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Y_2Rh_3Ge, a Rhombohedral Substitution Variant of the $MgCu_2$ Type*

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The structure of Y_2Rh_3Ge has been determined and refined from single-crystal X-ray diffraction data ($R = 0.042$). It is a rhombohedral, ternary, ordered variant of the cubic Laves structure type $MgCu_2$, with space group $R\bar{3}m$, $Z = 3$, $a = 5.552(3)$ and $c = 11.82(1)$ Å for the triple hexagonal cell. The c/a ratio (2.13) is significantly lower than the value for the triple hexagonal cell of the cubic lattice of the parent structure type (2.45), resulting in shorter distances between Rh and Ge atoms than between Rh atoms. The isotypy of Pr_2Rh_3Si, Er_2Rh_3Si, Pr_2Rh_3Ge, and Er_2Rh_3Ge has been established from Guinier films. The Y_2Rh_3Ge structure is compared with the binary compound YRh_2, crystallizing with the $MgCu_2$ structure, and with three other simple, ternary, ordered substitution derivatives of the Laves phase types $MgZn_2$ and $MgCu_2$.

Introduction

The Laves (or Friauf) phases with $MgZn_2$ or $MgCu_2$ structure type (*1–3*), or a stacking variant of these, are frequently found among binary intermetallic compounds with composition AB_2. According to Teslyuk (*4*) there can exist in principle two different kinds of very simple ternary substitution variants of each of the base types $MgZn_2$ and $MgCu_2$ having the compositions $A_2B_3B^*$ and AA^*B_4. A substitution variant with composition AA^*B_4, based on the cubic $MgCu_2$ type, has been observed, for example, with $MgSnCu_4$ (*5*), which may also be considered as a substitution variant of the $AuBe_5$ type (*6*). $MnInCu_4$ has been reported to crystallize with the $MgZn_2$-type structure (see (*4*)); however, the ordered atom distribution needs to be proven. The substitution variant with composition $A_2B_3B^*$ of the hexagonal $MgZn_2$ type, for which a large number of isotypes have been identified (see (*7*)), is known under the name Mg_2Cu_3Si type (*8*). We report here on the $A_2B_3B^*$ variant of the cubic $MgCu_2$ type. It was once believed that such an ordering variant occurs with Mn_2Cu_3Al (see (*4*)); however, later reinvestigations of this compound (*9*) indicate that the Cu and Al atoms are not ordered.

Structure Resolution and Single-Crystal Refinement

A sample of nominal composition Y_2Rh_3Ge was prepared from the elements (Y 99.99, Rh 99.9, Ge 99.999%) in an arc furnace under Ar atmosphere, and further wrapped in Ta foil and annealed in a quartz tube at 1073 K for 10 days. A single crystal of irregular shape (mean radius 10 μm) was

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TABLE I

ATOMIC COORDINATES IN THE TRIPLE HEXAGONAL CELL AND ISOTROPIC DISPLACEMENT PARAMETERS FOR Y_2Rh_3Ge WITH SPACE GROUP $R\bar{3}m$

		x	y	z	$100U$ (Å^2)
Rh	in 9(d)	1/2	0	1/2	0.6(1)
Y	in 6(c)	0	0	0.3718(3)	1.0(1)
Ge	in 3(a)	0	0	0	0.5(1)

Note. The temperature factor is expressed as $T = \exp[-2\pi^2U(2\sin\theta/\lambda)^2]$. e.s.d.'s are given in parentheses.

mounted on a Philips PW1100 diffractometer with graphite monochromatized Mo$K\alpha$ radiation. Laue symmetry $\bar{3}m1$; systematic absences at $-h + k + l \neq 3n$, leading to possible space groups $R32$, $R3m$ and $R\bar{3}m$; 274 reflections were collected out to $\sin\theta/\lambda = 0.70$ Å^{-1} ($0 \leq h, k \leq 7; 0 \leq l \leq 16$ and all antireflections) in the ω-2θ scan mode, yielding 135 independent reflections ($R_{\text{int}} = 0.054$), of which 97 were considered significant [$|I| \geq 3\sigma(I)$]. Standard reflections were 2 −2 −2 and −2 2 2 (max. intensity variation ±1.7%); spherical absorption correction was $\mu = 46.6$ mm^{-1}; $\mu R = 0.466$; $1.943 \leq A^* \leq 1.977$. Structure solution was obtained by direct methods, with the program MULTAN80 (*10*). Full matrix refinement in $R\bar{3}m$ used $|F|$ values of 114 independent reflections (including 17 less-thans calculated greater than observed). One positional parameter and three isotropic displacement parameters, listed in Table I, one scale factor and one correction factor for isotropic secondary extinction (Gaussian distribution, mosaic spread parameter $G = 1.1(4) \times 10^{-5}$ °) were refined to a final $R = 0.042$ ($S = 2.50$; shift/error in the last cycle ≤ 0.0002; max. (min.) height of final residual electron density map = 5.8 (−6.1) e Å^{-3}). Atomic scattering factors for neutral atoms, f' and f'', were from the "International Tables for X-Ray Crystallography" (1974); programs used for data reduction and structure refinement were from the XRAY76 system (*11*).

