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# The Stannides $RE_2Ni_2Sn$ ( $RE = Pr, Ho, Er, Tm$ ) – Structural Transition from the $W_2B_2Co$ to the $Mo_2B_2Fe$ Type as a Function of the Rare Earth Size

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The stannides  $RE_2Ni_2Sn$  ( $RE = Pr, Ho, Er, Tm$ ) were synthesized by arc-melting of the elements and characterized by powder X-ray diffraction.  $Pr_2Ni_2Sn$  crystallizes with the orthorhombic  $W_2B_2Co$ -type structure,  $Immm$ ,  $a = 443.8(1)$ ,  $b = 572.1(1)$ ,  $c = 855.1(2)$  pm,  $wR2 = 0.0693$ , 293  $F^2$  values, 13 variables. A structural transition to the tetragonal  $Mo_2B_2Fe$  type occurs for the heavier rare earth elements. The structures of  $Ho_2Ni_2Sn$  ( $a = 729.26(9)$ ,  $c = 366.66(7)$  pm,  $wR2 = 0.0504$ , 250  $F^2$  values, 12 variables),  $Er_2Ni_2Sn$  ( $a = 727.2(2)$ ,  $c = 364.3(1)$  pm,  $wR2 = 0.0397$ , 262  $F^2$  values, 12 variables), and  $Tm_2Ni_2Sn$  ( $a = 725.2(1)$ ,  $c = 362.8(1)$  pm,  $wR2 = 0.0545$ , 258  $F^2$  values, 12 variables) were refined from single-crystal diffractometer data. The switch in structure type is driven by the size of the rare earth element. The  $[Ni_2Sn]$  substructures are composed of  $Ni_2Sn_2$  squares and  $Ni_4Sn_2$  hexagons in  $Pr_2Ni_2Sn$ , and of  $Ni_3Sn_2$  pentagons in  $Er_2Ni_2Sn$ . The  $Ni_4Sn_2$  hexagons and  $Ni_3Sn_2$  pentagons exhibit  $Ni_2$  pairs with Ni–Ni distances of 247 pm in  $Pr_2Ni_2Sn$ , and of 250 pm in  $Er_2Ni_2Sn$ .

**Key words:** Stannides, Crystal Structure, Lanthanoid Contraction

## Introduction

The ternary rare earth ( $RE$ ) compounds of the general composition  $RE_2T_2X$  ( $T =$  electron-rich transition metal;  $X = Mg, Zn, Cd, Al, Ga, In, Sn, Pb$ ) crystallize with three different structure types, depending on the size of the atoms and the valence electron concentration (VEC): (i) the tetragonal  $Mo_2B_2Fe$  type, space group  $P4/mbm$  [1] (a ternary ordered version of the  $U_3Si_2$  structure), (ii) the orthorhombic  $Mn_2B_2Al$  type [2], space group  $Cmmm$ , and (iii) the orthorhombic  $Co_2B_2W$  type [3], space group  $Immm$ . Most representatives occur for the  $Mo_2B_2Fe$  type [4]. The common structural motif of these three structure types are transition metal-centered trigonal prisms. Exemplarily we present projections of the  $Pr_2Ni_2Sn$ ,  $Er_2Ni_2Sn$ , and  $Er_2Ni_2Pb$  [5] structures in Fig. 1.

Several series of the  $RE_2T_2X$  intermetallics show structural transitions as a function of the rare earth element (lanthanoid contraction) or the chemical composition. If the radii criteria do not match for a  $Mo_2B_2Fe$ -

type structural arrangement, superstructure formation with small distortions is possible. This has first been observed for the ternary stannides  $Er_2Au_2Sn$  [6] and  $U_2Pt_2Sn$  [7]. Other compounds show the formation of defects on the transition metal site, e. g.  $RE_2Ni_{2-x}Cd$  [8, 9] and  $RE_2Ni_{2-x}In$  [10]. In case of the indides, the phases with a nickel defect crystallize with the tetragonal  $Mo_2B_2Fe$  type, while those with the ideal composition adopt the orthorhombic  $Mn_2B_2Al$  structure. The cadmium compounds [9] crystallize with a tetragonal  $Mo_2B_2Fe$  type and an orthorhombic  $Mn_2B_2Al$  type, respectively, in the low- and the high-temperature modification. This phase transition is of reconstructive nature.

