

## The New Ternary Silicide $\text{ErCo}_3\text{Si}_2$

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The new ternary silicide  $\text{ErCo}_3\text{Si}_2$  adopts the  $\text{ErRh}_3\text{Si}_2$  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  $\text{CeCo}_3\text{B}_2$  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  $\text{CaCu}_5$  type (Pearson symbol *hP6*, space group *P6/mmm*) [1]. The simplest ternary derivative is the  $\text{CeCo}_3\text{B}_2$  type, which is the ordered variant of the  $\text{CaCu}_5$  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  $\text{CeCo}_3\text{B}_2$  type. Such derivatives usually have larger cells and lower symmetry. An example of such a structure is  $\text{ErRh}_3\text{Si}_2$  (Pearson symbol *oI24*, space group *Imma*) [3]. Some of the representatives of this type are distinguished in their physical properties. For example,  $\text{CeRh}_3\text{Si}_2$  is characterized by a multi-step character of the magnetic ordering [4].  $\text{CeIr}_3\text{Si}_2$  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  $\text{ErCo}_3\text{Si}_2$ .

### Experimental

Single crystals of  $\text{ErCo}_3\text{Si}_2$  were obtained as a by-product during the synthesis of  $\text{ErCoIn}$  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  $2 \text{ K h}^{-1}$ ) 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  $\text{MoK}_\alpha$  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  $\text{ErCo}_3\text{Si}_2$ . 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  $\text{ErCo}_3\text{Si}_2$  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  $\text{ErCo}_3\text{Si}_2$  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 ( $\text{CuK}_\alpha$  radiation, graphite monochromator,  $2\theta$  range  $20.00$ – $100.00^\circ$ , 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.* ErCo<sub>3</sub>Si<sub>2</sub> and ErCo<sub>2</sub>Si<sub>2</sub> [10]. The powder X-ray diffraction data of ErCo<sub>3</sub>Si<sub>2</sub> are in good agreement with single-crystal data:  $a = 6.954(2)$ ,  $b = 8.992(3)$ ,  $c = 5.229(2)$  Å,  $V = 908.9(4)$  Å<sup>3</sup>,  $R_{\text{Bragg}} = 8.31\%$ ,  $R_{\text{F}} = 7.72\%$ ,  $R_{\text{p}} = 7.67\%$ ,  $R_{\text{wp}} = 9.72\%$ . A part of the arc-melted sample was annealed at 870 K inside an evacuated quartz ampoule for one month. However, no sign of ErCo<sub>3</sub>Si<sub>2</sub> 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,

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-426847.

## Results and Discussion

ErCo<sub>3</sub>Si<sub>2</sub>, which is a new representative of the ErRh<sub>3</sub>Si<sub>2</sub> 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 ErCo<sub>3</sub>Si<sub>2</sub> 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 REIr<sub>3</sub>Ge<sub>2</sub> compounds ( $RE = \text{La, Ce, Pr, Nd}$ ) with the CeCo<sub>3</sub>B<sub>2</sub> type, which exist only in as-cast samples and decompose during annealing at  $T = 1070$  K with the formation of RE<sub>4</sub>Ir<sub>13</sub>Ge<sub>9</sub> (Ho<sub>4</sub>Ir<sub>13</sub>Ge<sub>9</sub> 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(Si<sub>6</sub>Co<sub>24</sub>Co<sub>18</sub>Er<sub>2</sub>)] is a slightly distorted variant of the calcium polyhedron in the CaCu<sub>5</sub> type. It is a hexagonal antiprism with Si-capped lateral sides and Er-capped bases. Here, in contrast to CaCu<sub>5</sub>, 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 1. Crystal data and structure refinement for ErCo<sub>3</sub>Si<sub>2</sub>.

Cell parameters	
$a$ , Å	6.950(1)
$b$ , Å	9.020(2)
$c$ , Å	5.230(1)
Cell volume $V$ , Å <sup>3</sup>	327.86(11)
Crystal system; space group; $Z$	orthorhombic; <i>Imma</i> ; 4
Molar mass, g mol <sup>-1</sup>	400.23
Calculated density, g cm <sup>-3</sup>	8.11
Absorption coefficient, mm <sup>-1</sup>	18.6
$F(000)$ , e	302
$\theta$ range, deg	4.5–29.0
Range in $hkl$	+9; +12; $\pm 7$
Measured reflections	424
Independent reflections/ $R_{\text{int}}$	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 <sup>-3</sup>	2.17/–2.62

Table 2. Atomic coordinates and equivalent displacement parameters (Å<sup>2</sup>) of ErCo<sub>3</sub>Si<sub>2</sub>.

