There is no significant difference between the structures of $NaNp_2F_9$ and KU_2F_9. In this case, U and Np have a similar behaviour, different from that of Th. This study confirms that compounds with U and Na at this stoichiometry are isomorphous with compounds containing U and K. The value of the ionic radius for Np^{IV} in nine coordination is not given by Shannon (1976). With regards to the Np—F distances, no great difference should be expected between ionic radii when going from eight ($r_{Np^{IV}}$ = 0·98 Å in eight coordination) to nine coordination.

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$La_3Rh_4Ge_4$ of Orthorhombic $U_3Ni_4Si_4$ Type

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Abstract. Trilanthanum tetrarhenium tetragermanide, $La_3Rh_4Ge_4$, orthorhombic, space group *Immm*, a = 4·1746 (3), b = 4·2412 (2), c = 25·234 (3) Å, $Z = 2$, D_x = 8·32 Mg m^{-3}, μ(Mo $K\alpha$) = 35·1 mm^{-1}, $F(000) = 958$, R = 0·035 (271 F_o). The structure is of the $U_3Ni_4Si_4$ type. A comparison with the $Gd_3Cu_4Ge_4$ type, reported for the $Sc_3Ni_4Si_4$ compound among others, is given.

Introduction. In the course of a systematic study of equiatomic ternary rare-earth transition-metal gallides, silicides and germanides (Hovestreydt, Engel, Klepp, Chabot & Parthé, 1982) the compounds *R*RhGe were investigated. It was found that from CeRhGe to TmRhGe a series of isotypic compounds with the TiNiSi structure type is formed. The powder diffraction diagram of the lanthanum compound was, however, completely different and could not be interpreted with any of the known ternary equiatomic structure types found in similar systems. Therefore it appeared necessary to undertake a single-crystal study.

A sample of nominal composition LaRhGe was prepared by arc melting stoichiometric amounts of high-purity elements (La: 99·9%, Rh: 99·99%, Ge: 99·999%) under purified Ar atmosphere. Microscopic investigation showed that the sample was not single phased. One component, however, was well crystallized. A single crystal of prismatic shape (50 × 60 × 100 μm) was selected and mounted on a computer-controlled single-crystal diffractometer (Philips PW 1100 with graphite-monochromated Mo $K\alpha$ radiation). Preliminary crystallographic investigations indicated an *I*-centered cell of Laue symmetry *mmm*. The only systematic absences were those of the body-centered Bravais lattice leading to *Immm*, *Imm*2, $I2_12_12_1$ or *I*222 as possible space groups. The lattice constants given in the *Abstract* were obtained by least-squares refinement of the 2θ values of 34 reflections measured with Mo $K\alpha_1$ radiation (λ = 0·7093 Å). Intensity data were collected using ω–2θ scans in one quadrant of reciprocal space ($6 \leq 2\theta \leq 54°$). Absorption was accounted for by a spherical absorption correction (μR = 1·4). Averaging of equivalent reflections yielded a unique set of 323 reflections of which 237 with $I > 3\sigma(I)$ were considered as significant.

Comparison of the unit-cell volume with those of the other *R*RhGe compounds assuming similar density led to an estimate of 20–24 atoms for the unit-cell content. Symmetry and the relative cell dimensions indicated a relationship with $U_3Ni_4Si_4$ (*oI*22, *Immm*) (Yarmolyuk, Akselrud, Grin, Fundamenskii & Gladyshevskii, 1979). Hence the atomic positions of this structure were used

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Table 1. *Atomic positions and thermal parameters* ($\times 10^2$) *for* $La_3Rh_4Ge_4$ *of* $U_3Ni_4Si_4$ *type* (*space group* *Immm*)

The equivalent isotropic temperature factors are expressed as $T = \exp[-2\pi^2 U(2\sin\theta/\lambda)^2]$ and were obtained from $U = \frac{1}{3}(U_{11} + U_{22} + U_{33})$. E.s.d.'s are given in parentheses.

	x	y	z	U (Å^2)
Rh(1) in 4(*j*)	0·5	0	0·10010 (7)	1·4 (1)
Ge(1) in 4(*j*)	0·5	0	0·1984 (1)	1·1 (1)
La(1) in 4(*j*)	0·5	0	0·35455 (5)	1·10 (7)
Rh(2) in 4(*i*)	0	0	0·24976 (7)	0·90 (8)
Ge(2) in 4(*i*)	0	0	0·4502 (1)	1·2 (1)
La(2) in 2(*a*)	0	0	0	1·07 (9)

Table 2. *Interatomic distances d* (Å) *up to* 1·3 $\sum r$ *and rounded values of* $\Delta(\equiv d - \sum r)$ (Å) *for* $La_3Rh_4Ge_4$ *of* $U_3Ni_4Si_4$ *type*

