

The New Ternary Silicide ErCo_3Si_2

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Z. Naturforsch. **2014**, 69b, 369–372

DOI: 10.5560/ZNB.2014-3295

Received October 22, 2013

The new ternary silicide ErCo_3Si_2 adopts the ErRh_3Si_2 structure type (space group *Imma*, Pearson code *oI24*, $Z = 4$, $a = 6.950(1)$, $b = 9.020(2)$, $c = 5.230(1)$ Å, $R_1 = 0.0565$, $wR_2 = 0.0355$, 253 F^2 values, 23 variables). It is a deformation derivative of the CeCo_3B_2 structure type. The coordination of the Er atom shows a normal 20-vertex polyhedron $[\text{Er}(\text{Si}_6\text{Co}_{12}\text{Er}_2)]$. The two similar coordination polyhedra of Co are a distorted icosahedron $[\text{Co}(\text{Si}_4\text{Co}_4\text{Er}_4)]$, and a distorted icosahedron with one capped face $[\text{Co}(\text{Si}_4\text{Co}_5\text{Er}_4)]$. The Si atom is surrounded by the polyhedron $[\text{Si}(\text{Co}_6\text{Si}_2\text{Er}_3)]$.

Key words: Erbium, Cobalt, Silicon, Crystal Structure

Introduction

A large number of ternary borides, aluminides, gallides, and silicides adopt a variety of structures which can be derived from the hexagonal CaCu_5 type (Pearson symbol *hP6*, space group *P6/mmm*) [1]. The simplest ternary derivative is the CeCo_3B_2 type, which is the ordered variant of the CaCu_5 structure where Co and B atoms occupy exclusively two copper sites (Pearson symbol *hP6*, space group *P6/mmm*) [2]. In turn, different distorted structures originate from the CeCo_3B_2 type. Such derivatives usually have larger cells and lower symmetry. An example of such a structure is ErRh_3Si_2 (Pearson symbol *oI24*, space group *Imma*) [3]. Some of the representatives of this type are distinguished in their physical properties. For example, CeRh_3Si_2 is characterized by a multi-step character of the magnetic ordering [4]. CeIr_3Si_2 is a Kondo-lattice compound with two magnetic transitions [5]. In this paper we report on the single-crystal structure determination of the new silicide ErCo_3Si_2 .

Experimental

Single crystals of ErCo_3Si_2 were obtained as a by-product during the synthesis of ErCoIn single crystals. Ingots of erbium (99.8 mass-%), cobalt (99.9 mass-%), and indium (99.9 mass-%) were used as starting materials for the preparation of the title compound. The sample with a mass of 2 g was synthesized in an arc-furnace on a water-cooled Cu plate under an argon atmosphere. The argon was purified over titanium sponge. The button was remelted two times to ensure homogeneity. The weight losses were less than 1 %. The sample was enclosed in an evacuated silica ampoule. The specimen was heated in a furnace at 1170 K for 5 h and held at this temperature for 5 h. Then it was cooled to 970 K (at a rate of 2 K h^{-1}) and held for 3 h. It was finally cooled to room temperature within 3 h. Reaction of the sample with the quartz tube was observed. The surface of the obtained sample was covered by crystals suitable for structural studies. Single crystals extracted from a crushed sample exhibited metallic luster while ground powders were dark grey.

Intensity data were collected on a Bruker Apex-11 diffractometer equipped with a graphite-monochromatized MoK_α source ($\lambda = 0.71073$ Å). The final lattice parameters were calculated from all reflections observed in the actual data collection. The structure was solved by Direct Methods, and refined by using the program SHELXL-97 [6, 7]. Some details of the data collection and refinement parameters are given in Table 1.

Analyses of the systematic absences in the single-crystal data led to the possible space groups *Ima2* (no. 46) and *Imma* (no. 74), and the structure refinement revealed that the last one is correct. The starting atomic parameters were deduced from an automatic interpretation of Direct Methods, and the structure was successfully refined with anisotropic atomic displacement parameters for all atoms. All crystallographic positions are fully occupied. Careful analysis of electron densities revealed no indium but silicon in the compound. The refined composition is ErCo_3Si_2 . No residual peaks, indicative of additional elements, were observed. The crystallographic data and details of the data collection are listed in Table 1. The coordination and displacement parameters of the atoms are presented in Tables 2 and 3.

