Erbium nickel trisilicide, ErNiSi$_3$

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Single crystals of ErNiSi$_3$ were synthesized from the corresponding elements by arc melting. The ternary inter-metallic compound crystallizes in the orthorhombic space group *Cmmm* and adopts the SmNiGe$_3$ structure type, with all atoms in special positions of site symmetry *m2m*.

Comment

Ternary intermetallics of rare-earth metals with the general formula $RETX_3$ (where RE is a rare earth metal, T is a transition metal and X is a p-block element) crystallize mostly in eight structure types, *viz.* orthorhombic ScNiSi$_3$, SmNiGe$_3$ and YNiAl$_3$, tetragonal BaNiSn$_3$, cubic CaTiO$_3$, LaRuSn$_3$, TmRuGa$_3$ and CeRuGe$_3$ (Parthé *et al.*, 1993–1994).

The $RETX_3$ phases have received special attention for their interesting magnetic and electric properties. An accurate determination of the crystal structure for phases of this
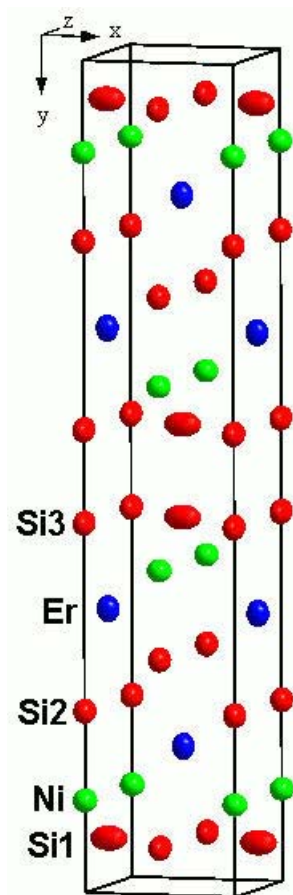

Figure 1
Clinographic projection of the ErNiSi$_3$ unit-cell contents, with displacement ellipsoids drawn at the 95% probability level.
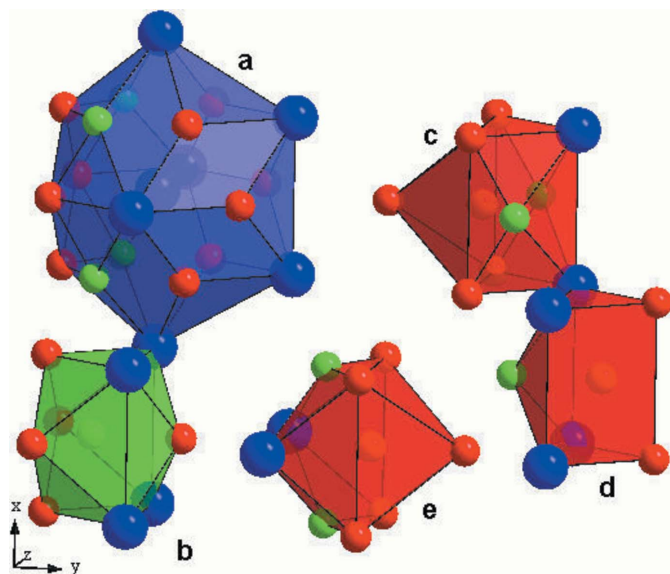
Figure 2
Coordination polyhedra around (*a*) the Er atom, (*b*) the Ni atom, and (c–e) the Si atoms. Er atoms are blue, Ni atoms are green and Si atoms are red.

composition is a basic requirement for the better understanding of their physical properties. The existence of the phase ErNiSi₃ was first reported by Gorelenko *et al.* (1977), who, on the basis of X-ray powder diffraction data, established that the crystal structure adopted the orthorhombic ScNiSi₃ structure type. In view of the closeness of the structure types ScNiSi₃ (space group *Amm*2) and SmNiGe₃ (space group *Cmmm*), it was necessary to determine precisely the structure type for ErNiSi₃ on the basis of single-crystal diffraction data, and we present these results here.

