

Superconductivity of the Platinum Metals and Their Alloys

A REVIEW SUMMARISING THE PUBLISHED SCIENTIFIC DATA

By Ch. J. Raub

Forschungsinstitut für Edelmetalle und Metallchemie, Schwäbisch Gmünd, West Germany

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 subse-

quently 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

Compound	$T_c \pm 0.1 K$
$Y_3Ru_4Ge_{13}$	1.7 – 1.4
$Y_3Os_4Ge_{13}$	3.9 – 3.7
$Lu_3Ru_4Ge_{13}$	2.3 – 2.2
$Lu_3Os_4Ge_{13}$	3.6 – 3.1

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 ± 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 Ru⁹⁹ and Ru¹⁰⁴ 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 \bar{M} of 99.2, 101.1 and 103.9 in magnetic fields up to 70 Oe gave the dependence: $T_c \approx M^{-1/8}$. At pressures up to 30,000 atmospheres the critical temperature is not affected by the applied pressure (11), while its volume dependence $\delta \ln(T_c/\theta_D)/\delta \ln V = -16$ (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 $\rho_{300}/\rho_{273} = 0.4$ 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 $T_c \approx M^{-0.2}$. The critical field is 80.9 Oe when $\bar{M} = 187.4$, and 80.2 Oe when $\bar{M} = 192.0$ (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 4.4×10^{-4} cm, and the penetration depth 3.9×10^{-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 $-(5.1 \pm 0.9) \times 10^{-4}$ 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 0.2×10^{-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 μ 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 10×10^{-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 ~ 10.7 K for palladium-deuterium samples (22). Ternary palladium-copper-hydrogen samples exhibited a maximum critical temperature at H:Pd₅₅

Cu₄₅ ≈ 0.8 of about 17 K. The values in the system palladium-silver-hydrogen are: H:Pd₇₀Ag₃₀ ≈ 0.8 and $T_c \approx 16$ K and in the system palladium-gold-hydrogen they are: H:Pd₈₄Au₁₆ ≈ 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-molybdenum and palladium-tungsten solid solutions (24). Ion-implantation experiments on Pd_{1-x}Al_x and Pd_{1-x}Ti_x alloys (H:Pd ≤ 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 $T_{c,D}/T_{c,H}$ 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 $\text{Ag}_2\text{Pd}_3\text{S}$, A13-type, $a = 7.235 \text{ \AA}$, has $T_c = 1.13 \text{ K}$ (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). Be_3Ru and Be_2Ru show critical temperatures of 1.3 and 1.35 K, respectively (35). Of the many beryllium-rhodium compounds only Be_2Rh is superconducting at 1.37 K (35). The transition temperatures of the beryllium compounds increase with beryllium content: for Be_3Os $T_c = 9.2$, for Be_2Os $T_c = 3.07$ and for $\text{Be}_{0.95}\text{Os}_{0.05}$ $T_c = 0.57 \text{ K}$ (7, 35). Among the beryllium phases with iridium only Be_3Ir is superconducting, with $T_c = 1.5 \text{ K}$ (35). The transition temperatures of the calcium compounds with C15-type Laves phase structure

are for CaRh_2 $T_c = 6.4$ and for CaIr_2 $T_c = 4$ to 6.15 K; for the corresponding strontium and barium phases SrRh_2 $T_c = 6.2$, SrIr_2 $T_c = 5.7$, SrPt_2 $T_c = 0.7$, and BaRh_2 $T_c = 6.0 \text{ K}$ (36, 37).

Cadmium, Mercury and Zinc

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

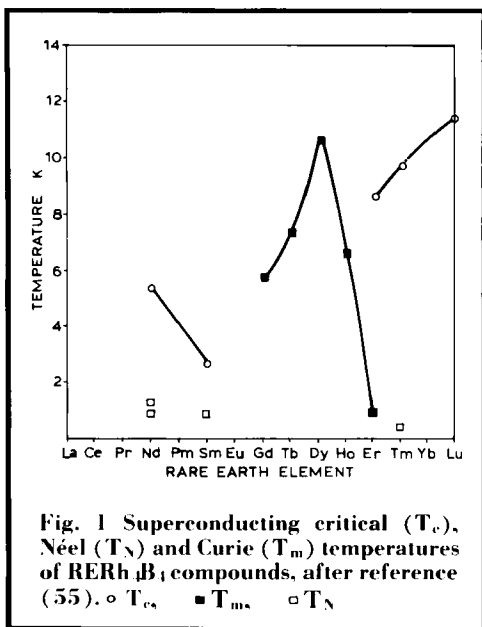
Aluminium, Boron, Gallium, Indium and Thallium