In continuation of our systematic studies of  $RE_2T_2X$  intermetallics we have recently investigated the  $RE_2Ni_2Sn$  series with the heavier rare earth elements. The representatives with the early rare earth elements [11–32] crystallize with the  $W_2B_2Co$ -type structure. Especially  $Ce_2Ni_2Sn$  [12–14, 16–18, 22–24, 26, 27] has intensively been studied. This stan-

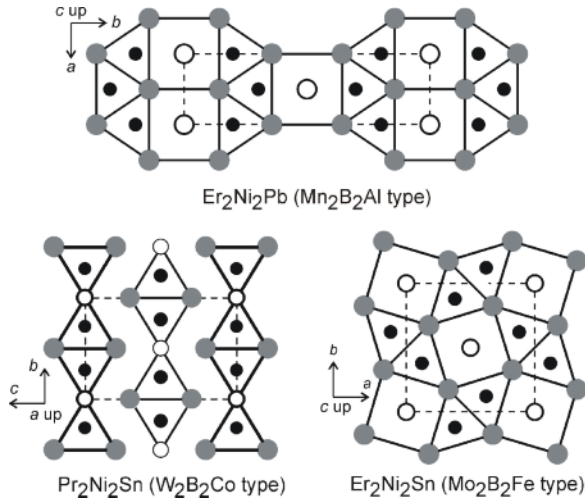


Fig. 1. Projections of the  $Pr_2Ni_2Sn$ ,  $Er_2Ni_2Sn$ , and  $Er_2Ni_2Pb$  structures along the short unit cell axis. Rare earth, nickel and tin (or lead) atoms are drawn as medium grey, black filled, and open circles, respectively. The trigonal prismatic slabs around the nickel atoms are emphasized.

nide behaves like a Kondo system and orders antiferromagnetically at  $T_N = 4.7$  K. Above  $T_N$ ,  $Ce_2Ni_2Sn$  shows a large negative magnetoresistance ( $\cong -20\%$  at 6 K and for an applied magnetic field of 9 T) mainly due to the Kondo effect.

The smallest rare earth element for which the  $W_2B_2Co$ -type structure is realized is dysprosium. Our current studies have revealed a switch in structure type from  $Ho_2Ni_2Sn$  on. The ternary holmium, erbium and thulium stannides reported herein crystallize with the tetragonal  $Mo_2B_2Fe$  type, similar to  $Lu_2Ni_2Sn$  [31]. Furthermore we obtained the new stannide  $Pr_2Ni_2Sn$  with the  $W_2B_2Co$  type.

## Experimental

### Synthesis

Starting materials for the syntheses of the  $RE_2Ni_2Sn$  stannides were sublimed pieces of the rare earth metals (Kelpin, Chempur, or smart elements,  $> 99.9\%$ ), nickel wire (Alfa-Aesar,  $\varnothing$  1 mm,  $> 99.5\%$ ), and tin granules (Merck,  $> 99.9\%$ ).  $Pr_2Ni_2Sn$  was obtained by arc-melting [33] pieces of the three elements under an argon atmosphere of ca. 700 mbar. The argon was purified over titanium sponge (900 K), silica gel, and molecular sieves. The arc-melted button was sealed in an evacuated silica tube and annealed at 1070 K for one week. Synthesis attempts for  $RE_2Ni_2Sn$  with

$RE = Ho, Er,$  and  $Tm$  with the ideal starting 2 : 2 : 1 composition resulted in considerable amounts of the equiatomic  $RENiSn$  phases (orthorhombic  $TiNiSi$  type) as by-products. No  $RE_2Ni_2Sn$  single crystals were obtained. After inspection of the  $RE-Ni-Sn$  phase diagrams with  $RE = Y$  [32],  $Nd$  [28],  $Gd$  [30],  $Dy$  [29], and  $Lu$  [31] we used the starting compositions  $42RE : 40Ni : 18Sn$  for the heavy rare earth elements. After arc-melting these samples we obtained the missing  $RE_2Ni_2Sn$  stannides. Only trace amounts of the  $RENiSn$  phases were evident. The  $RE_2Ni_2Sn$  stannides are air stable over months.

