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Superconductors, Superconductivity & Superconducting Materials

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ABSTRACT: A superconductor is a substance that conducts electricity without resistance when it becomes colder than a "critical temperature." At this temperature, electrons can move freely through the material. Superconductors are different from ordinary conductors, such as copper. Ordinary conductors lose their resistance (get more conductive) slowly as they get colder. In contrast, superconductors lose their resistance all at once. This is an example of a phase transition. High magnetic fields destroy superconductivity and restore the normal conducting state. Some examples of superconductors are the metals mercury and lead, ceramics and organic carbon nanotubes. 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. Superconductivity is a set of physical properties observed in certain materials where electrical resistance vanishes and magnetic flux fields are expelled from the material. Any material exhibiting these properties is a superconductor. Unlike an ordinary metallic conductor, whose resistance decreases gradually as its temperature is lowered, even down to near absolute zero, a superconductor has a characteristic critical temperature below which the resistance drops abruptly to zero

KEYWORDS: superconductors, superconductivity, materials, temperature, properties, resistance, periodic table

I. INTRODUCTION

Normally, a magnet moving by a conductor produces currents in the conductor by electromagnetic induction. But a superconductor actually pushes out magnetic fields entirely by inducing surface currents. Instead of letting the magnetic field pass through, the superconductor acts like a magnet pointing the opposite way, which repels the real magnet. This is called the Meissner effect, and it can be demonstrated by levitating a superconductor over magnets or vice versa. Physicists explain superconductivity by describing what happens when temperatures get cold.¹ The thermal energy in a solid or liquid shakes the atoms so they randomly vibrate, but this gets less as the temperature drops. Electrons carry the same negative electric charge which makes them repel each other. At higher temperatures each electron behaves as if it were a free particle. There is also however a very weak attraction between electrons when they are in a solid or liquid. At rather large distances² (many hundreds of nanometers apart) and low temperatures (near absolute zero), the attractive effect and lack of thermal energy allows pairs of electrons to hang together. This is called a cooper pair and it is a quasiparticle, that is it acts as if it were a new kind of particle in its own right even though it is made up of two fundamental electrons. Many overlapping cooper pairs can exist in the same nanometer sized space. Since paired electrons constitute a boson the motions of all of the cooper pairs within a single superconductor synchronize³ and they function as if they are a single entity. Small disturbances such as scattering of electrons are forbidden in this state, and it moves as one, showing no resistance to its motion. Thus, it is now a superconductor. The superconductivity phenomenon was discovered in 1911 by Dutch physicist Heike Kamerlingh Onnes. Like ferromagnetism and atomic spectral lines, superconductivity is a phenomenon which can only be explained

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by quantum mechanics.⁴ It is characterized by the Meissner effect, the complete ejection of magnetic field lines from the interior of the superconductor during its transitions into the superconducting state. The occurrence of the Meissner effect indicates that superconductivity cannot be understood simply as the idealization of perfect conductivity in classical physics.⁵

In 1986, it was discovered that some cuprate-perovskite ceramic materials have a critical temperature above 90 K (−183 °C). Such a high transition temperature is theoretically impossible for a conventional superconductor, leading the materials to be termed high-temperature superconductors. The cheaply available coolant liquid nitrogen boils at 77 K, and thus the existence of superconductivity at higher temperatures than this facilitates many experiments and applications that are less practical at lower temperatures. There are many criteria by which superconductors are classified.⁶ The most common are:

Response to a magnetic field

A superconductor can be Type I, meaning it has a single critical field, above which all superconductivity is lost and below which the magnetic field is completely expelled from the superconductor; or Type II, meaning it has two critical fields, between which it allows partial penetration of the magnetic field through isolated points.^[8] These points are called vortices.^[9] Furthermore, in multicomponent superconductors it is possible to have a combination of the two behaviours. In that case the superconductor is of Type-1.5.

