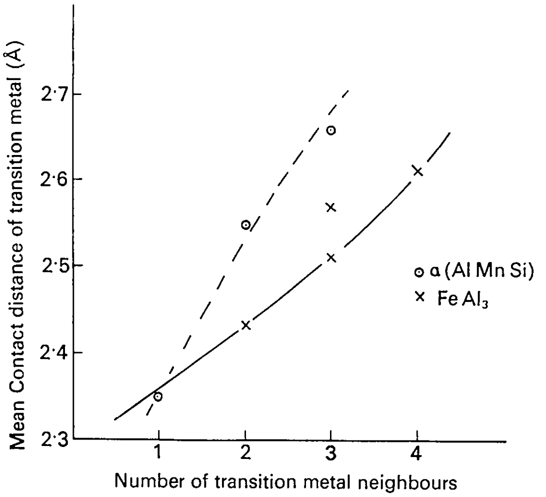

Fig. 3. Variation of the mean contact distances for neighbours of an Al atom in α(AlMnSi) and $FeAl_3$.

neighbours. The results are displayed in Fig. 3, together with those of Black for $FeAl_3$. Black discusses the trend in terms of a strong bond between unlike atoms.

The structure is a three-dimensional network of polyhedra. It can alternatively be described in terms of layers of manganese atoms parallel to the (100) planes, and linked by aluminum atoms, but in this case the layering is not as marked as in other aluminum alloys of transition metals.

Table 3. *Analysis of aluminum atom environments*

The standard deviation of a single Mn–Al bond is 0·03 Å

	Manganese contacts		
Atom	Number	Mean distance	Average
Al(4)	1	2·43	
Al(5)	1	2·27	2·35
Al(1)	2	2·58	
Al(2)	2	2·53	
Al(3)	2	2·46	
Al(8)	2	2·63	
Al(9)	2	2·60	2·55
Al(6)	3	2·59	
Al(7)	3	2·73	2·66

We are grateful to Professor N. F. Mott, F.R.S. and Dr W. H. Taylor for provision of facilities, and for their interest in the progress of the work; also to Dr P. J. Brown and other members of the Crystallographic Laboratory, Cambridge. Calculations on the EDSAC II computer were carried out by permission of Dr M.V. Wilkes and Mr E. N. Mutch, and with assistance from Mrs J. C. Matthewman. One of us (M. C.) acknowledges financial support from the United Kingdom Atomic Energy Authority for this work.

References

Bergman, G. (1951). *Nature, Lond.* **169**, 1057.
Black, P. J. (1955). *Acta Cryst.* **8**, 175.
Black, P. J. & Taylor, W. H. (1958). *Rev. Mod. Phys.* **30**, 57.
Bland, J. A. (1958). *Acta Cryst.* **11**, 236.
Buckle, H. (1938). *Aluminium Archiv.* **13**.
Cruickshank, D. W. J. (1959). In *International Tables for X-ray Crystallography* Vol. II, p. 330. Birmingham: Kynoch Press.
Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. & Truter, M. R. (1960). Paper 6 of the Glasgow Conference on *Computing Methods and the Phase Problem in X-ray Crystal Analysis.* Oxford: Pergamon Press, 1961.
Cruickshank, D. W. J. & Rollett, J. S. (1953). *Acta Cryst.* **6**, 705.
Forsyth, J. B. & Wells, M. (1959). *Acta Cryst.* **12**, 412.
Main, P. & Woolfson, M. M. (1963). *Acta Cryst.* **16**, 731.
Phillips, H. W. L. (1943). *J. Inst. Met.* **69**, 291.
Phragmen, G. (1950). *J. Inst. Met.* **77**, 489.
Pratt, J. N. & Raynor, G. V. (1951). *Proc. Roy. Soc.* A **205**, 103.
Robinson, K. (1952). *Acta Cryst.* **5**, 397.

Acta Cryst. (1966). **20**, 617

The Crystal Structure of Al_2Se_3

By G. A. Steigmann and J. Goodyear

Department of Physics, The University, Hull, England

(*Received* 21 *July* 1965)

The crystal structure of Al_2Se_3 has been determined from X-ray powder diffraction data. The unit cell is monoclinic, being centred on the *C* face, with parameters $a=11{\cdot}68_0$, $b=6{\cdot}73_3$, $c=7{\cdot}32_9$ Å and $\beta=121{\cdot}1_2°$. The space group is *Cc* and the structure is similar to that of α-Ga_2S_3.