### EDX data

Semiquantitative EDX analyses of the single crystals studied on the diffractometers were carried out in variable pressure mode with a Zeiss EVO<sup>®</sup> MA10 scanning electron microscope with the rare earth trifluorides, nickel, and tin as standards. The experimentally observed average compositions were close to the ideal ones. No impurity elements were detected.

### X-Ray diffraction

All polycrystalline  $RE_2Ni_2Sn$  samples were characterized by powder X-ray diffraction using the Guinier technique: imaging plate detector, Fujifilm BAS-1800,  $Cu K\alpha_1$  radiation and  $\alpha$ -quartz ( $a = 491.30$ ,  $c = 540.46$  pm) as an internal standard. The lattice parameters (Table 1) were refined from the Guinier powder data using a standard least-squares routine. The experimental patterns were compared to calculated ones [34] in order to assure correct indexing.

Small single crystals of  $Pr_2Ni_2Sn$  were selected from the crushed annealed sample, while those of  $Ho_2Ni_2Sn$ ,  $Er_2Ni_2Sn$ , and  $Tm_2Ni_2Sn$  were taken directly from the arc-melted samples. The crystals were glued to quartz fibers using beeswax and characterized on a Buerger camera (using white Mo radiation) to check their quality. The intensity data collection from suitable  $Pr_2Ni_2Sn$ ,  $Er_2Ni_2Sn$ , and  $Tm_2Ni_2Sn$  crystals was performed on a Stoe IPDS-II image plate system (graphite-monochromatized  $Mo K\alpha$  radiation;  $\lambda = 71.073$  pm) in oscillation mode. The  $Ho_2Ni_2Sn$  data set was measured on a Stoe Stadi Vari diffractometer equipped with a Mo micro focus source and a Pilatus detection system and scaled subsequently according to the Gaussian-shaped profile of the X-ray source. Numerical absorption corrections were applied to all data sets. Details about the data collections and the crystallographic parameters are summarized in Table 2.

### Structure refinements

Isotypism of  $Pr_2Ni_2Sn$  with  $W_2B_2Co$  and of  $RE_2Ni_2Sn$  ( $RE = Ho, Er, Tm$ ) with  $Mo_2B_2Fe$  was already evident