By theory of operation

It is conventional if it can be explained by the BCS theory or its derivatives, or unconventional, otherwise.^[11] Alternatively, a superconductor is called unconventional if the superconducting order parameter transforms according to a non-trivial irreducible representation of the point group or space group of the system.⁷

By critical temperature

A superconductor is generally considered high-temperature if it reaches a superconducting state above a temperature of 30 K (−243.15 °C);^[12] as in the initial discovery by Georg Bednorz and K. Alex Müller.^[7] It may also reference materials that transition to superconductivity when cooled using liquid nitrogen – that is, at only $T_c > 77$ K, although this is generally used only to emphasize that liquid nitrogen coolant is sufficient. Low temperature superconductors refer to materials with a critical temperature below 30 K, and are cooled mainly by liquid helium ($T_c > 4.2$ K).⁸ One exception to this rule is the iron pnictide group of superconductors which display behaviour and properties typical of high-temperature superconductors, yet some of the group have critical temperatures below 30 K.

By material

Superconductor material classes include chemical elements (e.g. mercury or lead), alloys (such as niobium–titanium, germanium–niobium, and niobium nitride), ceramics (YBCO and magnesium diboride), superconducting pnictides (like fluorine-doped LaOFeAs) or organic superconductors (fullerenes and carbon nanotubes; though perhaps these examples should be included among the chemical elements, as they are composed entirely of carbon).⁹

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.¹⁰

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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 .¹¹

II. DISCUSSION

Elementary properties of superconductors

Several physical properties of superconductors vary from material to material, such as the critical temperature, the value of the superconducting gap, the critical magnetic field, and the critical current density at which superconductivity is destroyed. On the other hand, there is a class of properties that are independent of the underlying material. The Meissner effect, the quantization of the magnetic flux or permanent currents, i.e. the state of zero resistance are the most important examples. The existence of these "universal" properties is rooted in the nature of the broken symmetry of the superconductor and the emergence of off-diagonal long range order. Superconductivity is a thermodynamic phase, and thus possesses certain distinguishing properties which are largely independent of microscopic details¹². Off diagonal long range order is closely connected to the formation of Cooper pairs. An article by V.F. Weisskopf presents simple physical explanations for the formation of Cooper pairs, for the origin of the attractive force causing the binding of the pairs, for the finite energy gap, and for the existence of permanent currents

Zero electrical DC resistance

The simplest method to measure the electrical resistance of a sample of some material is to place it in an electrical circuit in series with a current source I and measure the resulting voltage V across the sample. The resistance of the sample is given by Ohm's law as $R = V / I$. If the voltage is zero,¹³ this means that the resistance is zero. Superconductors are also able to maintain a current with no applied voltage whatsoever, a property exploited in superconducting electromagnets such as those found in MRI machines. Experiments have demonstrated that currents in superconducting coils can persist for years without any measurable degradation. Experimental evidence points to a current lifetime of at least 100,000 years. Theoretical estimates for the lifetime of a persistent current can exceed the estimated lifetime of the universe, depending on the wire geometry and the temperature.¹⁵ In practice, currents injected in superconducting coils have persisted for more than 27 years (as of August, 2013) in superconducting gravimeters.^{17][18]} In such instruments, the measurement principle is based on the monitoring of the levitation of a superconducting niobium sphere with a mass of 4 grams. In a normal conductor, an electric current may be visualized as a fluid of electrons moving across a heavy ionic lattice. The electrons are constantly colliding with the ions in the lattice, and during each collision some of the energy carried by the current is absorbed by the lattice and converted into heat, which is essentially the vibrational kinetic energy of the lattice ions. As a result, the energy carried by the current is constantly being dissipated. This is the phenomenon of electrical resistance and Joule heating.¹⁴

The situation is different in a superconductor. In a conventional superconductor, the electronic fluid cannot be resolved into individual electrons. Instead, it consists of bound pairs of electrons known as Cooper pairs. This pairing is caused by an attractive force between electrons from the exchange of phonons. This pairing is very weak, and small thermal vibrations can fracture the bond. Due to quantum mechanics, the energy spectrum of this Cooper pair fluid possesses an energy gap, meaning there is a minimum amount of energy ΔE that must be supplied in order to excite the fluid. Therefore, if ΔE is larger than the thermal energy of the lattice, given by kT , where k is Boltzmann's constant and T is the temperature, the fluid will not be scattered by the lattice.^{19]} The Cooper pair fluid is thus a superfluid,¹⁵ meaning it can flow without energy dissipation. In a class of superconductors known as type II superconductors, including all known high-temperature superconductors, an extremely low but nonzero resistivity appears at temperatures not too far below the nominal superconducting transition when an electric current is applied in conjunction with a strong magnetic