Introduction

The crystal structure of Al_2Se_3 was examined by Schneider & Gattow (1954), who used X-ray diffraction data obtained with a Debye–Scherrer camera of 5·74 cm diameter. They proposed a wurtzite-type structure which was deficient in cations, the parameters of the hexagonal cell being $a=3{\cdot}89$, $c=6{\cdot}30$ Å.

Table 1. *Observed and calculated powder data*

Column (i), Schneider & Gattow.
Column (ii), Steigmann & Goodyear.
In columns (iii) and iv) data were not calculated for reflexions with spacings less than 1·700 Å because these reflexions showed significant instrumental broadening, making observations on them less precise.
In column (iv) $I_c = |F_c|^2 p f_1(\theta) \times 10^{-4}$, where p is the multiplicity and $f_1(\theta)$ is the angular factor defined by Goodyear & Duffin (1957). The absorption factor was almost constant for all reflexions, and so no correction has been made for this.

(i)		(ii)		(iii)			(iv)	
d_o(Å)	I	d_o(Å)	I	d_c(Å)	hkl	I_c	I_c	I_o
		5·57	*w*	5·59	110	63	63	31
		5·00	w^-	5·00	200	32	47	34
		4·94	*vw*	4·94	$\bar{1}11$	15		
		3·671	*vw*	3·679	111	6	18	21
		3·647	*w*	3·635	$\bar{2}02$	12		
3·35	*s*	3·363	*vs*(*b*)	3·371	$\bar{3}11$	575	868	712
				3·368	020	293		
3·14	*s*	3·143	*s*	3·152	$\bar{1}12$	12	690	920
				3·138	002	678		
2·958	*vs*	2·986	*s*	2·987	310	625	1840	1578
		2·958	*vs*(*b*)	2·967	021	606		
				2·952	$\bar{3}12$	609		
		2·874	*w*(*b*)	2·878	$\bar{2}21$	10	10	10
		2·779	*w*	2·793	220	3	8	15
				2·776	$\bar{4}02$	5		
		2·497	*tr*	2·500	400	4	4	6
		2·472	w^-	2·469	$\bar{2}22$	2	2	9
		2·449	*w*	2·450	112	6	6	11
2·294	*ms*	2·311	m^+	2·315	221	5	409	656
				2·313	311	140		
		2·294	*s*	2·295	022	139		
		2·284	*m*	2·280	$\bar{3}13$	125		
		—	—	2·270	202	3	3	—
		2·185	*w*(*b*)	2·194	$\bar{4}21$	4	9	25
				1·190	130	⩽1		
				2·188	$\bar{5}12$	4		
				2·176	$\bar{1}13$	1		
		—	—	2·156	$\bar{5}11$	1	1	—
		2·140	w^-	2·144	$\bar{1}31$	5	6	9
				2·142	$\bar{4}22$	1		
		2·003	*tr*	2·007	420	1	6	13
				1·998	131	4		
		1·994	*tr*	1·986	$\bar{5}13$	1		
		1·971	*tr*	1·969	$\bar{2}23$	3	3	5
1·933	*s*	1·941	*vs*(*b*)	1·946	$\bar{6}02$	241	723	696
				1·944	$\bar{3}31$	482		
		1·915	*tr*	1·917	510	3	3	6
		1·903	*tr*(*b*)	1·899	$\bar{1}32$	⩽1	⩽1	—
				1·893	$\bar{4}23$	3	3	6
		—	—	1·862	330	< 1	< 1	—
		—	—	1·853	$\bar{3}32$	< 1	< 1	—
		—	—	1·839	222	1	1	—
		1·821	*tr*	1·817	$\bar{4}04$	1	1	—
		—	—	1·796	113	1	1	—
1·775	*s*	1·788	*m*	1·789	312	257	758	713
		1·779	*s*	1·783	$\bar{2}04$	1		
		1·770	*m*	1·777	023	253		
				1·766	$\bar{3}14$	247		
		1·726	*tr*	1·716	421	2	2	4
1·678	*w*	1·683	*m*					
		1·676	m^-					
1·653	*s*	1·665	*m*					
		1·656	*m*					
		1·652	m^+					
		1·645	*m*					
		1·631	*w*					
1·620	*m*	1·621	*m*					
		1·606	*tr*					
1·572	*w*	1·572	*w*					

The space group was $P6_3mc$, and selenium atoms were considered to be in a close-packed array with aluminum atoms occupying two-thirds of the tetrahedrally coordinated sites which are filled by zinc in wurtzite. Schneider & Gattow concluded that three-quarters of the aluminum atoms were in ordered positions, the rest randomly distributed amongst the remaining available sites.

