The Crystal Structures of Sc$_5$Si$_3$, Sc$_5$Ge$_3$, La$_5$Ge$_3$, and Ce$_5$Ge$_3$

By Joseph Arbuckle and Erwin Parthé

University of Pennsylvania, Metallurgy Department, Philadelphia, Pa., U.S.A.

The crystal structures of Sc$_5$Si$_3$, Sc$_5$Ge$_3$, La$_5$Ge$_3$, and Ce$_5$Ge$_3$ have been studied by means of Debye–Scherrer powder photographs. All compounds crystallize in the unfilled Mn$_5$Si$_3$(D8$_8$) structure type. The hexagonal lattice constants of Sc$_5$Si$_3$ are $a = 7 \cdot 861$ and $c = 5 \cdot 812$ Å; those of Sc$_5$Ge$_3$ are $a = 7 \cdot 939$ and $c = 5 \cdot 883$ Å. The dimensions of La$_5$Ge$_3$ are $a = 8 \cdot 958$ and $c = 6 \cdot 795$ Å while those of Ce$_5$Ge$_3$ are $a = 8 \cdot 875$ and $c = 6 \cdot 570$ Å. All of the above compounds have an unusually large c/a ratio.

Introduction

Due to the extreme difficulty of producing elementary scandium, few properties of this metal and its alloys are known at this time. A literature survey revealed that at present only about a score of scandium compounds are known. One might expect scandium to behave much like the rare earths with respect to properties and alloying ability, but this is not necessarily the case as scandium is almost 10% smaller than the smallest rare earth, lutecium.

This study on the structure of scandium silicides and germanides is the first paper in a series of investigations to reveal the crystal chemistry of scandium compounds.

The Mn$_5$Si$_3$ structure type has been the object of numerous recent investigations. It is geometrically related to the NiAs structure (Parthé, 1957; Jellinek, 1959) and to the σ phase (Aronsson & Lundstrøm, 1957). The results of some recent work on Y$_5$Si$_3$ and Y$_5$Ge$_3$ (Parthé, 1960) have prompted this study of D8$_8$ phases with other transition metals of the third group of the periodic system.

Sample preparation and experimental results

The scandium, lanthanum, and cerium used in these experiments were supplied by the A. D. Mackay Co. The scandium was 99% pure, 0·3% iron being the main impurity. Mixtures of scandium and powdered silicon in the proper proportion were arc-melted while scandium and powdered germanium were alloyed in an induction furnace. In both cases, the samples were under an inert atmosphere. The lanthanum and cerium were 99·9% pure. In each case, metal filings were pressed into a pill with the proper amount of germanium. The samples were then induction melted under inert atmosphere. The composition of all samples was checked by chemical analysis. The samples were homogenized by repeated induction heating to approximately 1300 °C.

Debye–Scherrer photographs of Sc$_5$Si$_3$, Sc$_5$Ge$_3$, La$_5$Ge$_3$, and Ce$_5$Ge$_3$ were indexed, and in each case the unit cell was found to be hexagonal. The lattice parameter, c/a ratios, and calculated densities are given below.

Compound	a (Å)	c (Å)	c/a	Density (g.cm.$^{-3}$)
Sc$_5$Si$_3$	7·861	5·812	0·739	1·98
Sc$_5$Ge$_3$	7·939	5·883	0·741	2·76
La$_5$Ge$_3$	8·958	6·795	0·759	3·72
Ce$_5$Ge$_3$	8·875	6·570	0·740	3·92

From the systematic extinctions, the space groups D_{6h}^3–$P6_3/mcm$, D_{3h}^2–$P\bar{6}c2$, C_{6v}^3–$P6_3cm$, D_{3d}^4–$P\bar{3}c1$, and C_{3v}^3–$P3c1$ were all found to be acceptable possibilities. The first of these was assumed for all of the compounds, the scandium (lanthanum or cerium) atoms being placed in equipoint 4d and 6g_{I} with $x_{\mathrm{I}} = 0·25$ and the silicon (or germanium) atoms in equipoint 6g_{II} with $x_{\mathrm{II}} = 0·61$. The calculated and observed intensities are in excellent agreement.* The calculated d values and observed intensities are shown in Table 1. All four compounds crystallize in the unfilled D8$_8$ structure type.

