Platinum-Based and Platinum-Doped Layered Superconducting Materials: Synthesis, Properties and Simulation

Experimental and theoretical results for newest group of high-temperature superconductors

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In 2011, the newest group of layered high-temperature superconductors were discovered: platinum-based quaternary 10-4-8 ($Ca_{10}(Pt_4As_8)(Fe_2As_2)_5$) and 10-3-8 ($(CaFe_{1-x}Pt_xAs)_{10}Pt_3As_8$) phases with superconducting transition temperatures (T_C) up to 35–38 K. Intensive studies have been carried out to investigate their preparation and properties. This finding stimulated much activity in search of related materials and has attracted increased attention to platinum as a component of layered superconductors. This review presents experimental and theoretical results devoted to two main groups of superconducting materials with platinum: Pt-based materials (where Pt forms individual sub-lattices inside building blocks of corresponding phases such as SrPtAs, $SrPt_2As_2$ and $LaPt_2B_2C$) and Pt-containing materials, where Pt acts as a dopant. Synthesis, basic properties and simulation of these materials are covered.

1. Introduction

Platinum and a rich series of Pt-based alloys and compounds (as bulk, films or nanostructured species) are well known as critical materials for many applications (besides jewellery and investment) – for example they are excellent catalysts for chemical processing, and have many uses in the automotive industry (for example, in catalytic converters, spark plugs and sensors), in electronics (for high-temperature and non-corrosive wires and contacts), in petroleum refining, and also in medicine, electrochemistry and fuel cells. However, the participation of Pt in the formation of superconducting materials is much less well known (1–3). Superconductors find use in applications such as magnetic levitation ('maglev') trains, magnetic resonance imaging (MRI) scanners and particle accelerators and have further potential for more efficient electricity generation and distribution as well as fast computing applications.

The face-centred cubic (fcc)-Pt metal remains non-superconducting (1) even at the lowest accessible temperatures of solid matter, T ~1.5 μK (4, 5). It is believed that one of the obstacles to a possible superconducting transition is the purity of the metal, especially with regard to the concentration of magnetic impurities (6). Strong electron-phonon coupling, favourable for the formation of Cooper pairs in fcc-Pt, may also be a factor. Enhanced electronic susceptibility and the Sommerfeld coefficient (owing to low-dispersive near-Fermi bands and high carrier concentration) bring Pt close to magnetic instability (Stoner factor ~4 (7)), when spin fluctuations may completely suppress superconductivity in this metal (4). A very low-temperature superconducting transition (at T_C ~1.9 mK) was observed for compacted high-purity Pt powder with average grain sizes of ~2 μm (6,7); for Pt powders with nanosized grains (~100–300 nm) T_C increases to ~20 mK (8,9). It is supposed that the granular structure and the lattice strains related to local inhomogeneity (which is incommensurate with the Fermi surface nesting vectors (10)) are the key factors for the occurrence of inter- and intragranular superconductivity in granular Pt (8–10). In any case, 'pure' Pt as a superconductor seems unlikely.

However, a new set of Pt-based alloys and compounds represent very attractive groups of modern superconducting materials, and these have become the subjects of much research interest, particularly owing to clear evidence of unconventional pairing mechanisms for these systems.

Traditional John Bardeen, Leon Cooper and Robert Schrieffer (BCS)-like theories of superconductivity hold that pairs of electrons within nonmagnetic materials are coupled to phonons. In the case of unconventional superconductors, various mechanisms without phonons are suggested. For example, the unusual properties of UPt_3 (11) including a heavy fermion state below T = 20 K, dynamic antiferromagnetism (AFM) with onset at magnetic transition temperature, T_N = 6 K, and an anisotropic superconducting state with three distinct superconducting phases, provide strong evidence for unconventional spin-triplet superconductivity. In turn, $CePt_3Si$ is the first heavy-fermion superconductor without inversion symmetry, and its discovery (12) has initiated widespread research activity in the field of so-called noncentrosymmetric superconductors (13–15). Recently such superconductors lacking a lattice inversion centre have been investigated for the possibility of spin-triplet dominated pairing symmetry. Related Pt-based noncentrosymmetric superconductors are also known: $BaPtSi_3$ (16), Li_2Pt_3B (17) and $LaPt_3Si$ (18).

Another exciting material is platinum hydride (PtH) (19–21), for which the superconducting transition was predicted at T_C ~12 K (19) – the highest superconducting transition temperature among known metal hydrides – at pressure P ~90 GPa. Recent theoretical estimates confirm that the critical temperature of the two high-pressure phases of PtH correlates with electron-phonon coupling (19). Another group of low-T_C (< 8.5 K) superconductors include germanium-platinum compounds with the skutterudite-like crystal structure MPt_4Ge_{12} (where M are alkaline earth metals (strontium or barium), rare earth metals, thorium or uranium) (23–26). The majority of the listed Pt-based materials (a) belong to three-dimensional (3D)-like crystals; and (b) adopt low-temperature superconductivity.

One of the most remarkable achievements in physics and materials sciences was the discovery of high-temperature superconductors with T_C values equal to or above the historical limit of T_C ~23 K for niobium-germanium (Nb_3Ge). Starting with the discovery of the superconducting transition at T_C = 35 K in Ba-doped La_2CuO_4 in 1986 (27), several exciting families of high-T_C materials were subsequently found. Among these are the discoveries of superconductivity in layered materials: MgB_2 (T_C ~39 K) in 2000 (28) and fluorine-doped LaFeAsO (T_C ~26 K) in 2008 (29). These discoveries have inspired worldwide research efforts and have been the subject of many reviews (30–51). Most recently, phases with considerably increased values of T_C ~56 K were synthesised ($Gd_{1-x}Th_xFeAsO$ (52), $Sr_{1-x}Sm_xFeAsF$ (53) and $Ca_{1-x}Nd_{1-x}FeAsF$ (54)), and these form a new class of so-called iron-based high-temperature superconductors. The unconventional superconductivity of these materials, including various types of pairing and the coexistence of superconductivity with magnetism, has been widely discussed.

