

Synthesis and Structure of $\text{Sr}_2\text{Pd}_2\text{In}$ and $\text{Sr}_2\text{Pt}_2\text{In}$

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The new intermetallic compounds $\text{Sr}_2\text{Pd}_2\text{In}$ and $\text{Sr}_2\text{Pt}_2\text{In}$ were synthesized from the elements in sealed tantalum tubes in a water-cooled sample chamber of an induction furnace. Both indides crystallize with the $\text{HT-Pr}_2\text{Co}_2\text{Al}$ -type structure: $C2/c$, $a = 1048.7(2)$, $b = 603.5(2)$, $c = 830.6(1)$ pm, $\beta = 103.68(2)^\circ$, $wR2 = 0.0492$, 743 F^2 values for $\text{Sr}_2\text{Pd}_2\text{In}$; $a = 1026.8(2)$, $b = 599.0(1)$, $c = 830.3(2)$ pm, $\beta = 103.17(1)^\circ$, $wR2 = 0.0666$, 885 F^2 values for $\text{Sr}_2\text{Pt}_2\text{In}$ with 25 variables per refinement. The shortest interatomic distances occur for the Pd–In (Pt–In) and Pd–Pd (Pt–Pt) contacts. The strontium atoms are embedded in complex three-dimensional polyanionic networks of compositions $[\text{Pd}_2\text{In}]$ and $[\text{Pt}_2\text{In}]$.

Key words: Strontium Intermetallics, Crystal Structure

Introduction

The europium-transition metal (T) indides $\text{Eu}_x\text{T}_y\text{In}_z$ have intensively been investigated in recent years with respect to their structural chemistry and their interesting magnetic and electrical properties. Prominent examples are the metamagnets EuPdIn ($T_N = 13$ K) [1, 2] and EuAuIn ($T_N = 21$ K) [1, 3], the antiferromagnet EuRh_2In_8 [4, 5], or the ferromagnet EuPt_4In [6]. Besides susceptibility measurements, the magnetic hyperfine interactions and the europium valence of these compounds can effectively be studied by ^{151}Eu Mössbauer spectroscopy. A large number of data are summarized in a recent review article [7].

A comparison of the ionic radii of Eu^{2+} (117 pm) and Sr^{2+} (118 pm) [8] implies, that divalent europium in such intermetallic and related compounds might be substituted by diamagnetic Sr^{2+} . Prominent examples for such a substitution are the oxides $\text{Eu}^{\text{II}}\text{Eu}^{\text{III}}_2\text{O}_4$ [9–11] and SrEu_2O_4 [9], where strontium completely substitutes for divalent europium. Therefore, a number of strontium-transition metal indides exist, which are isotopic with the corresponding europium compounds: SrTIn ($T = \text{Pd, Pt, Au}$) [12–14], SrTIn_2 ($T = \text{Rh, Pd, Ir, Pt}$) [15], SrTIn_4 ($T = \text{Ni, Pd, Ir, Pt}$) [16, 17], SrAu_3In_3 [18], $\text{Sr}_2\text{Au}_3\text{In}_4$ [19], the solid solution $\text{SrIn}_{4-x}\text{Au}_x$ [14, 20, 21], $\text{Sr}_2\text{Rh}_2\text{In}_3$ [22], SrRh_2In_8 [16], and SrT_7In_6 ($T = \text{Ni, Cu}$) [23, 24]. These strontium compounds do not contain strontium

as majority component. In view of the interesting crystal chemistry of the recently reported calcium-rich indides $\text{Ca}_2\text{Pd}_2\text{In}$, $\text{Ca}_2\text{Pt}_2\text{In}$ [25], and $\text{Ca}_3\text{Au}_3\text{In}$ [26], we were interested in the corresponding strontium-rich systems. Herein we report on the synthesis and structure refinements of $\text{Sr}_2\text{Pd}_2\text{In}$ and $\text{Sr}_2\text{Pt}_2\text{In}$ which are isotopic with the calcium compounds.