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field, which may be caused by the electric current. This is due to the motion of magnetic vortices in the electronic superfluid, which dissipates some of the energy carried by the current¹⁶. If the current is sufficiently small, the vortices are stationary, and the resistivity vanishes. The resistance due to this effect is tiny compared with that of non-superconducting materials, but must be taken into account in sensitive experiments. However, as the temperature decreases far enough below the nominal superconducting transition, these vortices can become frozen into a disordered but stationary phase known as a "vortex glass". Below this vortex glass transition temperature, the resistance of the material becomes truly zero.¹⁷

Phase transition

In superconducting materials, the characteristics of superconductivity appear when the temperature T is lowered below a critical temperature T_c . The value of this critical temperature varies from material to material. Conventional superconductors usually have critical temperatures ranging from around 20 K to less than 1 K. Solid mercury, for example, has a critical temperature of 4.2 K. As of 2015, the highest critical temperature found for a conventional superconductor is 203 K for H_2S , although high pressures of approximately 90 gigapascals were required.^[20] Cuprate superconductors can have much higher critical temperatures: $YBa_2Cu_3O_7$, one of the first cuprate superconductors to be discovered, has a critical temperature above 90 K, and mercury-based cuprates have been found with critical temperatures in excess of 130 K.¹⁸ The basic physical mechanism responsible for the high critical temperature is not yet clear. However, it is clear that a two-electron pairing is involved, although the nature of the pairing remains controversial.^[21]

Similarly, at a fixed temperature below the critical temperature, superconducting materials cease to superconduct when an external magnetic field is applied which is greater than the critical magnetic field. This is because the Gibbs free energy of the superconducting phase increases quadratically with the magnetic field while the free energy of the normal phase is roughly independent of the magnetic field.¹⁹ If the material superconducts in the absence of a field, then the superconducting phase free energy is lower than that of the normal phase and so for some finite value of the magnetic field (proportional to the square root of the difference of the free energies at zero magnetic field) the two free energies will be equal and a phase transition to the normal phase will occur. More generally, a higher temperature and a stronger magnetic field lead to a smaller fraction of electrons that are superconducting and consequently to a longer London penetration depth of external magnetic fields and currents.²⁰ The penetration depth becomes infinite at the phase transition. The onset of superconductivity is accompanied by abrupt changes in various physical properties, which is the hallmark of a phase transition. For example, the electronic heat capacity is proportional to the temperature in the normal (non-superconducting) regime. At the superconducting transition, it suffers a discontinuous jump and thereafter ceases to be linear. At low temperatures, it varies instead as $e^{-\alpha/T}$ for some constant, α . This exponential behavior is one of the pieces of evidence for the existence of the energy gap.²¹

The order of the superconducting phase transition was long a matter of debate. Experiments indicate that the transition is second-order, meaning there is no latent heat. However, in the presence of an external magnetic field there is latent heat, because the superconducting phase has a lower entropy below the critical temperature than the normal phase. It has been experimentally demonstrated^[22] that, as a consequence, when the magnetic field is increased beyond the critical field, the resulting phase transition leads to a decrease in the temperature of the superconducting material. Calculations in the 1970s suggested that it may actually be weakly first-order due to the effect of long-range fluctuations in the electromagnetic field. In the 1980s it was shown theoretically with the help of a disorder field theory, in which the vortex lines of the superconductor play a major role, that the transition is of second order within the type II regime and of first order (i.e., latent heat) within the type I regime, and that the two regions are separated by a tricritical point.^[23] The results were strongly supported by Monte Carlo computer simulations²²

III. RESULTS

Ruthenium

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The superconducting transition temperature of ruthenium has been placed between 0.40 and 0.509 ± 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 Ru^{99} and 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 \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 $\delta \ln(T_c/\theta_D)/\delta \ln V = -16$ ²³

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 $\rho/\rho_{273} = 0.4$ 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. Isotope effect measurements do not agree, even when apparently identical samples are checked (10, 13). 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.²⁴

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. However, for samples containing 50 ppm of iron $T_c = 0.10$ -0.11 K. 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.²⁵ 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

