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Sr_7Pt_3: An Orthorhombic Structure Formed by Pt-Centered Trigonal Prisms

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The phase Sr_7Pt_3 is orthorhombic, space group *Pnma*, with $a = 7.929$ (1), $b = 24.326$ (6), $c = 7.100$ (4) Å, $Z = 4$. Direct methods were used for the structure resolution and anisotropic refinement led to an R value of 0.065 for 535 reflections, collected on a four-circle diffractometer. The structure consists of trigonal prisms of Sr atoms centered by Pt and arranged in nets, analogous to those found in the Fe_3C and Mn_5C_2 types. Differently from Fe_3C (isolated nets) and Mn_5C_2 (double nets), the nets are here joined three by three through prism edges, forming slabs along the b axis. A description of the structure in terms of unit cell microtwinning is provided.

Introduction

The study of the binary phase diagram Sr–Pt (*1*) led to the discovery of four new intermetallic compounds, two of which (Sr_5Pt_4 and Sr_3Pt_2) were completely identified, while the remaining two (Sr_7Pt_3 and Sr_9Pt) showed unknown structures. Preliminary single crystal investigations on Sr_7Pt_3 led to its assignment to orthorhombic symmetry in the possible space group *Pnma*, and yielded approximate lattice constant values.

As several R_7X_3 phases are found for the rare earth–transition metal intermetallics, all crystallizing with the hexagonal Th_7Fe_3 type, it seemed useful to undertake the determination of the crystal structure of Sr_7Pt_3, which is the first phase formed by the alkaline earths with a transition element on this composition.

Experimental

The sample preparation was described elsewhere (*1*). A plate-like single crystal with approximate dimensions 0.08 × 0.07 × 0.02 mm was chosen and sealed under vacuum in a thin glass capillary. Cell constants were obtained by least squares from 25 reflections measured with an Enraf-Nonius CAD-4 automatic diffractometer, used also for the data collection (graphite-monochromated Mo$K\alpha$ radiation): $a = 7.929$ (1), $b = 24.326$ (6), $c = 7.100$ (4) Å. The orthorhombic symmetry and systematic extinctions were confirmed; $0kl$ reflections were present only for $k + l = 2n$, and $hk0$ present only for $h = 2n$ indicating that the space groups were $Pn2_1a$ and *Pnma*.

As the ratio between maximum and minimum intensity during the ψ scan of a top reflection was nearly six ($\mu = 60.3$ mm^{-1}),

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TABLE I

ATOMIC COORDINATES, EQUIVALENT TEMPERATURE FACTOR, AND ANISOTROPIC THERMAL PARAMETERS ($\times 10^3$) OF Sr_7Pt_3

	x	y	z	B_{eq} (Å^2)[a]	U_{11}[b]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr(1)	0.3212(7)[c]	0.1744(3)	0.1829(9)	1.45(1)	13(2)	17(3)	25(3)	−3(3)	−2(3)	0(2)
Sr(2)	0.3298(8)	0.0216(3)	0.1808(10)	1.89(2)	20(3)	25(4)	27(4)	−4(3)	5(2)	2(3)
Sr(3)	0.4590(7)	0.1158(3)	0.6514(9)	1.89(2)	12(3)	32(4)	28(4)	−1(3)	−6(3)	−1(3)
Sr(4)	0.1764(11)	$\frac{1}{4}$	0.6444(14)	2.55(3)	13(4)	59(8)	25(6)	0	5(4)	0
Pt(1)	0.1184(3)	0.0966(1)	0.4615(4)	2.03(1)	11(1)	40(2)	26(1)	2(2)	1(1)	1(1)
Pt(2)	0.0226(4)	$\frac{1}{4}$	0.0364(6)	2.00(1)	9(1)	43(3)	24(2)	0	1(2)	0

[a] The equivalent isotropic temperature factor is computed according to the relation $B_{eq} = \frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33})$.

[b] Thermal parameters are defined by $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^*)]$.