Compound	Structure type	Space group	$a$ (pm)	$b$ (pm)	$c$ (pm)	$V$ (nm <sup>3</sup> )	Reference
Sc <sub>2</sub> Ni <sub>2</sub> Sn	Mo <sub>2</sub> FeB <sub>2</sub>	$P4/mbm$	709.28(4)	$a$	338.00(3)	0.1700	[11]
Y <sub>2</sub> Ni <sub>2</sub> Sn	W <sub>2</sub> CoB <sub>2</sub>	$Immm$	425.7(2)	558.5(2)	835.1(4)	0.1985	[32]
Ce <sub>2</sub> Ni <sub>2</sub> Sn	W <sub>2</sub> CoB <sub>2</sub>	$Immm$	439.1(2)	573.0(3)	858.6(4)	0.2160	[27]
Ce <sub>2</sub> Ni <sub>2</sub> Sn	W <sub>2</sub> CoB <sub>2</sub>	$Immm$	439.1(1)	573.5(2)	859.1(3)	0.2163	[13]
Ce <sub>2</sub> Ni <sub>2</sub> Sn	W <sub>2</sub> CoB <sub>2</sub>	$Immm$	439.36(9)	573.96(9)	859.67(13)	0.2168	[12]
Pr <sub>2</sub> Ni <sub>2</sub> Sn	W <sub>2</sub> CoB <sub>2</sub>	$Immm$	438.0(1)	572.1(1)	855.1(2)	0.2171	this work
Nd <sub>2</sub> Ni <sub>2</sub> Sn	W <sub>2</sub> CoB <sub>2</sub>	$Immm$	436.2(2)	570.1(3)	850.3(5)	0.2114	[27]
Nd <sub>2</sub> Ni <sub>2</sub> Sn	W <sub>2</sub> CoB <sub>2</sub>	$Immm$	436.0(1)	569.5(2)	849.8(2)	0.2110	[14]
Nd <sub>2</sub> Ni <sub>2</sub> Sn	W <sub>2</sub> CoB <sub>2</sub>	$Immm$	435.8(2)	569.2(1)	849.5(3)	0.2107	[28]
Sm <sub>2</sub> Ni <sub>2</sub> Sn	W <sub>2</sub> CoB <sub>2</sub>	$Immm$	432.1(3)	567.0(3)	841.8(4)	0.2070	[27]
Gd <sub>2</sub> Ni <sub>2</sub> Sn	W <sub>2</sub> CoB <sub>2</sub>	$Immm$	429.1(3)	563.2(4)	839.1(7)	0.2028	[27]
Gd <sub>2</sub> Ni <sub>2</sub> Sn	W <sub>2</sub> CoB <sub>2</sub>	$Immm$	429.4(1)	563.8(1)	839.0(1)	0.2031	[20]
Tb <sub>2</sub> Ni <sub>2</sub> Sn	W <sub>2</sub> CoB <sub>2</sub>	$Immm$	427.7(3)	560.9(4)	832.3(5)	0.1996	[27]
Tb <sub>2</sub> Ni <sub>2</sub> Sn	W <sub>2</sub> CoB <sub>2</sub>	$Immm$	427.8(1)	561.4(1)	833.2(1)	0.2001	[20]
Dy <sub>2</sub> Ni <sub>2</sub> Sn	W <sub>2</sub> CoB <sub>2</sub>	$Immm$	424.7(1)	561.5(1)	827.3(1)	0.1973	[20]
Ho <sub>2</sub> Ni <sub>2</sub> Sn	Mo <sub>2</sub> FeB <sub>2</sub>	$P4/mbm$	729.26(9)	$a$	366.66(7)	0.1950	this work
Er <sub>2</sub> Ni <sub>2</sub> Sn	Mo <sub>2</sub> FeB <sub>2</sub>	$P4/mbm$	727.2(2)	$a$	364.3(1)	0.1927	this work
Tm <sub>2</sub> Ni <sub>2</sub> Sn	Mo <sub>2</sub> FeB <sub>2</sub>	$P4/mbm$	725.2(1)	$a$	362.8(1)	0.1908	this work
Lu <sub>2</sub> Ni <sub>2</sub> Sn	Mo <sub>2</sub> FeB <sub>2</sub>	$P4/mbm$	723.8(3)	$a$	360.2(1)	0.1887	[31]

Table 1. Lattice parameters (Guinier powder data) of  $RE_2Ni_2Sn$  compounds. Standard deviations are given in parentheses.

Table 2. Crystal data and structure refinement results for the stannides  $RE_2Ni_2Sn$ .

