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Disordered Microtwinned $(Sc_{1-x})Sc_4Co_6Sn_{18}$ $(x = 0.14)$*

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The crystal structure and composition of $(Sc_{1-x})Sc_4Co_6Sn_{18}$ (x = 0.14) were refined from single crystal X-ray diffraction data. The structure is disordered microtwinned tetragonal, $I4_1/acd$, a = 13.341(8), c = 26.69(2) Å, V = 4749.8 Å^3, Z = 8, D_x = 7.58 g cm^{-3}, M_r = 2708.5, μ = 23.85 mm^{-1}, 73 refined parameters, R = 0.0638 for 1639 observed unique reflections with $F_o > 4\sigma(F_o)$. The title compound belongs to a large series of stannides with formula $(M_{1-x}Sn_x)M_4M'_6Sn_{18}$ (M = rare earth, M' = Co, Ru, Rh, Ir, Os) and two related structures (tetragonal phase II with cell parameters $a \approx 13.7$, $c \approx 27.4$ Å and pseudo-cubic phase II' (earlier sometimes called phase III) with $a \approx 13.7$ Å, which was explained as microtwinned phase II). The crystal was microtwinned. The refined volume fractions of three twin domains were 0.381(7), 0.287(7) and 0.332(7), respectively. A microtwinning of phase II seems to be an intrinsic feature of its structure thus reducing the probability of the formation of the ideal cubic structure II' during the crystal growth.

Key words: scandium, rare earths, stannides, intermetallic compounds, crystal chemistry, twinning.

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* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

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INTRODUCTION

During systematic investigation of the phase equilibria in the Sc–Co–Sn ternary system,[1] a ternary compound with the tentative composition $ScCo_{1.1}Sn_{3.6}$ [2] was confirmed. It belongs to a large group of ternary stannides MM'_xSn_y where M = rare earth, Ca, Sr, Th and M' = Co, Ru, Rh, Os, Ir. Many of these compounds exhibit magnetic ordering and/or superconductivity.[2–7] Four different structure types have been characterized among these stannides. They were marked I, I', II and II' (in some earlier papers II' was called also phase III). The composition of phases I and I' is $M_3M'_4Sn_{13}$. Phase I is cubic, space group $Pm3n$, $a_{I} \approx 9.7$ Å. Phase I' is a slightly distorted structure of phase I. Its symmetry is either b.c.c. with $a_{I'} \approx 2a_{I}$ or tetragonal with $a_{I'} \approx a_{I} \cdot 2^{1/2}$ and $c_{I'} \approx a_{I}$.[7]

Phases II and II' have the composition $M_{5-x}M'_6Sn_{18+x}$ or $(M_{1-x}Sn_x)$-$M_4M'_6Sn_{18}$, as presented in Refs. 9 and 10. Phase II is tetragonal, sp. gr. $I4_1/acd$, $a_{II} \approx 13.7$ Å, $c_{II} \approx 2a_{II}$ while phase II' is cubic, sp. gr. $Fm3m$, $a_{II'} \approx a_{II}$.[10,11] Compound $ScCo_{1.1}Sn_{3.6}$ has been reported to be tetragonal, however only its pseudocubic lattice parameter a = 13.324 Å was presented.[2] We report herein the refined crystal structure of this compound. Its composition is $(Sc_{1-x})Sc_4Co_6Sn_{18}$ (x = 0.14).

EXPERIMENTAL DETAILS AND RESULTS

A single crystal of the title compound has been extracted from the alloy, prepared by means of arc melting of initial metals (purity not less than 99.9%) in an atmosphere of purified argon. After preparation, the alloy was homogenated at 600 °C for 720 h.

