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Single crystal investigation of the new phase $Er_{0.85}Co_{4.31}Si$ and of CoSi

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The crystal structure of the new phase $Er_{0.85}Co_{4.31}Si$ was determined by single-crystal X-ray diffraction (46 unique reflections, R1 = 0.0378, wR2 = 0.0697). The compound crystallizes in the $TbCu_7$ structure type: space group *P6/mmm*, *hP*8-1.85, with lattice parameters *a* = 4.8593(19), *c* = 3.9869(16) Å. A full investigation of the crystal structure was also performed for the known phase CoSi on single-crystal X-ray diffraction data (61 unique reflections, R1 = 0.0256, wR2 = 0.0548). CoSi crystallizes in the FeSi structure type: space group *P*$2_1$3, *cP*8, with lattice parameter *a* = 4.4500(5) Å.

Transition metal alloys and compounds / Crystal structure / X-ray diffraction

Introduction

This paper is part of a systematic study of the interaction of erbium and transition metals with silicon or germanium. The Er–Co–Si ternary system has not been completely investigated yet, but eight ternary compounds have been found to exist: tetragonal $ErCo_2Si_2$ [1-4] and $ErCo_9Si_2$ [5], orthorhombic ErCoSi [6,7], $ErCoSi_2$ [6,8,9] and $Er_2Co_3Si_5$ [10], monoclinic Er_2CoSi_2 [11], $Er_5Co_4Si_{14}$ ("$Er_3Co_2Si_7$") [6,12] and Er_3CoSi_3 [13]. Quite recently, the other new ternary phase, $ErCo_5Si_3$, was found and its crystal structure has been determined by X-ray single crystal method [14]. The solubility of silicon in the binary Er_2Co_{17} phase was studied in [15]. According to the accepted phase diagram of the Er–Co system [16], a hexagonal phase of composition $ErCo_5$ (structure type $CaCu_5$) exists in a limited temperature range; it forms peritectically at 1340°C and decomposes eutectoidally at 1240°C. It seemed of interest to study the influence of a third component on the formation and stability of this hexagonal phase.

The existence of the compound CoSi was firstly reported in [17], but a complete investigation of the crystal structure has not been performed. During our systematic studies of the Er–Co–Si system several single crystals were grown. This work presents the results of the X-ray investigation of single crystals of the new phase $Er_{0.85}Co_{4.31}Si$ and of the known phase CoSi.

Experimental

Single crystals of prismatic form were extracted from samples of compositions $Er_{16}Co_{69}Si_{15}$ and $Er_5Co_{47}Si_{48}$. The samples were melted from pieces of initial components of high purity (Er 99.86%, Co 99.99%, Si 99.999%) under an argon atmosphere (Ti-getter) in an arc furnace with a water-cooled copper crucible, and annealed in evacuated silica tubes at 800°C for 1 month. The single crystals suitable for X-ray analysis were at a preliminary step investigated by the Laue and Weissenberg methods (RKV-86 and RGNS-2 chambers, MoKα-radiation), then on an automatic single-crystal diffractometer (Oxford Diffraction Xcalibur3^{TM} CCD, MoKα-radiation, graphite monochromator, ω-scans). Data collection and reduction were performed using CrysAlis CCD [18] and CrysAlis RED [19] programs. The crystal structures were solved and refined using the SHELX-97 program package [20]. The crystallographic data were standardized with the program Structure Tidy [21]. Experimental and crystallographic data are given in Table 1.

Results and discussion

The structure of $Er_{0.85}Co_{4.31}Si$ was solved by direct methods. The first step of the solution of the structure revealed the atomic positions of the $CaCu_5$ structure type. However, the differential Fourier map contained additional electron density of about 13 e/Å^3 at 0 0 0.297 that is typical for the $TbCu_7$ structure type. After having included this peak into the atom list and applied the restraint $G(\mathrm{Er})+G(\mathrm{Co}_1) = 1$, the atomic parameters were refined in the anisotropic approximation down to R = 0.0378. The final values are listed in Table 2. The structure is characterized by strong disorder (about 65%), typical of the representatives of the $TbCu_7$ structure type.

A clinographic projection of the unit cell of $Er_{0.85}Co_{4.31}Si$ is shown in Fig. 1.

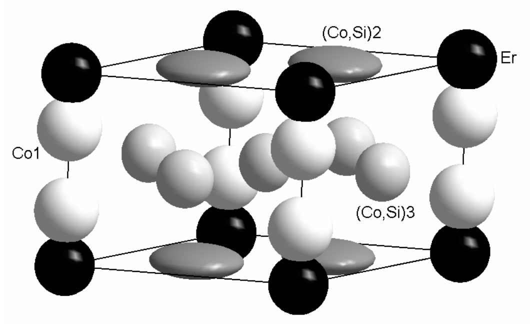

Fig. 1 Clinographic projection of the unit cell of $Er_{0.85}Co_{4.31}Si$ ($TbCu_7$-type structure) with displacement ellipsoids.