Compound	Pr <sub>2</sub> Ni <sub>2</sub> Sn	Ho <sub>2</sub> Ni <sub>2</sub> Sn	Er <sub>2</sub> Ni <sub>2</sub> Sn	Tm <sub>2</sub> Ni <sub>2</sub> Sn
Space group, $Z$	$Immm, 2$	$P4/mbm, 2$	$P4/mbm, 2$	$P4/mbm, 2$
Structure type	W <sub>2</sub> B <sub>2</sub> Co	Mo <sub>2</sub> B <sub>2</sub> Fe	Mo <sub>2</sub> B <sub>2</sub> Fe	Mo <sub>2</sub> B <sub>2</sub> Fe
Molar mass, g mol <sup>-1</sup>	517.93	565.97	570.63	573.97
Calculated density, g cm <sup>-3</sup>	7.92	9.64	9.84	9.99
Absorption coefficient, mm <sup>-1</sup>	36.0	55.6	58.8	61.9
$F(000), e$	448	480	484	488
Crystal size, $\mu\text{m}^3$	10 × 20 × 40	20 × 20 × 90	10 × 40 × 50	10 × 30 × 60
Transm. ratio (max / min)	0.782 / 0.379	0.474 / 0.211	0.593 / 0.125	0.502 / 0.218
Diffraktometer	IPDSII	StadiVari	IPDSII	IPDSII
X-Ray source, Mo	sealed tube	GeniX <sup>3D</sup>	sealed tube	sealed tube
Detector	Imaging Plate	PILATUS 100K	Imaging Plate	Imaging Plate
Detector distance, mm	60	70	60	60
Exposure time, sec	600	12	600	300
$\omega$ range increment, deg	1.0	0.3	1.0	1.0
Integr. parameter A, B, EMS	12.8, 3.0, 0.012	7.3, -5.3, 0.013	13.0, 3.0, 0.012	12.9, 3.0, 0.012
$\theta$ range, deg	4–35	4–34	4–35	4–35
Range in $hkl$	±7, ±9, ±13	±11, ±11, ±5	±11, ±11, +5	±11, ±11, ±5
Total no. reflections	1736	2823	1584	2847
Independent reflections / $R_{\text{int}}$	293 / 0.0728	250 / 0.0363	262 / 0.0119	258 / 0.0487
Reflections with $I > 2\sigma(I)/R_{\sigma}$	243 / 0.0476	220 / 0.0214	256 / 0.0092	234 / 0.0206
Data / parameters	293 / 13	250 / 12	245 / 12	258 / 12
Goodness-of-fit on $F^2$	0.994	1.017	1.341	1.164
$R1 / wR2$ for $I > 2\sigma(I)$	0.0303 / 0.0656	0.0211 / 0.0499	0.0180 / 0.0389	0.0254 / 0.0530
$R1 / wR2$ for all data	0.0417 / 0.0693	0.0244 / 0.0504	0.0208 / 0.0397	0.0317 / 0.0545
Extinction coefficient	0.0041(9)	0.0057(8)	0.0027(4)	0.0033(7)
Largest diff. peak / hole, e Å <sup>-3</sup>	2.10 / -2.40	1.66 / -1.73	2.11 / -1.36	2.38 / -3.34

from the Guinier powder data. The systematic extinctions of the data sets were compatible with space groups  $Immm$  and  $P4/mbm$ , respectively. The atomic parameters of orthorhombic Ce<sub>2</sub>Ni<sub>2</sub>Sn [12] and tetragonal Ce<sub>2</sub>Pt<sub>2</sub>In [35] were taken as starting values, and the four structures were refined with anisotropic displacement parameters for all atoms

with SHELXL-97 (full-matrix least-squares on  $F_o^2$ ) [36, 37]. Since the crystals of the  $RE_2Ni_2Sn$  stannides with the heavy rare earth elements were taken from samples of the starting compositions 42RE : 40Ni : 18Sn, the occupancy parameters were refined in separate series of least-squares cycles for all data sets. All sites were fully occupied within two

Table 3. Atomic coordinates and isotropic displacement parameters ( $\text{pm}^2$ ) of  $RE_2Ni_2Sn$  compounds.  $U_{13} = U_{23} = 0$ .  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Atom	Wyckoff position	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{eq}$
<b>Pr<sub>2</sub>Ni<sub>2</sub>Sn</b>									
Pr	4 <i>j</i>	1/2	0	0.29695(8)	145(3)	117(3)	116(3)	0	126(2)
Ni	4 <i>h</i>	0	0.2156(3)	1/2	158(7)	208(8)	149(7)	0	172(3)
Sn	2 <i>a</i>	0	0	0	128(5)	106(4)	125(4)	0	120(2)
<b>Ho<sub>2</sub>Ni<sub>2</sub>Sn</b>									
Ho	4 <i>h</i>	0.17493(4)	1/2 + $x$	1/2	137(2)	$U_{11}$	119(2)	-11(1)	131(2)
Ni	4 <i>g</i>	0.37885(14)	1/2 + $x$	0	172(4)	$U_{11}$	164(6)	-26(4)	169(3)
Sn	2 <i>a</i>	0	0	0	123(3)	$U_{11}$	172(5)	0	139(2)
<b>Er<sub>2</sub>Ni<sub>2</sub>Sn</b>									
Er	4 <i>h</i>	0.17434(3)	1/2 + $x$	1/2	107(1)	$U_{11}$	89(2)	-13(1)	101(1)
Ni	4 <i>g</i>	0.37864(12)	1/2 + $x$	0	137(3)	$U_{11}$	133(5)	-25(4)	136(2)
Sn	2 <i>a</i>	0	0	0	90(2)	$U_{11}$	139(3)	0	106(2)
<b>Tm<sub>2</sub>Ni<sub>2</sub>Sn</b>									
Tm	4 <i>h</i>	0.17403(5)	1/2 + $x$	1/2	113(2)	$U_{11}$	88(2)	-11(2)	105(2)
Ni	4 <i>g</i>	0.37843(17)	1/2 + $x$	0	143(5)	$U_{11}$	134(6)	-26(5)	140(3)
Sn	2 <i>a</i>	0	0	0	97(3)	$U_{11}$	132(4)	0	109(2)