Experimental Section

Synthesis

Starting materials for the synthesis of $\text{Sr}_2\text{Pd}_2\text{In}$ and $\text{Sr}_2\text{Pt}_2\text{In}$ were a strontium rod (Johnson Matthey, > 99.8 %), palladium and platinum powder or shot (Heraeus, > 99.9 %), and indium tear drops (Johnson Matthey, > 99.9 %). The elements were weighed in the ideal 2:2:1 atomic ratio and sealed in small tantalum tubes under an argon pressure of ca. 600 mbar [27]. The argon was purified before over molecular sieves, silica gel and titanium sponge (900 K). The ampoules were then placed in a water-cooled sample chamber of a high-frequency furnace (Hüttinger Elektronik, Freiburg, type TIG 1.5/300) under flowing argon [28], were rapidly heated to 1600 K and kept at that temperature for about 1 min followed by slow cooling to 900 K. Finally the samples were annealed for 4 h at that temperature. The temperature was controlled through a Sensor Therm Methis MS09 pyrometer with an accuracy of ± 30 K. The samples could easily be separated from the crucible material. No reaction with tantalum was observed. Well-shaped single crystals of $\text{Sr}_2\text{Pd}_2\text{In}$ and $\text{Sr}_2\text{Pt}_2\text{In}$ are stable in air over several days. Polycryst-

Table 1. Crystal data and structure refinement for Sr₂Pd₂In and Sr₂Pt₂In, space group *C2/c* (No. 15), *Z* = 4, Pearson code *mC20*.

Empirical formula	Sr ₂ Pd ₂ In	Sr ₂ Pt ₂ In
Molar mass	502.86	680.24
Unit cell dimensions (Guinier powder data)		
<i>a</i> , pm	1048.7(2)	1026.8(2)
<i>b</i> , pm	603.5(2)	599.0(1)
<i>c</i> , pm	830.6(2)	830.3(2)
β , deg	103.68(2)	103.17(1)
<i>V</i> , nm ³	0.5108	0.4973
Calculated density, g cm ⁻³	6.54	9.09
Crystal size, μm^3	40 × 40 × 50	20 × 60 × 80
Detector distance, mm	60	—
ω Range; increment, deg	0–180; 1	—
Exposure time, min	5	—
Integr. Param. A, B, EMS	13.2; 3.5; 0.010	—
Transmission (max/min)	1.80	1.91
Absorption coefficient, mm ⁻¹	31.9	44.3
<i>F</i> (000), e	868	1124
θ Range for data collection	3 to 30°	3 to 25°
Range in <i>hkl</i>	–13 ≤ <i>h</i> ≤ 14 –7 ≤ <i>k</i> ≤ 8 –11 ≤ <i>l</i> ≤ 11	–15 ≤ <i>h</i> ≤ 15 0 ≤ <i>k</i> ≤ 9 –12 ≤ <i>l</i> ≤ 12
Total no. reflections	2581	1766
Independent reflections	743	885
<i>R</i> _{int}	0.0676	0.0609
Reflections with <i>I</i> ≥ 2σ(<i>I</i>)	391	609
<i>R</i> _σ	0.1399	0.0815
Data / ref. parameters	743 / 25	885 / 25
Goodness-of-fit on <i>F</i> ²	0.489	0.957
Final <i>R</i> indices [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0238 <i>wR</i> 2 = 0.0422	<i>R</i> 1 = 0.0391 <i>wR</i> 2 = 0.0598
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0720 <i>wR</i> 2 = 0.0492	<i>R</i> 1 = 0.0747 <i>wR</i> 2 = 0.0666
Extinction coefficient	0.0015(1)	0.0028(2)
Largest diff. peak and hole, e Å ⁻³	1.03 / –1.35	2.46 / –2.69

talline samples and powders slowly hydrolyze in humid air. Single crystals exhibit metallic lustre while ground powders are light grey.

X-Ray diffraction

The samples were studied through Guinier powder patterns (imaging plate technique, Fujifilm BAS-1800) using CuK α 1 radiation and α -quartz (*a* = 491.30 and *c* = 540.46 pm) as an internal standard. The lattice parameters (Table 1) were obtained from least-squares fits of the powder data. To ensure correct indexing, the experimental patterns were compared to calculated ones [29], taking the atomic positions from the structure refinements. The lattice parameters determined on the single crystal diffractometers (*a* = 1049.9(2), *b* = 603.1(1), *c* = 829.3(2) pm, β = 103.62(3)° for Sr₂Pd₂In and *a* = 1025.7(1), *b* = 598.2(1), *c* = 829.8(1) pm, β = 103.14(1)° for Sr₂Pt₂In) were in agreement with the powder data (Table 1).