A single crystal was investigated by the Laue, rotation and precession methods using Cu-Kα and Mo-Kα radiation. According to the results of preliminary X-ray investigation, the crystal was assumed to be cubic with a = 13.342(5) Å. However, long-term precession photographs showed the presence of weak intermittent streaks at the positions where reflections which are responsible for the doubling of the c axis along each of the three pseudocubic directions <100>, <010> and <001> are expected, as observed by Miraglia *et al.*[10] for $(Tb_{1-x}Sn_x)Tb_4Rh_6Sn_{18-y}$ (x = 1.0, y = 0.4) single crystals. Lattice parameters of the tetragonal cell were determined to be a = 13.341(8) c = 26.69(2) Å, space group $I4_1/acd$, Z = 8, D_x = 7.58 g cm^{-3}, M_r = 2708.5. Intensity measurements were carried out on a Philips PW-1100 four-circle diffractometer. Experimental conditions and the parameters of refinements as well as the final agreement factors are given in Table I.

TABLE I

Parameters of data collections and structure refinements

Radiation	Graphite monochromated Mo-Kα
Radiation wavelength	0.71073 Å
Absorption coefficient	23.85 mm^{-1}
Total number of reflections	4011
Total number of contributing reflections ($F_o > 4\sigma(F_o)$)	1639
$\theta_{min} - \theta_{max}$	3.05° – 24.97°
Structure refinement program	SHELXL-97
Number of variables	73
Number of restraints	60
R_F	0.0638
wR_F	0.0979
Goodness of fit	0.993

The doubling of the c axis along each of the three pseudocubic directions in phase II was explained earlier in Ref. 9 as the result of twinning by the pseudothreefold axes $[1\,1\,1]_c$, $[\bar{1}\bar{1}1]_c$, $[1\bar{1}\bar{1}]_c$ and $[\bar{1}1\bar{1}]_c$ of the pseudocubic $2a_{II} \times 2a_{II} \times c_{II}$ lattice. Twin formation has to be expected in the tetragonal phase II since the difference between $2a_{II}$ and c_{II} is very small. For instance for $(Er_{1-x}Sn_x)Er_4Rh_6Sn_{18}$ ($x = 0.68$), it is equal to 0.048 Å.[9] Precise structural studies by electron and X-ray diffraction of the phase II' single crystals $(R_{1-x}Sn_x)R_4Rh_6Sn_{18}$ (R = Tb, Dy) showed that they are disordered microtwinned phases II.[10] A similar observation was made for the investigated crystal of $(Sc_{1-x})Sc_4Co_6Sn_{18}$ ($x = 0.14$) compound. The volume fractions of three twin domains were found to be 0.381(7), 0.287(7) and 0.332(7), respectively. The stoichiometry of compound $(Sc_{1-x})Sc_4Co_6Sn_{18}$ ($x = 0.14$) was refined from the X-ray diffraction data. Refined atomic parameters are given in Table II. Anisotropic thermal parameters were refined too.*

DISCUSSION

A projection of the crystal structure $(Sc_{1-x})Sc_4Co_6Sn_{18}$ ($x = 0.14$) on the (100) plane and coordination polyhedra (CP) of atoms are shown in Figure 1.

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* Additional material to this paper can be ordered referring to no. CSD 410123, names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Lists of Fo/Fc-data are available from the authors up to one year after the publication has appeared.

TABLE II

Atomic coordinates, equivalent isotropic thermal (U_{eq} /Å^2) and occupation (G /%) parameters

Atom	Site	x	y	z	U_{eq}	G
Sc1	8(*b*)	0	1/4	1/8	0.023(2)	86(2)
Sc2	32(*g*)	0.1314(5)	0.1178(5)	0.3082(3)	0.0073(7)	100
Sn2	32(*g*)	0.0897(2)	0.1605(2)	0.4199(1)	0.0083(3)	100
Sn31	16(*f*)	0.1731(3)	0.4231(3)	1/8	0.019(1)	100
Sn32	16(*f*)	0.3265(3)	0.5765(3)	1/8	0.013(1)	100
Sn33	32(*g*)	0.1726(4)	0.2531(2)	0.0393(2)	0.0128(9)	100
Sn34	32(*g*)	0.0033(2)	0.0762(4)	0.0384(2)	0.0133(9)	100
Sn4	16(*e*)	0.2819(2)	0	1/4	0.0156(8)	100
Co1	16(*d*)	0	1/4	0.2525(5)	0.005(2)	100
Co2	32(*g*)	0.0008(3)	0.0084(5)	0.3749(4)	0.006(1)	100

