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# $R_3T_2$ Compounds ($R$ = Rare Earth or Y; $T$ = Rh, Pd, Pt) with the Rhombohedral $Er_3Ni_2$ Structure Type

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$Sm_3Rh_2$ crystallizes with the $Er_3Ni_2$ structure type. Space group $R\bar{3}$, $a = 8{\cdot}701$ (2), $c = 16{\cdot}526$ (7) Å, $Z = 9$, $D_x = 9{\cdot}06$ g cm$^{-3}$; $\mu$(Mo $K\alpha$) = 430 cm$^{-1}$. Direct methods, absorption correction, least-squares refinement. $R = 0{\cdot}11$ for 451 independent reflexions. $Ce_3Rh_2$, $Pr_3Rh_2$, $Nd_3Rh_2$, $La_3Pt_2$, $Ce_3Pt_2$, $Pr_3Pt_2$, $Nd_3Pt_2$ and $Y_3Pd_2$ are isostructural with $Sm_3Rh_2$. The $Er_3Ni_2$ structure type is compared with the $U_3Si_2$ structure type which has been found with rare-earth–palladium compounds. Both structures are characterized by transition-metal-centred trigonal double prisms and rare-earth-centred cubes.

## Introduction

Phase diagrams have been published for the systems La–Rh and Nd–Rh (Singh & Raman, 1969, 1970), for Er–Rh (Ghassem & Raman, 1973*a*) and for Gd–Rh (Loebich & Raub, 1976). Intermediate phases have been reported for some other rare-earth–Rh systems (Ghassem & Raman, 1973*b*). The structures of the numerous compounds with a Rh content between 37·5 and 50 at.% were all unknown before 1974. Raman (1976) has recently recognized that the compounds with formula $R_5Rh_4$ ($R$ = La, Ce, Nd, Sm, Gd) crystallize in the orthorhombic $Gd_5Si_4$-type structure. At the same time, Moreau, Paccard & Parthé (1976) analysed structurally the compounds with formula $R_3Rh_2$ ($R$ = Gd, Tb, Dy, Ho, Er, Y) which crystallize in the new tetragonal $Y_3Rh_2$-type structure. There was still an unknown structure for compounds of the same composition formed with light rare-earth elements. Phase-diagram studies in the system Y–Pd by Loebich & Raub (1973) indicate the presence of a compound $Y_3Pd_2$ with unknown structure. No phase-diagram data for $R$–Pt systems are known. It was thus necessary to perform systematic investigations in order to find out what compounds exist.

## Experimental

The compounds were prepared by the conventional arc-melting technique. The initial stoichiometry was $R_5Rh_3$ ($R$ = La, Ce, Pr, Nd, Sm) and $Y_3Pd_2$ according to phase diagrams and $R_3Pt_2$ ($R$ = La, Ce, Pr, Nd) for Pt compounds. Powder was obtained from the crushed button and X-ray patterns were taken with a Guinier–de Wolff camera and Cu $K\alpha$ radiation. The diagrams show that all these compounds are isotypic, except $La_5Rh_3$. A single crystal was isolated from the $Sm_5Rh_3$ melt. Its hexagonal lattice constants and intensities were measured with graphite-monochromated Mo $K\alpha$ radiation on a

Philips PW 1100 computer-controlled four-circle goniometer. Possible space groups are $R3$ and $R3$. $\theta$–$2\theta$ scans were used to collect 569 non-equivalent intensities out to a limit of $\sin\theta/\lambda = 0{\cdot}7$ Å$^{-1}$. An empirical absorption correction based on the comparison of several sets of equivalent reflexions was applied with the program *CAMEL JOCKEY* (Flack, 1975). The structure was solved by direct methods (in $R\bar{3}$) with the program *LSAM* (Main, Woolfson & Germain, 1972), and relativistic Hartree–Fock scattering factors (Cromer & Mann, 1968). All positional and isotropic thermal parameters refined satisfactorily with the least-squares programs *CRYLSQ* (XRAY system, 1976). $R$ $(= \Sigma\ |\Delta F|/\Sigma\ |F_o|)$, calculated from 451 observed reflexions ($|F_o| > 2\sigma$) with isotropic thermal parameters, was 0·11. The final positional and thermal parameters are listed in Table 1.*

The isotypism of $Ce_3Rh_2$, $Pr_3Rh_2$, $Nd_3Rh_2$, $La_3Pt_2$, $Ce_3Pt_2$, $Pr_3Pt_2$, $Nd_3Pt_2$ and $Y_3Pd_2$ with $Sm_3Rh_2$ was established by comparing observed and calculated powder diffraction intensities with the *LAZY PULVERIX* program (Yvon, Jeitschko & Parthé, 1977). The lattice parameters reported in Table 2 were obtained with *PARAM* (XRAY system, 1976). The reflexions were measured on films, calibrated with Si, taken with a Guinier–de Wolff camera and Cu $K\alpha$ radiation. The variation of the cell parameters is a consequence of the normal lanthanide contraction.

