Acta Cryst. (1987). C**43**, 1455–1457

$Er_3Ru_4Si_{12}$: a New Structural Type of Orthorhombic Symmetry

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(*Received* 27 *October* 1986; *accepted* 18 *March* 1987)

Abstract. Erbium ruthenium silicide, $M_r = 1243{\cdot}1$, orthorhombic, *Bbcm*, $a = 8{\cdot}072$ (3), $b = 8{\cdot}076$ (3), $c = 18{\cdot}39$ (1) Å, $V = 1199$ (1) Å^3, $Z = 4$, $D_m = 6{\cdot}75$ (5), $D_x = 6{\cdot}89$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 27{\cdot}15$ mm^{-1}, $F(000) = 2192$, $T = 298$ K, $R = 0{\cdot}036$ for 1084 independent reflections. Isostructural compounds are $M_3Ru_4Si_{12}$ with M = Gd, Tb, Dy, Ho and Y. This new structural type shows some similarities with those of $BaNiSn_3$ and $Yb_3Rh_4Sn_{13}$. The Er atoms occupy two kinds of sites, either surrounded by 12 Si atoms forming a slightly distorted cubooctahedron, or within a 16-atom coordination polyhedron formed by 4 Ru and 12 Si atoms.

Introduction. Recently we have reported two new series of ternary silicides with formulae $MTSi_3$ and $M_3T_4Si_{13}$, where M is a rare earth and T a transition element such as Co, Rh, Ir, Ru, Os (Wang, Lloret, Ng, Chevalier, Etourneau & Hagenmuller, 1985; Lloret, Chevalier, Lejay & Etourneau, 1986). Some of these silicides exhibit low-temperature superconducting properties. The existence of these compounds depends on the relative sizes of the M and T atoms. The $MTSi_3$ silicides crystallize with the tetragonal $BaNiSn_3$ structure type and appear only for the large-size rare earths. In contrast, the $M_3T_4Si_{13}$ compounds, which adopt the cubic $Yb_3Rh_4Sn_{13}$ structure type (Vandenberg, 1980), occur only for M = Ho, Er, Lu and T = Os, Ir.

The investigation of the Er–Ru–Si system led us to prepare a new ternary silicide $Er_3Ru_4Si_{12}$, which crystallizes with a novel structure. This new crystal structure is reported here and compared with those of $BaNiSn_3$ and $Yb_3Rh_4Sn_{13}$.

Experimental. $Er_3Ru_4Si_{12}$ prepared by arc melting from high-purity metals and silicon in an oxygen-free argon atmosphere, and annealing at 1073 K for two weeks. Samples examined by conventional X-ray diffractometry and with a Guinier–Hägg camera (Cu $K\alpha$). Microprobe analysis used to check the homogeneity of the samples and to determine their exact composition. D_m obtained by hydrostatic pressure measurements.

A parallelepipedic single crystal (60 × 90 × 120 μm) was isolated by mechanical fragmentation from the solidified melt after slow cooling, and then mounted on an automatic three-circle diffractometer (Enraf–Nonius CAD-3). Cell parameters obtained by least-squares refinement of 2θ values of 24 reflections ($40 < 2\theta < 64°$) collected by the automatic diffractometer. As $a \simeq b$, the powder diagram was indexed with a tetragonal unit cell. However, single-crystal photographs (Weissenberg, precession) showed that the symmetry was orthorhombic not tetragonal. 10 580 reflections collected by θ–2θ scanning [$(\sin\theta)/\lambda < 0{\cdot}807$ Å^{-1}, $-12 < h < 13$, $-12 < k < 13$, $-5 < l < 29$] with an angular width of $(0{\cdot}85 + 0{\cdot}50 \tan\theta)°$. Intensities of three standard reflections checked successively every 100 reflections, with no significant fluctuation observed and a maximum relative deviation of 5%. Absorption correction using *SHELX*76 (Sheldrick, 1976), idealized crystal shape (seven faces) and size, and incident and diffracted beam direction cosines: $0{\cdot}156 < T < 0{\cdot}398$. $R_{\rm int} = 6{\cdot}5$ and $3{\cdot}6$% before and after correction. Conditions for reflections, $h + l = 2n$ for hkl, $k = 2n$ for $0kl$, $h = 2n$ for $h0l$, consistent with two possible space groups *Bbcm* and *Bba*2 [inconsistencies: 0 with $I/\sigma(I) > 4$, 28 with $4 > I/\sigma(I) > 3$]. 1084 unique reflections with $I/\sigma(I) > 3$. Atomic scattering factors for neutral atoms and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