Rhodium

In the purities generally available commercially, rhodium is not superconducting at 0.086 K (13) nor at 0.003 K. 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. 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

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become a superconductor at a temperature of 0.2×10^{-3} K, a temperature predicted to be “at least a decade away”. With significantly improved refrigeration facilities it has recently been established that polycrystalline rhodium is in fact superconducting at a critical temperature of $325 \mu\text{K}$.²⁶

Palladium and Platinum

Even extra purified palladium and platinum are not superconducting. The lowest test temperature published is 0.1 K 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.²⁷

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 8.8K for palladium-hydrogen and ~ 10.7 K for palladium-deuterium samples. 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. 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. 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. 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. 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. 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. 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. 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. The pressure coefficient of palladium-hydrogen alloys $\delta \ln T_c / \delta P$ is -0.01 K/bar. 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. 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. 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, confirming observations by Raub and Loebich.²⁸

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. Electrolytically loading palladium-lithium solid solution samples with hydrogen did not produce superconductivity above 1.9 K.

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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. The ternary phase $\text{Ag}_2\text{Pd}_3\text{S}$, A13-type, $a = 7.235 \text{ \AA}$, has $T_c = 1.13 \text{ K}$.²⁹

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. Be_{13}Ru and Be_2Ru show critical temperatures of 1.3 and 1.35 K, respectively. Of the many beryllium-rhodium compounds only Be_2Rh is superconducting at 1.37 K. The transition temperatures of the beryllium compounds increase with beryllium content: for Be_5Os $T_c = 9.2$, for Be_2Os $T_c = 3.07$ and for $\text{Be}_{0.95}\text{Os}_{0.05}$ $T_c = 0.57 \text{ K}$. Among the beryllium phases with iridium only Be_5Ir is superconducting, with $T_c = 1.5 \text{ K}$. 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 $T_c = 6.0 \text{ K}$.³⁰

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.

Group III Elements

Aluminium, Boron, Gallium, Indium and Thallium

The compound B_3Ru is superconducting at 2.58 and B_2Ru at 1.6 K. None of the binary borides of platinum or palladium shows superconductivity above 1.2 K. Superconducting ternary palladium-hydrogenboron alloys can be prepared by ion-implantation techniques. OsB_2 has a critical temperature of about 2 K, 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 . 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. Among osmium-aluminium phases OsAl and $\text{Os}_4\text{Al}_{13}$ become superconducting at 0.9 and 3.3 K, respectively. The critical temperature of 5.9 K for OsAl_3 is probably the same for $\text{Os}_4\text{Al}_{13}$.³¹

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. It was first shown by V. B. Compton and B. T. Matthias 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 CeRu_2 (C15-type) for which $T_c = 4.9 \text{ K}$. The simultaneous

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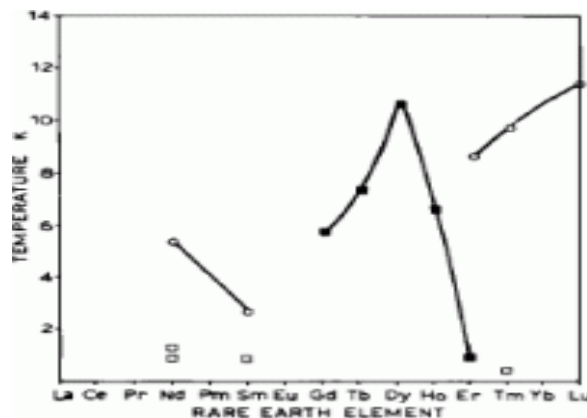
occurrence of superconductivity and ferromagnetism in pseudo-binary systems has been investigated in a series of papers on C15-type YOs_2 - $GdOs_2$, $CeRu_2$ - $PrRu_2$ and $CeRu_2$ - $GdRu_2$ alloys. Among the C15 phases of the noble metals with Group III elements, $CeRu_2$ and $LaOs_2$ exhibit the highest critical temperature, this being 6.5 K. Among C14-type phases they are YOs_2 and $LuOs_2$ with $T_c = 4.7$ and 3.49 K, respectively. Among the Os_2 -rare earth compounds the Curie temperature is highest at $OsGd_2$ (80 K). It drops down evenly to near 0 K at $OsLu_2$. The magnetic moments show two maxima at Ru_2Pr and Ru_2Dy and a minimum for europium compounds. This behaviour is equalled by that of the iridium and osmium rare earth C15-type phases. 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_3Y or Ir_4Y . Ir_2Y_3 is superconducting at 1.61 K and Ir_2Y 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_4Y . Nevertheless the behaviour is still somewhat unclear. Scandium-rich rhodium alloys show superconductivity beginning (partial superconductivity) near 0.9 K. 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. 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.³²