Later, a sample with the composition ErCo_3Si_2 was prepared in an arc-furnace under an argon atmosphere from the ingots of erbium (99.8 mass-%), cobalt (99.9 mass-%), and silicon (99.9 mass-%). The ErCo_3Si_2 sample is stable in moist air over months in powdered as well as in polycrystalline form. The powder X-ray diffraction data for the structure refinement were collected on a Bruker D8 advance diffractometer (CuK_α radiation, graphite monochromator, 2θ range $20.00\text{--}100.00^\circ$, step size in $2\theta = 0.03^\circ$,

scan time 23 s per step). Phase analysis was performed using the program POWDERCELL [8], and refinement of the cell parameters was achieved with the program FULLPROF [9]. The phase analysis revealed the presence of two phases, *viz.* ErCo₃Si₂ and ErCo₂Si₂ [10]. The powder X-ray diffraction data of ErCo₃Si₂ are in good agreement with single-crystal data: $a = 6.954(2)$, $b = 8.992(3)$, $c = 5.229(2)$ Å, $V = 908.9(4)$ Å³, $R_{\text{Bragg}} = 8.31\%$, $R_F = 7.72\%$, $R_p = 7.67\%$, $R_{\text{wp}} = 9.72\%$. A part of the arc-melted sample was annealed at 870 K inside an evacuated quartz ampoule for one month. However, no sign of ErCo₃Si₂ was detected in the annealed sample in accordance with previous data [11].

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe,

Table 1. Crystal data and structure refinement for ErCo₃Si₂.

Cell parameters	
a , Å	6.950(1)
b , Å	9.020(2)
c , Å	5.230(1)
Cell volume V , Å ³	327.86(11)
Crystal system; space group; Z	orthorhombic; <i>Imma</i> ; 4
Molar mass, g mol ⁻¹	400.23
Calculated density, g cm ⁻³	8.11
Absorption coefficient, mm ⁻¹	18.6
$F(000)$, e	302
θ range, deg	4.5–29.0
Range in hkl	+9; +12; ±7
Measured reflections	424
Independent reflections/ R_{int}	253/0.0358
Reflections with $I > 2\sigma(I)/R_\sigma$	209/0.0656
Data/refined parameters	253/23
Goodness-of-fit on F^2	0.920
R_1 [$F^2 > 2\sigma(F^2)$]	0.0565
wR_2 (F^2) (all data)	0.0355
Largest diff. peak/hole, e Å ⁻³	2.17 / -2.62

76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-426847.

Results and Discussion

ErCo₃Si₂, which is a new representative of the ErRh₃Si₂ type, was synthesized for the first time, and its crystal structure was determined by single-crystal X-ray methods. The analysis of the powder X-ray diffraction patterns of arc-melted and annealed samples has pointed out that, most likely, this compound exists within only a limited temperature range. It has to be noted that ErCo₃Si₂ was not found during the investigation of the isothermal section of the Er-Co-Si system at $T = 873$ K [11]. A similar situation is observed for related REIr₃Ge₂ compounds (RE = La, Ce, Pr, Nd) with the CeCo₃B₂ type, which exist only in as-cast samples and decompose during annealing at $T = 1070$ K with the formation of RE₄Ir₁₃Ge₉ (Ho₄Ir₁₃Ge₉ type, Pearson symbol *oP52*, space group *Pmmn*) [12].

A projection of the unit cell and the coordination polyhedra of the atoms are shown in Fig. 1. The coordination polyhedron of the erbium atoms [Er(Si₆Co₄Co₁₈Er₂)] is a slightly distorted variant of the calcium polyhedron in the CaCu₅ type. It is a hexagonal antiprism with Si-capped lateral sides and Er-capped bases. Here, in contrast to CaCu₅, the cobalt hexagons are corrugated. Two similar types of polyhedra were observed for the Co1 and Co2 atoms on Wyckoff sites 8g and 4c,

Table 2. Atomic coordinates and equivalent displacement parameters (Å²) of ErCo₃Si₂.