Interatomic distances are presented in Table III. Sc1 atoms are inside cuboctahedra, each formed by 12Sn. Coordination number (CN) of Sc2 atoms is 13. Its CP is derived from a cuboctahedron with one extra atom. CNs of both Co1 and Co2 atoms are 8. They are inside slightly distorted trigonal prisms [Sn_6], two side faces of which are capped with Sc atoms. All Co–Sn distances are remarkably shortened in comparison with the sum of their metallic radii ($r_{Sn} + r_{Co} = 1.58 + 1.25 = 2.83$ Å) while Co–Sc distances are larger than the sum of their metallic radii ($r_{Sc} + r_{Co} = 1.64 + 1.25 = 2.89$ Å).

CNs of Sn atoms are different. They vary from 10 for Sn4 to 16 for Sn2. Intermediate values of CNs are also observed: 12 for Sn32, 13 for Sn33 and Sn34, 14 for Sn31. The shapes of CP of Sn atoms are very different too (see Figure 1). They are usually irregular. Only separate Sc–Sn and Sn–Sn distances are contracted in the structure. Some of them are slightly contracted, *e.g.* Sc2–Sn2, Sc2–Sn32, Sc2–Sn34, and some are considerably contracted, *e.g.* Sn31–Sn32, Sn33–Sn33, Sc2–Sn4 (see Table III). Thus, the values of interatomic distances correspond to the mixed type of bonding – metallic and covalent in the structure.

In general, 128 Sn atoms (Sn2, Sn31, Sn32, Sn33 and Sn34) form a threedimensional array of corner-sharing trigonal prisms centered by the Co atoms. Each prism is connected with eight other trigonal prisms. These 128 Sn and 48 Co atoms form nearly cubic sublattices. A similar network of corner-sharing trigonal prisms is observed in the cubic phase I ($Yb_3Rh_4Sn_{13}$),[8] with which the structure of phase II is closely related. The layers of corner sharing [M'Sn_6] trigonal prisms in both I and II structures are shown in Figure 2. There is a similar fragment (fragment *A*) in both