Several groups in this class of Fe-based superconductors are now known. The majority of them are iron-pnictide (*Pn*) (or chalcogenide (*Ch*)) phases (Fe-Pn or Fe-Ch, respectively). These materials can be categorised into the following major groups. From the chemical point of view, the simplest of them are binaries: 11-like phases (such as $FeSe_x$ (45,55)); ternary 111-like (such as AFeAs, where A are alkali metals (56)) and 122-like (such as BFe_2Pn_2, where B are alkali earth metals (57), or $A_xFe_{2-y}Ch_2$ (58)) materials; and a

wide group of quaternary 1111-like superconductors including pnictide oxides or pnictide fluorides such as *R*FeAsO (*R* are rare earth metals) and *B*FeAsF.

Recently, more complex materials such as $B_3Sc_2Fe_2As_2O_5$ (32225 phases) (59) and $B_4M_2Fe_2Pn_2O_6$ (*M* are *d* block metals) (42226 (or 21113) phases) were proposed (60,61) as parent phases for new high-T_C superconductors (46). For some of these, relatively high transition temperatures were established, for example T_C ~17 K for $Sr_4Sc_2Fe_2P_2O_6$ (60) and T_C ~37 K for $Sr_4V_2Fe_2P_2O_6$ (61). This family was further expanded when new pnictide oxides such as $Ca_{n+2}(Al,Ti)_nFe_2As_2O_y$ ($n = 2,3,4$) (62), $Ca_4Al_2Fe_2(P,As)_2O_{6-y}$ (63), $Sr_4(Sc,Ti)_3Fe_2As_2O_8$, $Ba_4Sc_3Fe_2As_2O_{7.5}$, $Ba_3Sc_2Fe_2As_2O_5$ (64), $Ca_4(Mg,Ti)_3Fe_2As_2O_y$ (65), $Sr_4MgTiFe_2Pn_2O_6$ (66, 67), and $Ba_4Sc_2Fe_2As_2O_6$ (68) were successfully prepared and studied (69–77).

For all the listed iron-based superconducting materials:

(a) The crystal structure includes two-dimensional (2D)-like (Fe-*Pn*) (or Fe-*Ch*) blocks, which are separated by *A* or *B* atomic sheets (for 111- and 122-like phases, respectively) or by (*R*O), ($B_3M_2O_5$) or (B_2MO_3) blocks for more complex 1111, 32225 or 21113 phases; the simplest 11-like binaries consist of stacked (Fe-*Ch*) blocks;

(b) The electronic bands in the window around the Fermi level are formed mainly by the states of (Fe-*Pn*) (or Fe-*Ch*) blocks, which are responsible for superconductivity, whereas the *A* and *B* atomic sheets or oxide blocks, which are often termed also as spacer layers, serve as insulating 'charge reservoirs'; and

(c) These materials have high chemical flexibility to a large variety of constituent elements together with high structural flexibility, and atomic substitution inside the blocks (electron or hole doping) is one of the main strategies for designing new superconducting systems with desirable properties (30–51).

The next promising step in expanding of this family of high-temperature superconductors was made in 2011, when a unique group of Pt-based materials: 10-4-8 ($Ca_{10}(Pt_4As_8)(Fe_2As_2)_5$) and 10-3-8 ($(CaFe_{1-x}Pt_xAs)_{10}Pt_3As_8$) phases was discovered (78–80) and intensive studies of their properties were initiated (81–85). For these materials superconductivity has been detected up to T_C ~35–38 K, which is probably induced either by Pt doping of the blocks (FeAs) in the 10-3-8 phase or by indirect electron doping in the 10-4-8 phase owing to additional Pt^{2+} in the platinum arsenide blocks (78–80). Thus, the role of Pt in the formation of superconducting materials becomes very intriguing.

Pt as a component of layered superconducting materials has been investigated for a long time, and Pt has been found to play a triple role: (a) as a dopant, (b) as a component of non-superconducting blocks (spacer layers), and (c) as a component of superconducting blocks. Thus, all superconductors with Pt can be divided onto two groups: Pt-based materials (where Pt forms individual sub-lattices inside blocks) and Pt-containing materials, where Pt acts as a dopant.

The following sections will focus on the above mentioned materials to cover the basic issues of their synthesis, main properties and simulation.

2. Pt-Based Superconducting Materials

Besides the 10-3-8 and 10-4-8 phases, some other Pt-based superconductors are known, such as SrPtAs (86), $SrPt_2As_2$ (87) and RPt_2B_2C (where *R* are rare earth metals or Th) (88–94), see **Table I**.

2.1 1221 Phases (Borocarbides)

Historically, the systematic study of layered Pt-based superconducting materials began with borocarbides RPt_2B_2C (1221 phases) in the mid-1990s and was continued in the new millennium (87–99). These phases crystallise in the tetragonal $LuNi_2B_2C$-type structure, which is an interstitial modification of the $ThCr_2Si_2$-type, and attract attention mainly because of the coexistence of various types of magnetic ordering and superconductivity. Since data about the properties of these materials are discussed in detail in a set of available reviews (100–104), here only the structural and superconducting parameters for known Pt-based superconductors are listed (**Table I**). All these materials belong to the class of low T_C superconductors.

2.2 SrPtAs

In 2011, the hexagonal phase SrPtAs was discovered (86) as a new low-temperature superconductor with T_C ~4.2 K. Polycrystalline samples of SrPtAs were prepared (86) by a solid-state reaction with $PtAs_2$ as a precursor mixed with Sr and Pt powders using several steps of heating. SrPtAs adopts a hexagonal structure (space group $P6_3/mmc$, #194) derived from the well-known AlB_2-type structure and can be schematically described as a sequence of two honeycomb planar sheets, where one plane is formed by Sr atoms, and the other (PtAs) by hexagonal Pt_3As_3, see **Figure 1**. The

Table I

Pt-Based Layered Superconducting Materials: Structural Properties and Critical Temperatures, T_C

