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Sc_5Ga_3 and Y_5Ga_3 with $D8_8$ structure.

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In continuation of an investigation on the occurrence of compounds with $D8_8$ structure (Parthé, 1957, 1958, 1959, 1960; Arbuckle & Parthé, 1962; Boller & Parthé, 1963*a*, *b*) the phases Sc_5Ga_3 and Y_5Ga_3 have been synthesized. Induction melting of the metals mixed in proper weight proportions in a boron nitride crucible under argon has given homogeneous samples of Sc_5Ga_3 and Y_5Ga_3.

The X-ray diffraction patterns of the gallides could be indexed with a hexagonal unit cell with dimensions

$$Sc_5Ga_3: \; a = 8\cdot074 \pm 0\cdot002, \; c = 5\cdot951 \pm 0\cdot002 \text{ Å} \text{ with } c/a = 0\cdot737.$$

$$Y_5Ga_3: \; a = 8\cdot576 \pm 0\cdot006, \; c = 6\cdot479 \pm 0\cdot004 \text{ Å} \text{ with } c/a = 0\cdot755.$$

The systematic extinctions $h0\bar{h}l$ with $l = 2n+1$ lead to possible space groups $P6_3/mcm$ (D^3_{6h}), $P\bar{6}c2$ (D^2_{3h}), $P6_3cm$ (C^3_{6v}), and $P\bar{3}c1$ (D^4_{3d}).

The visual comparison with the powder patterns of Sc_5Ge_3 and Y_5Ge_3 suggested immediately that the gallides are isotypic with the germanides. The latter were shown before to crystallize with the $D8_8$ structure (Parthé, 1960; Arbuckle & Parthé, 1962). Thus an intensity calculation was performed for Sc_5Ga_3 assuming space group $P6_3/mcm$ (D^3_{6h}) and placing 4Sc in 4(*d*), 6Sc in $6(g_{\mathrm{I}})$ with $x_{\mathrm{I}} = 0\cdot25$ and 6Si in $6(g_{\mathrm{II}})$ with $x_{\mathrm{II}} = 0\cdot61$. Table 1 allows a comparison between calculated and observed intensities. The good agreement leaves no doubt that Sc_5Ga_3 crystallizes with the $D8_8$ structure. No intensity calculations have been made for Y_5Ga_3. It was not felt necessary to do so as there was good agreement between the diffraction pattern of Y_5Ge_3 and that of Y_5Ga_3.

Table 1. *Intensity calculation for* Sc_5Ga_3 *with* $D8_8$ *structure* (Cr $K\alpha$ radiaton)