The isotropic displacement parameters and the residual electron density map corresponding to the refinement above are in good agreement with the occupation of the sites in Wyckoff positions 9(d) and 3(a) by Rh and Ge atoms, respectively. However, a refinement of the population parameters of these two sites was carried out as a check. The population parameter for the site in 9(d) refined to 101(2)% Rh and that for the site in 3(a) to 102(4)% Ge. The R factor and the displacement parameters were similar to the values of the preceding refinement. No attempt has been made to look for a homogeneity range.

Isotypic Compounds

Cell parameters of the isotypic compounds Pr_2Rh_3Si, Er_2Rh_3Si, Pr_2Rh_3Ge, and Er_2Rh_3Ge are given in Table II. All compounds were prepared at the stoichiometric composition in an arc furnace and annealed for 7 days at 1273 K. The isotypy was established by comparing Guinier films with the diffraction patterns calculated by the program LAZY PULVERIX (*12*) for the Y_2Rh_3Ge type. The lattice parameters of Y_2Rh_3Ge were determined from single-crystal diffractometer data, the remaining ones from Guinier films using Si (a = 5.4307

TABLE II

PARAMETERS OF THE TRIPLE HEXAGONAL CELLS FOR GERMANIDES AND SILICIDES CRYSTALLIZING WITH THE Y_2Rh_3Ge TYPE AND EXPERIMENTAL CONDITIONS FOR THEIR DETERMINATION

Compound	a (Å)	c (Å)	c/a	λ (Å)	Refl.	2θ range
Pr_2Rh_3Si	5.615(1)	11.785(4)	2.099	1.5418	15	31–68°
Er_2Rh_3Si	5.500(1)	11.562(3)	2.102	1.5418	17	32–70°
Y_2Rh_3Ge	5.552(3)	11.82(1)	2.129	0.7093	14	36–55°
Pr_2Rh_3Ge	5.626(2)	11.993(4)	2.132	1.5418	17	22–67°
Er_2Rh_3Ge	5.523(1)	11.762(3)	2.130	1.5418	16	22–69°

Å) as internal standard. The program FINAX (*13*) was used for their refinement. It can also be seen from Table II that the axial ratios of all compounds are significantly smaller than the value $2^{1/2} \cdot 3^{1/2} \approx 2.45$ for the triple hexagonal cell of the cubic $MgCu_2$ type.

Description of the Four Simple Ternary Laves Phase Substitution Derivatives

Figure 1 shows the arrangement of the atoms in the Y_2Rh_3Ge structure in a projection on the $(1\ 1\ \bar{2}\ 0)$ plane of the triple hexagonal cell, together with the three other simple ternary substitution variants of the $MgCu_2$ and the $MgZn_2$ types in similar projections. The upper two structures are derived from the $MgZn_2$ type and the two on the bottom from the $MgCu_2$ type; the structures to the left have the composition $A_2B_3B^*$ and those to the right AA^*B_4. The idealized atom coordinates of these four structure types are given in Table III. In the case of the $MgZn_2$-derivative $MnInCu_4$ there is no complete proof that this compound really has an ordered Laves-type structure.

The Laves phases may be described as built up of slabs, perpendicular to the c-axis of the (triple) hexagonal cell (their interfaces are indicated with dashed lines in Fig. 1). As in the case of the close-packed