Atom	Wyckoff position	x	y	z	U_{eq}
Er	4e	0	1/4	0.7732(2)	0.0087(3)
Co1	8f	0.7269(3)	0	0	0.0099(4)
Co2	4c	1/4	1/4	1/4	0.0135(8)
Si	8h	0	0.9171(4)	0.7144(9)	0.0146(9)

Table 3. Anisotropic displacement parameters (Å²) of ErCo₃Si₂^a.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}
Er	0.0093(4)	0.0096(5)	0.0071(5)	0	0
Co1	0.0114(10)	0.0093(9)	0.0088(8)	-0.0004(6)	0
Co2	0.0228(13)	0.0065(13)	0.0112(13)	0	0.0010(13)
Si	0.0083(13)	0.0204(18)	0.015(2)	0.0040(17)	0

^a $U_{12} = 0$.

namely, a distorted icosahedron with one capped face [Co1(Si₄Co₂Co₁Er₄)] and a distorted icosahedron [Co₂(Si₄Co₁Er₄)]. The silicon atoms have 11 neighbors [Si(Co₁Co₂Si₂Er₃)]. This polyhedron can be described as a distorted trigonal prism of cobalt atoms with all lateral faces and two lateral edges capped by Er and Si atoms, respectively.

As mentioned above, the structure of ErCo₃Si₂ is a deformation variant of the CeCo₃B₂ type which itself is a substitution variant of the CaCu₅ type. This structure represents multilayers of atoms that are alternately stacked along the shortest direction (Fig. 2). The first layer is formed by Co Kagomé nets and cor-

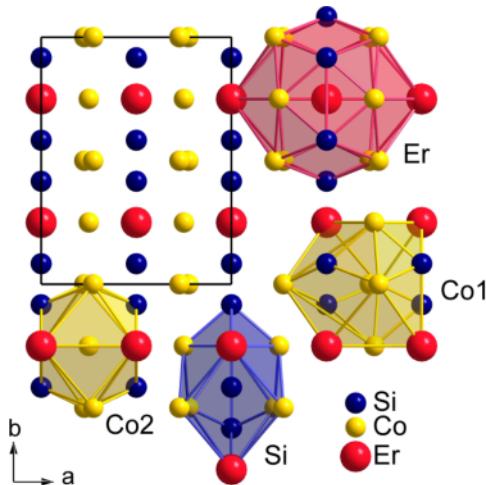


Fig. 1 (color online). A projection of the ErCo₃Si₂ unit cell onto the *ab* plane and a view of the coordination polyhedra of the atoms.

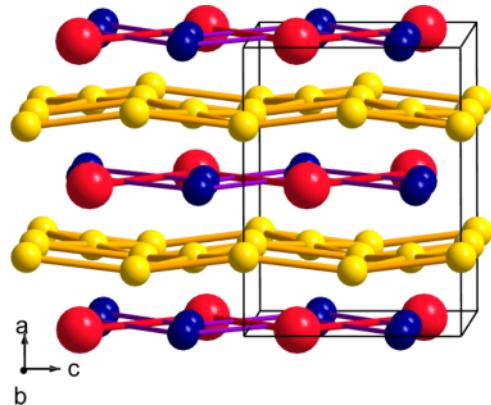


Fig. 2 (color online). Structure of ErCo₃Si₂ showing the stacked nets of atoms.

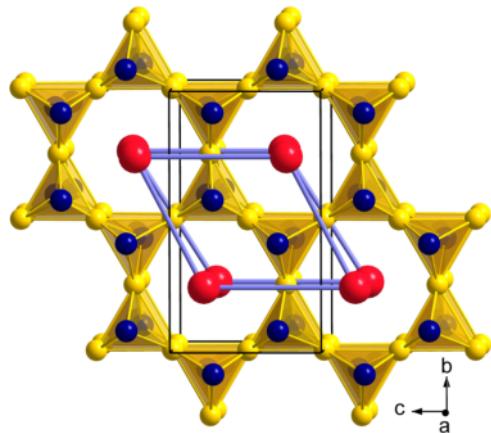


Fig. 3 (color online). The hexagonal rings of trigonal bipyramids [Si₂Co₂₂Co₁] in the ErCo₃Si₂ structure. The unit cell of the CeCo₃B₂ structure is indicated by blue lines.