Type	Material	Space group	Lattice constants, Å			T_C, K	Refs.
			a	*b*	*c*		
1221	YPt_2B_2C	*I*4/*mmm*	–	–	–	10–11	(88, 89)
	$LaPt_2B_2C$	*I*4/*mmm*	3.875	3.875	10.705	10.5–11	(88)
	$PrPt_2B_2C$	*I*4/*mmm*	3.837	3.837	10.761	6–6.5	(88, 89)
	$NdPt_2B_2C$	*I*4/*mmm*	3.826	3.826	10.732	2.5	(90, 91)
	$ThPt_2B_2C$	*I*4/*mmm*	3.83	3.83	10.853	6.7–7	(92–94)
111	SrPtAs	*P*6$_3$/*mmc*	4.244	4.244	8.989	4.2	(86)
122	$SrPt_2As_2$	*P*4/*nmm*	4.46	4.51	9.81	5.2	(87)
10-4-8	$(CaFe_{1-x}Pt_xAs)_{10}Pt_{4-y}As_8$; α-phase	*P*4/*n*	8.716	8.716	10.462	~11–31	(80)
	$(CaFe_{1-x}Pt_xAs)_{10}Pt_{4-y}As_8$; β-phase, x ~0.13	*P*1	8.7282	8.7287	11.049	~30	(80)
	$(CaFe_{1-x}Pt_xAs)_{10}Pt_{4-y}As_8$; x ~0.36	*P*1	8.719	8.727	11.161	32.7–38	(88)
10-3-8	$(CaFe_{1-x}Pt_xAs)_{10}Pt_3As_8$; x ~0.05	*P*1	8.776	8.781	10.689	~11–35	(80)
	$(CaFe_{1-x}Pt_xAs)_{10}Pt_3As_8$; x ~0.16	*P*1	8.795	8.789	21.008	13.7	(83)

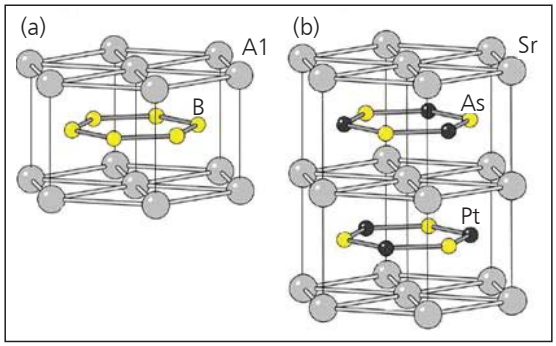

Fig. 1. Crystal structures of: (a) AlB_2 and (b) SrPtAs. The structure of SrPtAs can be described as an ordered variant of the AlB_2-type structure, where the Al sites are occupied by Sr and the boron sites are occupied either by Pt or As atoms so that they alternate in the honeycomb layer as well as along the c-axis (86)

atomic coordinates are Sr: 2*a* (0;0;0), Pt: 2*c* (⅓;⅔;¼), and As: 2*d* (⅔;⅓;¼), the lattice constants are a = 4.244 Å and c = 8.989 Å (86, 105).

Some theoretical efforts have been undertaken to predict the electronic and some other properties of SrPtAs (106–108). It is thought that this material should be characterised as a quasi-2D ionic metal (106), which consists of metallic-like (PtAs) sheets alternating with Sr atomic sheets coupled by ionic interactions. The near-Fermi valence bands are derived from the Pt 5*d* states with an admixture of the As 4*p* states. The Fermi surface of SrPtAs is formed by two quasi-2D (cylindrical-like) sheets parallel to the k_z direction (along the Γ-*A* direction) and by two sheets at the zone corners (around *K*-*H*). All the Fermi surfaces are hole-like. A very small closed electronic-like pocket was found around *K*, see **Figure 2**.

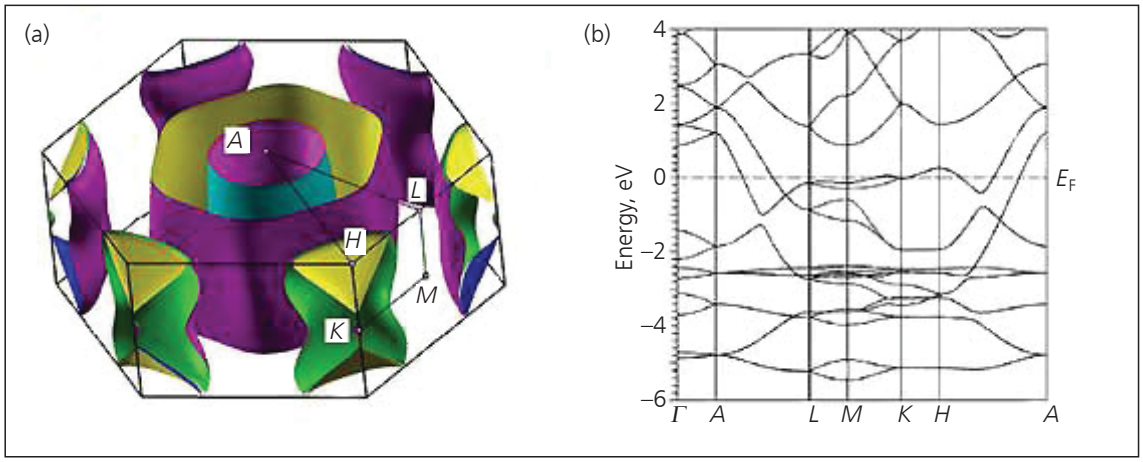

Fig. 2. (a) Fermi surface; and (b) Electronic bands of SrPtAs (106)

Taking into account the relativistic effects, this small electronic-like pocket disappears (102), and the Fermi surface of SrPtAs becomes fully hole-like. This feature distinguishes SrPtAs from other layered pnictogen-containing superconductors. It was also pointed out that SrPtAs provides a prime example of a superconductor with locally broken inversion symmetry (107). The calculated anisotropy in Fermi velocity, conductivity and plasma frequency related to the layered structure were found to be enhanced owing to spin-orbit coupling; further, it was predicted that electron doping would be favourable for an increase in T_C (108). Finally, SrPtAs was found (106) as a mechanically stable and soft material with high compressibility lying on the border of brittle/ductile behaviour, and the parameter limiting its mechanical stability is the shear modulus G, **Table II**.