standard deviations, and the ideal compositions were assumed again in the following cycles. The final difference Fourier syntheses revealed no residual peaks. The refined atomic positions, equivalent isotropic displacement parameters, and interatomic distances (exemplarily for  $Pr_2Ni_2Sn$  and  $Er_2Ni_2Sn$ ) are given in Tables 3 and 4.

Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; E-mail: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de), [http://www.fiz-karlsruhe.de/request\\_for\\_deposited\\_data.html](http://www.fiz-karlsruhe.de/request_for_deposited_data.html)) on quoting the deposition number CSD-425429 ( $Pr_2Ni_2Sn$ ), CSD-425430 ( $Ho_2Ni_2Sn$ ), CSD-425431 ( $Er_2Ni_2Sn$ ), and CSD-425432 ( $Tm_2Ni_2Sn$ ).

Table 4. Interatomic distances (pm) of  $Pr_2Ni_2Sn$  and  $Er_2Ni_2Sn$ , calculated with the powder lattice parameters. Standard deviations are all equal or less than 0.2 pm.

$Pr_2Ni_2Sn$			$Er_2Ni_2Sn$				
Pr:	2	Ni	301.6	Er:	2	Ni	278.1
	4	Ni	307.6		4	Ni	284.4
	2	Sn	334.6		4	Sn	324.6
	2	Sn	337.2		1	Er	358.6
	1	Pr	347.3		2	Er	364.3
	4	Pr	370.8		4	Er	379.9
Ni:	1	Ni	246.7	Ni:	1	Ni	249.6
	2	Sn	275.2		2	Er	278.1
	2	Pr	301.6		4	Er	284.4
	4	Pr	307.6		2	Sn	289.1
Sn:	4	Ni	275.2	Sn:	4	Ni	289.1
	4	Pr	334.6		8	Er	324.6
	4	Pr	337.2				

## Discussion

The series of  $RE_2Ni_2Sn$  stannides has been completed with the synthesis of the members with praseodymium, holmium, erbium, and thulium as rare earth elements. Our own phase-analytical studies gave no hint for the formation of a corresponding lanthanum compound. This is in full agreement with the phase analytical studies of Zhuang *et al.* [38]. Also no such compounds form with europium and ytterbium, since these two elements prefer divalent oxidation states. The course of the unit cell volumes is presented in Fig. 2. In agreement with the lanthanoid contraction the volume decreases from  $Ce_2Ni_2Sn$  to  $Lu_2Ni_2Sn$ . The plot shows no anomaly for the cerium compound, in accord with the trivalent ground state accompanied by magnetic ordering at  $T_N = 4.7$  K [12–14, 16–18, 22–24, 26, 27]. The volume of  $Y_2Ni_2Sn$  fits in between  $Tb_2Ni_2Sn$  and  $Dy_2Ni_2Sn$ , similar to examples of several other 2-2-1 series [4].  $Sc_2Ni_2Sn$  shows by far the smallest cell volume in the  $RE_2Ni_2Sn$  series.

