP)</td>
</tr>
<tr>
<td>Rh_{x}As</td>
<td>0.56</td>
<td>hexagonal</td>
</tr>
<tr>
<td>Pd_{x}P</td>
<td>0.75</td>
<td>orthorhombic (Fe_{3}C)</td>
</tr>
<tr>
<td>Pd_{x}P_{3} (h.t.)</td>
<td>1.0</td>
<td>rhombohedral</td>
</tr>
<tr>
<td>Pd_{x}P_{3} (l.t.)</td>
<td>0.7</td>
<td>?</td>
</tr>
<tr>
<td>Pd_{x}As_{2}</td>
<td>0.46</td>
<td>?</td>
</tr>
<tr>
<td>Pd_{x}As (h.t.)</td>
<td>1.7</td>
<td>hexagonal (Fe_{3}P)</td>
</tr>
<tr>
<td>Pd_{x}As (l.t.)</td>
<td>0.6</td>
<td>hexagonal</td>
</tr>
</tbody>
</table>
phases Ti$_{0.57}$Rh$_{0.28}$O$_{0.14}$ and Ti$_{0.37}$Ir$_{0.28}$O$_{0.14}$ ($T_c = 3.37$ and 5.5 K, respectively), also Zr$_{0.61}$Rh$_{0.26}$O$_{0.135}$, Zr$_{0.61}$Pd$_{0.26}$O$_{0.135}$ and Zr$_{0.65}$Ir$_{0.265}$O$_{0.085}$ ($T_c = 11.8$, 2.09 and 2.30 K, respectively) (32). The A15 phases Ti$_3$Ir and Ti$_3$Pt become superconducting at 5.4 and 0.58 K, respectively (32). Among the C14-type phases HfO$_2$ and ZrO$_2$ ($T_c = 2.69$ and 3.00 K respectively) show superconductivity at higher temperatures than the C15 phases ZrIr$_2$ and ThIr$_2$ ($T_c = 4.10$ and 6.5 K, respectively) (32). Data for the D10$_2$-type phases are for Th$_3$Rh$_3$ $T_c = 2.15$, for Th$_3$Os$_3$ $T_c = 1.51$ and for Th$_3$Ir$_3$ $T_c = 1.52$ K. Th$_3$Pt$_3$ is not superconducting above 1.02 K (32). In the system titanium-platinum, depending on sample preparation, a critical temperature between 0.4 and 4.5 K is measured. Ternary superconducting solid solutions based on body-centred cubic titanium-rhodium and zirconium-rhodium have been investigated (43, 87); in all cases the critical temperature was reduced by the presence of platinum group metals.

**Group V Elements**

**Phosphorus, Arsenic, Antimony and Bismuth**

Superconductivity data for binary phosphides and arsenides of the platinum metals are listed in Table IV. It is interesting to note the difference between the critical temperature of the high and low temperature forms of Pd$_7$P$_3$ and Pd$_1$As, where the high temperature form always exhibits a slightly higher critical temperature. Among the antimonides only the B8$_1$-type phases Pd$_5$Sb and Pt$_5$Sb are superconducting with $T_c = 1.5$ and 2.1 K, respectively (88). Among the
bismuthides, β-PdBi₂ has a higher critical temperature than α-PdBi₂, T_c = 4.2 and 1.7 K, respectively (7, 13). A review on the superconductivity of binary compounds of the platinum metals with elements of Groups IV, V and VI has been published elsewhere (89).

Ternary hexagonal phosphides and arsenides of ruthenium and osmium constitute a new class of ternary superconductors discovered in 1980 (90). Transition temperatures and lattice parameters of the known superconducting ternary phosphides are listed in Table V and of the corresponding arsenides in Table VI (90, 91). The proposed structure of the hexagonal ternary phosphide ZrRuP is shown as Figure 4 (90).