2.3 $SrPt_2As_2$

For the chemically similar phase $SrPt_2As_2$ (110), low-T_C superconductivity (~5.2 K) has also been found (87), and this phase seems very attractive as the first superconductor from the wide family of related Pt-containing 122-like materials: for example, $ThPt_2Si_2$, $YbPt_2Si_2$, UPt_2Si_2, RPt_2Si_2 (R = La, Nd, Er, Dy, Ce), $ThPt_2Ge_2$, $YbPt_2Si_2$, UPt_2Ge_2 and RPt_2Ge_2 (112).

Polycrystalline samples of $SrPt_2As_2$ were synthesised using stoichiometric amounts of Sr, $PtAs_2$ and Pt powders by a solid-state reaction (87). $SrPt_2As_2$ adopts a tetragonal $CaBe_2Ge_2$-type structure (space group $P4/nmm$, #129) (87, 110, 111). The atomic positions are Sr: 2*c* (¼, ¼, z_{Sr}); 2*a* (¾, ¼, 0); Pt2: 2*c* (¼, ¼, z_{Pt}); As1: 2*b* (¾, ¼, ½); and As2: 2*c* (¼, ¼, z_{As}), where $z_{Sr,Pt,As}$ are the internal coordinates. The lattice parameters are listed in **Table I**. This structure can be

Table II

Calculated Bulk Modulus (B, in GPa), Compressibility (β, in GPa^{-1}), Shear Modulus (G, in GPa), and Pugh's Indicator (G/B) for SrPtAs (106) and $SrPt_2As_2$ (113)

Phase/parameter	SrPtAs	$SrPt_2As_2$[b]	$SrPt_2As_2$[c]
$B_{V,R,VRH}$[a]	79/10/44.5	101/99/100	71/71/71
β	0.023	0.010	0.014
$G_{V,R,RVH}$[a]	30/15/22.5	27/25/26	29/5/17
G/B	0.51	0.26	0.24

[a] *$B(G)_{V,R,RVH}$ as calculated within Voigt (V)/Reuss (R)/Voigt-Reuss-Hill (VRH) approximations, see for example (109)*

[b] *For $SrPt_2As_2$ polymorphs of $CaBe_2Ge_2$-type*

[c] *For $SrPt_2As_2$ polymorphs of $ThCr_2Si_2$-type*

schematically described as a sequence of Sr sheets and $[Pt_2As_2]$ and $[As_2Pt_2]$ blocks consisting of $\{PtAs_4\}$ and $\{AsPt_4\}$ tetrahedrons: …$[Pt_2As_2]$/Sr/$[As_2Pt_2]$/Sr/$[Pt_2As_2]$/Sr/$[As_2Pt_2]$… as shown in **Figure 3**.

For $SrPt_2As_2$, superconductivity coexists with the charge density wave (CDW) state (87) and this material exhibits a CDW transition at about 470 K (110).

Theoretical probes (113, 114) predict that $SrPt_2As_2$ is essentially a multiple-band system, with the Fermi level (E_F) crossed by Pt 5*d* states with a rather strong admixture of As 4*p* states, **Figure 4**. It was found (113) that $CaBe_2Ge_2$-type $SrPt_2As_2$ is a unique system with an 'intermediate'-type Fermi surface (**Figure 3**), which consists of electronic pockets having a cylinder-like (2D) topology (typical of 122 FeAs phases) together with 3D-like electronic and hole pockets. The latest are characteristic of $ThCr_2Si_2$-like iron-free low-T_C superconductors. The non-monotonic behaviour of the density of states (DOS, see **Figure 4**) near the E_F suggests the possibility of significant changes of T_C due to various (electron or hole) doping.

Analysis (113) revealed that other features of $CaBe_2Ge_2$-like $SrPt_2As_2$ are as follows:

(a) Essential differences in contributions to the near-Fermi region from the $[Pt_2As_2]$ and $[As_2Pt_2]$ blocks when conduction is anisotropic and occurs mainly in $[Pt_2As_2]$ blocks;

(b) Formation of a 3D system of strong covalent Pt-As bonds (inside and between $[Pt_2As_2]$/$[As_2Pt_2]$ blocks, see **Figure 3**), which is responsible for enhanced stability of this polymorph – in comparison with the competing $ThCr_2Si_2$-like phase; and

(c) Essential charge anisotropy between adjacent $[Pt_2As_2]$ and $[As_2Pt_2]$ blocks.

It has also been predicted that $CaBe_2Ge_2$-like $SrPt_2As_2$ will be a mechanically stable and relatively soft material with high compressibility, which will behave in a ductile manner, **Table II**. However, the $ThCr_2Si_2$-type $SrPt_2As_2$ polymorph, which contains only $[Pt_2As_2]$ blocks, is less stable and will be a ductile material with high elastic anisotropy.

A family of higher-order polytypes has been proposed (113), which can be formed as a result of various stacking arrangements of the two main types of building blocks ($[Pt_2As_2]$ and $[As_2Pt_2]$) in different combinations along the *z* axis. This may provide an interesting platform for further theoretical and experimental work in the search for new Pt-based superconducting materials.

In 2012, a new family of related ternary platinum phosphides APt_3P (*A* = calcium (Ca), strontium (Sr) or lanthanum (La)) was discovered (115). These phases crystallise in a tetragonal structure, where