The atomic radii (r) used for La, Rh and Ge are 1·87, 1·34 and 1·37 Å respectively. E.s.d.'s are given in parentheses.

	d	Δ		d	Δ
La(1)–4Rh(1)	3·1880 (8)	−0·02	Rh(2)–2Ge(1)	2·457 (2)	−0·25
–2Ge(2)	3·191 (2)	−0·05	–2Ge(1)	2·492 (2)	−0·22
–4Ge(1)	3·262 (1)	0·02	–4Rh(2)	2·9756 (1)	0·30
–Ge(1)	3·940 (3)	0·70	–2La(1)	3·369 (2)	0·16
–2Rh(2)	3·369 (2)	0·16	–2La(1)	3·380 (2)	0·17
–2Rh(2)	3·380 (2)	0·17			
			Ge(1)–2Rh(2)	2·457 (2)	−0·25
La(2)–8Ge(2)	3·230 (1)	−0·01	–2Rh(2)	2·492 (2)	−0·22
–4Rh(1)	3·277 (1)	0·07	–Rh(1)	2·481 (3)	0·23
			–4La(1)	3·262 (1)	0·02
Rh(1)–2Ge(2)	2·471 (2)	−0·24	–La(1)	3·940 (3)	0·70
–Ge(1)	2·481 (3)	−0·23			
–4La(1)	3·1880 (8)	−0·02	Ge(2)–2Rh(1)	2·471 (2)	0·24
–2La(2)	3·277 (1)	0·07	–Ge(2)	2·514 (4)	−0·23
			–2La(1)	3·191 (2)	−0·05
			–4La(2)	3·230 (1)	−0·01

as starting values for a least-squares refinement, which converged after a few cycles to a conventional R of 0·05. Further refinements with anisotropic thermal parameters led to a final $R = \sum|\Delta F|/\sum|F_o|$ of 0·035 $\{R_w = 0{\cdot}046,\ w = 1/[\sigma(F) + 0{\cdot}01F|^2\}$.* A final electron density difference map was featureless. The atomic parameters and equivalent isotropic temperature factors are given in Table 1. Interatomic distances are listed in Table 2.

All calculations were performed with programs of the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Scattering factors for neutral atoms were taken from Cromer & Mann (1968), anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Discussion. A projection of the $La_3Rh_4Ge_4$ structure along the a axis is shown in Fig. 1. As already observed by Yarmolyuk, Akselrud, Grin, Fundamenskii & Gladyshevskii (1979) the structure may be considered as a periodic intergrowth of ordered AlB_2 and ordered $BaAl_4$ segments. The only two compounds known to crystallize with this structure type are $U_3Ni_4Si_4$ and $La_3Rh_4Ge_4$. However, Bodak & Gladyshevskii (1969) reported a $Ce_6Ni_6Si_7$ with space group *Immm* and unit-cell parameters $a = 4{\cdot}047$, $b = 4{\cdot}092$ and $c = 23{\cdot}16$ Å. The similarity of composition and lattice parameters makes the isotypy with $U_3Ni_4Si_4$ likely.

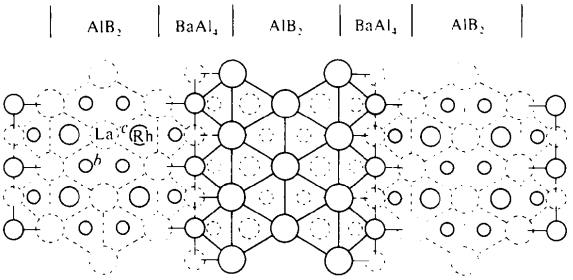

Fig. 1. $La_3Rh_4Ge_4$ of $U_3Ni_4Si_4$ type. Large circles: La, medium circles: Rh, small circles: Ge. Fully drawn circles at $x = \frac{1}{2}$, broken circles at $x = 0$.

The other rare-earth compounds known to have the composition ratio 3:4:4 are $Sc_3Ni_4Si_4$ (Bodak, Kotur & Gladyshevskii, 1976), $R_3Cu_4Si_4$ with R = Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Sc (Hanel & Nowotny, 1970) and $R_3Cu_4Ge_4$ with R = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y (Rieger, 1970; Hanel & Nowotny, 1970). These compounds crystallize with the $Gd_3Cu_4Ge_4$ structure type (Rieger, 1970) which has the same space group and Z value as the $U_3Ni_4Si_4$ type but different unit-cell ratios and atomic coordinates.