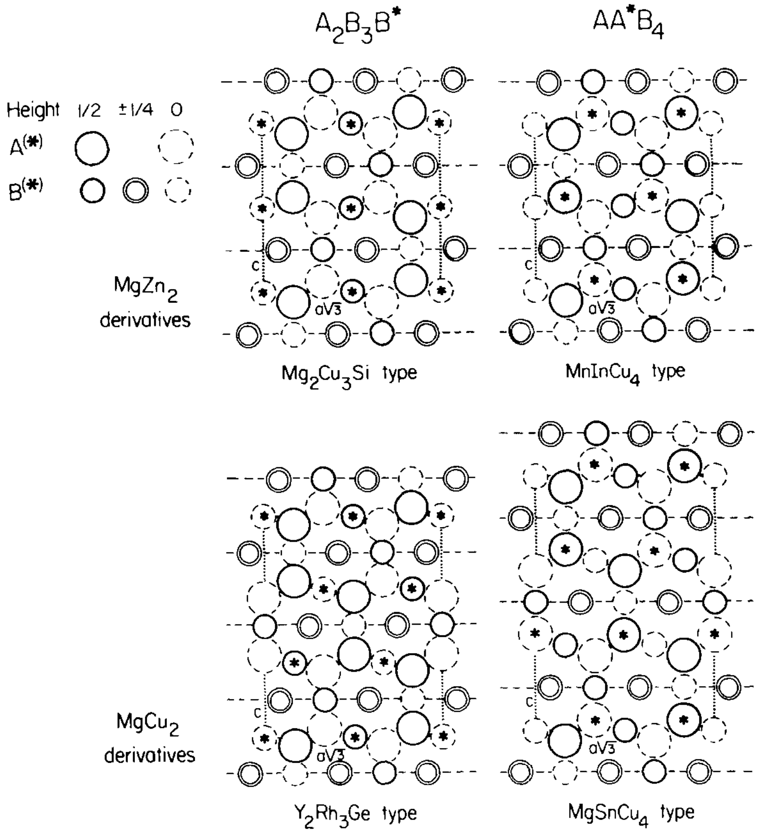

FIG. 1. The four simple substitution variants of the Laves types $MgCu_2$ and $MgZn_2$ in projections on the $(1\ 1\ \bar{2}\ 0)$ plane of the (triple) hexagonal cells.

TABLE III

CRYSTALLOGRAPHIC DATA (IDEALIZED) FOR THE TERNARY ORDERED SUBSTITUTION VARIANTS OF THE $MgZn_2$ AND $MgCu_2$ TYPES WITH COMPOSITIONS $A_2B_3B^*$ AND AA^*B_4

	$A_2B_3B^*$	AA^*B_4
$MgZn_2$ derivatives	Mg_2Cu_3Si type	$MnInCu_4$? type
	$hP12$, $P6_3/mmc$	$hP12$, $P6_3mc$
	$c/a \simeq 2(2/3)^{1/2}$	$c/a \simeq 2(2/3)^{1/2}$
	A 4(f) 1/3 2/3 ~9/16	A 2(b) 1/3 2/3 ~1/16
	B 6(h) ~1/6 1/3 1/4	A^* 2(b) 1/3 2/3 ~7/16
	B^* 2(a) 0 0 0	B 6(c) ~5/6 $-x$ ~1/4
		B 2(a) 0 0 0
$MgCu_2$ derivatives	Y_2Rh_3Ge type	$MgSnCu_4$ type
	$hR18$, $R\bar{3}m$	$cF24$, $F\bar{4}3m$
	$c/a \simeq 3(2/3)^{1/2}$	c/a(hex) = $3(2/3)^{1/2}$
	A 6(c) 0 0 ~3/8	A 4(a) 0 0 0
	B 9(d) 1/2 0 1/2	A^* 4(c) 1/4 1/4 1/4
	B^* 3(a) 0 0 0	B 16(e) ~5/8 x x

structures of the elements the relative shift of these slabs results in numerous possible stacking variants. We will limit our attention here to the two simplest stacking variants $MgCu_2$ and $MgZn_2$. It can be seen from the projection of the structure of Y_2Rh_3Ge in Fig. 1 that in the ternary compound the transition metal atoms occupy all the sites at the interfaces of the stacked slabs while the main group element is found at the sites inside the slabs (indicated with an asterisk). The same site distribution between the transition metal and the main group element is also observed for silicides, germanides, and gallides crystallizing with the Mg_2Cu_3Si type, see, for example, Sc_2Co_3Si (*14*); however, in the case of aluminides the transition metal and main group sites are in certain cases interchanged. It is frequently observed among ternary intermetallic compounds containing a rare earth (or a similar large electropositive element), a transition metal, and a main group element such as Al, Ga, Si, or Ge, that aluminides crystallize with the same structure type as silicides, germanides, or gallides, but with the transition metal and the main group element sites interchanged (*15*). Considering ternary Laves phases occurring with similar elements this seems to be true only to a certain extent since, for example, both U_2Cu_3Al (*16*) and Sc_2RuAl_3 (*17*) have been reported to crystallize with the Mg_2Cu_3Si type.