From  $Dy_2Ni_2Sn$  to  $Ho_2Ni_2Sn$  we observed a switch from the orthorhombic  $W_2B_2Co$ - [3] to the tetragonal  $Mo_2B_2Fe$ -type [1] structure. This structural transition has drastic influences on the near-neighbor coordination of the atoms. The coordination polyhedra for  $Pr_2Ni_2Sn$  and  $Er_2Ni_2Sn$  are presented in Fig. 3. If one considers only the nickel-tin coordination (these atoms have the shortest distances to the rare earth elements),  $Pr_2Ni_2Sn$  shows coordination of Pr by

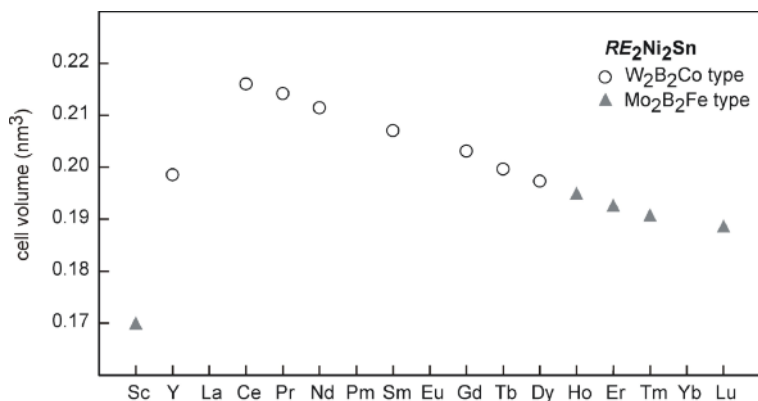


Fig. 2. Course of the cell volumes in the series of  $RE_2Ni_2Sn$  compounds.

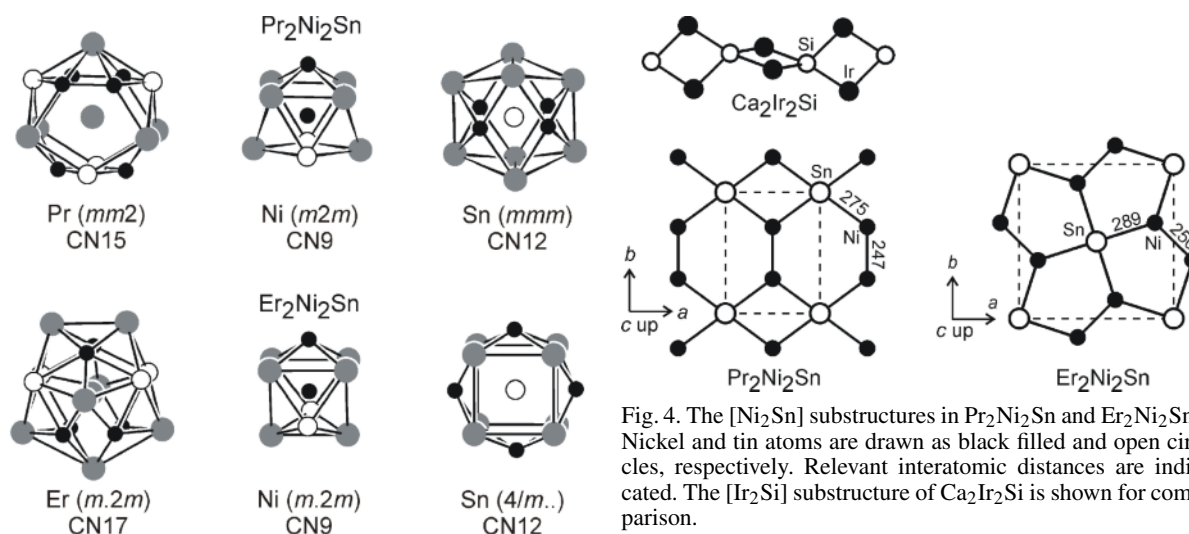


Fig. 3. The coordination polyhedra in the structures of  $Pr_2Ni_2Sn$  and  $Er_2Ni_2Sn$ . Rare earth, nickel and tin atoms are drawn as medium grey, black filled and open circles, respectively. Site symmetries are indicated.

a  $Ni_4Sn_2$  hexagon and a  $Ni_2Sn_2$  square, while Er in  $Er_2Ni_2Sn$  has two parallel  $Ni_3Sn_2$  pentagons in the first coordination shell.  $Er_2Ni_2Sn$  has two more rare earth atoms in its coordination shell as compared to  $Pr_2Ni_2Sn$  (Table 4). The nickel atoms in both stannides have coordination number 9 in the form of tri-capped trigonal prisms. The tin atoms in  $Pr_2Ni_2Sn$  and  $Er_2Ni_2Sn$  have four nickel and eight rare earth neighbors, but with different site symmetry.