Discussion

The compounds in this study all showed unusually high c/a ratios. In D8$_8$ phases with transition metals of Group IV or greater, the distance between metal atoms in the 4d and 6g positions is relatively large. With metals of Group III, atoms in these positions come very close to touching one another, and, in some cases, even overlap. A compression of the a axis results, causing the unusually large c/a ratio. This aspect and others will be discussed in detail in a forthcoming paper on the occurrence and lattice dimensions of D8$_8$ phases (Arbuckle & Parthé; in preparation).

---
* This data and sin$^2 \theta$ values may be obtained by writing to the authors.

Table 1. *Calculated d values and observed intensities*
(Cr Kα radiation)

hkil	Sc_5Si_3 d_c (Å)	I_o	Sc_5Ge_3 d_c (Å)	I_o
$10\bar10$	6·808	vw	6·875	w
$11\bar20$	3·930	—	3·969	vw
$20\bar20$	3·404	w	3·438	—
$11\bar21$	3·257	vw	3·290	m
0002	2·906	vw	2·941	m
$10\bar12$	2·673	mw	2·705	m
$21\bar30$	2·573	m	2·599	m
$21\bar31$	2·353	vvs	2·377	vvs
$11\bar22$	2·337	vvs	2·363	vs
$30\bar30$	2·269	s	2·292	s
$20\bar22$	2·210	vw	2·235	w
$22\bar40$	1·965	—	1·985	—
$21\bar32$	1·926	—	1·947	—
$31\bar40$	1·888	vw	1·907	—
$22\bar41$	1·862	vw	1·880	vw
$31\bar41$	1·796	vw	1·814	m
$30\bar32$	1·788	—	1·808	—
$11\bar23$	1·738	—	1·758	—
$40\bar40$	1·702	—	1·719	—
$22\bar42$	1·628	m	1·645	w
$31\bar42$	1·583	—	1·600	—
$32\bar50$	1·562	—	1·577	—
$21\bar33$	1·548	m	1·565	m
$32\bar51$	1·508	w	1·524	vw
$41\bar50$	1·486	w	1·500	—
$40\bar42$	1·469	mw	1·484	—
0004	1·453	w	1·471	w
$41\bar51$	1·439	—	1·454	—
$10\bar14$	1·421	—	1·438	—
$22\bar43$	1·380	—	1·395	—
$32\bar52$	1·376	vw	1·390	vw
$11\bar24$	1·363 }	vw	1·379 }	vw
$50\bar50$	1·362 }		1·375 }	
$31\bar43$	1·352	vw	1·367	w
$20\bar24$	1·336	—	1·352	—
$41\bar52$	1·323	vw	1·337	vw
$33\bar60$	1·310	—	1·323	—
$42\bar60$	1·287	mw	1·299	w
$33\bar61$	1·278	mw	1·291	vw
$21\bar34$	1·265	mw	1·280	vw
$42\bar61$	1·256	w	1·269	m
$50\bar52$	1·233	m, d	1·246	s, d
$30\bar34$	1·224 }	s, d	1·238 }	s, d
$51\bar60$	1·223 }		1·235 }	
$32\bar53$	1·216	mw	1·229	—
$51\bar61$	1·197 }	s, d	1·209 }	m, d
$33\bar62$	1·194 }		1·207 }	
$41\bar53$	1·179	—	1·192	—
$42\bar62$	1·176 }	vw, d	1·189	w, d
$22\bar44$			1·182	—