The structure was determined on the basis of the *Bbcm* group by Patterson-function deconvolution and heavy-atom methods for Er and Ru. Si atoms located with several difference Fourier syntheses. All calculations performed with *SHELX*76. Several cycles carried out with unit weights, varying the positional and isotropic thermal parameters for all atoms. At this stage the R factor was 0·066. A trial with anisotropic thermal parameters for Er and Ru gave unsatisfactory values and comparison between F_o and F_c showed that the strong reflections occurring at low θ angles were affected by extinction. In the following cycles a weighting relation, $w = 1/\sigma^2(F_o)$, and an empirical isotropic extinction parameter x [$F_c = F(1 - 10^{-4}xF^2/\sin\theta)$] were applied. Calculations with individual isotropic thermal parameters yielded $R = 0{\cdot}039$ and $wR = 0{\cdot}046$. The structure was refined down to $R = 0{\cdot}036$ and $wR = 0{\cdot}044$ with anisotropic factors for Er and Ru atoms [extinction parameter $x = 50\,(1) \times 10^{-5}$; max. shift/

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e.s.d. in last cycle <0·001].* Calculations with the non-centrosymmetric group *Bba*2 did not improve the model. The residual electron density (−6·2 to 3·7 e Å^{-3}, with maximum values near the Er and Ru atoms) and the non-significant variations observed on the refined data of the site occupation factors, confirmed the 3:4:12 formula type. Atomic parameters are given in Table 1, and selected bond lengths in Table 2.

Powder patterns of $M_3Ru_4Si_{12}$ (M = Gd, Tb, Dy, Ho, Y) show that these silicides are isostructural with $Er_3Ru_4Si_{12}$. For these phases the *a* and *b* parameters are also very similar and the indexing cannot distinguish (*hkl*) from (*khl*). Tetragonal refinements of $M_3Ru_4Si_{12}$ lattice constants are given in Table 3. The newly obtained structural type does not exist for the largest rare earths, *i.e.* La→Sm.

Discussion. The Er atoms occupy two kinds of sites as shown in Figs. 1(*a*) and 1(*b*).

The Er(1) atoms are surrounded by twelve Si atoms forming a slightly distorted cubooctahedron with Er(1)—Si distances ranging from 3·005 to 3·069 Å. The Ru atoms form a second-nearest-neighbor polyhedron, namely an octahedron with Er(1)—Ru distances ranging from 3·124 to 3·183 Å (Fig. 1*a*). Each Ru atom caps a pseudorectangular face of the Si cubooctahedron.

The Er(2) atoms are within the 16-atom coordination polyhedron formed by four Ru and twelve Si atoms (Fig. 1*b*).

Frameworks of Si (or similar) atoms around Er also occur in many other ternary silicides, germanides or stannides containing rare earths and transition elements. An Si cubooctahedron is found for instance in $Er_3Os_4Si_{13}$ (Lloret *et al.*, 1986), which crystallizes in the $Yb_3Rh_4Sn_{13}$ structure type. In the ternary superconducting stannide $(Er_{1-x}Sn_x)Er_4Rh_6Sn_{18}$ (Hodeau, Marezio & Remeika, 1984) the site which is occupied statistically by Er and one of the Sn atoms is formed by an Sn cubooctahedron and an Rh octahedron. The structure of this ternary stannide derives from that of $Yb_3Rh_4Sn_{13}$. The 16-atom Er(2) polyhedron type is known to occur in many structures derived from the $BaAl_4$ type such as $ThCr_2Si_2$, $CaBe_2Ge_2$ and $BaNiSn_3$ (Parthé, Chabot, Braun & Engel, 1983). In particular, in the MTSi$_3$ phases of $BaNiSn_3$-type structure (Wang *et al.*, 1985), the rare-earth *M* coordination is also a polyhedron constituted by twelve Si (or analogous) and four transition-element *T* atoms in the same way as for Er(2) in the $Er_3Ru_4Si_{12}$ structure.

A projection of the $Er_3Ru_4Si_{12}$ structure along the *a* axis is given in Fig. 2. The layers of the 16-atom polyhedra are parallel to the *x*0*y* plane and connected along the *c* axis *via* the Si cubooctahedron. The $Er_3Ru_4Si_{12}$ structure is characterized by large segments of cubic $Yb_3Rh_4Sn_{13}$-type and tetragonal $BaNiSn_3$-type arrangements.