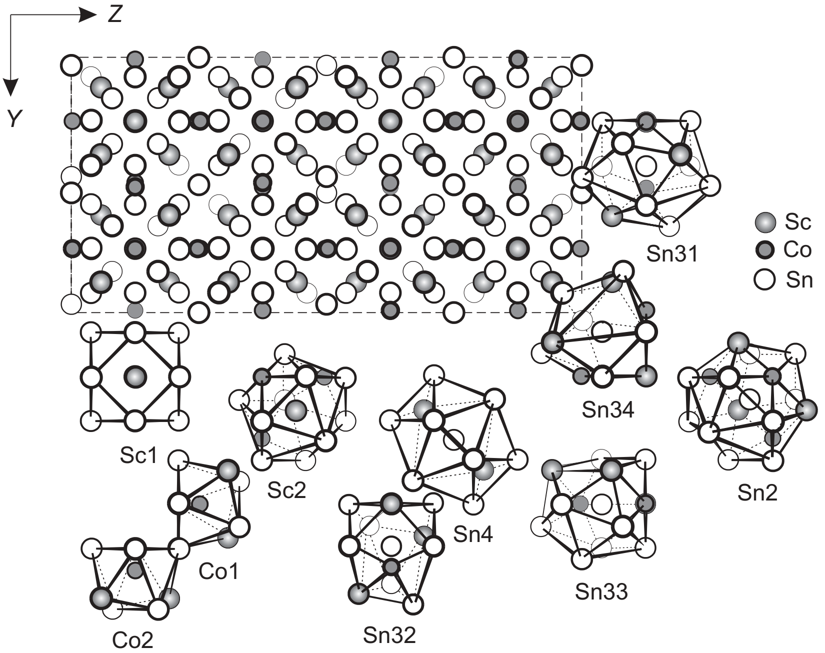


Figure 1. Projection of the crystal structure (Sc$_{1-x}$)Sc$_4$Co$_6$Sn$_{18}$ (x = 0.14) on the (100) plane and coordination polyhedra of atoms.

structures. This is indicated in Figure 2 by dotted lines. Structure II contains also fragment *A'*. It is indicated by double dotted lines in Figure 2. Fragments *A* and *A'* have the same composition, but they are rotated around the centers of the fragments by 90° with respect to each other. Structures I and II contain also a second layer of trigonal prisms. Both layers in structure I are identical. They are formed of fragments *A*. The second layer of trigonal prisms in structure II is shown in Figure 3. It consists of four different fragments: *B*, *C*, *D* and *E*. Connections of different fragments in two layers in structures I and II are shown in Figure 4.

There are three types of holes in the trigonal prisms [CoSn$_6$] network in the (Sc$_{1-x}$)Sc$_4$Co$_6$Sn$_{18}$ (x = 0.14) structure. The centers of these holes are at sites 8(b) 0, 1/4, 1/8; 8(a) 0, 1/4, 3/8 and 16(e) x, 0, 1/4 ($x \approx 1/4$). The 8(b) site is partially occupied by the Sc1 atoms (G = 86(2)%). In the Er–Rh–Sn phase II, this site is occupied randomly by the Er and Sn atoms in the ratio Er/Sn = 32/68 ≈ 1/2 [9] while in the Tb–Rh–Sn phase II' it is occupied by the Tb atoms only.[10] These data indicate a different stoichiometry of phases II and II' occurring in different ternary systems, for example Er$_{5-x}$Rh$_6$Sn$_{18}$ (x = 0.68), Tb$_5$Rh$_6$Sn$_{18-y}$ (y = 0.4), Sc$_{5-x}$Co$_6$Sn$_{18}$ (x = 0.14). Homogeneity ranges of these phases are also possible. As it was shown by Miraglia *et al.*,[11] the occupation