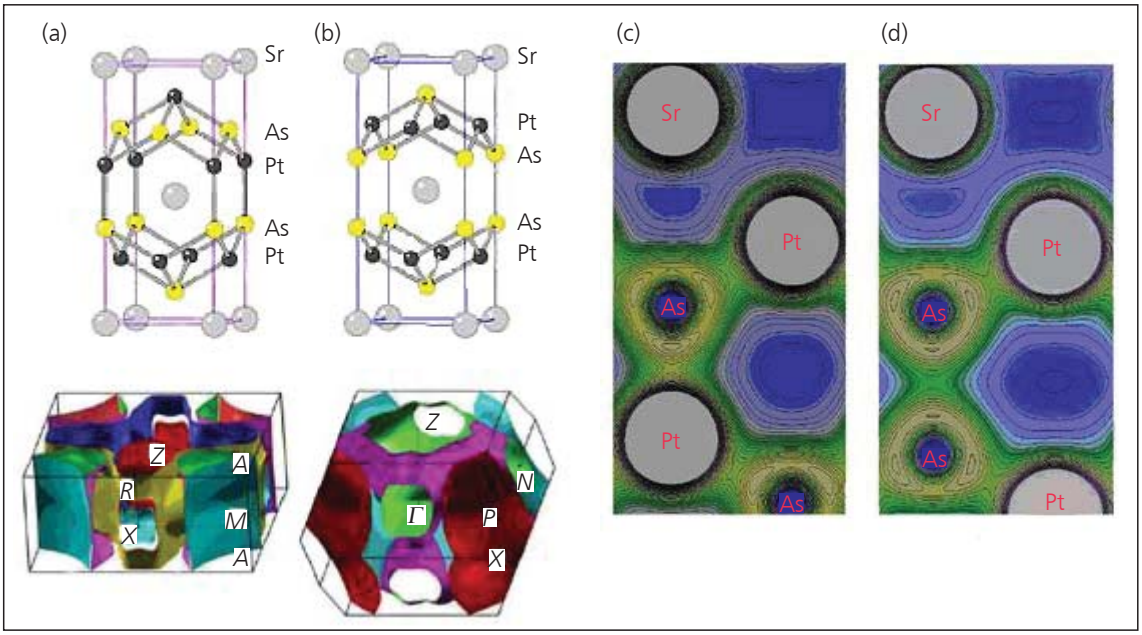

Fig. 3. Left: Crystal structures of: (a) $SrPt_2As_2$ with $CaBe_2Ge_2$-type; and (b) $ThCr_2Si_2$-type structures (87) and the corresponding Fermi surfaces (113). Right: Charge density maps of $SrPt_2As_2$ polymorphs illustrating the formation of directional "inter-block" covalent bonds: (c) As-Pt bonds for $CaBe_2Ge_2$-type; and (d) As-As bonds for $ThCr_2Si_2$-type structures (113)

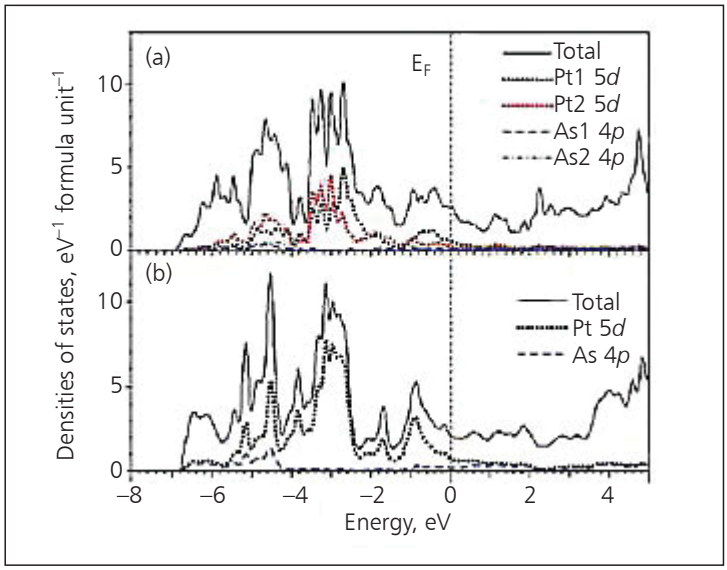

Fig. 4. Total and partial densities of states (DOSs) of $SrPt_2As_2$ polymorphs with structures of: (a) $CaBe_2Ge_2$-type; and (b) $ThCr_2Si_2$-type (113)

the anti-perovskite units Pt_6P are placed between Sr sheets. All three materials showed low-temperature superconductivity. The highest T_C ~8.4 K was found for $SrPt_3P$. Local-density approximation (LDA) calculations (116) reveal the 3D-like multiple band structure of APt_3P phases. The increase of T_C for $SrPt_3P$ with hole doping (for example, by partial replacement of Sr with potassium (K), rubidium (Rb) or caesium (Cs)) was predicted.

2.4 Quaternary 10-4-8 and 10-3-8 Superconducting Phases

In 2011, superconductivity with T_C ~25 K was reported for the tetragonal phase $Ca_{10}(Pt_4As_8)(Fe_2As_2)_5$ formed in the quaternary Ca-Pt-Fe-As system (76). Very soon, additional reports (78, 80) became available, where the related Ca-Pt-Fe-As systems are examined and enhanced superconductivity with transition temperatures up to T_C ~38 K, achieved by substitution of Pt for Fe in the (Fe_2As_2) blocks, is reported.

One of the most intriguing features of these new Pt-based materials (78–85) is the presence of (Fe_2As_2) blocks, which are typical of the family of Fe-*Pn* superconductors, together with oxygen-free blocks $[Pt_nAs_m]$.

Based on Zintl's chemical concept of ion electron counting, it was proposed (79, 80) that $[Pt_4As_8]$ and $[Fe_2As_2]$ blocks in the $Ca_{10}(Pt_4As_8)(Fe_2As_2)_5$ phase are metallic-like (i.e. both blocks will give appreciable contributions to the density of states at E_F) leading to enhanced inter-block coupling and thus to an enhanced transition temperature of this system. It has also been suggested that similar phases with additional metallic-like blocks might provide an interesting platform for the discovery of novel high-T_C superconducting materials.

Single crystals of $Ca_{10}(Pt_nAs_8)(Fe_{2-x}Pt_xAs_2)_5$ were grown (78) by heating a mixture of Ca, FeAs, Pt and As powders. The mixture was placed in an alumina crucible, sealed in an evacuated quartz tube, and heated in one of two ways. Heating at 700ºC for 3 h and then at 1000ºC for 72 h followed by slow cooling to room temperature yielded an α-phase with T_C ~38 K, whereas heating at 1100ºC and slow cooling to 1050ºC for 40 h yielded a β-phase with T_C ~13 K (78).