hkil	d_c (Å)	$1000.\sin^2\theta_c$	$1000.\sin^2\theta_o$	I_c	I_o
$10\bar{1}0$	6·995	26,8	27,2	19·9	*vw*
$11\bar{2}0$	4·038	80,4	80,7	8·0	*vvw*
$20\bar{2}0$	3·497	107,2	—	0·029	—
$11\bar{2}1$	3·341	117,4	118,1	17·8	*vw*
0002	2·977	148,0	147,7	32·8	*w*
$10\bar{1}2$	2·739	174,8	174,6	6·8	*vvvw*
$21\bar{3}0$	2·644	187,6	188,1	20·2	*vw*
$21\bar{3}1$	2·416	224,6	224,8	100	*s*
$11\bar{2}2$	2·395	228,4	229,1	81·3	*ms*
$30\bar{3}0$	2·331	241,2	241,0	52·3	*m*
$20\bar{2}2$	2·266	255,2	254,5	11·9	*vvw*
$22\bar{4}0$	2·019	321,6	—	0·018	—
$21\bar{3}2$	1·976	335,6	—	0·080	—
$31\bar{4}0$	1·940	348,4	348,8	5·7	*vvvw*
$22\bar{4}1$	1·912	358,6	358,8	9·2	*vvw*
$31\bar{4}1$	1·844	385,4	385,8	22·7	*vw*
$30\bar{3}2$	1·835	389,2	389,2	5·5	*vvvw*
$11\bar{2}3$	1·781	413,4	—	2·8	—
$40\bar{4}0$	1·749	428,8	—	0·250	—
$22\bar{4}2$	1·671	469,6	468,6	15·4	*vvw*
$31\bar{4}2$	1·625	496,4	—	0·020	—
$32\bar{5}0$	1·604	509,2	—	0·250	—
$21\bar{3}3$	1·587	520,6	520,9	27·4	*w*
$32\bar{5}1$	1·549	546,2	546,2	9·0	*vvw*
$41\bar{5}0$	1·526	562,8	—	2·7	—
$40\bar{4}2$	1·508	576,8	576,5	5·7	*vvvw,d*
0004	1·488	592,0	592,0	13·2	*vvw*
$41\bar{5}1$	1·478	599,8	—	1·4	—
$10\bar{1}4$	1·456	618,8	—	0·6	—
$22\bar{4}3$	1·415	654,6	657,8	5·2	*vvw,d*
$32\bar{5}2$	1·412	657.2		10·6	
$50\bar{5}0$	1·3986	670,0	669,4	8·7	*vvw*
$11\bar{2}4$	1·3960	672,4	—	1·1	—
$31\bar{4}3$	1·3868	681,4	680,8	14·6	*vvw*
$20\bar{2}4$	1·3691	699,2	—	0·020	—
$41\bar{5}2$	1·3578	710,8	710,5	8·3	*vvvw,d*
$33\bar{6}0$	1·3458	723,6	—	1·2	—
$42\bar{6}0$	1·3215	750,4	750,0	14·4	*vvw*
$33\bar{6}1$	1·3127	760,6	760,5	10·7	*vvw*
$21\bar{3}4$	1·2966	779,6	779,6	8·8	*vvvw*
$42\bar{6}1$	1·2902	787,4	786,8	23·2	*vw*
$50\bar{5}2$	1·2657	818,0	817,4	44·1	*w,d*
$51\bar{6}0$	1·2560	830,8	832,0	6·9	*w,d*
$30\bar{3}4$	1·2542	833,2		39·3	
$32\bar{5}3$	1·2475	842,2	842,3	11·6	*vvw*
$51\bar{6}1$	1·2289	867,8	868,0	18·8	*vvw,d*
$33\bar{6}2$	1·2263	871,6		6·4	
$41\bar{5}3$	1·2095	895,8	—	2·3	—
$42\bar{6}2$	1·2078	898,4	898,3	11·2	*vvvw*
$22\bar{4}4$	1·1977	913,6	—	0·020	—

Including Sc_5Ga_3 and Y_5Ga_3 the total number of known $D8_8$ phases has now increased to 46. An extensive analysis of the $D8_8$ structure, its filled-in variations, the so-called Nowotny phases and the Ti_5Ga_4-type compounds, its structural relationship to Ca_5Pb_3 and the apatite ($H5_7$) structure and its variations will be discussed at a later time when studies on other $D8_8$ phases have been completed. Now only comments in relation to gallides with $D8_8$ structure will be made.

Gallides with $D8_8$ structure are known with transition metals of the *3rd group*: Sc_5Ga_3, Y_5Ga_3; *4th group*: Ti_5Ga_3, Zr_5Ga_3 and Hf_5Ga_3 (Boller & Parthé, 1963*a*); and *5th group*: $V_5Ga_3C_x$, $Nb_5Ga_3C_x$ and $Ta_5Ga_3C_x$ (Jeitschko, Nowotny & Benesovsky, 1963; Schubert, Frank, Gohle, Maldonado, Meissner, Raman & Rossteutscher, 1963). In analogy to $D8_8$ silicides, the gallides of the 5th group need small amounts of carbon or oxygen atoms as stabilizers. The 5th group $D8_8$ phases do not form as binary compounds, while gallides with transition metals of the 4th group seemingly do not need stabilizer atoms or only in extremely small amounts. The 3rd-group compounds Sc_5Ga_3 and Y_5Ga_3 are true binary phases. However, samples of Sc_5Ga_3, which were annealed in evacuated (10^{-4} mmHg) quartz tubes at 1200 °C for 4 hours showed a change in the lattice constants to: $a = 8\cdot059 \pm 0\cdot001$, $c = 6\cdot033 \pm 0\cdot001$ Å and $c/a = 0\cdot749$. This is probably caused by the insertion of oxygen atoms from the quartz into the $D8_8$ structure. In agreement with this assumption is the observation that samples which were heated for a longer time (40 hours) under the same conditions have completely reacted with quartz, thereby forming elementary silicon and scandium oxide.

The axial ratios of the unit cells of Sc_5Ga_3 and Y_5Ga_3 agree with the axial ratios of the six other known $D8_8$ phases containing Sc, Y or rare earth metals: Sc_5Si_3, Sc_5Ge_3, Y_5Si_3, Y_5Ge_3, La_5Ge_3 and Ce_5Ge_3. All these phases have very high axial ratios of about 0·75 while the axial ratios of the other known $D8_8$ phases are between 0·68 and 0·70. The characteristic high axial ratio of a $D8_8$ phase with a metal of the third group is nearly the same for gallide, silicide and germanide phase, but changes slightly with the transition metal component.