[c] e.s.d. in parentheses.

and taking into account the particular shape of the crystal, the data collection was carried out with the option FLAT, allowing each reflection to be measured at the appropriate ψ angle minimizing absorption. Intensities of 3136 hkl and $\bar{h}kl$ reflections were collected in the ω-scan mode, with scan width 1° and θ range from 2 to 27.5°. After applying Lorentz and polarization corrections, equivalent reflections were averaged, giving 1602 independent ones.

Structure Determination

Comparing the cell volume with that calculated with the elemental atomic values, four Sr_7Pt_3 formulae per cell could be assigned. The MULTAN 80 (*2*) and SHELX 76 (*3*) programs were employed for the structure resolution and refinement, respectively, taking atomic scattering factors and anomalous dispersion corrections from (*4*). MULTAN gave rise to an acceptable model in the centrosymmetric space group *Pnma*, indicated by statistical tests as the most probable one, allowing 28 Sr and 12 Pt atoms to be located.

Three cycles of isotropic least squares refinement were followed by three other cycles of anisotropic refinement of 49 parameters over 535 reflections with $F_0 > 2\sigma(F_0)$ and weights $w = [\sigma^2(F_0) + 0.024\, F_0^2]^{-1}$, obtaining at convergence a final R index of 0.065. Table I lists the positional and anisotropic thermal parameters.[1]

Discussion

In the structure of Sr_7Pt_3, shown in projection along the c axis in Fig. 1, the Sr atoms occupy the vertices of trigonal prisms, which are centered by Pt and arranged in nets perpendicular to the b axis. The nets are joined by prism edges to form three-membered slabs along the same b axis.

There is a close relationship between this structure and the well known orthorhombic Fe_3C and monoclinic Mn_5C_2 types (*5*), found for numerous rare earth–transition metal compounds. The same nets of trigonal prisms are present, but linked in a different way in the three structures: isolated nets in Fe_3C, nets joined two by two in Mn_5C_2, and nets joined three by three in Sr_7Pt_3. Thus, the c/a ratio between the lattice constants of the orthorhombic phases (or b/c of the monoclinic ones) is nearly equal, despite the change in stoichiometry

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[1] The list of observed and calculated structure factors can be obtained from the authors.

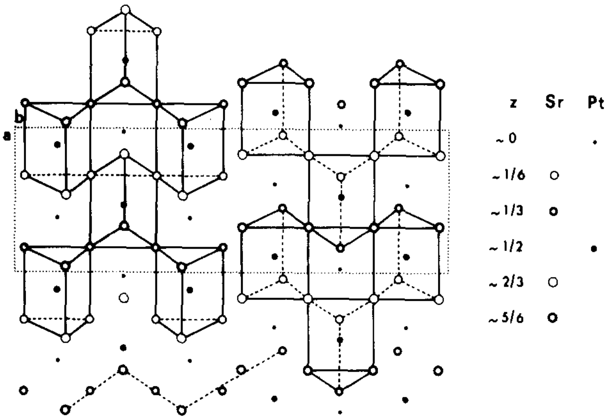

FIG. 1. Projection of the structure of Sr_7Pt_3 along the *c* axis, showing the Pt-centered Sr trigonal prisms. In the lower part the untwinned segment sequence is indicated by dashed lines (see text).

and in the alloying partners, while the different linkage of the prism nets along the third direction regulates the value of the lattice constant *b* for the orthorhombic phases (or *a* for the monoclinic ones).

Andersson and Hyde (*6*) and Parthé (*7*) derived and related a great number of structures using the unit cell twinning concept. They demonstrated that the application of periodic twin planes to a hexagonal or cubic close-packed lattice of atoms leads to structures characterized by different size and sequence of the untwinned segments, where the trigonal prismatic holes created on the twin planes can be occupied by the alloying partner. In particular, for the Fe_3C and Mn_5C_2 structures, obtained from a hexagonal close-packed lattice of Fe or Mn atoms, Andersson and Hyde (*6*) specified the segment sequence 4,4,4, . . . and 3,4,3,4, . . ., respectively. The same criterion may be applied to the structure of Sr_7Pt_3, also based on a hexagonal close-packed lattice of Sr atoms, and in the lower part of Fig. 1 the segment sequence is outlined: 3,3,4,3,3,4, ... Likewise Sr_7Pt_3, the hexagonal Th_7Fe_3 structure type (*5*), adopted by many rare earth–transition metal intermetallic phases, involves Fe-centered trigonal prisms of Th, and is derivable (*8*) with the periodic twinning concept, starting from a hexagonal close-packed lattice, but with a different twin mechanism: in place of parallel twin planes, in Th_7Fe_3 three twin planes intersect according to a threefold symmetry and give rise to a triple twinning.