In contrast to the previous examination (Gorelenko *et al.*, 1977), ErNiSi₃ does not crystallize in the ScNiSi₃ structure type, but adopts the SmNiGe₃ structure type (Bodak *et al.*, 1985). A clinographic projection of the unit cell is shown in Fig. 1. The coordination sphere around Er (site symmetry $m2m$) consists of 20 atoms if bonding interactions are considered for distances < 4.0 Å, resulting in a polyhedron with 20 apices [ErSi₄Ni₄Si₆Er₆] (Fig. 2*a*). The coordination polyhedron around the nickel atom (site symmetry $m2m$) is a tetragonal antiprism [NiSi₅Er₄] if bonding interactions are considered for distances < 3.1 Å. The antiprism is made up of 4 Er atoms in one basal plane with an additional Si atom, and 4 Si atoms in the second basal plane (Fig. 2*b*). The coordination polyhedra around the Si atoms (site symmetry $m2m$) are trigonal prisms (bonding interactions < 3.1 Å): tricapped [Si1Ni₂Si₅Er₂] with one additional Si and two Ni as the capping atoms (Fig. 2*c*), monocapped [Si2NiSi₂Er₄] with one additional Ni as the capping atom (Fig. 2*d*), and tricapped [Si3Ni₂Si₅Er₂] with one additional Si and two Er as the capping atoms (Fig. 2*e*). The interatomic distances are in good agreement with the sums of the atomic radii (Pauling, 1967). The shortest distance (Table 1) is observed between atoms Ni and Si2 (93% of the sum of the atomic radii of the corresponding atoms).

Experimental

The single crystal used in this work was extracted from an alloy with nominal composition Er₁₀Ni₂₅Si₆₅, which was prepared by arc melting of the initial components (purity better than 99.9%) in an electric arc furnace with a water-cooled copper bottom (Ti-getter) under an argon atmosphere and annealed at 870 K. A preliminary crystal investigation was performed using Laue and rotation methods (RKV-86 and RGNS-2 chambers, Mo *Kα* radiation).

Crystal data

ErNiSi₃	Mo *Kα* radiation
$M_r = 310.24$	Cell parameters from 1395
Orthorhombic, *Cmmm*	reflections
$a = 3.9152$ (5) Å	$\theta = 5.2$–32.7°
$b = 20.948$ (3) Å	$\mu = 32.50$ mm⁻¹
$c = 3.9313$ (6) Å	$T = 295$ (2) K
$V = 322.42$ (8) Å³	Prism, metallic light grey
$Z = 4$	$0.07 \times 0.05 \times 0.04$ mm
$D_x = 6.391$ Mg m⁻³	

Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer	360 independent reflections
	358 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.028$
Absorption correction: analytical CrysAlis RED (Oxford Diffraction, 2005)	$\theta_{max} = 32.7°$
	$h = -5 \rightarrow 5$
	$k = -30 \rightarrow 30$
$T_{min} = 0.187$, $T_{max} = 0.274$	$l = -3 \rightarrow 5$
1407 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0156P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.016$	$+ 8.1601P]$
$wR(F^2) = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
360 reflections	$\Delta\rho_{max} = 1.37$ e Å⁻³
22 parameters	$\Delta\rho_{min} = -1.37$ e Å⁻³
	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.0108 (5)

Table 1
Selected interatomic distances (Å).

Er—Si2ⁱ	2.9586 (7)	Ni—Si2	2.247 (2)
Er—Niⁱⁱ	3.0300 (4)	Ni—Si3ⁱ	2.2671 (11)
Er—Si1ⁱⁱ	3.0707 (15)	Ni—Si1ᵛⁱ	2.2759 (11)
Er—Si3	3.0729 (15)	Si1—Si1ᵛⁱⁱ	2.340 (4)
Er—Si2	3.0823 (15)	Si1—Si3ⁱⁱ	2.7742 (3)
Er—Erⁱⁱⁱ	3.9152 (5)	Si2—Si2ᵛⁱⁱⁱ	2.376 (2)
Er—Erⁱᵛ	3.9254 (6)	Si3—Si3ⁱˣ	2.347 (4)
Er—Erᵛ	3.9313 (6)		

Symmetry codes: (i) $-x - \frac{1}{2}, -y + \frac{1}{2}, -z$; (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $x + 1, y, z$; (iv) $-x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (v) $x, y, z + 1$; (vi) $x, y, z - 1$; (vii) $-x, -y, -z + 1$; (viii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (ix) $-x, -y + 1, -z$.

The structure refinement of ErNiSi₃ clearly indicates that this phase crystallizes in space group *Cmmm*, adopting the SmNiGe₃ structure type. Refinement in space group *Amm*2 (ScNiSi₃ structure type) was less satisfactory and resulted in higher *R* factors and atomic displacement parameters. The highest maximum residual electron density is located at a distance of 0.68 Å from the Er atom, and the deepest hole is 1.99 Å from the same atom.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg,

1999); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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