Interatomic Distances and Coordinations

In Table IV the interatomic distances (d) up to 4 Å in Y_2Rh_3Ge are compared with those observed in the binary compound YRh_2 which, like $PrRh_2$ (*18*) and $ErRh_2$ (*19*), crystallizes with the cubic $MgCu_2$ type, a = 7.498 Å (a_h = 5.302, c_h = 12.98 Å) (*20*). The values of $\Delta = (d - \Sigma r)/\Sigma r$ have been calculated, using the radii (r) of 12-coordinated atoms (*21*), in order to estimate the contraction of the distances.

In the binary Laves phase structures the A site, generally occupied by the larger atom kind, is surrounded by 12 B sites distributed on the vertices of a truncated tetrahedron, and by 4 A sites situated above its hexagonal faces. This kind of 16-atom coordination is generally called a Friauf

TABLE IV

INTERATOMIC DISTANCES (d) UP TO 4 Å AND $\Delta = (d - \Sigma r)/\Sigma r$ FOR Y_2Rh_3Ge AND YRh_2, THE LATTER WITH $MgCu_2$-TYPE STRUCTURE

Y_2Rh_3Ge			YRh_2		
	d (Å)	Δ (%)		d (Å)	Δ (%)
Y—3 Rh	2.907(4)	−7.6	Y—12 Rh	3.109	−1.2
Y	3.030(7)	−15.9	4 Y	3.247	−9.9
6 Rh	3.162(2)	+0.5			
3 Ge	3.237(2)	+2.1			
3 Y	3.332(2)	−7.5			
Rh—2 Ge	2.540(2)	−6.4	Rh—6 Rh	2.651	−1.5
4 Rh	2.776(1)	+3.2	6 Y	3.109	−1.2
2 Y	2.907(4)	−7.6			
4 Y	3.162(2)	+0.5			
Ge—6 Rh	2.540(2)	−6.4			
6 Y	3.237(2)	+2.1			

Note. e.s.d.'s are given in parentheses. Atomic radii (r) used are 1.801 (Y), 1.345 (Rh), and 1.369 Å (Ge), respectively (*21*).

polyhedron. The *B* sites form tetrahedra linked to each other by vertices ($MgCu_2$ stacking) or by faces and vertices ($MgZn_2$ stacking). Each atom at a *B* site has 6 nearest *B* neighbors, which together with 6 atoms from surrounding *A* sites, form an icosahedron. It can be seen from Table IV that in the case of YRh_2 all the distances between the central atoms and the atoms belonging to the coordination polyhedra are shorter than the sum of the atomic radii.

In the substitution variants with composition $A_2B_3B^*$ the B^* atoms are distributed in such a way that there is no contact between them. The coordination for the different sites are $9B + 3B^* + 4A$ for the *A* site, $4B + 2B^* + 6A$ for the *B* site and $6B + 6A$ for the B^* site. The parameters of the triple hexagonal cell of Y_2Rh_3Ge are about 5% longer (*a*) and 10% shorter (*c*) than those of the related cell of YRh_2, resulting in a significantly smaller *c*/*a* ratio (2.13 instead of 2.45). As a consequence of this, the distances between Rh and Ge atoms are shorter than those observed between Rh atoms. Furthermore, looking at the interatomic distances of Y_2Rh_3Ge in Table IV, it appears that the former show a contraction of 6.4%, while the latter are no longer contracted as in YRh_2. The general contraction of the structure along the *c*-axis, as compared with the cubic parent type, is also reflected in the very short distances parallel to this axis between Y atoms, $d(\text{Y–Y}) = 3.030(7)$ Å ($\Delta = -15.9\%$), which is even shorter than the sum of covalent radii, $2r_{\text{cov}}(\text{Y}) = 3.24$ Å. However, similar very short distances between Y atoms have also been observed, for example, with YCo_3B_2, crystallizing with the $CeCo_3B_2$ type, where $d(\text{Y–Y})$ has been reported to be 3.038(2) (*22*) or 3.027(2) Å (*23*). The average contraction of the distances between Y atoms in Y_2Rh_3Ge is about the same as in YRh_2. Considering the complete coordination of the Y atoms, it can be seen that the distances to the 9 Rh atoms are shorter than those to the three Ge atoms, also when comparing the relative distances taking into account the atomic radii.

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Note added in proof. The same rhombohedral structuure as Y_2Rh_3Ge was recently found with Mg_2Ni_3Si (*24*); however, it was not described as a substitution variant of the $MgCu_2$ type. Assigning four valence electrons to Si the valence electron concentration of Mg_2Ni_3Si is 1.33 for which a cubic stacking is to be expected with Mg-base Laves phases (*25, 26, 27*).

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