Table 2. Atomic coordinates and isotropic displacement parameters (pm²) of Sr₂Pd₂In and Sr₂Pt₂In. *U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Atom	Wyckoff site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Sr ₂ Pd ₂ In					
Sr	8 <i>f</i>	0.35144(7)	0.1396(2)	0.35214(8)	72(2)
Pd	8 <i>f</i>	0.13313(6)	0.13567(19)	0.00301(7)	82(2)
In	4 <i>e</i>	0	0.1345(2)	1/4	62(2)
Sr ₂ Pt ₂ In					
Sr	8 <i>f</i>	0.35182(10)	0.1412(3)	0.35222(14)	106(2)
Pt	8 <i>f</i>	0.13609(5)	0.13773(10)	0.00256(6)	98(2)
In	4 <i>e</i>	0	0.1312(3)	1/4	98(3)

Table 3. Interatomic distances (pm) in the structures of Sr₂Pd₂In and Sr₂Pt₂In, calculated with the lattice parameters obtained from X-ray powder data. Standard deviations are all equal or smaller than 0.2 pm. All distances within the first coordination spheres are listed.

Sr ₂ Pd ₂ In				Sr ₂ Pt ₂ In			
Sr:	1	Pd	321.6	Sr:	1	Pt	318.9
	1	Pd	322.3		1	Pt	320.1
	1	Pd	324.2		1	Pt	322.6
	1	Pd	326.1		1	Pt	324.0
	1	Pd	328.5		1	Pt	324.3
	1	Pd	330.6		1	Pt	325.8
	1	In	356.3		1	In	349.8
	1	In	357.4		1	In	351.8
	1	In	358.1		1	In	357.7
	1	In	361.5		1	In	359.9
	2	Sr	384.8		1	Sr	379.9
	1	Sr	384.8		1	Sr	380.7
Pd:	1	Sr	386.8		2	Sr	382.1
	1	Sr	388.5		1	Sr	383.9
	1	In	274.1	Pt:	1	Pt	270.7
	1	In	276.3		1	In	273.6
	1	Pd	282.4		1	In	275.9
	1	Sr	321.6		1	Sr	318.9
	1	Sr	322.3		1	Sr	320.1
	1	Pd	322.7		1	Sr	322.6
	1	Sr	324.2		1	Pt	323.8
	1	Sr	326.1		1	Sr	324.0
	1	Sr	328.5		1	Sr	324.3
	1	Sr	330.6		1	Sr	325.8
	2	Pd	274.1	In:	2	Pt	273.6
In:	2	Pd	276.3		2	Pt	275.9
	2	Sr	356.3		2	Sr	349.8
	2	Sr	357.4		2	Sr	351.8
	2	Sr	358.1		2	Sr	357.7
	2	Sr	361.5		2	Sr	359.9

Single crystal intensity data of Sr₂Pt₂In were collected at r.t. by use of a four-circle diffractometer (CAD4) with graphite-monochromatized AgK α (56.086 pm) radiation and a scintillation counter with pulse height discrimination. The scans were taken in the $\omega/2\theta$ mode. Intensity data for Sr₂Pd₂In were measured at r.t. on a Stoe IPDS-II image plate system in oscillation mode. Numerical absorption cor-

rections were applied to both data sets. All relevant details concerning the data collections and evaluations are listed in Table 1.

Structure refinements

Small, irregularly shaped single crystals of $\text{Sr}_2\text{Pd}_2\text{In}$ and $\text{Sr}_2\text{Pt}_2\text{In}$ were selected from the annealed samples by mechanical fragmentation and examined by use of a Buerger camera equipped with an image plate system (Fujifilm BAS-1800) in order to establish suitability for intensity data collection. The isotypy with the monoclinic $\text{HT-Pr}_2\text{Co}_2\text{Al}$ -type [30], space group $C2/c$, was already evident from the powder patterns.

The atomic parameters of $\text{Ca}_2\text{Pd}_2\text{In}$ [25] were taken as starting values and both structures were refined using SHELXL-97 [31] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all atoms. The occupancy parameters were refined in separate series of least-squares cycles. All sites were fully occupied within two standard deviations and the ideal occupancies were assumed again in the last cycles. The final difference Fourier syntheses were flat (Table 1). The positional parameters and interatomic distances of the refinements are listed in Tables 2 and 3.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-391432 ($\text{Sr}_2\text{Pd}_2\text{In}$) and CSD-391433 ($\text{Sr}_2\text{Pt}_2\text{In}$).