The compound B_3Ru is superconducting at 2.58 (7) and B_2Ru 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). OsB_2 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 B_2IrMo_2 with $T_c = 1.25$, $\text{B}_2\text{Ir}_{1.2}\text{V}_{1.8}$ $T_c = 1.25$ and B_2IrV_2 $T_c = 1.12 \text{ K}$. The corresponding ruthenium compounds are B_2RuMo_2 with $T_c = 2.48$ to 2.57, $\text{B}_2\text{RuW}_{1.5}$ $T_c = 2.83$ to 3.28, B_2RuW_2 $T_c = 3.32$ to 3.42 K (39). The hexagonal phases $\text{Ba}_{0.67}\text{Pt}_3\text{B}_2$, $\text{Sr}_{0.67}\text{Pt}_3\text{B}_2$ and $\text{Ca}_{0.67}\text{Pt}_3\text{B}_2$ are superconductors below 5.6, 2.7 and 1.57 K, respectively (40).

Among osmium-aluminium phases OsAl and $\text{Os}_4\text{Al}_{13}$ become superconducting at 0.9 and 3.3 K, respectively (32, 41). The critical temperature of 5.9 K for OsAl_3 is probably the same for $\text{Os}_4\text{Al}_{13}$ (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,



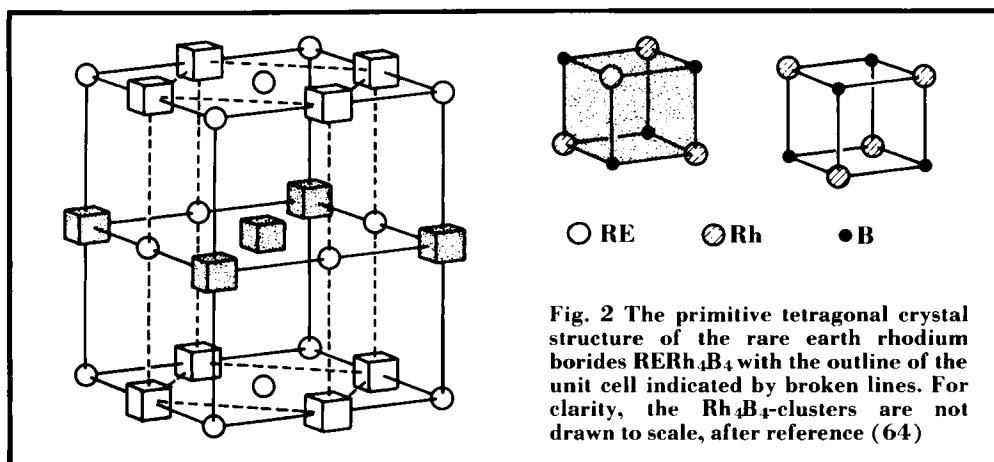
13, 32, 43, 44, 45, 46, 47). It was first shown by V. B. Compton and B. T. Matthias (48) that the C₁₄- and C₁₅-type Laves phases of the platinum metals and the rare earths, and the Group III metals without free 4f electrons, exhibit superconductivity, while those with free 4f electrons, that is the elements from praseodymium to ytterbium exhibit ferromagnetism, an exception being CeRu₂ (C₁₅-type) for which $T_c = 4.9$ K (32, 48). The simultaneous occurrence of superconductivity

and ferromagnetism in pseudo-binary systems has been investigated in a series of papers on C₁₅-type YO₂-GdOs₂, CeRu₂-PrRu₂ and CeRu₂-GdRu₂ alloys (44-51).

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 YO₂ 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 Ru₂Pr and Ru₂Dy 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 Ir₃Y or Ir₄Y. Ir₂Y₃ is superconducting at 1.61 K and Ir₄Y is superconducting in its homogeneity range, from 0.88 to 2.18 K. The composition of the superconducting phase richest in iridium is near Ir₄Y (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 $RERh_4B_4$

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 $CeCo_4B_4$ type (55, 56). As with the binary C_{15} 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 T_m which is below the superconducting transition temperature T_c . The superconducting transition temperatures and the ferromagnetic Curie temperatures of the $RERh_4B_4$ 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 $Er_{1-x}Ho_xRh_4B_4$ (58) and $Sm_{1-x}Er_xRh_4B_4$ (55).

