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Sc₁₁Al₂Ge₈, a Ternary Substitution Variant of the Tetragonal Ho₁₁Ge₁₀ Type

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Abstract. Sc₁₁Al₂Ge₈, $M_r = 1129.20$, tetragonal, $tR84$, $I4/mmm - n^2mjh^2e^2d$, $a = 10.419$ (1), $c = 14.974$ (2) Å, $V = 1625.6$ (3) Å³, $Z = 4$, $D_x = 4.614$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 19.738$ mm⁻¹, $F(000) = 2052$, $T = 300$ K, $wR = 0.045$ for 369 contributing unique reflections. Sc₁₁Al₂Ge₈ is a new ternary substitution variant of the Ho₁₁Ge₁₀ type with the Al atoms substituting for the Ge atoms on one crystallographic site.

Introduction. From the study of the crystal structures of the binary or ternary rare-earth-transition-metal-non-metal compounds, with the non-metal being Si or Ge, it is known that the Al atoms, when introduced as a third or fourth component, do not always simply substitute for Si or Ge atoms but often prefer sites with different coordinations. To obtain more information on the site occupations of the Al atoms it was considered of interest to study the structures of rare-earth aluminium germanides.

Experimental. The sample of nominal composition Sc₂Al₂Ge was prepared by arc melting under argon atmosphere (Sc 99.99, Al 99.99 and Ge 99.99%). The weight loss was 0.6%. A single crystal with irregular shape (mean radius: 0.008 mm) obtained from the as-cast sample was mounted on a Philips PW1100 automatic four-circle diffractometer, Mo $K\alpha$ radiation with graphite monochromator. The cell parameters were refined from 2θ values of 22 reflections (Mo $K\alpha$, $\lambda = 0.71073$ Å, $15 < 2\theta < 35^\circ$) using the pro-

gram *LATCON* (Schwarzenbach, 1966). 2696 reflections were collected out to $(\sin\theta)/\lambda = 0.702$ Å⁻¹ ($0 \leq h \leq 14$, $0 \leq k \leq 14$, $0 \leq l \leq 20$ and the antireflections) in the ω - 2θ scan mode, yielding 721 unique reflections ($R_{\text{int}} = 0.13$). Two standard reflections (330 and 006) were measured with maximum intensity variations of 1.05 and 1.2%, respectively. A spherical absorption correction was made using the program *ABSORB* (Davenport, Spadaccini & Stewart, 1989) with max. and min. transmission factors of 0.7468 and 0.7407. The anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). From the resemblance of the unit cell and the possible space groups $I422$, $I4mm$, $\bar{I}4m2$, $\bar{I}42m$, $I4/mmm$ (*International Tables for Crystallography*, 1983, Vol. A), we were led to assume that the structure is isotypic to the Ho₁₁Ge₁₀ type (Smith, Johnson & Tharp, 1967). The space group $I4/mmm$, the Wyckoff position and the atom coordinates of Ho₁₁Ge₁₀ were used as starting values for the refinement. The refinement was based on $|F|$ values and isotropic atomic displacement parameters using the program *CRYLSQ* (Olthof-Hazekamp, 1989). During the first step of the refinement it was found that the displacement parameter of the Ge atoms at the $8(h)$ position was very high and there was a large hole at this position on the difference electron density map. This led us to place Al atoms in this site. The final refinement of the structure confirmed the substitution. 22 variables refined to $R = 0.059$ and $wR = 0.045$ [$w = 1/$

Table 1. Atomic positional and displacement parameters for the $\text{Sc}_{11}\text{Al}_2\text{Ge}_8$ structure, space group $I4/mmm$, and the site occupations in $\text{Ho}_{11}\text{Ge}_{10}$, $\text{Sc}_7\text{Cr}_{4+x}\text{Si}_{10-x}$ ($x = 0.8$), $\text{Sc}_7\text{Mn}_{4+x}\text{Ge}_{10-x}$ ($x = 1.3$) and $\text{Sc}_7\text{Re}_{4-x}\text{Si}_{10+x}$ ($x = 0.65$)

The isotropic atomic displacement factors are expressed as $T = \exp\{-2\pi^2 U[(\sin\theta)/\lambda]^2\}$. E.s.d.'s are given in parentheses.