The shortest interatomic distances in both structures occur for the nickel atoms, which form pairs with Ni–Ni distances of 247 pm in  $Pr_2Ni_2Sn$  and 250 pm in  $Er_2Ni_2Sn$  (Table 4), close to the Ni–Ni distance of

249 pm in *fcc* nickel [39]. Each nickel atom coordinates to two tin atoms, leading to the  $[Ni_2Sn]$  substructures with four-, five-, and six-membered rings as presented in Fig. 4. The tin atoms have square-planar  $SnNi_4$  coordination with Ni–Sn distances of 289 pm in  $Er_2Ni_2Sn$ , but a planar  $SnNi_4$  rectangle in  $Pr_2Ni_2Sn$  with a distance of 275 pm for Ni–Sn. These Ni–Sn distances are all significantly longer than the sum of the covalent radii of 255 pm [40]. Especially for  $Er_2Ni_2Sn$  the Ni–Sn bonding is weak and will not significantly contribute to the overall stability of the structure. Nevertheless, this weakness (in comparison with  $Pr_2Ni_2Sn$ ) is compensated by short Er–Ni distances of 278 and 284 pm, close to the sum of the covalent radii of 272 pm [40].

A third structure type (HT- $Pr_2Co_2Al$  [41, 42] and  $Ca_2Ir_2Si$  [43]) exists for the 2-2-1 composition, how-

ever, with another polyanionic substructure. As an example we present the  $[Ir_2Si]$  substructure of  $Ca_2Ir_2Si$  in Fig. 4. The silicon atoms have four nearest iridium neighbors in strongly distorted tetrahedral coordination within the one-dimensional polyanion. Flattening of these chains followed by condensation through  $T-T$  bonding leads to the substructure of the  $W_2B_2Co$  type. Indeed,  $Pr_2Co_2Al$  is dimorphic with a  $W_2B_2Co$ -type low-temperature modification and a monoclinic (space group  $C2/c$ ) high-temperature modification.

The orthorhombic structure type  $W_2B_2Co$  exists for a small range of valence electron concentrations (VEC) from 26 (*e. g.*  $Ca_2Pt_2Cd$  [44]) to 30 ( $Pr_2Ni_2Sn$  [this work]), while a slightly larger VEC range from 26 (*e. g.*  $La_2Rh_2Cd$  [45]) to 32 (*e. g.*  $Er_2Au_2Sn$  [6]) applies to the  $Mo_2B_2Fe$ -type compounds. This is probably related to the larger number of representatives [4] for the latter type. Both structure types have flexibility for the geometry within the planar polyanionic layers, accounting for the difference in size and electronegativ-

ity, as is evident from electronic structure calculations on  $Ca_2Pt_2Cd$  [44] and  $Ca_2Cu_2Ga$  [46].

Similar to the series of equiatomic stannides  $RENiSn$  [47],  $REPtSn$  [48],  $REAgSn$  [49], and  $REPtSn$  [50], one might think of high-temperature or high-pressure modifications for those rare earth elements, where the transition in structure type takes place. Careful inspection of the Guinier powder diagrams of the melted and quenched  $Ho_2Ni_2Sn$  samples gave no hint for a  $W_2B_2Co$ -type high-temperature modification. We have therefore planned high-pressure high-temperature studies on  $Dy_2Ni_2Sn$ , expecting to find a  $Mo_2B_2Fe$ -type high-pressure modification. Since the whole  $RE_2Ni_2Sn$  series has the same VEC, the switch in structure types is most likely driven by the course of the lanthanoid contraction.

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