Rhodium can be replaced at least partially by ruthenium (59) or iridium (60). For the phase $Ho(Ir_{0.6}Rh_{0.4})_4B_4$ 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 YRh_4B_4 - $LuRh_4B_4$ - $ThRh_4B_4$ 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 $RERh_4B_4$ is shown in Figure 2 (64).

Group IV Elements

Germanium, Lead, Silicon and Tin

Among these compounds the only superconductors are $PdSi$, where $T_c = 0.93$ K; $PtSi$, $T_c = 0.8$ K; Rh_3Ge_3 , $T_c = 2.12$ K (7, 13, 32); together with $RhGe$, $T_c = 0.96$ K (65); $IrGe$, $T_c = 4.7$ K (66); $PtGe$, $T_c = 0.4$ K (32); and $RhSn_2$, $T_c = 0.60$ K (67). Ternary superconductors are the ruthenium and osmium germanides $Y_3Ru_4Ge_{13}$ and $Y_3Os_4Ge_{13}$, having a $Yb_3Rh_4Sn_3$ 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 $Sc_3Co_4Si_{10}$ type of structure, show a similar behaviour (68, 69, 70). The superconducting transition temperatures of the $RE_3T_4Ge_{13}$ phases are shown in Table I and the magnetic ordering temperatures in Table II (68, 69, 70).

Osmium compounds	$T_m \pm 0.1$ K	Ruthenium compounds	$T_m \pm 0.1$ K
$Ce_3Os_4Ge_{13}$	6.1	$Ce_3Ru_4Ge_{13}$	6.7
$Pr_3Os_4Ge_{13}$	16.0	$Pr_3Ru_4Ge_{13}$	14.2
$Nd_3Os_4Ge_{13}$	1.9		
$Eu_3Os_4Ge_{13}$	10.1		
$Tb_3Os_4Ge_{13}$	14.1		
$Dy_3Os_4Ge_{13}$	2.1		
$Er_3Os_4Ge_{13}$	1.9	$Er_3Ru_4Ge_{13}$	

Compound	T_c K	T_m K
$Sc_5Co_4Si_{10}$	5.0 – 4.8	
$Sc_5Rh_4Si_{10}$	8.54 – 8.45	
$Sc_5Ir_4Si_{10}$	8.46 – 8.38	
$Y_5Ir_4Si_{10}$	3.0 – 2.3	
$Lu_5Ir_4Si_{10}$	3.76 – 3.72	
$Tm_5Ir_4Si_{10}$		1.0
$Er_5Ir_4Si_{10}$		2.3
$Ho_5Ir_4Si_{10}$		1.5
$Dy_5Ir_4Si_{10}$		5.0
$Y_5Ir_4Si_{10}$	2.62 – 2.58	
$Y_5Os_4Ge_{10}$	8.68 – 8.41	

The superconducting transition and magnetic ordering temperatures of $Sc_5Co_4Si_{10}$ 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 $RERh_{1.1}Sn_{3.6}$ and $REOs_xSn_y$, respectively (71–81). Both $ErOs_xSn_y$ and $ErRh_{1.1}Sn_{3.6}$ 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 $Pm\bar{3}n$ with a lattice constant $a = 9.7 \text{ \AA}$; I' compounds are distorted cubic; II are tetragonal with $a_{II} = 13.75$ and $c_{II} = 27.4 \text{ \AA}$ while III are cubic with $a_{III} = 13.7 \text{ \AA}$ (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 $T_c = 0.97 \text{ K}$ and

$T_m = 0.57 \text{ K}$). Phase II of yttrium and scandium are superconducting at 3.2 and 4.5 K, respectively (80).