	x	y	z	$U(\text{\AA}^2 \times 100)$	$\text{Ho}_{11}\text{Ge}_{10}$	$\text{Sc}_7\text{Cr}_{4+x}\text{Si}_{10-x}$	$\text{Sc}_7\text{Mn}_{4+x}\text{Ge}_{10-x}$	$\text{Sc}_7\text{Re}_{4-x}\text{Si}_{10+x}$
Sc(1)	16(n)	0	0.2507 (4)	0.3102 (2)	0.48 (7)	Ho	Sc	Sc
Sc(2)	16(n)	0	0.3356 (3)	0.1024 (2)	0.32 (7)	Ho	Cr	Mn
Ge(1)	16(m)	0.2047 (1)	0.2047 (1)	0.1711 (1)	1.00 (5)	Ge	Si	Ge
Ge(2)	8(f)	0.1470 (3)	$\frac{1}{2}$	0	0.60 (7)	Ge	Si	Ge
Al	8(h)	0.1270 (6)	0.1270 (6)	0	0.80 (18)	Ge	$\text{Si}_{0.6}\text{Cr}_{0.4}$	$\text{Mn}_{0.64}\text{Ge}_{0.36}$
Sc(3)	8(h)	0.3272 (4)	0.3272 (4)	0	0.63 (11)	Ho	Sc	Sc
Sc(4)	4(e)	0	0	0.1688 (6)	0.55 (16)	Ho	Sc	Sc
Ge(3)	4(e)	0	0	0.3815 (3)	0.39 (9)	Ge	Si	Ge
Ge(4)	4(d)	0	$\frac{1}{4}$	0.32 (8)	0.32 (8)	Ge	Si	Ge

Table 2. Interatomic distances up to 3.5 Å in $\text{Sc}_{11}\text{Al}_2\text{Ge}_8$; e.s.d.'s are given in parentheses

Sc(1)—Ge(4)	2.750 (1)	Al—2Al	2.646 (9)
Ge(3)	2.822 (2)	2Ge(1)	2.805 (3)
2Ge(1)	3.020 (4)	Sc(3)	2.951 (7)
Ge(2)	3.035 (4)	4Sc(2)	2.971 (6)
2Ge(1)	3.125 (4)	2Sc(4)	3.144 (8)
Sc(2)	3.236 (5)		
Sc(4)	3.363 (6)	Ge(1)—Ge(1)	2.716 (3)
2Sc(2)	3.376 (3)	2Sc(2)	2.732 (3)
2Sc(3)	3.461 (4)	Al	2.805 (3)
		Sc(4)	3.016 (1)
Sc(2)—2Ge(1)	2.732 (3)	2Sc(1)	3.020 (4)
2Ge(2)	2.762 (3)	2Sc(1)	3.125 (4)
Ge(4)	2.797 (3)	Sc(3)	3.134 (3)
2Al	2.971 (6)		
Sc(2)	3.066 (4)	Ge(2)—2Sc(3)	2.601 (4)
Sc(1)	3.236 (5)	4Sc(2)	2.762 (3)
2Sc(1)	3.376 (3)	2Sc(1)	3.035 (4)
Sc(2)	3.426 (5)	Sc(2)	3.064 (5)
Sc(3)—2Ge(2)	2.601 (4)	Ge(3)—4Sc(1)	2.822 (2)
Al	2.951 (7)	4Sc(3)	3.103 (4)
2Ge(3)	3.103 (4)	Sc(4)	3.186 (9)
2Ge(1)	3.134 (3)		
4Sc(1)	3.461 (4)	Ge(4)—4Sc(1)	2.750 (1)
		4Sc(2)	2.797 (3)
Sc(4)—4Ge(1)	3.016 (1)		
4Al	3.144 (8)		
Ge(3)	3.186 (9)		
4Sc(3)	3.363 (6)		

$\sigma^2(|F_{\text{rel}}|)$, $S = 1.503$, considering 369 contributing reflections with $|F_{\text{rel}}| > 3\sigma(|F_{\text{rel}}|)$. The maximum shift/e.s.d. in the last cycle was 0.00005, and the final residual electron density + 6.61 (− 5.84) $e \text{\AA}^{-3}$. The programs used to refine the structures were all from the *XTAL2.6* system (Hall & Stewart, 1989). The atomic positional parameters were standardized by using the *STRUCTURE TIDY* program (Gelato & Parthé, 1987). The atomic positional and displacement parameters are given in Table 1* and the interatomic distances up to 3.5 Å in Table 2.

* Lists of structure factors and isotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53330 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

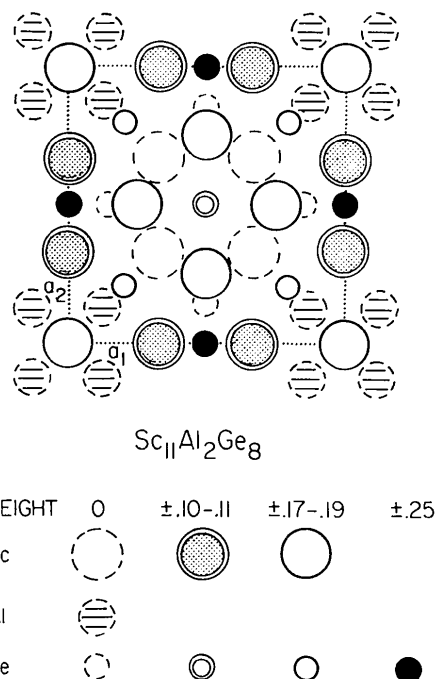


Fig. 1. The [001] projection of half a unit cell of $\text{Sc}_{11}\text{Al}_2\text{Ge}_8$ ($-0.25 \leq z \leq +0.25$). The Al atoms form squares around the origin. Large shaded circles correspond to sites which are occupied by transition elements in other $\text{Ho}_{11}\text{Ge}_{10}$ substitution variants.