Atom	Wyckoff position	$x$	$y$	$z$	$U_{\text{eq}}$
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 (Å<sup>2</sup>) of ErCo<sub>3</sub>Si<sub>2</sub><sup>a</sup>.

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

<sup>a</sup>  $U_{12} = 0$ .

namely, a distorted icosahedron with one capped face [Co1(Si<sub>4</sub>Co<sub>2</sub>Co<sub>1</sub>Er<sub>4</sub>)] and a distorted icosahedron [Co2(Si<sub>4</sub>Co<sub>1</sub>Er<sub>4</sub>)]. The silicon atoms have 11 neighbors [Si(Co<sub>1</sub>Co<sub>2</sub>Si<sub>2</sub>Er<sub>3</sub>)]. 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 ErCo<sub>3</sub>Si<sub>2</sub> is a deformation variant of the CeCo<sub>3</sub>B<sub>2</sub> type which itself is a substitution variant of the CaCu<sub>5</sub> 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-

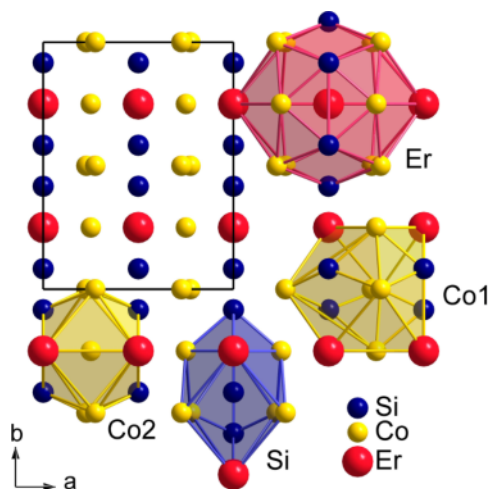


Fig. 1 (color online). A projection of the ErCo<sub>3</sub>Si<sub>2</sub> unit cell onto the *ab* plane and a view of the coordination polyhedra of the atoms.

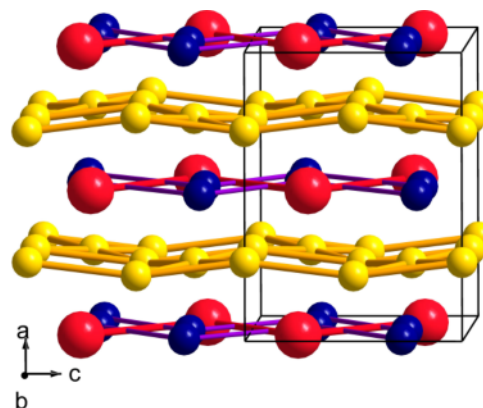


Fig. 2 (color online). Structure of ErCo<sub>3</sub>Si<sub>2</sub> showing the stacked nets of atoms.

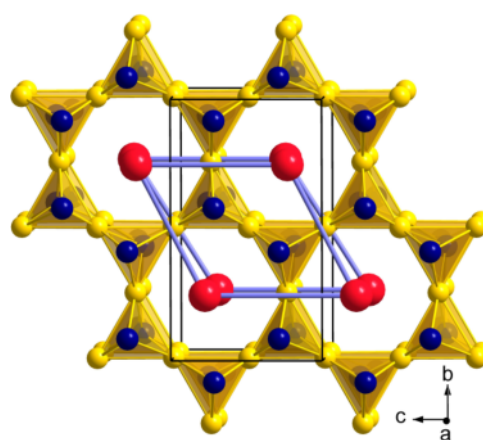


Fig. 3 (color online). The hexagonal rings of trigonal bipyramids [Si<sub>2</sub>Co<sub>2</sub>Co<sub>1</sub>] in the ErCo<sub>3</sub>Si<sub>2</sub> structure. The unit cell of the CeCo<sub>3</sub>B<sub>2</sub> structure is indicated by blue lines.

Table 4. Interatomic distances (*d*, Å), Δ values ( $\Delta = 100(d - \Sigma r)/\Sigma r$ , where  $\Sigma r$  is the sum of the respective atomic radii) and coordination numbers (CN) of the atoms for ErCo<sub>3</sub>Si<sub>2</sub>.

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	
	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	11	
	4 Co1	3.101(1)	3.00		Si	2 Co1	2.074(3)		-14.38
	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		
Co1	2 Er	3.484(7)	-0.89	13	1 Si	2.696(6)	15.19		
	2 Si	2.074(3)	-14.38		1 Er	2.962(5)	1.20		
	2 Si	2.528(3)	4.35		1 Si	3.015(5)	28.82		
	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  $\text{ErSi}_2$  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  $[\text{Si}_2\text{Co}_2\text{Co}_1]$  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  $\text{CeCo}_3\text{B}_2$  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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