Scanning electron microscopy

The bulk samples of $\text{Sr}_2\text{Pd}_2\text{In}$ and $\text{Sr}_2\text{Pt}_2\text{In}$ and the single crystals investigated on the diffractometers were analyzed in a LEICA 420 I scanning electron microscope equipped with an OXFORD EDX analyzer. Since the crystals were mounted by beeswax on glass fibres, they were first coated with a carbon film. SrF_2 , Pd, Pt, and InAs were used as standards for the semiquantitative EDX measurements. The analyses (41 ± 2 at.-% Sr: 39 ± 2 at.-% Pd: 20 ± 2 at.-% In and 38 ± 2 at.-% Sr: 41 ± 2 at.-% Pt: 21 ± 2 at.-% In) were in good agreement with the ideal composition and no impurity elements were observed.

Results and Discussion

$\text{Sr}_2\text{Pd}_2\text{In}$ and $\text{Sr}_2\text{Pt}_2\text{In}$ crystallize with the monoclinic $\text{HT-Pr}_2\text{Co}_2\text{Al}$ -type structure [30] and they are isotypic with $\text{Ca}_2\text{Pd}_2\text{In}$ and $\text{Ca}_2\text{Pt}_2\text{In}$ [25]. Due to the larger size of strontium, the cell volumes increase for $\text{Sr}_2\text{Pd}_2\text{In}$ and $\text{Sr}_2\text{Pt}_2\text{In}$ with respect to the calcium

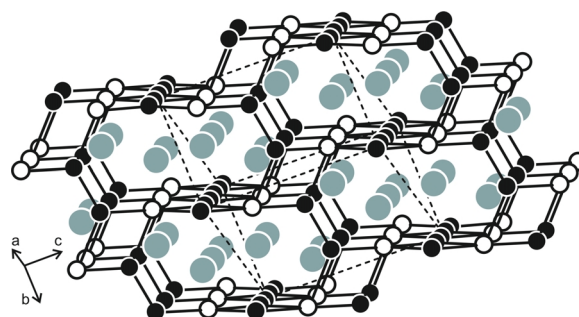


Fig. 1. The crystal structure of $\text{Sr}_2\text{Pt}_2\text{In}$. The strontium, platinum, and indium atoms are drawn as medium grey, black, and open circles, respectively. The three-dimensional $[\text{Pt}_2\text{In}]$ network is emphasized. For details see text.

compounds. As an example, a view of the $\text{Sr}_2\text{Pt}_2\text{In}$ structure approximately along the $[110]$ direction is shown in Fig. 1. The shortest interatomic distances in this structure occur for Pt–Pt (271 pm) and Pt–In (273–276 pm). Together, the platinum and indium atoms build up a three-dimensional polyanionic network which consists of Pt_2 dumb-bells that are bridged *via* the indium atoms. Larger channels within this network extend along the $[110]$ direction. They are filled by the strontium atoms. In agreement with the course of the electronegativities, bonding of strontium to the $[\text{Pt}_2\text{In}]$ network proceeds *via* shorter Sr–Pt contacts (319–326 pm), similar to SrPtIn [13]. For a more detailed discussion on the coordination polyhedra in this structure type we refer to the previous work on $\text{Ca}_2\text{Pd}_2\text{In}$ and $\text{Ca}_2\text{Pt}_2\text{In}$ [25].

Finally we revert to the differences between the palladium and platinum compounds in both series. Although the Pt–Pt distances are slightly longer in *fcc* platinum with respect to *fcc* palladium [32] (the same holds true for the course of the covalent radii [33]), the cell volumes of $\text{Ca}_2\text{Pt}_2\text{In}$ and $\text{Sr}_2\text{Pt}_2\text{In}$ are about 2 % smaller than those of the corresponding palladium compounds. Similar volume reduction occurs for the pairs SrPtIn [13] and SrPdIn [12] as well as for the binary alkaline earth (AE) compounds $\text{AEPd}_5 \rightleftharpoons \text{AEPt}_5$ and $\text{AEPd}_2 \rightleftharpoons \text{AEPt}_2$ [34]. This peculiar behavior is most likely related to the relativistically caused contraction (stabilization) of the platinum 6s orbitals [35, 36].