The atomic structures of the α-phase $Ca_{10}(Pt_4As_8)$-$(Fe_{2-x}Pt_xAs_2)_5$ (termed also as 10-4-8 phase) and the β-phase $Ca_{10}(Pt_3As_8)(Fe_{2-x}Pt_xAs_2)_5$ (10-3-8 phase) are depicted in **Figure 5**; the lattice parameters are listed in **Table I**.

These structures can be schematically described as a sequence of 2D-like $[Pt_4As_8]$ ($[Pt_3As_8]$) and $[Fe_2As_2]_5$ blocks separated by Ca sheets; in turn, platinum-arsenide blocks $[Pt_4As_8]$ ($[Pt_3As_8]$) are formed by corner-shared $\{PtAs_4\}$ squares, whereas iron-arsenide blocks consist of $\{FeAs_4\}$ tetrahedrons. In both cases $[Pt_4As_8]$ ($[Pt_3As_8]$) and $[Fe_2As_2]_5$ blocks contain a set of non-equivalent types of Fe, Pt and As atoms (78–85).

Further studies of superconducting gap anisotropy (82), low energy electronic structure, and Fermi surface topology (using angle resolved photoemission spectroscopy, see **Figure 5**) (117), the critical magnetic fields (118), and some transport properties (84, 119) together with theoretical calculations of the electronic

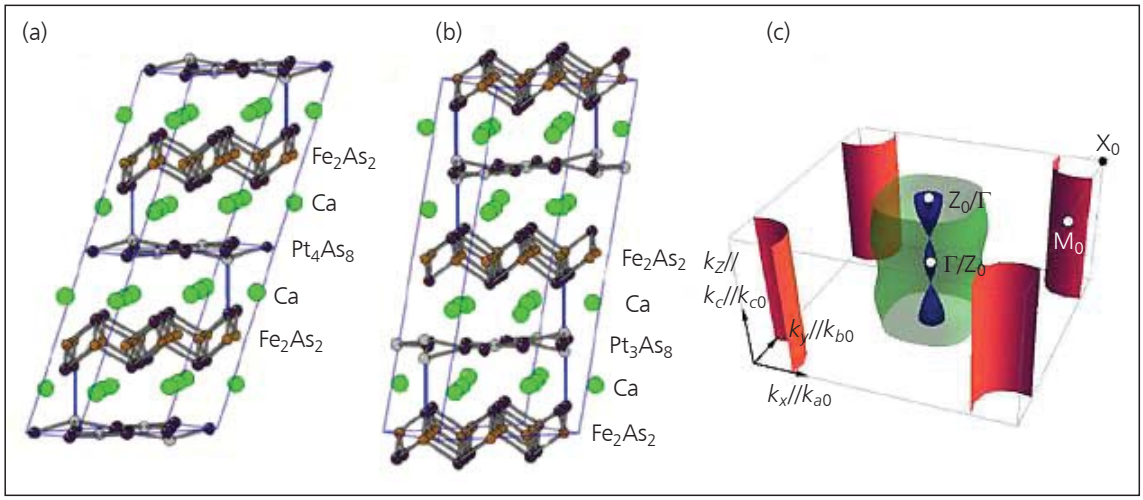

Fig. 5. Crystal structures of: (a) 10-4-8 phase (α-phase $Ca_{10}(Pt_4As_8)(Fe_{2-x}Pt_xAs_2)_5$); (b) 10-3-8 phase (β-phase $Ca_{10}(Pt_3As_8)(Fe_{2-x}Pt_xAs_2)_5$) (83); and (c) Experimentally-derived Fermi surface for the β-phase (117)

band structure and parameters of interatomic bonds (80, 81) reveal some interesting features of these materials. In particular, Pt doping into FeAs blocks was found to play a critical role for the occurrence of superconductivity. This doping-dependent evolution of the superconducting state is illustrated in **Figure 6**, where the electronic phase diagram for $Ca_{10}(Pt_3As_8)$-$(Fe_{2-x}Pt_xAs_2)_5$ is depicted. About 2 wt% Pt doping produces superconductivity, and the superconducting transition temperature reaches its maximum T_C ~13.6 K in the doping range $0.050 < x < 0.065$. With further Pt doping, T_C slowly decreases.

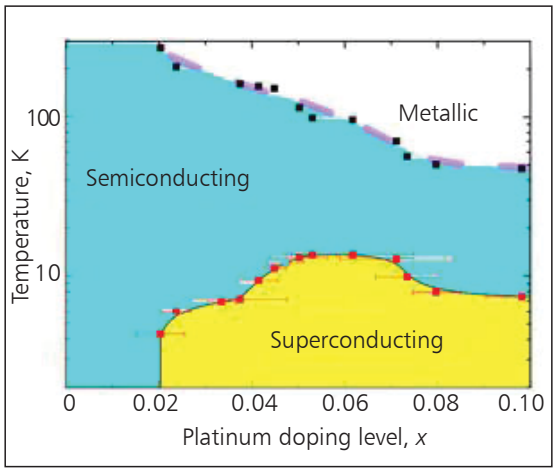

Fig. 6. Electronic phase diagram for $Ca_{10}(Pt_3As_8)$-$(Fe_{2-x}Pt_xAs_2)_5$ (84) which illustrates the doping-dependent formation of semiconducting, metallic-like, and superconducting states for this material

The first studies of electronic properties and interatomic bonding (80, 81) reveal that for $Ca_{10}(Pt_4As_8)(Fe_2As_2)_5$:

(a) The electronic bands in the window around the Fermi level are formed mainly by the Fe 3*d* states of $[Fe_2As_2]_5$ blocks;
(b) The $[Pt_4As_8]$ blocks will behave as semi-metals with very low densities of states at the Fermi level;
(c) The near-Fermi bands adopt a 'mixed' character: simultaneously with quasi-flat bands, a series of high-dispersive bands which intersect the Fermi level was found; and
(d) The chemical bonding in $Ca_{10}(Pt_4As_8)(Fe_2As_2)_5$ is complicated and includes an anisotropic mixture of covalent, metallic and ionic interatomic and inter-block interactions, see **Figure 7**.