TABLE III

Interatomic distances /Å up to 3.6 Å

Sc1–	4Sn33	3.245(5)
	2Sn31	3.266(6)
	4Sn34	3.274(5)
	2Sn32	3.274(6)
Sc2–	Co2	2.886(11)
	Co1	2.896(11)
	Co2	2.914(11)
	Sn4	2.987(4)
	Sn2	3.057(7)
	Sn2	3.068(7)
	Sn2	3.084(8)
	Sn34	3.151(10)
	Sn32	3.195(9)
	Sn33	3.203(10)
	Sn31	3.206(9)
	Sn33	3.208(10)
	Sn34	3.209(10)
Co1–	2Sn33	2.560(8)
	2Sn34	2.564(8)
	2Sn2	2.673(12)
	2Sc2	2.896(11)
Co2–	Sn33	2.555(11)
	Sn32	2.568(6)
	Sn34	2.574(11)
	Sn31	2.584(6)
	Sn2	2.638(8)
	Sn2	2.643(8)
	Sc2	2.886(11)
	Sc2	2.914(11)
Sn2–	Co2	2.638(8)
	Co2	2.643(8)
	Co1	2.673(12)
	Sc2	3.057(7)
	Sc2	3.068(7)
	Sc2	3.084(8)
	Sn2	3.381(9)
	2Sn2	3.39(2)
	Sn4	3.477(14)
	Sn34	3.541(11)
	Sn33	3.546(11)
	Sn32	3.561(11)
	Sn31	3.563(11)
	Sn33	3.56(2)
	Sn34	3.580(10)
Sn31–	2Co2	2.584(6)
	Sn32	2.894(10)
	2Sc2	3.206(9)
	2Sn33	3.220(5)
	Sc1	3.266(6)
	2Sn34	3.298(5)
	2Sn4	3.54(2)
	2Sn2	3.563(11)
Sn32–	2Co2	2.568(6)
	Sn31	2.894(10)
	2Sc2	3.195(9)
	2Sn34	3.240(5)
	Sc1	3.274(6)
	2Sn33	3.284(5)
	2Sn2	3.561(11)
Sn33–	Co2	2.555(11)
	Co1	2.560(8)
	Sn33	2.945(9)
	Sc2	3.203(10)
	Sc2	3.208(10)
	Sn31	3.220(5)
	Sn4	3.224(4)
	Sc1	3.245(5)
	Sn34	3.268(6)
	Sn34	3.270(6)
	Sn32	3.284(5)
	Sn2	3.546(11)
	Sn2	3.56(2)
Sn34–	Co1	2.564(8)
	Co2	2.574(11)
	Sc2	3.151(10)
	Sc2	3.209(10)
	Sn32	3.240(5)
	Sn33	3.268(6)
	Sn33	3.270(6)
	Sc1	3.274(5)
	Sn31	3.298(5)
	Sn2	3.541(11)
	Sn2	3.58(2)
	Sn4	3.580(10)
Sn4–	2Sc2	2.987(4)
	2Sn33	3.224(4)
	2Sn2	3.477(14)
	2Sn31	3.54(2)
	2Sn34	3.580(10)