Table 1 Experimental and crystallographic data for $Er_{0.85}Co_{4.31}Si$ and CoSi.

Compound	$Er_{0.85(2)}Co_{4.31(7)}Si_{0.99(6)}$	CoSi
Structure type	$TbCu_7$	FeSi
Space group	*P*6/*mmm*	$P2_13$ [a]
Z, Pearson symbol	1, hP8-1.85	4, cP8
Lattice parameters, Å	*a* = 4.8593(19) *c* = 3.9869(16)	*a* = 4.4500(5)
Crystal size, mm	0.10 × 0.08 × 0.05	0.14 × 0.08 × 0.04
Crystal color	Metallic dark grey	
Absorption coefficient, mm^{-1}	45.444	9.805
Absorption correction	Analytical	
θ range for data collection	4.83 to 25.16°	6.48 to 25.47°
Limiting indices	$5 \leq h \leq 5$, $-5 \leq k \leq 4$, $-4 \leq l \leq 4$	$-5 \leq h \leq 4$, $-5 \leq k \leq 5$, $-5 \leq l \leq 5$
Reflections collected/unique	455 / 46 [R(int) = 0.1648]	533 / 61 [R(int) = 0.1582]
Completeness to θ	100.0 % [b]	100.0 %
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	46 / 1 / 16	61 / 0 / 8
Goodness-of-fit on F^2	1.124	1.214
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0697	R1 = 0.0256, wR2 = 0.0548
R indices (all data)	R1 = 0.0416, wR2 = 0.0709	R1 = 0.0256, wR2 = 0.0548
Extinction coefficient	0.09(3)	0.010(18)
Largest diff. peak and hole	0.980 and -1.861 e Å^{-3}	0.713 and -0.667 e Å^{-3}

[a] Absolute structure parameter -0.02(10).

[b] Transformed from an initial orthorhombic cell (*a* = 3.9869(16), *b* = 4.8578(19), *c* = 8.4211(35) Å).

Table 2 Atomic positional and displacement parameters for $Er_{0.85}Co_{4.31}Si$.

Atom	Site	*x*	*y*	*z*	Displacement parameters [a], Å^2 ×10^3					*G*
					U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	
Er	1*a*	0	0	0	18(1)	18(2)	18(2)	18(3)	9(1)	0.85(2)
Co_1	2*e*	0	0	0.288(8)	21(12)	– [b]	–	–	–	0.15(2)
$(Co,Si)_2$	2*c*	1/3	2/3	0	31(3)	44(3)	44(3)	5(3)	22(2)	*G*(Co) = 0.85(7) *G*(Si) = 0.15(7)
$(Co,Si)_3$	3*g*	1/2	0	1/2	16(2)	16(2)	14(3)	17(2)	7(1)	*G*(Co) = 0.77(5) *G*(Si) = 0.23(5)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2\mathbf{a}^{*2}U_{11} + ... + 2hk\mathbf{a}^*\mathbf{b}^*U_{12}]$, $U_{13} = U_{23} = 0$, $U_{12} = U_{22}/2$.

[b] Anisotropic displacements were not refined.

Table 3 Interatomic distances for $Er_{0.85}Co_{4.31}Si$.

Atoms	δ, Å	Atoms	δ, Å
Er – $2Co_1$	1.148(32) [a]	$(Co,Si)_2$ – $6(Co,Si)_3$	2.4375(7)
– $6(Co,Si)_2$	2.8055(11)	– $3(Co,Si)_2$	2.8055(11)
– $2Co_1$	2.839(32)	– 3Er	2.8055(11)
– $12(Co,Si)_3$	3.1428(9)	$(Co,Si)_3$ – $4(Co,Si)_3$	2.4297(9)
– 2Er	3.9869(16)	– $4(Co,Si)_2$	2.4375(7)
Co_1 – Er	1.148(32) [a]	– 4 Co_1	2.57(1)
– Co_1	1.690(45) [a]	– 4Er	3.1428(9)
– Co_1	2.296(45)		
– $6(Co,Si)_3$	2.57(1)		
– Er	2.839(32)		
– $6(Co,Si)_2$	3.031(12)		

[a] These distances do not realize physically.

Table 4 Atomic positional and displacement parameters for CoSi.