Both structure types contain structural segments of the AlB_2 type. The essential difference concerns the Cu and the Rh coordinations. In $Gd_3Cu_4Ge_4$ all Cu atoms are in the center of a Ge_4 tetrahedron; however, in $La_3Rh_4Ge_4$ only the Rh in the $BaAl_4$ segments are tetrahedrally surrounded by Ge atoms, while the Rh atoms in the AlB_2 segment are surrounded by only three Ge atoms in a trigonal planar configuration.

Surprisingly the $Gd_3Cu_4Ge_4$ structure is isotypic with $Sr_3Li_4Sb_4$ and $Ba_3Li_4Sb_4$ (Liebrich, Schäfer & Weiss, 1970), a polyanionic valence compound with $(VEC)_A = 7\frac{1}{2}$ and the corresponding crystal chemical formula $Sr_3Li_4Sb_2^{[+0]}Sb_2^{[+1]}$. $La_3Rh_4Ge_4$ neither has the same structure as $Sr_3Li_4Sb_4$ nor can be considered a valence compound. However, as one can see in Table 2, each Ge(1) is isolated but each Ge(2) has one close Ge(2) neighbor. Thus the crystal chemical formulae of the $Gd_3Cu_4Ge_4$ and $U_3Ni_4Si_4$ structure types are identical as far as the homonuclear coordination of Ge or Si is concerned.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36733 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Caesium Tetrachlorodioxoneptunate(V)

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Abstract. $Cs_3[NpCl_4O_2]$, monoclinic, $C2/c$, $a = 15{\cdot}468\,(9)$, $b = 7{\cdot}275\,(4)$, $c = 12{\cdot}757\,(6)$ Å, $\beta = 117{\cdot}23\,(4)°$, $U = 1276{\cdot}4\,(3{\cdot}0)$ Å^3, $Z = 4$, $D_c = 4{\cdot}21$ g cm^{-3}, $\mu(\text{Mo } K\alpha) = 144{\cdot}6$ cm^{-1}, $R = 0{\cdot}036$ ($R_w = 0{\cdot}033$) for 951 reflections. The complex contains $[NpCl_4O_2]^{3-}$ ions with *trans* oxygen atoms in the linear NpO_2^+ group [Np—O = 1·814 (34) Å]. The Np—Cl distances are 2·752 (13) and 2·760 (19) Å.

Introduction. As part of an investigation of the structural chemistry of neptunyl(V) and (VI) the structure of $Cs_3[NpCl_4O_2]$ has been redetermined. The high R value, 0·17, reported for the earlier investigation (Vodovatov, Ladygin, Lychev, Mashirov & Suglobov, 1975) suggested that the data would not be sufficiently precise to allow a meaningful comparison with the structure recently determined for $NpCl_2O_2$.2tppo (Alcock, Roberts & Brown, 1982*a*) to identify the effects of the additional *f* electron on bond lengths in the NpO_2^{n+} groups and those in the equatorial planes around them.

Suitable crystals of $Cs_3[NpCl_4O_2]$ were obtained by allowing $Cs_2[NpCl_4O_2]$ dissolved in an ethanol–water mixture to undergo spontaneous reduction. Turquoise, needle-like crystals grew as the solution slowly evaporated during a three or four day period. Suitable crystals were mounted on quartz fibres and encapsulated in glass capillaries which were then coated with Araldite. These operations were performed in a glove box to afford protection from the α-activity associated with ^{237}Np.

Reflections were collected at 153 K on a Syntex $P2_1$ automatic four-circle diffractometer with an attached LT-1 low-temperature device, using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). A crystal of dimensions 0·18 × 0·06 × 0·08 mm bounded by faces (110) and $(\bar{1}\bar{1}0)$ was used, which gave transmission factors in the range 0·346–0·505.

Accurate cell parameters were obtained by least-squares calculations based on the positions of 15 reflections in the range $25 \leq 2\theta \leq 27°$. The θ–2θ scan technique was used, with scan rates varying from 1·0 to 29·3° min^{-1}, depending on the intensity of a 2s pre-scan. The scan range was ±1·0° around both the $K\alpha_1$ and $K\alpha_2$ positions. 1229 reflections were collected in the range $0 \leq 2\theta < 50°$, of which 951 were considered observed [$I/\sigma(I) \geq 3{\cdot}0$] and used in the refinement. Three standard reflections monitored every 100 reflections showed no appreciable decrease in intensity.

The systematic absences $h + k \neq 2n$ for hkl and $l \neq 2n$ for $h0l$ reflections indicated the space group $C2/c$. The coordinates of the atoms were obtained from the published crystal structure of $Cs_3[NpCl_4O_2]$ in space group $B2/b$ (Vodovatov, Ladygin, Lychev, Mashirov & Suglobov, 1975) by an appropriate transformation.