The relatively high residual electron densities may be caused by the following (a) since the sample was not annealed the collected data set was not good enough ($R_{\text{int}} = 0.13$) to permit an anisotropic structure refinement and (b) the spherical absorption correction for the irregular crystal was only an approximation. The distance between the largest peak and hole is ca 1.2 Å. Some holes were found at nearly the same positions as the peaks. The positions of the largest peak and hole are between the Sc(4) and Ge(3) atoms along the c axis. From Table 2 we can see that the coordinations of these two atoms are noticeably different from the other Sc and Ge atoms.

Discussion. The Sc₁₁Al₂Ge₈ structure can be considered as a ternary substitution variant of the Ho₁₁Ge₁₀ type. The four Sc sites correspond to the Ho sites and the four Ge sites together with the Al site to the Ge sites in Ho₁₁Ge₁₀. The projection of half a unit cell of Sc₁₁Al₂Ge₈ is shown in Fig. 1. Sets of four Al atoms form a square around the origin. These squares of tightly bonded Al atoms are also found in YbMo₂Al₄ (Fornasini & Palenzona, 1976). The interatomic distances of the Al atoms in Sc₁₁Al₂Ge₈ are 2.646 Å and in YbMo₂Al₄ 2.65 Å, respectively. These distances are 5–5% smaller than the sum of the metallic radii of the Al atoms. Similar short distances are, however, also found in the structures with the Ho₁₁Ge₁₀ type and its other substitution variants without Al.

Four ternary compounds which are substitution variants of the Ho₁₁Ge₁₀ type have been reported: Sc₇Cr_{4+x}Si_{10-x} ($x = 0.8$) (Kotur, Bodak & Zavodnik, 1985), both Sc₇Mn_{4+x}Ge_{10-x} ($x = 1.3$) and Sc₇Cr_{4+x}Ge_{10-x} ($x = 1.2$) (Kotur, Andrusyak & Zavodnik, 1988) and Sc₇Re_{4-x}Si_{10+x} ($x = 0.65$) (Zhao, Chabot & Parthé, 1988) for which the site occupations are also given in Table 1. A substitution of the Ho₁₁Ge₁₀ structure has been observed on two sites only, that is one 16(*n*) Ho site (marked in Fig. 1 by large shaded circles) and the 8(*h*) Ge site (occupied by Al in Sc₁₁Al₂Ge₈). The transition elements substitute essentially on the Ho site; however, Cr and

Mn, to a lesser degree also Re, partially occupy also the 8(*h*) Ge site.

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Structure of (μ -I)₂Os₂(CO)₆I₂

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Abstract. Hexacarbonyl-1 κ^3 C,2 κ^3 C-di- μ -iodo-1 κ I-2 κ I-diiiodo-1 κ I,2 κ I-diosmium, [Os₂(CO)₆I₄], monoclinic, *C*2/*m*, $a = 11.082$ (2), $b = 7.740$ (5), $c = 9.711$ (3) Å, $\beta = 107.22^\circ$, $V = 795.6$ Å³, $Z = 2$, $D_x = 4.408$ g cm⁻³, $M_r = 1056.08$, $F(000) = 896$, $M_o K\alpha$, $\lambda = 0.71703$ Å, $\mu = 237$ cm⁻¹, room temperature, $R_f = 0.037$ for 841 reflections. The molecular structure of the title compound consists of two (CO)₃Os units bridged by two iodines. The symmetry around the Os atoms was found to be octahedral.

Introduction. Although there have been reports for the synthesis of (μ -I)₂Os₂(CO)₆I₂ (Psaro, Ugo, Zanderighi, Besson, Smith & Basset, 1981) by the reac-

tion of [Os(CO)₃Cl₂] with LiI, by the reaction of osmium oxidide with copper turnings at 403 K under CO pressure for 24 h (Hales & Irving, 1967), and also by dimerization of *cis*-[Os(CO)₄I₂] at 403 K (Moss, Niven & Sutton, 1988), there is no conclusive evidence for the molecular structure of the compound synthesized. Here we report the molecular structure of (μ -I)₂Os₂(CO)₆I₂. This compound was isolated from the reaction of (μ -H)Os₃(CO)₁₁ with CH₂ClI in the presence of BCl₃.

Experimental. Light yellow, single crystals were obtained from CH₂Cl₂ at 298 K. For X-ray examination and data collection, a suitable crystal of approx-