Table 1. *Atomic parameters for* $Sm_3Rh_2$ *with e.s.d.'s in parentheses*

The Debye–Waller factor is defined as
$\exp[-2\pi^2 \times 10^{-2} U(2 \sin\theta/\lambda)^2]$.
Space group $R\bar{3}$.

| | Equipoint | $x$ | $y$ | $z$ | $U$ (Å$^2$) |
|---|---|---|---|---|---|
| Sm(1) | 3 (*b*) | 0 | 0 | $\frac{1}{2}$ | 1·5 (1) |
| Sm(2) | 6 (*c*) | 0 | 0 | 0·2962 (3) | 1·4 (1) |
| Sm(3) | 18 (*f*) | 0·2417 (3) | 0·9861 (3) | 0·0924 (2) | 1·4 (1) |
| Rh | 18 (*f*) | 0·5940 (6) | 0·9802 (6) | 0·0695 (3) | 1·8 (1) |

Table 2. *Lattice constants for compounds isotypic with* $Er_3Ni_2$

E.s.d.'s are in parentheses, $V$ = volume of the unit cell, $n$ = number of atoms in the unit cell.

| | $a$ (Å) | $c$ (Å) | $(V/n)^{1/3}$ | Reference |
|---|---|---|---|---|
| $Ce_3Rh_2$ | 8·835 (7) | 16·76 (2) | 2·93 | (*a*) |
| $Pr_3Rh_2$ | 8·784 (4) | 16·68 (2) | 2·91 | (*a*) |
| $Nd_3Rh_2$ | 8·761 (8) | 16·64 (2) | 2·90 | (*a*) |
| $Sm_3Rh_2$ | 8·701 (2) | 16·526 (7) | 2·89 | (*a*) |
| $Ho_3Ni_2$ (h.t.) | 8·52 (1) | 15·75 (2) | 2·80 | (*b*) |
| $Er_3Ni_2$ | 8·472 (2) | 15·680 (2) | 2·79 | (*b*) |
| $Eu_3Pd_2$ | 9·204 | 17·384 | 3·05 | (*c*) |
| $Y_3Pd_2$ | 8·750 (2) | 16·468 (5) | 2·89 | (*a*) |
| $La_3Pt_2$ | 9·096 (2) | 17·303 (8) | 3·01 | (*a*) |
| $Ce_3Pt_2$ | 8·981 (2) | 17·078 (8) | 2·98 | (*a*) |
| $Pr_3Pt_2$ | 8·959 (2) | 16·980 (8) | 2·97 | (*a*) |
| $Nd_3Pt_2$ | 8·893 (2) | 16·871 (8) | 2·95 | (*a*) |

(*a*) This work. (*b*) Moreau, Paccard & Gignoux (1974). (*c*) Iandelli & Palenzona (1975).

## Discussion

The refined parameters of Table 1 show clearly that this structure is isotypic with $Er_3Ni_2$ (Moreau, Paccard & Gignoux, 1974). Unit-cell parameters of other compounds crystallizing with the same structure type are reported in Table 2. Crystal structures of $R_xT$ compounds with $x \geq 1$, where $R$ = rare earth and $T$ = Co, Ni, Rh, Pd, can be characterized by the nature of the coordination polyhedron of the $T$ atom (Parthé & Moreau, 1977). In $Sm_3Rh_2$, each Rh atom is surrounded by a trigonal prism of Sm atoms. Figs. 1 and 2 show how these prisms are connected in the structure. Only Sm(2) and Sm(3) participate in the formation of the prisms; Sm(1) is at the centre of a cube with Sm(2) and Sm(3) at each corner and one Rh outside the centre of each face (CN = 14).