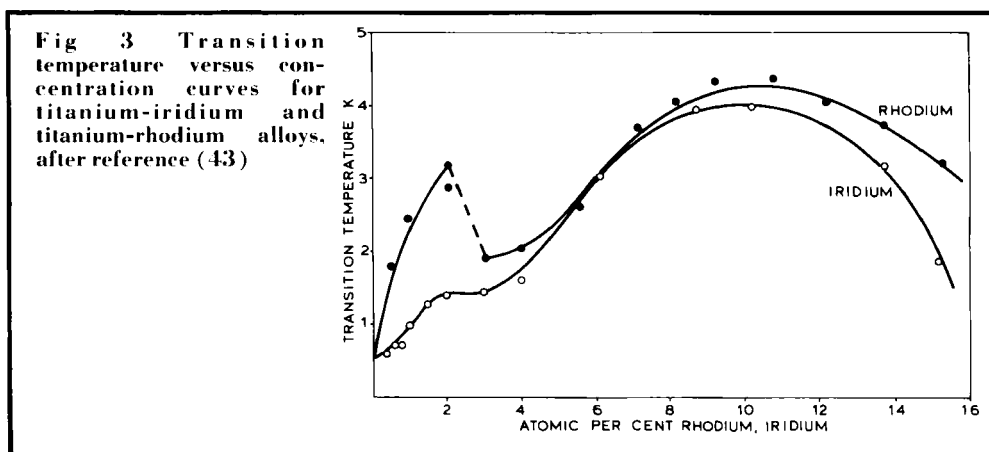
Ternary compounds of the $MnCu_2Al$ (Heusler) type YPd_2M (where M is tin, lead, indium and antimony) are superconducting. Superconducting transition temperatures are YPd_2Sn 3.72 YPd_2Pb 4.76 and YPd_2In 0.85 K (82).

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 α -phase (43, 84), see Figure 3. Most of these effects are caused by superconducting filaments or shields of the β -phase or α/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

Compound	T_c K	Structure
Rh_2P	1.3	cubic (CaF_2)
Rh_4P_3	2.5	orthorhombic
$RhAs$	0.58	orthorhombic (MnP)
$Rh_{1.4}As$	0.56	hexagonal
Pd_3P	0.75	orthorhombic (Fe_3C)
Pd_7P_3 (h.t.)	1.0	rhombohedral
Pd_7P_3 (l.t.)	0.7	?
Pd_5As_2	0.46	?
Pd_2As (h.t.)	1.7	hexagonal (Fe_2P)
Pd_2As (l.t.)	0.6	hexagonal



phases $\text{Ti}_{0.573}\text{Rh}_{0.287}\text{O}_{0.14}$ and $\text{Ti}_{0.573}\text{Ir}_{0.287}\text{O}_{0.14}$ ($T_c = 3.37$ and 5.5 K, respectively), also $\text{Zr}_{0.61}\text{Rh}_{0.285}\text{O}_{0.105}$, $\text{Zr}_{0.61}\text{Pd}_{0.285}\text{O}_{0.105}$ and $\text{Zr}_{0.65}\text{Ir}_{0.265}\text{O}_{0.085}$ ($T_c = 11.8$, 2.09 and 2.30 K, respectively) (32). The A_{15} phases Ti_3Ir and Ti_3Pt become superconducting at 5.4 and 0.58 K, respectively (32). Among the C_{14} -type phases HfOs_2 and ZrOs_2 ($T_c = 2.69$ and 3.00 K respectively) show superconductivity at higher temperatures than the C_{15} phases ZrIr_2 and ThIr_2 ($T_c = 4.10$ and 6.5 K, respectively) (32). Data for the D_{10_2} -type phases are for Th_7Rh_3 $T_c = 2.15$, for Th_7Os_3 $T_c = 1.51$ and for Th_7Ir_3 $T_c = 1.52$ K. Th_7Pt_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_7P_3 and Pd_2As , where the high temperature form always exhibits a slightly higher critical temperature. Among the antimonides only the $B8_1$ -type phases PdSb and PtSb are superconducting with $T_c = 1.5$ and 2.1 K, respectively (88). Among the