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- [1] R. Pöttgen, *J. Mater. Chem.* **1996**, 6, 63.
- [2] T. Ito, S. Nishigori, I. Hiromitsu, M. Kurisu, *J. Magn. Magn. Mater.* **1998**, 177, 1079.
- [3] R. Müllmann, B. D. Mosel, H. Eckert, G. Kotzyba, R. Pöttgen, *J. Solid State Chem.* **1998**, 137, 174.
- [4] R. Pöttgen, D. Kußmann, *Z. Anorg. Allg. Chem.* **2001**, 627, 55.
- [5] V. Fritsch, S. Bobev, N. O. Moreno, Z. Fisk, J. D. Thompson, J. L. Sarrao, *Phys. Rev. B* **2004**, 70, 052410.
- [6] S. K. Malik, R. Vijayaraghavan, D. T. Adroja, B. D. Padalia, A. S. Edelstein, *J. Magn. Magn. Mater.* **1990**, 92, 80.
- [7] Ya. M. Kalychak, V. I. Zaremba, R. Pöttgen, M. Lukachuk, R.-D. Hoffmann in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 34 (Eds.: K. A. Gschneidner Jr., V. K. Pecharsky, J.-C. Bünzli), Elsevier, Amsterdam, **2005**, chapter 218.
- [8] R. D. Shannon, *Acta Crystallogr.* **1976**, A32, 751.
- [9] H. Bärnighausen, G. Brauer, *Acta Crystallogr.* **1962**, 15, 1059.
- [10] R. C. Rau, *Acta Crystallogr.* **1966**, 20, 716.
- [11] H. H. Wickman, E. Catalano, *J. Appl. Phys.* **1968**, 39, 1248.
- [12] S. Cirafici, A. Palenzona, F. Canepa, *J. Less-Common Met.* **1985**, 107, 179.
- [13] R.-D. Hoffmann, R. Pöttgen, *Z. Anorg. Allg. Chem.* **1999**, 625, 994.
- [14] I. Muts, V. I. Zaremba, R. Pöttgen, *Z. Anorg. Allg. Chem.* **2007**, 633, 2234.
- [15] R.-D. Hoffmann, U. Ch. Rodewald, R. Pöttgen, *Z. Naturforsch.* **1999**, 54b, 38.
- [16] I. Muts, V. I. Zaremba, R. Pöttgen, *Z. Anorg. Allg. Chem.*, in press.
- [17] I. Muts, V. I. Zaremba, V. V. Baran, R. Pöttgen, *Z. Naturforsch.* **2007**, 62b, 1407.
- [18] I. R. Muts, F. M. Schappacher, W. Hermes, V. I. Zaremba, R. Pöttgen, *J. Solid State Chem.* **2007**, 180, 2202.
- [19] R.-D. Hoffmann, R. Pöttgen, C. Rosenhahn, B. D. Mosel, B. Künnen, G. Kotzyba, *J. Solid State Chem.* **1999**, 145, 283.
- [20] S. Liu, J. D. Corbett, *Inorg. Chem.* **2004**, 43, 4988.
- [21] A. V. Tkachuk, A. Mar, *J. Solid State Chem.* **2007**, 180, 2298.
- [22] R.-D. Hoffmann, D. Kußmann, R. Pöttgen, *Int. J. Inorg. Mater.* **2000**, 2, 135.
- [23] V. I. Zaremba, I. R. Muts, R.-D. Hoffmann, R. Pöttgen, *Z. Anorg. Allg. Chem.* **2003**, 629, 2330.
- [24] I. Muts, R.-D. Hoffmann, R. Pöttgen, Ya. M. Kalychak, V. I. Zaremba, *IXth International Conference on Crystal Chemistry of Intermetallic Compounds*, Lviv, **2005**, P62.
- [25] I. Muts, V. I. Zaremba, R. Pöttgen, *Z. Anorg. Allg. Chem.*, in press.
- [26] I. Muts, V. I. Zaremba, R. Pöttgen, *Z. Anorg. Allg. Chem.*, in press.
- [27] R. Pöttgen, Th. Gulden, A. Simon, *GIT Labor-Fachzeitschrift* **1999**, 43, 133.
- [28] D. Kußmann, R.-D. Hoffmann, R. Pöttgen, *Z. Anorg. Allg. Chem.* **1998**, 624, 1727.
- [29] K. Yvon, W. Jeitschko, E. Parthé, *J. Appl. Crystallogr.* **1977**, 10, 73.
- [30] M. Pani, F. Merlo, M. L. Fornasini, *Z. Kristallogr.* **2002**, 217, 415.
- [31] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.
- [32] J. Donohue, *The Structures of the Elements*, Wiley, New York, **1974**.
- [33] J. Emsley, *The Elements*, Oxford University Press, Oxford, **1999**.
- [34] Th. Heumann, M. Kniepmeyer, *Z. Anorg. Allg. Chem.* **1957**, 290, 191.
- [35] P. Pykkö, *Chem. Rev.* **1988**, 88, 563.
- [36] N. Wiberg, *Holleman-Wiberg, Lehrbuch der Anorganischen Chemie*, 102nd Ed. **2007**, p. 340.