The Er—Ru and Er—Si distances are smaller for the Er(1) site [Er(1)—Ru = 3·163 Å, Er(1)—Si = 3·047 Å] than for the Er(2) site [Er(2)—Ru = 3·213 Å, Er(2)—

Table 1. *Atomic parameters for* $Er_3Ru_4Si_{12}$, *space group Bbcm*

For each atom position are given site symmetry, fractional coordinates and isotropic thermal parameters of the temperature factors $T = \exp\{-B_{\rm iso}[(\sin\theta)/\lambda]^2\}$ (equivalent values for Er and Ru are calculated according to

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \sum_{i=1}^{3}\sum_{j=1}^{3} a_i^* a_j^* U_{ij}\mathbf{a}_i.\mathbf{a}_j).$$

	Position	Site symmetry	*x*	*y*	*z*	$B_{\rm eq}$ or $B_{\rm iso}$ (Å^2)
Er(1)	4(*a*)	..2/*m*	0	0	0	0·41
Er(2)	8(*d*)	2..	0·24639 (6)	$\frac{1}{4}$	$\frac{1}{4}$	0·44
Ru(1)	8(*e*)	..2	0	0	0·16990 (4)	0·28
Ru(2)	8(*f*)	..*m*	0·37335 (9)	0·12687 (9)	0	0·27
Si(1)	8(*e*)	..2	0	0	0·2952 (2)	0·45 (4)
Si(2)	8(*f*)	..*m*	0·1673 (4)	0·3330 (4)	0	0·54 (4)
Si(3)	16(*g*)	1	0·4936 (3)	0·2294 (3)	0·1171 (1)	0·54 (3)
Si(4)	16(*g*)	1	0·2705 (3)	0·0068 (3)	0·1170 (1)	0·56 (3)

Table 2. *Selected distances* (Å) *in* $Er_3Ru_4Si_{12}$

The e.s.d. values are in parentheses.

Er(1)—Ru(1)	2×	3·124 (2)	Er(2)—Ru(1)	2×	3·194 (2)
Ru(2)	2×	3·183 (2)	Ru(1^{v})	2×	3·231 (2)
Ru(2^{i})	2×	3·182 (2)	Si(1)	2×	2·953 (2)
Si(2)	2×	3·009 (3)	Si(1^{v})	2×	2·993 (2)
Si(2^{i})	2×	3·005 (3)	Si(3)	2×	3·159 (3)
Si(3^{i})	4×	3·069 (3)	Si(3^{i})	2×	3·188 (3)
Si(4)	4×	3·066 (3)	Si(4)	2×	3·143 (3)
			Si(4^{v})	2×	3·209 (3)
Ru(1)—Er(1)	1×	3·124 (2)	Ru(2)—Er(1)	1×	3·183 (2)
Er(2)	2×	3·194 (2)	Er(1^{ii})	1×	3·182 (2)
Er(2^{i})	2×	3·231 (2)	Ru(2^{iii})	1×	2·895 (2)
Si(1)	1×	2·304 (3)	Si(2)	1×	2·353 (3)
Si(3^{i})	2×	2·392 (3)	Si(2^{ii})	1×	2·395 (3)
Si(4)	2×	2·391 (3)	Si(2^{iv})	1×	2·396 (3)
			Si(3)	2×	2·504 (3)
			Si(4)	2×	2·502 (3)
Si(1)—Er(2)	2×	2·953 (2)	Si(2)—Er(1)	1×	3·009 (3)
Er(2^{i})	2×	2·993 (2)	Er(1^{ii})	1×	3·005 (3)
Ru(1)	1×	2·304 (3)	Ru(2)	1×	2·353 (3)
Si(3^{vi})	2×	2·457 (3)	Ru(2^{i})	1×	2·395 (3)
Si(4^{vi})	2×	2·458 (3)	Ru(2^{v})	1×	2·396 (3)
			Si(3^{i})	2×	2·619 (3)
			Si(4^{v})	2×	2·618 (3)

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

Table 3. *Lattice constants of* $M_3Ru_4Si_{12}$ *silicides with the* $Er_3Ru_4Si_{12}$ *structural type*

Phase	*a*,*b* (Å)	*c* (Å)
$Gd_3Ru_4Si_{12}$	8·128 (3)	18·50 (1)
$Tb_3Ru_4Si_{12}$	8·117 (3)	18·48 (1)
$Dy_3Ru_4Si_{12}$	8·102 (3)	18·47 (1)
$Ho_3Ru_4Si_{12}$	8·082 (3)	18·43 (1)
$Er_3Ru_4Si_{12}$	8·067 (3)	18·42 (1)
$Y_3Ru_4Si_{12}$	8·105 (3)	18·46 (1)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43899 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Si = 3·108 Å] (Table 2). The existence of these two Er sites in $Er_3Ru_4Si_{12}$ may explain the stability of the compound. It is worthwhile pointing out that phases with 1:1:3 and 3:4:13 compositions do not exist in the Er–Ru–Si system, probably because only one site is available for Er atoms in the corresponding structures.