Inside $[Fe_2As_2]_5$ blocks covalent Fe-As and metallic-like Fe-Fe bonds take place, whereas inside $[Pt_4As_8]$ blocks a system of covalent Pt-As and As-As bonds emerges. Further, inside these blocks interatomic ionic interactions occur owing to charge transfer Fe → As and Pt → As. The inter-block charge transfer occurs from the electropositive Ca ions to $[Pt_4As_8]$ and $[Fe_2As_2]_5$ blocks. It is important that the charge transfer $Ca_{10} \rightarrow [Pt_4As_8]$ is much greater than the transfer $Ca_{10} \rightarrow [Fe_2As_2]_5$, i.e. in contrast to the majority of known superconducting Fe-containing materials (38–43, 51), the new phase $Ca_{10}(Pt_4As_8)$-$(Fe_2As_2)_5$ includes two negatively charged blocks, where the charge of the conducting $[Fe_2As_2]_5$ blocks is much smaller than for the Pt-As blocks. The chemical modification of Pt_nAs_8 blocks may lead

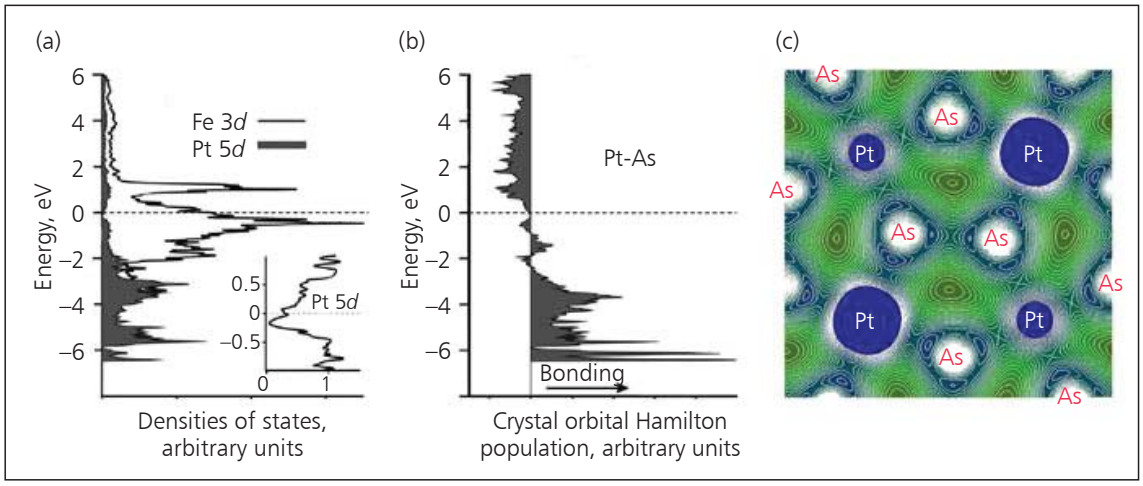

Fig. 7. (a) Partial density of states; and (b) Crystal orbital Hamilton population (COHP) of the Pt-As bonds (80); and (c) Charge density map for $Ca_{10}(Pt_4As_8)(Fe_2As_2)_5$ phase, which illustrates the formation of directional covalent As-As bonds inside (Pt_4As_8) blocks (81)

to the discovery of similar materials with increased T_C (83).

3. Platinum-Doped Layered Superconducting Materials

The first attempts to investigate Pt as a dopant which can optimise the properties of layered superconductors were undertaken as early as the 1990s when the high-temperature superconductor cuprates were examined (120, 121). Next, the effects induced by Pt doping of 1221 phases (borocarbides), which exhibit a rich variety of phenomena associated with superconductivity, magnetism, and their interplay, were studied (122–131).

For non-magnetic superconductors such as YNi_2B_2C and $LuNi_2B_2C$, the introduction of Pt atoms at the nickel sites leads to modifications of their superconducting properties. For series of single crystals of $YNi_{2-x}Pt_xB_2C$ (x = 0.02, 0.06, 0.1, 0.14 and 0.2), which were grown by the travelling solvent floating zone method (125), with an increase in the Pt content the critical temperature decreases from T_C ~15.9 K to T_C ~13 K for x = 0.14, **Figure 8**. The results were explained (125) assuming the increase in inter-band scattering in the multi-band superconductor YNi_2B_2C.

Pseudo-quaternary samples $Y(Pd_{1-x}Pt_x)_2B_2C$ were prepared by mechanical alloying followed by a thermal treatment (126). It was found that Pt stabilises

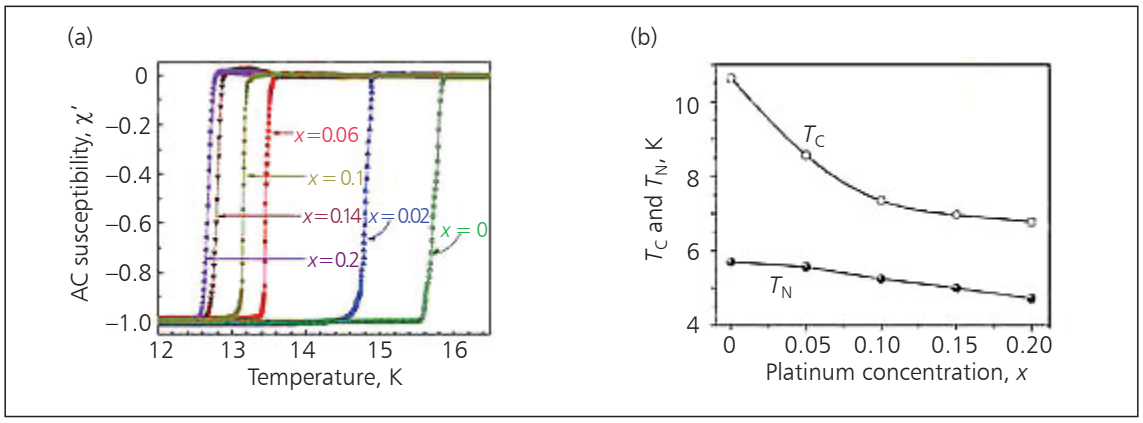

Fig. 8. (a) Normalised real part of alternating current (AC) susceptibility as a function of temperature in $YNi_{2-x}Pt_xB_2C$ (125); and (b) Superconducting transition temperature (T_C) and magnetic transition temperature (T_N) in $Er(Ni_{1-x}Pt_x)_2B_2C$ as functions of the Pt concentration, x (131)

the formation of the tetragonal superconducting phase YPd_2B_2C (which adopts the highest T_C ~23 K among the borocarbides), when an almost single-phase material with T_C near 15 K for $Y(Pd_{0.8}Pt_{0.2})_2B_2C$ was formed after annealing at 1273 K.