Depending on their preparation and heat treatment, some of the superconducting phosphides and arsenides show high or low temperature modifications, which in most cases have now been fully identified and reported (91). No superconductivity was observed for the LaFe₄P₁₂ type compounds RERuP₁₂ (RE = cerium, praseodymium or neodymium). The influence of oxygen on the critical temperature of ZrRuP has been investigated (92). Oxygen is not taken into the lattice, but reduces the phosphorus concentration, which itself determines critical temperature. By specific heat measurements, the following critical temperature data were obtained: for ZrRuP T_c = 13, for HfRuP T_c = 10.8 and for TiRuP T_c = 1.2 K. The relatively low critical temperature of TiRuP may be caused by some kind of magnetic interaction (93).

Vanadium, Niobium and Tantalum

Solid solutions of elements of Groups V and VI in the Periodic Table, when present in ruthenium and osmium reduce their critical temperatures.

### Table V

<table>
<thead>
<tr>
<th>Compound</th>
<th>T_c K</th>
<th>Structure</th>
<th>Lattice constants Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiRuP</td>
<td>1.33</td>
<td>ZrRuSi</td>
<td>a ± 0.006</td>
</tr>
<tr>
<td>ZrRuP</td>
<td>12.34 - 10.56</td>
<td>ZrRuSi</td>
<td>c ± 0.004</td>
</tr>
<tr>
<td>HfRuP</td>
<td>12.70 - 11.08</td>
<td>ZrRuSi</td>
<td></td>
</tr>
<tr>
<td>TiOsP</td>
<td>&lt;1.2</td>
<td>ZrRuSi</td>
<td></td>
</tr>
<tr>
<td>ZrOsP</td>
<td>7.44 - 7.1</td>
<td>ZrRuSi</td>
<td></td>
</tr>
<tr>
<td>HfOsP</td>
<td>6.10 - 4.96</td>
<td>ZrRuSi</td>
<td></td>
</tr>
</tbody>
</table>

### Table VI

<table>
<thead>
<tr>
<th>Compound</th>
<th>T_c K</th>
<th>Structure</th>
<th>Lattice constants Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiRuAs (900°C)</td>
<td>&lt;0.35</td>
<td>TiFeSi</td>
<td>a</td>
</tr>
<tr>
<td>ZrRuAs (flux)</td>
<td>11.90 - 10.03</td>
<td>ZrRuSi</td>
<td>b</td>
</tr>
<tr>
<td>HfRuAs</td>
<td>3.2</td>
<td>ZrRuSi</td>
<td>c</td>
</tr>
<tr>
<td>ZrOsAs</td>
<td>4.93 - 4.37</td>
<td>ZrRuSi</td>
<td></td>
</tr>
<tr>
<td>HfOsAs</td>
<td>8.0</td>
<td>ZrRuSi</td>
<td></td>
</tr>
</tbody>
</table>

*Platinum Metals Rev., 1984, 28, (2)*
temperatures (43). In vanadium-rich solutions the presence of 10 atomic per cent palladium or platinum reduces the critical temperature of vanadium to below 1.5 K (94).

**Intermetallic Phases**

Since the last review article on the superconductivity of the platinum metals and their alloys practically no new binary superconductors have been found (43). Some work has been concerned with the influence of additions on the behaviour of pseudo-binary phases (7, 13, 32, 43, 100). Critical temperatures of the δ-phases in the systems niobium-rhodium and tantalum-rhodium have been shown to be 2.95 K for the homogeneous phase Nb0.652Rh0.348, and 424 K for the heterogeneous sample Nb0.637Rh0.363 (96). This may be caused by a very narrow homogeneity range.

The δ-phase in the tantalum-rhodium system is not superconducting, however (96). Alphaphases with the highest transition temperatures among these compounds are Nb3Pt and Mo0.7Ir0.76 with \( T_c = 9.3 \) and 9.05 K, respectively. Special attention should be given to the peculiar A15-type phase Os0.84Vo0.15 which has a critical temperature of 5.15 K (7, 13, 32, 43, 97).