The $Er_3Ni_2$ structure type of $Sm_3Rh_2$ is closely related to the $U_3Si_2$ structure type (Zachariasen, 1949) also characterized by cubes and centred trigonal double prisms. The $U_3Si_2$ structure has been reported for $Gd_3Pd_2$, $Dy_3Pd_2$, $Ho_3Pd_2$ and $Er_3Pd_2$ (Loebich & Raub, 1973). In Fig. 3 the structure of $U_3Si_2$ is compared with a corresponding structural element of the $Er_3Ni_2$ structure type. The essential difference is the presence of infinite columns of cubes and infinite columns of

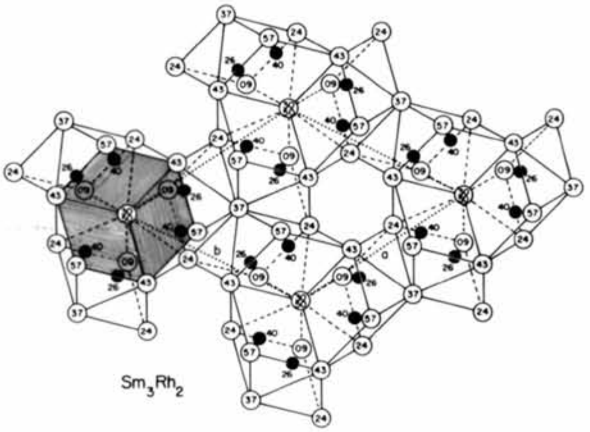

Fig. 1. The linkage of the trigonal double prisms in $Sm_3Rh_2$ with the $Er_3Ni_2$ structure type; projection along **c**. Only prisms in the lower half of the unit cell are shown. Filled circles correspond to Rh atoms. The three shaded faces form the lower part of the cube around a Sm(1) atom at $z = \frac{1}{2}$.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32480 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

trigonal prisms in $U_3Si_2$, while in $Er_3Ni_2$ all six faces of the cube are also trigonal prism faces. They are identical in shape because they are related by the threefold axis.

It has been shown (Hohnke & Parthé, 1966; Parthé, 1970) that the relative dimensions of the trigonal prism depend on the type of element at its centre. 'Stretched' prisms occur with borides, silicides and germanides, while 'squeezed' prisms are found in compounds with transition elements at the prism centres. The $U_3Si_2$ structure type can accommodate stretched or squeezed trigonal double prisms by slightly stretching or squeezing the cubes along the tetragonal $c$ axis. The type of trigonal prism in the $U_3Si_2$ structure can be directly deduced from the value of the $c/a$ ratio. One obtains perfect cubes and trigonal prisms if $c/a = 0{\cdot}518$ [on the assumption that $x = 0{\cdot}18$ for the equipoint 4($h$) occupied by U atoms]. The cubes and trigonal prisms are stretched if $c/a > 0{\cdot}518$ (borides, silicides, germanides) or squeezed if $c/a < 0{\cdot}518$ (transition elements inside the prisms). In Table 3 the $c/a$ ratio and relative prism or cube dimensions are given for a few representative compounds with the $U_3Si_2$ structure type.

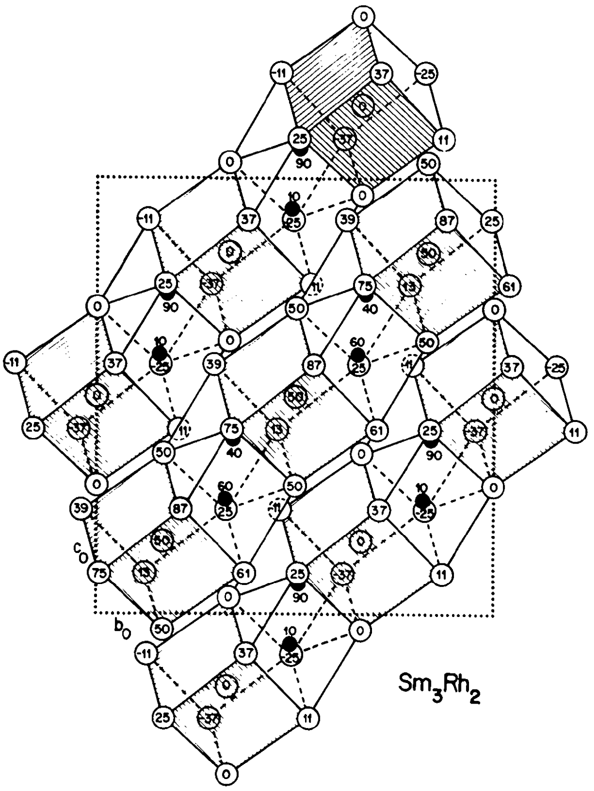


Fig. 2. The linkage of cubes and double prisms in $Sm_3Rh_2$. For a better visualization, the structure is described here with an orthohexagonal unit cell ($a_O = a_H$, $b_O = a_H\sqrt{3}$, $c_O = c_H$). The projection along the orthohexagonal $a_O$ axis corresponds to a projection on the (11$\bar{2}$0) plane in the hexagonal description. Filled circles correspond to Rh atoms. Double prisms along the directions perpendicular to the chains have been omitted.