For magnetic superconductors such as $ErNi_2B_2C$, the introduction of Pt atoms influences both T_C and T_N (129–131). For example the measurements for $Er(Ni_{1-x}Pt_x)_2B_2C$ (polycrystalline samples with Pt content x = 0.0, 0.05, 0.10, 0.15 and 0.20 were synthesised by standard arc melting under protective argon atmosphere (131)) reveal that the variation of T_C as a function of x contains two intervals, see **Figure 8**. At the first step, a strong decrease in T_C in the range $0 \leq x < 0.10$ occurs, whereas a much weaker drop of T_C was observed with a further increase of x (131). The value of T_N, by contrast, decreases almost monotonically. Thus, the Pt impurities in superconducting 1221 borocarbides usually lead to reduction of T_C. The explanation of the observed effects requires further studies.

A different effect accompanies the introduction of Pt inside layered 122-like Fe-based pnictides such as BFe_2Pn_2 (132–136). It is known that 'pure' BFe_2Pn_2 phases (parent materials for Fe-based superconductors) are located on the border of magnetic instability and commonly exhibit temperature-dependent structural and magnetic transitions with the formation of collinear AFM spin ordering, whereas superconductivity emerges either as a result of hole or electron doping into these parent compounds (38–43, 47). Accordingly, this effect was observed for some Pt-doped 122-like phases. Polycrystalline samples of $SrFe_{2-x}Pt_xAs_2$ ($0 \leq x \leq 0.4$) were prepared by a solid-state reaction method using SrAs, FeAs and metallic powders of Fe and Pt as reagents. The mixture was pressed into a Ta capsule, sealed in an evacuated quartz tube, and heated at 1000ºC for 48 h. The measurements demonstrated that as a result of Pt doping, the magnetic order of the parent phase $SrFe_2As_2$ is suppressed, superconductivity for $SrFe_{2-x}Pt_xAs_2$ emerges at approximately x = 0.15, and T_C reaches a maximum of 16 K at x = 0.2 (132).

A similar effect was detected for the related system $BaFe_{2-x}Pt_xAs_2$ (133), where at the doping level of x ~0.1 the maximum transition temperature T_C ~25 K was achieved. This situation is well illustrated in **Figure 9**, where the electronic phase diagram of $BaFe_{2-x}Pt_xAs_2$ for the doping range x = 0–0.25 is depicted. In a simplified way, these effects can be interpreted in terms of the difference in the number of valence

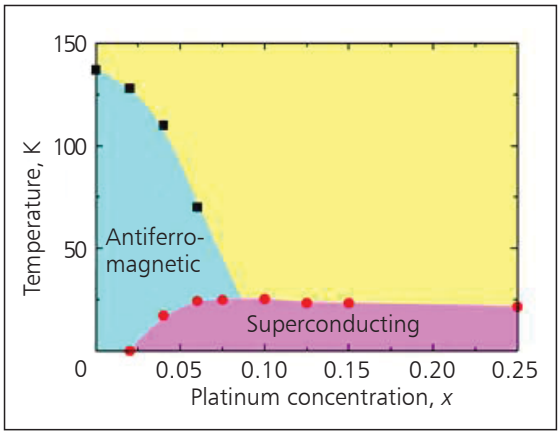

Fig. 9. Phase diagram of $BaFe_{2-x}Pt_xAs_2$ for the doping level x = 0–0.25 (133). At x < 0.02 a magnetic state with AF spin fluctuations exists. Superconductivity appears at x = ~0.02, and T_C reaches its maximum value (25 K) at x = 0.1

electrons between the doped transition metal (Pt) and iron, i.e. the chemical scaling of the electronic phase diagram (137, 138).

However, some exceptions can exist here: for the related system $CaFe_{2-x}Pt_xAs_2$ it was established (134) that the substitution of Pt is ineffective in the reduction of AFM ordering as well as for inducing of superconductivity up to a solubility limit at x ~0.08. This challenge calls for further studies.

4. Conclusions

This overview has covered the relatively little-known role of platinum in design and modification of modern superconducting materials. The main goal was to highlight recent experimental and theoretical results that may give an insight into the current status and possible development of layered superconducting materials with Pt.

To date, two types of such materials have been discovered: Pt-based materials (where Pt forms individual sub-lattices inside building blocks of corresponding phases such as SrPtAs, $SrPt_2As_2$, $LaPt_2B_2C$ and $(CaFe_{1-x}Pt_xAs)_{10}Pt_3As_8$) and Pt-containing materials (such as $Y(Pd_{1-x}Pt_x)_2B_2C$ or $SrFe_{2-x}Pt_xAs_2$), where Pt acts as a dopant. The role of Pt can be radically different. For example, the Pt impurity in superconducting borocarbides usually leads to a reduction of T_C; whereas the introduction of Pt inside layered Fe-based pnictides such as BFe_2Pn_2 leads to the occurrence of superconductivity (with high transition temperatures to T_C ~25 K) in these non-superconducting parent materials. A very promising

step in expanding the family of superconducting materials with Pt was made in 2011, when the unique quaternary phases: 10-4-8 ($Ca_{10}(Pt_4As_8)(Fe_2As_2)_5$) and 10-3-8 ($((CaFe_{1-x}Pt_xAs)_{10}Pt_3As_8$) with highest T_C ~35–38 K were discovered.

The author hopes that this overview will be useful as a compendium to guide further research into layered superconducting materials with Pt, which seem interesting and challenging systems for providing new and promising superconductors.

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