**Group VI Elements**

**Sulphur, Selenium and Tellurium**

A review of the superconductivity of sulphur, selenium and tellurium compounds has been presented (98). Superconductivity was discovered only among the selenides of palladium (for Pd6.7-Se \( T_c = 0.66 \) and for Pd-Se \( T_c = 0.42 \) K) and the tellurides of palladium, platinum and iridium. Data on the latter are given in Table VII.

The decrease of the critical temperature of the B8 phase PdTe with tellurium concentration within its homogeneity range, is peculiar. The coefficient of the electronic specific heat \( \gamma \) drops from 13.5 to 9.9 cal/mol/degree\(^2\), while \( \theta_D \), the Debye temperature, is reduced from 277 to 239 K in the same range (98).

Apparently there is a sharp peak in the density of states and energy at the stoichiometric composition.

**Chromium, Molybdenum and Tungsten**

In the system ruthenium-chromium the critical temperature of the 20 atomic per cent chromium alloy is 0.3 K, while at 30 atomic per cent it is higher at 1.65 K (99). Both RuCr\(_2\) and RuCr\(_3\) are superconducting, at 2.0 and 3.3 K, respectively (99).

Solid solutions of molybdenum and tungsten with ruthenium show an increase in the critical temperature with increasing ruthenium content (43); the critical temperature of the δ-phase with 50 atomic per cent molybdenum is 10.6 K (100).

Further work on superconductivity in the ruthenium-molybdenum system has previously been summarised (44). The δ-phase Ru0.6W0.40 is superconducting in the range 4.67 to 5.2 K (32). Among osmium-chromium alloys the δ-phase and also the A15-phase OsCr\(_3\) are superconductors with critical temperatures of 1.03 and 4.03 K, respectively (7, 13). The δ-phases of osmium with molybdenum and tungsten have critical temperatures of 5.65 and 3.81 K, respectively (101). Superconducting iridium-chromium alloys are IrCr\(_3\), of δ-W type, with \( T_c = 0.75 \); IrMo\(_3\) with critical temperatures in the range of 8.17 to 8.8 K, depending on ordering and the δ-phase Ir0.28Mo0.72 with a critical temperature of 4.46 K (7, 13, 43). The A12-type compound Nb0.40Pd0.60 exhibits superconductivity at 2.04 to 2.47 K (101).

<table>
<thead>
<tr>
<th>Table VII</th>
<th>Superconducting Tellurides of the Platinum Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>( T_c, K )</td>
</tr>
<tr>
<td>Pd(_3)Te</td>
<td>0.76</td>
</tr>
<tr>
<td>Pd(_{1.1})Te</td>
<td>4.07</td>
</tr>
<tr>
<td>PdTe</td>
<td>3.85</td>
</tr>
<tr>
<td>PdTe(_{1.02})</td>
<td>2.56</td>
</tr>
<tr>
<td>PdTe(_{1.08})</td>
<td>1.88</td>
</tr>
<tr>
<td>Pd(_{1.6})Te</td>
<td>1.69</td>
</tr>
<tr>
<td>PtTe</td>
<td>0.59</td>
</tr>
<tr>
<td>IrTe(_3)</td>
<td>1.18</td>
</tr>
</tbody>
</table>
Group VII Elements

No superconducting phases are known between the platinum group metals and Group VII elements. Only small amounts of rhenium in iridium reduce its critical temperature, while a few atomic per cent iridium in rhenium seem to have little influence on its critical temperature \( T_{\text{c}} \).

Group VIII Elements

Iron, cobalt and nickel, when present in solid solution, all considerably reduce the critical temperature of the superconducting platinum metals. The influence on non-superconducting platinum and palladium is less \( T_{\text{c}} \). Superconducting compounds are unknown.

Summary

The platinum metals and their compounds exhibit an extremely wide variety of behaviour at low temperatures. This ranges from the four elements which are superconducting to new classes of superconducting platinum metal hydrides, borides, silicides, stannides, phosphides and arsenides. Since some of the phases show the co-existence of magnetism and superconductivity, their investigation has resulted in a wide interest in low temperature materials research. In addition to increasing the understanding of the phenomenon of superconductivity, these investigations will no doubt result in time in applications which are not yet visualised.