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. The compounds are tetragonal in structure, of the $CeCo_4B_4$ type. 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. 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 .³³ The superconducting transition temperatures and the ferromagnetic Curie temperatures of the $RERh_4B_4$ compounds (Fig.1.)

Fig. 1

Superconducting critical (T_c), Néel (T_N) and Curie (T_m) temperatures of $RERh_4B_4$ compounds, after reference (55).
 \circ T_c , \blacksquare T_m , \square T_N



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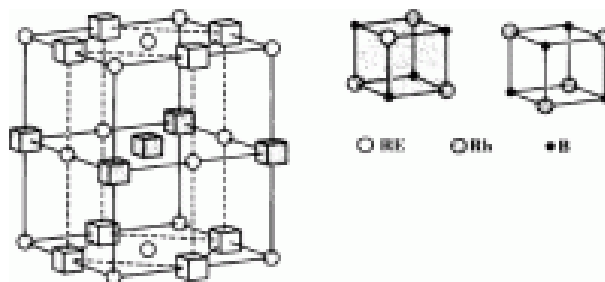
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A wide range of pseudo-binary compounds of these phases was investigated for the interaction between superconductivity, magnetic ordering and “crystalline field splitting”, for example $\text{Er}_{1-x}\text{Ho}_x\text{Rh}_4\text{B}_4$ and $\text{Sm}_{1-x}\text{Er}_x\text{Rh}_4\text{B}_4$. Rhodium can be replaced at least partially by ruthenium, or iridium. For the phase $\text{Ho}(\text{Ir}_{0.6}\text{Rh}_{0.4})_4\text{B}_4$ co-existence between superconductivity and antiferromagnetism was observed, the Néel temperature being higher than the critical temperature. 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. The structure of RERh_4B_4 is shown in Figure 2.

Fig. 2

The primitive tetragonal crystal structure of the rare earth rhodium borides RERh_4B_4 with the outline of the unit cell indicated by broken lines. For clarity, the Rh_4B_4 -clusters are not drawn to scale, after reference (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_5Ge_3 , $T_c = 2.12$ K (7, 7, 7); together with RhGe, $T_c = 0.96$ K (65); IrGe, $T_c = 4.7$ K (66); PtGe, $T_c = 0.4$ K; and RhSn_2 , $T_c = 0.60$ K. Ternary superconductors are the ruthenium and osmium germanides $\text{Y}_3\text{Ru}_4\text{Ge}_{13}$ and $\text{Y}_3\text{Os}_4\text{Ge}_{13}$, having a $\text{Yb}_3\text{Rh}_4\text{Sn}_3$ type structure. Ternary silicides and germanides with ruthenium, rhodium and osmium and the rare earths, of the $\text{Sc}_5\text{Co}_4\text{Si}_{10}$ type of structure, show a similar behaviour. Similar superconductivity/magnetic ordering behaviour is shown by ternary stannides $\text{RERh}_{1.1}\text{Sn}_{3.6}$ and REOs_xSn_y , respectively. Both ErOs_xSn_y and $\text{ErRh}_{1.1}\text{Sn}_{3.6}$ for example show re-entrant superconductivity. The phases in the system Me-tin show at least four different structures: I, I', II, and III depending on the kind of Me. Phase I compounds are cubic, space group $\text{Pm}\bar{3}\text{n}$ with a lattice constant $a = 9.7$ Å; I' compounds are distorted cubic; II are tetragonal with $a_{\text{II}} = 13.75$ and $c_{\text{II}} = 27.4$ Å while III are cubic with $a_{\text{III}} = 13.7$ 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. 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 K, YPd_2Pb 4.76 K and YPd_2In 0.85 K. The phases RhPb_2 and PdPb_2 , being C16- or CuAl_2 -type are superconducting at 2.66 and 2.95 K, respectively.³¹