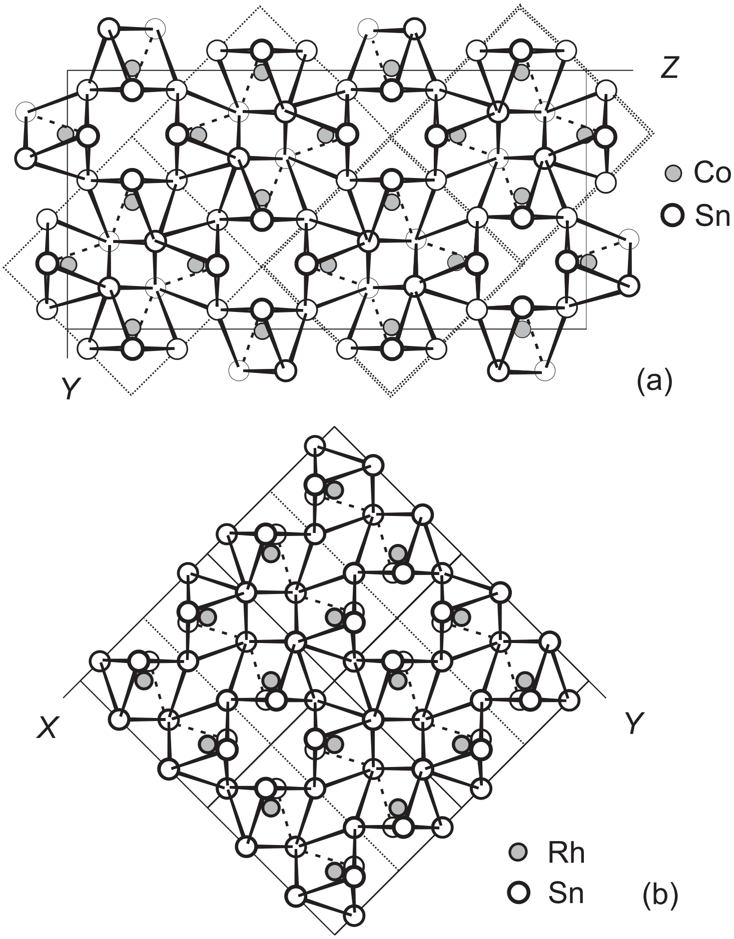


Figure 2. Layers of trigonal prisms $[CoSn_6]$ and $[RhSn_6]$ in the structures (Sc_{1-x})-$Sc_4Co_6Sn_{18}$ (x = 0.14) (a) and $Yb_3Rh_4Sn_{13}$ (b), respectively. Other atoms in both structures are not indicated. Similar fragments in both structures are indicated by dotted lines. Projection on the (100) plane of atoms with $-0.2 < x < 0.2$ (a) and projection on the (001) plane of atoms with $0.5 < z < 1.0$ (b).

of site 8(b) influences significantly the physical properties (superconducting and magnetic) of Er–Rh–Sn phase II.

Two larger holes in the trigonal prisms $[CoSn_6]$ network in the $(Sc_{1-x})Sc_4Co_6Sn_{18}$ (x = 0.14) structure are filled with Sc2 and Sn4 atoms. As a result, a Sc2 sublattice forms distorted tetrahedra with centers at site 8(a). Sn2 atoms also form a sublattice of distorted tetrahedra with centers at site 8(a). These atoms are capping the faces of $[Sc2_4]$ tetrahedra forming

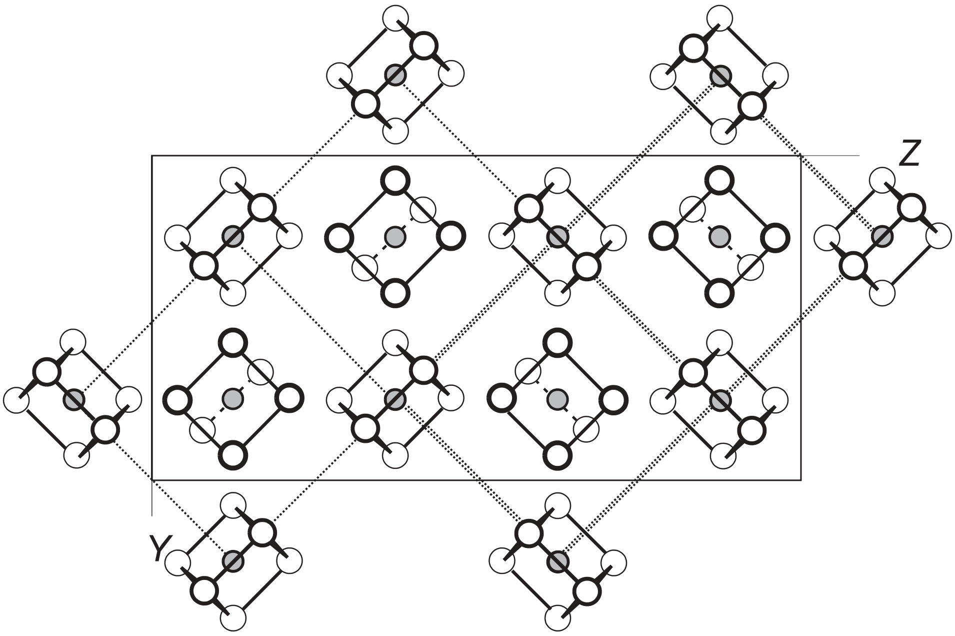
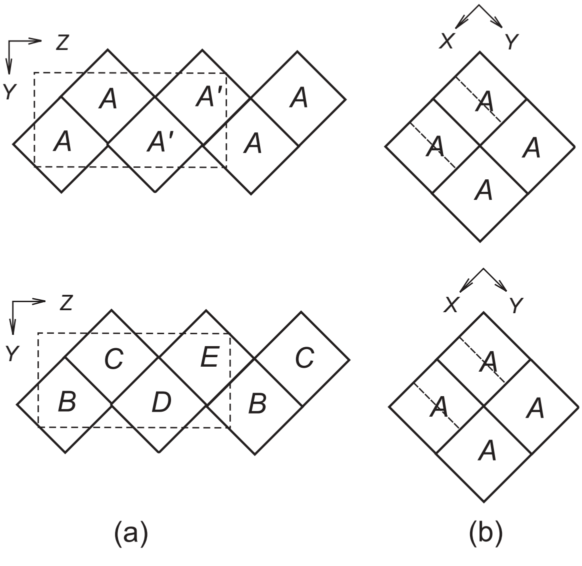