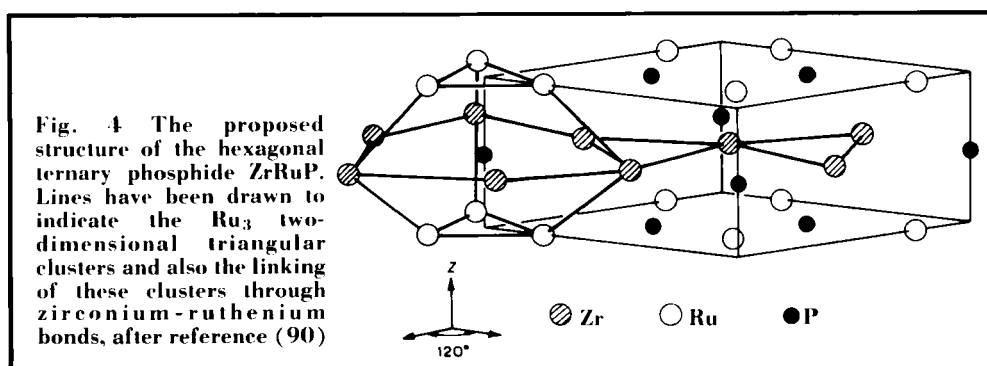


Table V Superconducting Ternary Phosphides of Ruthenium and Osmium				
Compound	T_c K	Structure	Lattice constants Å	
			$a \pm 0.006$	$c \pm 0.004$
TiRuP	1.33	ZrRuSi	6.325	3.542
ZrRuP	12.34 – 10.56	ZrRuSi	6.459	3.778
HfRuP	12.70 – 11.08	ZrRuSi	6.414	3.753
TiOsP	<1.2	ZrRuSi	6.285	3.625
ZrOsP	7.44 – 7.1	ZrRuSi	6.460	3.842
HfOsP	6.10 – 4.96	ZrRuSi	6.417	3.792

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

Table VI Superconducting Ternary Arsenides of Ruthenium and Osmium					
Compound	T_c K	Structure	Lattice constants Å		
			a	b	c
TiRuAs	<0.35	TiFeSi	7.287	11.227	6.515
ZrRuAs (900°C)	11.90 – 10.03	ZrRuSi	6.586		3.891
ZrRuAs (flux)	3.2	ZrRuSi	6.624		3.823
HfRuAs	4.93 – 4.37	ZrRuSi	6.568		3.842
ZrOsAs	8.0	ZrRuSi	6.602		3.794
HfOsAs	3.2	ZrRuSi	6.569		3.808

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 $\text{Nb}_{0.652}\text{Rh}_{0.348}$, and 424 K for the heterogeneous sample $\text{Nb}_{0.637}\text{Rh}_{0.363}$ (96). This may be caused by a very narrow homogeneity range.

The δ -phase in the tantalum-rhodium system is not superconducting, however (96). A15-phases with the highest transition temperatures among these compounds are Nb_3Pt and $\text{Mo}_{0.74}\text{Ir}_{0.76}$ with $T_c = 9.3$ and 9.05 K, respectively. Special attention should be given to the peculiar A15-type phase $\text{Os}_{0.5}\text{V}_{0.5}$ 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 Pd_{6-7}Se $T_c = 0.66$ and for Pd_4Se $T_c = 0.42$ 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 γ drops from 13.5 to 9.9 cal/mol/degree², while θ_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 $\text{Ru}_{0.4}\text{W}_{0.60}$ 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 β -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 $\text{Ir}_{0.28}\text{Mo}_{0.72}$ with a critical temperature of 4.46 K (7, 13, 43). The A12-type compound $\text{Nb}_{0.60}\text{Pd}_{0.40}$ exhibits superconductivity at 2.04 to 2.47 K (101).

Compound	T_c K	Structure
Pd_3Te	0.76	—
$\text{Pd}_{1.1}\text{Te}$	4.07	hexagonal (B8.)
PdTe	3.85	hexagonal (B8.)
$\text{PdTe}_{1.02}$	2.56	hexagonal (B8.)
$\text{PdTe}_{1.08}$	1.88	hexagonal (B8.)
PdTe_2	1.69	trigonal (C6.)
PtTe	0.59	orthorhombic
IrTe_3	1.18	cubic (C2.)

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 (102, 103).

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 (102, 103). 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.

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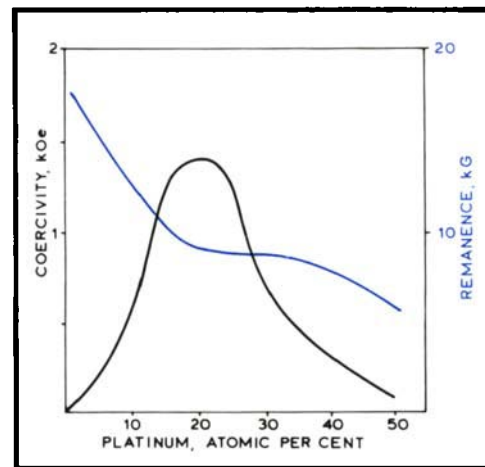
Sputtered Cobalt-Platinum Thin Magnetic Films

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 2×10^{-6} and 5×10^{-3} Torr, respectively.