hkil	La_5Ge_3 d_c (Å)	I_o	hkil	Ce_5Ge_3 d_c (Å)	I_o
$10\bar10$	7·758	—	$10\bar10$	7·686	—
$11\bar20$	4·479	--	$11\bar20$	4·437	–
$20\bar20$	3·879	vvw	$20\bar20$	3·843	vw
$11\bar21$	3·741	w	$11\bar21$	3·677	vw
0002	3·398	m	0002	3·284	vw
$10\bar12$	3·111	ms	$10\bar12$	3·021	m
$21\bar30$	2·932	s	$21\bar30$	2·905	m
$11\bar22$	2·707	vvs	$21\bar31$	2·657 }	vvs
$21\bar31$	2·692	vvs	$11\bar22$	2·640 }	
$30\bar30$	2·586	s	$30\bar30$	2·562	ms
$20\bar22$	2·556	vvw	$20\bar22$	2·497	—
$22\bar40$	2·240	vvw	$22\bar40$	2·219	—
$21\bar32$	2·220	—	$21\bar32$	2·176	—
$31\bar40$	2·151	vvw	$31\bar40$	2·132	—
$22\bar41$	2·127	w	$22\bar41$	2·102	vvw
$30\bar32$	2·058 }	w	$31\bar41$	2·028	vvw
$31\bar41$	2·051 }		$30\bar32$	2·020	—
$11\bar23$	2·021	vvw	$11\bar23$	1·964	—
$40\bar40$	1·939	vvw	$40\bar40$	1·921	vvw
$22\bar42$	1·870	ms	$22\bar42$	1·839	w
$31\bar42$	1·818	vw	$31\bar42$	1·788	vvw
$21\bar33$	1·793 }	s	$32\bar50$	1·763 }	m
$32\bar50$	1·780 }		$21\bar33$	1·749 }	
$32\bar51$	1·722	w	$32\bar51$	1·703	vw
0004	1·699	m	$41\bar50$	1·677	vw
$41\bar50$	1·693	m	$40\bar42$	1·659	w
$40\bar42$	1·684	m	0004	1·642	vw
$10\bar14$	1·659	—	$41\bar51$	1·625	—
$41\bar51$	1·643	—	$10\bar14$	1·606	—
$22\bar43$	1·593	vvw	$22\bar43$	1·559	—
$11\bar24$	1·588	—	$32\bar52$	1·554	—
$32\bar52$	1·577	vvw	$11\bar24$	1·540	—
$31\bar43$	1·560	vvw	$50\bar50$	1·537	vvw
$20\bar24$	1·556 }	w	$31\bar43$	1·528	—
$50\bar50$	1·552 }		$20\bar24$	1·510	—
$41\bar52$	1·515	vw	$41\bar52$	1·494	vvw
$33\bar60$	1·493	—	$33\bar60$	1·479	—
$21\bar34$	1·470	w	$42\bar60$	1·453	vw
$42\bar60$	1·466	w	$33\bar61$	1·443	vw
$33\bar61$	1·458	w	$21\bar34$	1·430	vw
$42\bar61$	1·433	vvw	$42\bar61$	1·418	—
$30\bar34$	1·420	m, d	$50\bar52$	1·392 }	ms
$50\bar52$	1·411	w	$30\bar34$	1·383 }	
$32\bar53$	1·399	w	$51\bar60$	1·380 }	
$51\bar60$	1·393	vw	$32\bar53$	1·373	vw
$33\bar62$	1·367 }	ms	$51\bar61$	1·351 }	m
$51\bar61$	1·365 }		$33\bar62$	1·349 }	
$41\bar53$	1·356	--	$41\bar53$	1·332	—
$22\bar44$	1·353	--	$42\bar62$	1·328	—
$42\bar62$	1·346	vvw	$22\bar44$	1·320	—
$31\bar44$	1·333	vvw	$31\bar44$	1·301	—
$11\bar25$	1·300	—	$60\bar60$	1·281	—
$60\bar60$	1·293	—	$51\bar62$	1·273	—
$51\bar62$	1·289	—	$43\bar70$	1·264	—
$40\bar44$	1·278 }	vw	$11\bar25$	1·260	—
$43\bar70$	1·275 }		$40\bar44$	1·249	vvw
$43\bar71$	1·253	vvw	$43\bar71$	1·241	—
$33\bar63$	1·247	w	$52\bar70$	1·231 }	w
$52\bar70$	1·242	vw	$33\bar63$	1·226 }	
$21\bar35$	1·233 }	ms, d	$42\bar63$	1·210 }	s, d
$42\bar63$	1·231 }		$52\bar71$	1·210 }	
$32\bar54$	1·229 }		$32\bar54$	1·202 }	
$52\bar71$	1·222	m, d	$21\bar35$	1·197 }	s, d
$60\bar62$	1·208	m, d	$60\bar62$	1·193 }	
$41\bar54$	1·199 }	s, d	$43\bar72$	1·179 }	s, d
$43\bar72$	1·194 }		$41\bar54$	1·173 }	
$51\bar63$	1·187	m, d	$61\bar70$	1·172 }	s, d
$61\bar70$	1·183	m, d	$51\bar63$	1·168 }	

References

ARONSSON, B. & LUNDSTRÖM, T. (1957). *Acta Chem. Scand.* **11**, 365.