References

22. B. Stritzker and W. Buckel, Z. Phys., 1972, 1
23. B. Stritzker, Z. Phys., 1974, 261
24. H. R. Khan and Ch. J. Raub, Naturwissenschaften, 1971, 58, 565
28. T. Skoskiewicz, Proc. 5th Int. Conf. on High Pressure and Technology High-Temperature-High Pressures, 1977, 7, 684
29. B. Baranowski, op. cit., ref. 25, 188
31. Ch. J. Raub and O. Loebrich, unpublished
32. B. T. Matthias, T. H. Geballe and V. B. Compton, Rev. Mod. Phys., 1963, 39, 1
33. H. R. Khan and Ch. J. Raub unpublished results
36 B. T. Matthias and E. Corenzwit, Phys. Rev., 1957, 107, 1558
37 Ch. J. Raub and B. T. Matthias, 1965, unpublished results
40 R.N. Shelton, J. Less-Common Met., 1978, 62, 191
43 Ch. J. Raub, Z. Metall., 1964, 55, 195
47 V. B. Compton and B. T. Matthias, Acta Crystallogr., 1959, 12, 651
53 T. H. Geballe, NATO-Summer School-Low Temp. 3rd Course, Erice, Italy, 1982, 389, and private communication
59 H. C. Ku and H. Barz, op. cit., 209
63 O. Fisher and M. B. Maple, op. cit., Vol. I, 10
64 S. Geller, Acta Crystallogr., 1955, 8, 15
65 B. T. Matthias, Phys. Rev., 1953, 92, 874
67 H. F. Braun, op. cit., ref. 59, 225
70 H. F. Braun and C. U. Segre, op. cit., ref. 59, 239
71 H. R. Ott, W. Odoni, Z. Fisk and J. P. Remeika, op. cit., ref. 59, 251
81 N. Ishikawa, J. L. Jorda and A. Junod, op. cit., ref. 61, 141
Sputtered Cobalt-Platinum Thin Magnetic Films

It has long been known that certain cobalt-platinum alloys possess useful magnetic properties which can, to some extent, be selected by choosing an appropriate alloy composition and varying the heat treatment given. In the annealed condition these alloys can be machined or rolled and drawn to size without difficulty. As a result they are used for a number of very specialised applications where worthwhile economic advantage can result from harnessing the powerful magnetic properties of these intrinsically valuable alloys.

A thin magnetic film possessing high coercivity and remanence and with high hysteresis loop squareness could find application as a high density magnetic recording medium, and in many magnetic devices. However, in contrast to bulk cobalt-platinum, the coercivity of electrodeposited cobalt-platinum films is too low to be useful for such purposes. Now Masahiro Kitada and Noboru Shimizu of the Central Research Laboratory of Hitachi Limited have reported on the development of r.f. sputtered cobalt-platinum thin films which exhibit good magnetic properties (J. Appl. Phys., 1983, 54, (12), 7089-7094).

The films were prepared using a conventional r.f. sputtering system in which the target was either a sintered cobalt-platinum disc or a cobalt disc upon which a calculated amount of platinum was placed, so enabling the composition of the target to be changed readily.

The magnetic properties and microstructure of the sputtered films, and the influence of sputtering conditions upon these were studied. High coercivity cobalt-platinum films were obtained with compositions in the range 5-35 atomic per cent platinum. A maximum coercivity of 1800 Oe was obtained for a cobalt-20 atomic per cent platinum alloy, which had a remanence of about 9500 G.

The coercivity and remanence of alloy films with a thickness of 800Å are shown here in the Figure; vacuum pressure prior to introduction of the argon sputtering gas and argon pressure during sputtering were $2 \times 10^{-6}$ and $5 \times 10^{-3}$ Torr, respectively.