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The length of the I–Cl bond in tetramethylammonium dichloroiodide.

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The polyhalide ions in $KICl_4.H_2O$ (Mooney, 1937) and in $N(CH_3)_4ICl_2$ (Mooney, 1939) aroused our interest as the reported bond lengths are remarkably short in comparison with those in other polyhalide ions (Elema, de Boer & Vos, 1963). Refinement of the crystal structure of $KICl_4.H_2O$ (Elema *et al.*, 1963) showed that the I–Cl bonds in the ICl_4^- ion range from 2·42 to 2·60 Å and are thus considerably longer than the value determined by Mooney, 2·34 Å. It will appear from this paper that also in ICl_2^- the bonds are long.

$N(CH_3)_4ICl_2$ is tetragonal, space group $P\bar{4}2_1m$, with the two $N(CH_3)_4$ and ICl_2 groups in special positions (Mooney, 1939). Cell dimensions determined from a powder diffractogram with CaF_2 as a reference are $a=9{\cdot}35$, $c=5{\cdot}94$ Å with an e.s.d. of 2 $^0/_{00}$.

Fig. 3 in Mooney's paper shows that the I–Cl bond length in the ICl_2^- ion with symmetry 2 can be obtained both from the [001] and from the $[1\bar{1}0]$ projection. Intensities of 56 *hk*0 reflexions were measured from a single crystal of dimensions $0{\cdot}17\times0{\cdot}25\times0{\cdot}28$ mm by counter techniques, 34 *hhl* reflexions were obtained from integrated zero-layer Weissenberg photographs about the $[1\bar{1}0]$ axis of a crystal with dimensions $0{\cdot}18\times0{\cdot}10\times0{\cdot}20$ mm. Molybdenum radiation, with balanced Zr and Y filters and Zr-filtered Mo radiation respectively, was used. Corrections for the Lorentz and polarization effect and for absorption ($\mu=35{\cdot}6$ cm^{-1}) were applied.

The [001] projection was refined first. Isotropic refinement by successive Fourier syntheses failed to yield satisfactory agreement between the observed and calculated values of the individual structure factors. Good agreement ($R=0{\cdot}041$) was achieved by anisotropic least-squares refinement which was kindly carried out by Dr J. S. Rollett on the Mercury computer at Oxford.

The final coordinates listed in Table 1 and the thermal parameters U_{ij} (Cruickshank, 1956*a*) in Table 2 were obtained by anisotropic least-squares refinement of the 34 reflexions *hhl* and the 56 more accurately measured reflexions *hk*0; a weighting scheme corresponding to rough estimates of the experimental accuracy was applied. F_o-F_c syntheses of the two projections calculated after the refinement showed only small changes, less than 0·004 Å, in the I–Cl bond length. The calculated structure factors in Table 3 correspond to the parameters in Tables 1 and 2. $R=0{\cdot}045$.

Table 1. *Final coordinates*

Atom	x	e.s.d.	y	e.s.d.	z	e.s.d.
I	0		0·5		$0{\cdot}103_9$	0·001
Cl	$0{\cdot}193_1$	0·0015	$0{\cdot}693_1$	0·0015	$0{\cdot}105_5$	0·0025
N	0		0		0·5	
C	0·108	0·003	0·063	0·003	0·350	0·005

Table 2. *Thermal parameters* U_{ij} (Å^2) *relative to* [110] (1), $[1\bar{1}0]$ (2) *and* z(3)

The e.s.d. for U_{ii}(I) and U_{ii}(Cl) are 0·002 and 0·004 Å^2 respectively

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I	0·084	0·031	0·053	0	0	0
Cl	0·064	0·052	0·053	0	0	0*
N	0·042	0·042	0·058	0	0	0
C	0·058	0·091	0·097	0·004	0·023	0·000

* U_{13}(Cl) was assumed to be zero during the refinement in agreement with a rigid body description of the ICl_2^- ion; the remaining zeroes are due to symmetry.

In calculating the I–Cl bond length no correction for thermal motion (Cruickshank, 1956*b*) could be applied as may be seen from the parameters U_{ij} in Table 2 (Cl–I–Cl along [110]). The difference $U_{22}(Cl)-U_{22}(I)$, which might be ascribed to libration, is approximately