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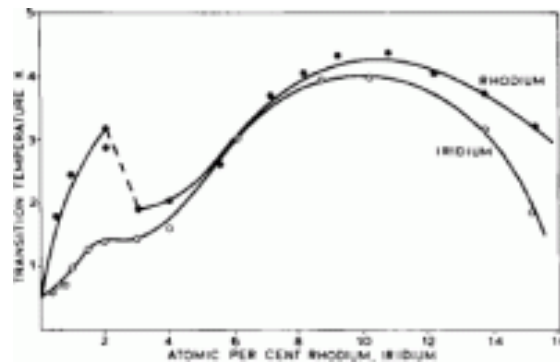
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Titanium, Zirconium, Hafnium and Thorium

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 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 and recently discussed. 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 phases $Ti_{0.573}Rh_{0.287}O_{0.14}$ and $Ti_{0.573}Ir_{0.287}O_{0.14}$ ($T_c = 3.37$ and 5.5 K, respectively), also $Zr_{0.61}Rh_{0.285}O_{0.105}$, $Zr_{0.61}Pd_{0.285}O_{0.105}$ and $Zr_{0.65}Ir_{0.265}O_{0.085}$ ($T_c = 11.8$, 2.09 and 2.30 K, respectively). The A15 phases Ti_3Ir and Ti_3Pt become superconducting at 5.4 and 0.58 K, respectively. Among the C14-type phases $HfOs_2$ and $ZrOs_2$ ($T_c = 2.69$ 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). Data for the D10₂-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. 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, in all cases the critical temperature was reduced by the presence of platinum group metals.³⁰

Fig. 3

Transition temperature versus concentration curves for titanium-iridium and titanium-rhodium alloys.



Group V Elements

Phosphorus, Arsenic, Antimony and Bismuth

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 B8₁-type phases $PdSb$ and $PtSb$ are superconducting with $T_c = 1.5$ and 2.1 K, respectively. Among the bismuthides, β - $PdBi_2$ has a higher critical temperature than a α - $PdBi_2$, $T_c = 4.2$ 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.²⁸

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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. 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.

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. Some work has been concerned with the influence of additions on the behaviour of pseudo-binary phases. 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 $\text{Nb}_{0.637}\text{Rh}_{0.363}$. This may be caused by a very narrow homogeneity range. The δ -phase in the tantalum-rhodium system is not superconducting, however, 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.²⁶

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 $\text{Pd}_{6.7}\text{Se}$ $T_c = 0.66$ and for Pd_4Se $T_c = 0.42$ K) and the tellurides of palladium, platinum and iridium.

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. Solid solutions of molybdenum and tungsten with ruthenium show an increase in the critical temperature with increasing ruthenium content; the critical temperature of the δ -phase with 50 atomic per cent molybdenum is 10.6 K. Further work on superconductivity in the ruthenium-molybdenum system has previously been summarised. The δ -phase $\text{Ru}_{0.4}\text{W}_{0.60}$ is superconducting in the range 4.67 to 5.2 K. 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. 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. The A12-type compound $\text{Nb}_{0.60}\text{Pd}_{0.40}$ exhibits superconductivity at 2.04 to 2.47 K.²⁴

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.

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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. Superconducting compounds are unknown. 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.²²

IV. IMPLICATIONS

When a superconductor is placed in a weak external magnetic field H , and cooled below its transition temperature, the magnetic field is ejected. The Meissner effect does not cause the field to be completely ejected but instead, the field penetrates the superconductor but only to a very small distance, characterized by a parameter λ , called the London penetration depth, decaying exponentially to zero within the bulk of the material. The Meissner effect is a defining characteristic of superconductivity. For most superconductors, the London penetration depth is on the order of 100 nm.