JELLINEK, F. (1959). *Öst. Chem. Ztg.* **60**, 311.

PARTHÉ, E. (1957). *Powder Metall. Bull.* **8**, 23.— Errata and additions (1958). *Powder Metall. Bull.* **8**, 70.

PARTHÉ, E. (1960). *Acta Cryst.* **13**, 868.

A Redetermination of the Orthorhombic IF₇ Structure

BY R. D. BURBANK

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.

The idealized molecular configuration in orthorhombic IF_7 has the point symmetry mm and can be derived from dodecahedral 8-coordination by allowing two atoms at one end of the $\bar{4}$ axis to coalesce into one. There are five bonds at 1·825 Å, $\sigma = 0·03$ Å, and two bonds at 1·97 Å, $\sigma = 0·04$ Å, in keeping with the chemical properties of IF_7 and IF_5. The same configuration has recently been observed in the ethylenediamine tetraacetoaquoferrate (III) ion. The revised structure was determined following a careful evaluation of the intensity data which entered into an earlier $3d$ Fourier difference analysis. Serious, non-calculable, systematic errors were found in the precession camera experiment. The most erroneous class of observations, the upper levels, were discarded. The zero levels were analyzed by least squares. The systematic errors for each zero level were treated as a separate problem in scaling and weighting analysis.

Introduction

Over a decade ago the writer and F. N. Bensey undertook a program of study of the polyfluoride branch of the interhalogen compounds. The crystal structures of ClF_3, BrF_3, and BrF_5 at low temperatures were determined in a relatively straightforward manner. The most interesting member of the group, IF_7, proved to be quite troublesome. In a preliminary report (Burbank & Bensey, 1953b) a structure was described which could have a symmetry no higher than that of the point group mm. This conclusion was unaltered in the final results of a $3d$ Fourier difference analysis (Burbank & Bensey, 1957a, b). The molecular structure found in the crystalline state was not in agreement with the interpretations given to a variety of other physical measurements.

Lord *et al.* (1950) studied the Raman spectra of the liquid and the infrared spectra of the gas, both at room temperature. Within the limited resolution of the spectra they stated that there was no noticeable departure from the selection rules for the point group symmetry D_{5h}, a pentagonal bipyramid. Gutowsky & Hoffman (1951) studied the nuclear magnetic resonance of the liquid at room temperature. The multiple F^{19} absorption lines were unexpectedly broad for a liquid. The simplest interpretation is that the F^{19} nuclei are in non-equivalent structural positions,

which is not inconsistent with a D_{5h} structure. Overlap of individual lines prevented more detailed analysis. Bauer (1952) assumed a D_{5h} structure to analyze the electron diffraction of the gas at -65 °C. In a revised analysis of the same data LaVilla & Bauer (1960) considered it necessary to introduce displacements of the five girdle atoms in directions perpendicular to the plane of the girdle.

Donohue (1959) made the categorical statement that the interpretation of the crystal structure was incorrect and that the molecular symmetry in orthorhombic IF_7 was D_{5h}. Recently Lohr & Lipscomb (1962) have reported a recalculation based on the Burbank & Bensey (1957a) data using the Busing–Levy (1959a) least squares program. It is claimed that the recalculation provides a quantitative statistical basis for Donohue's statement. However, this claim is compromised by the following factors:

1. The data contain serious and unknown systematic errors.

2. Under these circumstances the weighting system used is entirely arbitrary.

3. A complete set of anisotropic thermal parameters was introduced under circumstances in which they can have no physical meaning and in which they may interact seriously with the positional parameters.