Atom	Site	*x*	*y*	*z*	Displacement parameters [a], $Å^2 \times 10^3$		
					U_{eq}	$U_{11} = U_{22} = U_{33}$	$U_{23} = U_{13} = U_{12}$
Co	4*a*	0.3934(1)	0.3934(1)	0.3934(1)	5(1)	5(1)	0(1)
Si	4*a*	0.0935(3)	0.0935(3)	0.0935(3)	6(1)	6(1)	1(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form: $-2\pi^2\ [h^2\mathbf{a}^{*2}U_{11} + ... + 2hk\mathbf{a}^*\mathbf{b}^*U_{12}]$

Table 5 Interatomic distances and coordination numbers (C.N.) for CoSi.

Atoms	δ, Å	C.N.	Atoms	δ, Å	C.N.
Co – Si	2.312(3)	13	Si – Co	2.312(3)	13
– 3Si	2.3431(18)		– 3Co	2.3431(18)	
– 3Si	2.4514(10)		– 3Co	2.4514(10)	
– 6Co	2.7349(3)		– 6Si	2.7538(7)	

According to the results of the refinement of the occupation factor *G*, 15% of the Er atoms that could occupy position 1*a* are replaced by Co-Co dumb-bells in position 2*e*. The structure contains three types of net, emphasized in Fig. 2: a 6^3 net formed by $(Co,Si)_2$ atoms in 2*c*, a 3636 (Kagomé) net formed by $(Co,Si)_3$ atoms in 3*g*, and a 3^6 net formed by Er atoms in 1*a* (the latter being in part replaced by Co_1 atoms). The interatomic distances are in good agreement with the sums of the atomic radii of the elements [22] and are listed in Table 3.

The structure of CoSi was also solved by direct methods; the atomic parameters and interatomic distances are presented in Tables 4 and 5, respectively. A projection of the unit cell content of this compound, which adopts the cubic FeSi structure type, and the coordination polyhedrons of the two kinds of atom are shown in Fig. 3. For the cobalt as for the silicon atoms, the coordination polyhedrons have 13 apexes $[CoSi_7Co_6]$ and $[SiCo_7Si_6]$.

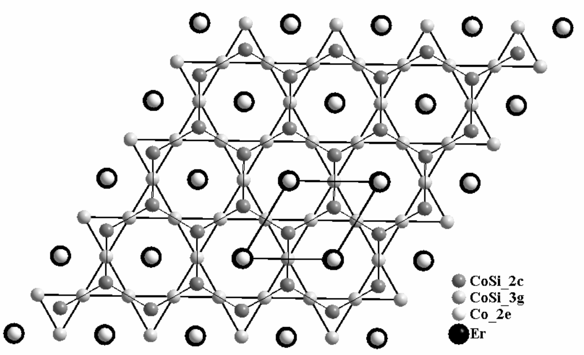

Fig. 2 6^3 net formed by $(Co,Si)_2$ atoms in the 2*c*-site, 3636 net (Kagomé) formed by $(Co,Si)_3$ atoms in the 3*g*-site and 3^6 net formed by Er atoms in the 1*a*-site (*G* = 0.85; in part replaced by Co_1 atoms in the 2*e*-site with *G* = 0.15).

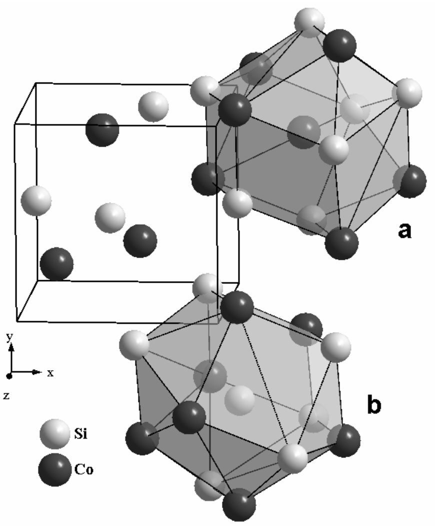

Fig. 3 Clinographic projection of the unit cell of CoSi (FeSi-type structure) and coordination polyhedra of the atoms: a) 13-apex polyhedron $[CoSi_7Co_6]$, b) 13-apex polyhedron $[SiCo_7Si_6]$.

Conclusions

Full X-ray single crystal investigations have been carried out for the new compound $Er_{0.85}Co_{4.31}Si$ in the ternary Er–Co–Si system and for the known compound CoSi. As a next step, it would be interesting to investigate the homogeneity range, temperature interval of existence and structural changes of the hexagonal phase $Er_{1-x}(Co_{1-y}Si_y)_{5+2x}$.

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