The Meissner effect is sometimes confused with the kind of diamagnetism one would expect in a perfect electrical conductor: according to Lenz's law, when a changing magnetic field is applied to a conductor, it will induce an electric current in the conductor that creates an opposing magnetic field. In a perfect conductor, an arbitrarily large current can be induced, and the resulting magnetic field exactly cancels the applied field.²⁰

The Meissner effect is distinct from this – it is the spontaneous expulsion that occurs during transition to superconductivity. Suppose we have a material in its normal state, containing a constant internal magnetic field. When the material is cooled below the critical temperature, we would observe the abrupt expulsion of the internal magnetic field, which we would not expect based on Lenz's law. A superconductor with little or no magnetic field within it is said to be in the Meissner state. The Meissner state breaks down when the applied magnetic field is too large. Superconductors can be divided into two classes according to how this breakdown occurs. In Type I superconductors, superconductivity is abruptly destroyed when the strength of the applied field rises above a critical value H_c . Depending on the geometry of the sample, one may obtain an intermediate state^[25] consisting of a baroque pattern of regions of normal material carrying a magnetic field mixed with regions of superconducting material containing no field. In Type II superconductors, raising the applied field past a critical value H_{c1} leads to a mixed state (also known as the vortex state) in which an increasing amount of magnetic flux penetrates the material, but there remains no resistance to the flow of electric current as long as the current is not too large. At a second critical field strength H_{c2} , superconductivity is destroyed. The mixed state is actually caused by vortices in the electronic superfluid, sometimes called fluxons because the flux carried by these vortices is quantized. Most pure elemental superconductors, except niobium and carbon nanotubes, are Type I, while almost all impure and compound superconductors are Type II. Conversely, a spinning superconductor generates a magnetic field, precisely aligned with the spin axis. The effect, the London moment, was put to good use in Gravity Probe B. This experiment measured the magnetic fields of four superconducting gyroscopes to determine their spin axes. This was critical to the experiment since it is one of the few ways to accurately determine the spin axis of an otherwise featureless sphere.²⁶

V. CONCLUSIONS

Superconducting magnets are some of the most powerful electromagnets known. They are used in MRI/NMR machines, mass spectrometers, the beam-steering magnets used in particle accelerators and plasma confining magnets in some tokamaks. They can also be used for magnetic separation, where weakly magnetic particles are extracted from a background of less or non-magnetic particles, as in the pigment industries. They can also be used

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in large wind turbines to overcome the restrictions imposed by high electrical currents, with an industrial grade 3.6 megawatt superconducting windmill generator having been tested successfully in Denmark.²⁸

In the 1950s and 1960s, superconductors were used to build experimental digital computers using cryotron switches. More recently, superconductors have been used to make digital circuits based on rapid single flux quantum technology and RF and microwave filters for mobile phone base stations. Superconductors are used to build Josephson junctions which are the building blocks of SQUIDS (superconducting quantum interference devices), the most sensitive magnetometers known. SQUIDS are used in scanning SQUID microscopes and magnetoencephalography.³⁰ Series of Josephson devices are used to realize the SI volt. Superconducting photon detectors can be realised in a variety of device configurations. Depending on the particular mode of operation, a superconductor–insulator–superconductor Josephson junction can be used as a photon detector or as a mixer. The large resistance change at the transition from the normal- to the superconducting state is used to build thermometers in cryogenic micro-calorimeter photon detectors. The same effect is used in ultrasensitive bolometers made from superconducting materials. Superconducting nanowire single-photon detectors offer high speed, low noise single-photon detection and have been employed widely in advanced photon-counting applications.³²

Other early markets are arising where the relative efficiency, size and weight advantages of devices based on high-temperature superconductivity outweigh the additional costs involved. For example, in wind turbines the lower weight and volume of superconducting generators could lead to savings in construction and tower costs, offsetting the higher costs for the generator and lowering the total levelized cost of electricity (LCOE). Promising future applications include high-performance smart grid, electric power transmission, transformers, power storage devices, electric motors (e.g. for vehicle propulsion, as in vactrains or maglev trains), magnetic levitation devices, fault current limiters, enhancing spintronic devices with superconducting materials, and superconducting magnetic refrigeration. However, superconductivity is sensitive to moving magnetic fields, so applications that use alternating current (e.g. transformers) will be more difficult to develop than those that rely upon direct current. Compared to traditional power lines, superconducting transmission lines are more efficient and require only a fraction of the space, which would not only lead to a better environmental performance but could also improve public acceptance for expansion of the electric grid. Another attractive industrial aspect is the ability for high power transmission at lower voltages. Advancements in the efficiency of cooling systems and use of cheap coolants such as liquid nitrogen have also significantly decreased cooling costs needed for superconductivity.³³

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