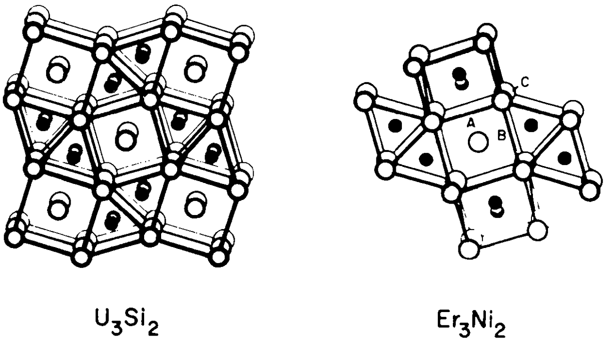
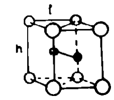


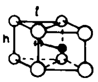
Fig. 3. Comparison between the $U_3Si_2$ and $Er_3Ni_2$ structure types. ($a$) A clinographic projection of the $U_3Si_2$ structure. ($b$) A corresponding structural element of $Er_3Ni_2$. Only four of the six trigonal double prisms surrounding a cube are shown. For a structure with squeezed trigonal prisms only ($h < l$), the conditions for the three prisms having $h$ or $l$ equal to $A$, $B$ or $C$ are (see also Fig. 1) $A < C$, $C < B$, $B < A$ which is impossible; then $A = B = C$.

Table 3. *Axial ratios and relative prism dimensions for a few representative compounds with the tetragonal* $U_3Si_2$ *structure type*

Stretched trigonal double prisms



Squeezed trigonal double prisms



| | $c/a$ | $h/l$ | | $c/a$ | $h/l$ |
|---|---|---|---|---|---|
| $U_3Si_2$ | 0·5321 | 1·03 | $Gd_3Pd_2$ | 0·496 | 0·96 |
| $Ta_3B_2$ | 0·5318 | 1·03 | $Dy_3Pd_2$ | 0·501 | 0·97 |
| $Th_3Ge_2$ | 0·527 | 1·02 | $Ho_3Pd_2$ | 0·506 | 0·97 |

Table 4. *Structure types found in R*–Rh *alloys (up to 50 at. %* Rh*) together with their characteristic* Rh*-centred rare-earth polyhedra*

| | | | | | | |
|---|---|---|---|---|---|---|
| Large $R$ | $Fe_3C$<br>Trigonal prisms | $Th_7Fe_3$<br>Trigonal prisms | | $Er_3Ni_2$<br>Trigonal prisms | $Gd_5Si_4$<br>Trigonal prisms | CrB<br>Trigonal prisms |
| Small $R$ | $Fe_3C$<br>Trigonal prisms | $Th_7Fe_3$<br>Trigonal prisms | $Mn_5Si_3$<br>Square antiprisms | $Y_3Rh_2$<br>Four different types of polyhedra | | CsCl<br>Cubes |

In the $Er_3Ni_2$ structure type all six cube faces are also trigonal prism faces. In such cases neither stretched nor squeezed trigonal prisms are permitted. If one trigonal prism requires one particular cube edge to be changed in length, the trigonal prism on the neighbouring cube face requires the same cube edge to be changed in an opposite direction (which can be verified by a study of the $Er_3Ni_2$ segment in Fig. 3). Thus, this structure type will be formed only with ideal trigonal prisms having square contact faces with the cube. This might be the reason why this structure type is rare and has never been found before.

In Table 4 we report structure types found in $R_x$Rh compounds ($x \geq 1$) with their characteristic Rh-centred rare-earth polyhedra. Omitted from the table is the *anti* $Th_3P_4$ type characterized by square antiprisms and found only with $La_4Rh_3$. It is an exception because in all other structures formed by larger rare-earth elements the Rh atoms are exclusively at the centres of trigonal prisms. With the smaller rare-earth elements, only the $Fe_3C$ and $Th_7Fe_3$ structure types have trigonal prisms alone. In $Y_3Rh_2$ there are mixtures of prisms and cubes together with other polyhedra, while in the equiatomic compounds there are only Rh-centred rare-earth cubes.

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