Table 4. Interatomic distances (*d*, Å), Δ values ($\Delta = 100(d - \Sigma r)/\Sigma r$, where Σr is the sum of the respective atomic radii) and coordination numbers (CN) of the atoms for ErCo₃Si₂.

Atom		<i>d</i> (Å)	Δ (%)	CN	Atom		<i>d</i> (Å)	Δ (%)	CN
Er	2 Si	2.962(5)	1.20	20	Co2	4 Si	2.308(2)	-4.75	12
	2 Si	3.019(4)	3.12		4 Co1	2.612(1)	4.21		
	2 Co2	3.039(1)	0.97		2 Er	3.039(1)	0.97		
	2 Si	3.075(5)	5.04		2 Er	3.241(1)	7.68		
	4 Co1	3.101(1)	3.00		Si	2 Co1	2.074(3)	-14.38	11
	4 Co1	3.177(1)	5.55		2 Co2	2.308(2)	-4.75		
	2 Co2	3.241(1)	7.68		2 Co1	2.528(3)	4.35		
	2 Er	3.484(7)	-0.89		1 Si	2.696(6)	15.19		
	2 Si	2.074(3)	-14.38	13	1 Er	2.962(5)	1.20		
	2 Si	2.528(3)	4.35		1 Si	3.015(5)	28.82		
Co1	2 Co2	2.612(1)	4.21		1 Er	3.019(4)	3.12		
	2 Co1	2.635(1)	5.13		1 Er	3.075(5)	5.04		
	2 Er	3.101(1)	3.00						
	1 Co1	3.154(3)	25.85						
	2 Er	3.177(1)	5.55						

rugated along the *a* direction. The ErSi₂ triangles form the second layer.

Interatomic distances are in good correlation with the respective sum of the atomic radii [13] (Table 4). Strong bonding is observed between the Co and Si atoms with a maximum distance reduction of –14.4 % in comparison with the sum of the atomic radii. Thus, this structure can be considered as a packing of dis-

torted trigonal bipyramids [Si₂Co₂Co1] which are connected through silicon atoms along the *c* direction and through cobalt atoms in the *bc* plane. Six bipyramids build up ring units within the *bc* plane, which are similar to the respective hexagonal units in the CeCo₃B₂ structure. Er atoms fill holes in the hexagonal rings (Fig. 3) with all the distances comparable to the sum of atomic radii.

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- [1] H. Nowotny, *Z. Metallkd.* **1942**, *34*, 247–253.
 - [2] Yu. B. Kuzma, P. I. Kripyakevich, N. S. Bilonizhko, *Dopov. Akad. Nauk Ukr. RSR Ser. A* **1969**, 939–941.
 - [3] K. Cenzual, B. Chabot, E. Parthé, *Acta Crystallogr.* **1988**, *C44*, 221–226.
 - [4] A. P. Pikul, D. Kaczorowski, *Acta Phys. Polon. A* **2009**, *115*, 235–237.
 - [5] Y. Muro, Y. Ohno, T. Okada, K. Motoya, *J. Magn. Magn. Mater.* **2007**, *310*, 389–390.
 - [6] G. M. Sheldrick SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.
 - [7] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.
 - [8] W. Kraus, G. Nolze, POWDERCELL for Windows, Berlin **1999**.
 - [9] J. Rodríguez-Carvajal, FULLPROF.2K (version 3.70), A Program for Rietveld Refinement and Pattern Matching Analysis, Jul2006-ILL JRC, **2006**.
 - [10] P. Demchenko, J. Konczyk, O. Bodak, B. Marciniak, R. Matvijishyn *Acta Crystallogr.* **2005**, *E61*, i218–i220.
 - [11] R. Matvijishyn, P. Demchenko, V. Pavlyuk, *Visnyk. Lviv. Univ., Ser. Chem.* **2009**, *65*, 59–65.
 - [12] M. Yarema, O. Zaremba, R. Gladyshevskii, V. Hlukhy, T. F. Fässler, *J. Solid State Chem.* **2012**, *196*, 72–78.
 - [13] J. Emsley, *The Elements*, 2nd edition, Clarendon Press, Oxford **1991**.