The Ru(1) sites are surrounded by five Er and five Si atoms (Fig. 1*c*) with a double-pyramidal coordination. The other structural unit is an Si(1) pseudo-tetragonal antiprism $Si(1)Er_4Si_4$ (Fig. 1*e*). It consists of four Er(2) atoms forming a rectangular face and four Si atoms with a nearly square-planar configuration. Ru(1) atoms complete these antiprisms to give $Si(1)Er_4Si_4Ru$ units. Such double-pyramidal and antiprismatic coordinations are also found for the $BaNiSn_3$ structure type.

The Ru(2) atoms have a new ten-atom coordination type (Fig. 1*d*): (two Er + one Ru) and three Si atoms (Ru–Si = 2·381 Å) constitute two opposite triangles in the mirror plane, and four Si atoms form a rectangle with the longest side perpendicular to the mirror plane (Ru–Si = 2·503 Å). The Si(2) nine-atom coordination polyhedron is represented in Fig. 1(*f*). Si(3) and Si(4) have quite similar nine-coordinated surroundings (three Er, two Ru, four Si) with no simple characteristic polyhedra.

As for the other ternary silicides, the bonding distances between Si and Ru atoms are shorter than the sum of their covalent radii (Table 2). This fact shows the existence of strong covalent interactions.

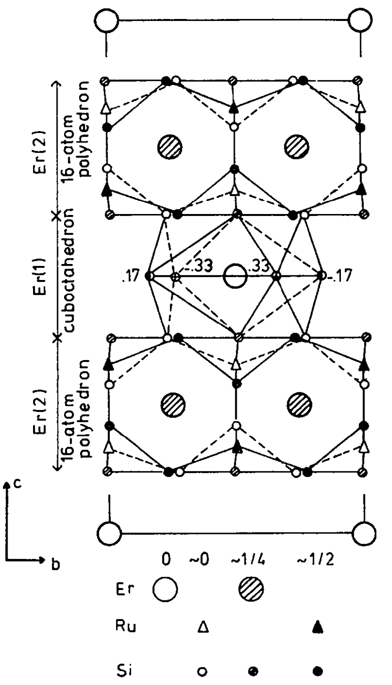

Fig. 2. Projection of the $Er_3Ru_4Si_{12}$ structure along [100].

The $Er(1)Si_{12}$ and $Er(2)Ru_4Si_{12}$ building blocks of $Er_3Ru_4Si_{12}$-type are common structural elements of several superconducting ternary silicides *e.g.* $LaRhSi_3$ (Lejay, Higashi, Chevalier, Etourneau & Hagenmuller, 1984), $Lu_3Os_4Si_{13}$ (Lloret *et al.*, 1986), $Y_2Fe_3Si_5$ and $Sc_5Co_4Si_{10}$ (Braun, 1981). The determination of this new structural type hopefully opens a new way for understanding the influence of structural and electronic factors on superconductivity. A study of the physical properties of isostructural phases containing in particular Y and Lu is now in progress.

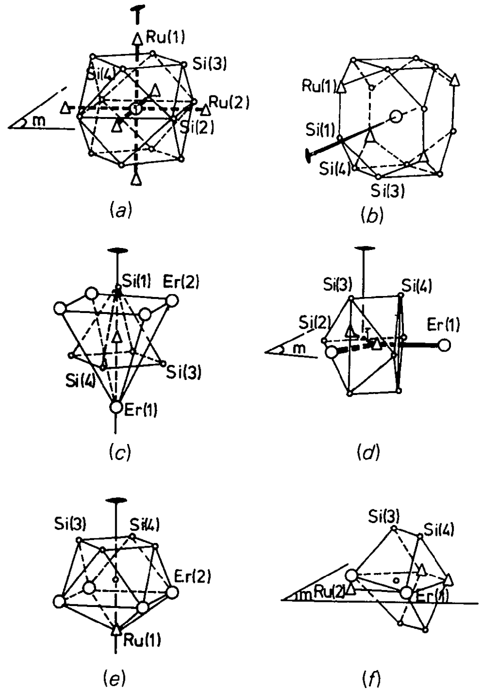

Fig. 1. Main coordination types in $Er_3Ru_4Si_{12}$: (*a*) Si cubo-octahedron and Ru octahedron around Er(1), (*b*) 16-atom polyhedron around Er(2), (*c*) double pyramid around Ru(1), (*d*) polyhedra around Ru(2), (*e*) antiprism around Si(1), and (*f*) polyhedra around Si(2).

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