Table II lists the interatomic distances in Sr_7Pt_3. The closest Sr–Pt distances (3.03 to 3.19 Å) involve Sr atoms belonging to the trigonal prisms, while other Sr atoms emerge from the lateral faces of the prisms, one at 3.30 Å for Pt(1), and two at 3.56 Å for Pt(2). The Sr–Sr bonds range in length from 3.68 to 4.52 Å, while no Pt–Pt bonds are present. The shortest Sr–Sr contact, contracted by 14% with respect to a Sr diameter (*9*), is not unusual; in the literature other similar values can be found, e.g., 3.54 Å in Sr_2Bi (*10*) and in Sr_2Sb (*11*), and 3.71 Å in Sr_5Sb_3 (*12*).

In the Sr–Pt system the structures of the Sr-rich phases, excepting Sr_9Pt, are now all known. The Pt element is always surrounded by a trigonal prism of Sr atoms, with some further atom capping the lateral faces. Concerning the Pt–Pt interactions, one should note that couples of Pt occur in Sr_5Pt_4 (Pu_5Rh_4-type) and in Sr_3Pt_2 (Er_3Ni_2-type), whereas "isolated" Pt occurs in

Sr_7Pt_3. This is the normal situation: decreasing the Pt content, decreases also the number of Pt–Pt contacts in the corresponding structure.

TABLE II

INTERATOMIC DISTANCES (Å) IN Sr_7Pt_3[a]

Sr(1)–	Pt(2)	3.15
	– Pt(2)	3.17
	– Pt(1)	3.17
	– Pt(1)	3.19
	– Sr(1)	3.68
	– Sr(2)	3.72
	– Sr(3)	3.78
	– Sr(4)	3.93
	– Sr(3)	3.99
	–2Sr(1)	4.08
	– Sr(4)	4.09
	– Sr(3)	4.18
	– Sr(4)	4.40
Sr(2)–	Pt(1)	3.10
	– Pt(1)	3.18
	– Pt(1)	3.30
	– Sr(1)	3.72
	– Sr(2)	3.87
	–2Sr(2)	3.91
	– Sr(3)	3.92
	– Sr(3)	4.06
	–2Sr(2)	4.08
	– Sr(3)	4.18
	– Sr(3)	4.41
	– Sr(3)	4.52
Pt(1)–	Sr(3)	3.05
	– Sr(3)	3.06
	– Sr(2)	3.10
	– Sr(1)	3.17
	– Sr(2)	3.18
	– Sr(1)	3.19
	– Sr(2)	3.30
Sr(3)–	Pt(1)	3.05
	– Pt(1)	3.06
	– Pt(2)	3.56
	– Sr(1)	3.78
	– Sr(2)	3.92
	– Sr(4)	3.96
	– Sr(4)	3.97
	– Sr(1)	3.99
	– Sr(2)	4.06
	– Sr(2)	4.18
	– Sr(1)	4.18
	–2Sr(3)	4.20
	– Sr(2)	4.41
	– Sr(2)	4.52
Sr(4)–	Pt(2)	3.03
	– Pt(2)	3.04
	–2Sr(1)	3.93
	–2Sr(3)	3.96
	–2Sr(3)	3.97
	–2Sr(1)	4.09
	–2Sr(4)	4.24
	–2Sr(1)	4.40
Pt(2)–	Sr(4)	3.03
	– Sr(4)	3.04
	–2Sr(1)	3.15
	–2Sr(1)	3.17
	–2Sr(3)	3.56

[a] The e.s.d. are less equal to 0.01 Å.

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