Figure 3. Layer of trigonal prisms [CoSn$_6$] in the structure (Sc$_{1-x}$)Sc$_4$Co$_6$Sn$_{18}$ (x = 0.14). The prisms with the atoms with $0.17 < x < 0.42$ are in projection on the (100) plane. The fragments of the layer are indicated by dotted lines.



(a) (b)

Figure 4. Connections of different fragments in the layers 1 and 2 in the structures of phases II (a) and I (b). For description of fragments *A*, *A’*, *B*, *C*, *D* and *E* see text.

together with them a sublattice of interpenetrating tetrahedra $[Sc2_4Sn2_4]$, which is responsible for the tetragonal symmetry of the whole structure.[10] All Sc2–Sn2 distances are contracted (see Table III). Just these two Sc2 and Sn2 sublattices can interchange, easily forming twin domains. The mechanism of microtwinning is explained in more detail elsewhere.[9,10] We think that this intrinsic feature of the crystal structure of phase II is very important. It provides the probability of the ideal cubic structure II' vanishing during the crystal growth. To our knowledge, nobody has reported to date obtaining ideal cubic crystals of phase II'. Maybe, all crystals of phases II' are pseudocubic, microtwinned disordered ones, consisting of domains of different size of tetragonal phase II. Partial disorder in the structure along the domain walls in the Sc2 and Sn2 positions increases with the decreasing domain size. Influence of microtwinning, disorder and size of tetragonal domains on the physical properties of phases II and II' seems to be evident too. But it needs additional investigations to be proved.

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SAŽETAK

Nered u mikrosraštenom $(Sc_{1-x})Sc_4Co_6Sn_{18}$ (x = 0,14)

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Kristalna struktura i sastav $(Sc_{1-x})Sc_4Co_6Sn_{18}$ (x = 0,14) utočnjeni su na temelju podataka dobivenih rentgenskom difrakcijom na jediničnom kristalu. Ustanovljeno je da se u strukturi mikrosraštenih tetragonskih kristala javlja nered. Spoj kristalizira s prostornom grupom $I4_1/acd$, s parametrima jedinične ćelije a = 13,341(8), c = 26,69(2) Å, V = 4749,8 Å^3, Z = 8, D_x = 7,58 g cm^{-3}, M_r = 2708,5 i μ = 23,85 mm^{-1}. Utočnjavanjem 73 promjenljiva parametra uz 1639 opaženih jediničnih refleksa [$F_o \geq 4\sigma(F_o)$] postignut je faktor nepouzdanosti R = 0,0638. Istraživani spoj pripada velikoj skupini stanida opće formule $(M_{1-x}Sn_x)M_4M'_6Sn_{18}$ (M = element niza rijetkih zemalja, M' = Co, Ru, Rh, Ir, Os) i dvjema srodnim strukturama: tetragonskoj fazi II s približnim parametrima jedinične ćelije $a \approx 13,7$ i $c \approx 27,4$ Å i lažno kubičnoj fazi II' (prije katkada zvanom fazom III) s $a \approx 13,7$ Å koja je opisana kao mikrosraštena faza II. Za kristale je znakovito mikrosraštanje. Utočnjeni volumni udjeli triju sraštenih domena iznose 0,381(7), 0,287(7) odnosno 0,332(7). Mikrosraštanje faze II vjerojatno je prirodna značajka njezine strukture; po svemu sudeći, ono dovodi do nestajanja idealne kubične strukture faze II' tijekom rasta kristala.