Powder data, obtained with a crystal focusing camera of 22·9 cm effective diameter, for specimens of Al_2Se_3 prepared by the present authors include additional reflexions which are consistent with a monoclinic cell related to the hexagonal cell of Schneider & Gattow. The difference between the new data and those of the latter is considered to be due to a difference in diffraction technique and not in the actual specimens examined.

Preparation of specimens and their X-ray powder data

Specimens of Al_2Se_3 were prepared in two ways as follows:

(i) A mixture, containing appropriate amounts of aluminum and selenium, was heated in an evacuated tube at 1000°C for 24 hours.

(ii) Equivalent amounts of aluminum and selenium were contained separately in silica boats in an evacuated tube, the temperature of the aluminum being maintained about 100°C higher than that of the selenium. The temperature of the aluminum was held at 750°C for 5 hours and was then raised at the rate of 70°C/hr to 950°C and maintained at this temperature for 13 hours. Al_2Se_3 formed in the boat initially containing the aluminum.

Each method yielded Al_2Se_3 as a grey polycrystalline mass which required only very light grinding prior to examination by the X-ray powder method. Since the material decomposed rapidly when in contact with the atmosphere, the X-ray camera was continuously evacuated during exposures. Both samples were found to give identical powder patterns.

The X-ray powder data, obtained with crystal-monochromatized Cu $K\alpha$ radiation, are given in column (ii) of Table 1, and for comparison the data of Schneider & Gattow are listed in column (i). The chief differences between the powder patterns of Al_2Se_3 in columns (i) and (ii) lie in the observation of additional weak reflexions and the resolution of several of Schneider & Gattow's single reflexions into two or more closely spaced reflexions. The extra detail in the new data can be attributed to the high resolving power and low background of the present X-ray technique.

Quantitative measurements of the intensities of the X-ray reflexions were made with a microdensitometer and are given in column (iv) of Table 1.

Structural considerations

A close similarity between the powder pattern of Al_2Se_3 and that of α-Ga_2S_3 (Goodyear & Steigmann, 1963) suggested that these materials might well have the same crystal structure. The aluminum selenide data were indexed to give a C-face-centred monoclinic cell with parameters $a=11{\cdot}68_0$ $b=6{\cdot}73_3$, $c=7{\cdot}32_9$ Å and $\beta=121{\cdot}1_2$°. This cell closely resembles in size and shape that of α-Ga_2S_3, whose dimensions are $a=11{\cdot}14_0$, $b=6{\cdot}41_1$, $c=7{\cdot}03_8$ Å and $\beta=121{\cdot}2_2$° according to Goodyear & Steigmann. Calculated d values are shown in column (iii) of Table 1. With 4 molecules per unit cell, the calculated density is 3·915 g.cm^{-3}, which is in good agreement with the value of 3·91 ± 0·03 g.cm^{-3} observed by Schneider & Gattow.

The intensities of X-ray reflexions have been calculated by assuming a structure essentially similar to that of α-Ga_2S_3, *i.e.* a wurtzite-type structure with 4 ordered cation vacancies per unit cell, the space group being Cc. In these calculations, the idealized atomic coordinates given in Table 2 and atomic scattering factors listed by Wilson (1960) were used. Temperature factors of 0·2 Å^2 and 1·0 Å^2 were assumed for selenium and aluminum, respectively. Observed and calculated intensities are compared in column (iv) of Table 1.

Table 2. *Atomic parameters*

Origin in glide-plane C

Atom	x/a	y/b	z/c
Al(1)	1/24	5/12	1/8
Al(2)	5/24	11/12	1/8
Se(1)	0	1/12	0
Se(2)	1/6	7/12	0
Se(3)	1/3	1/12	0

The agreement between the observed and calculated powder data in Table 1 is sufficiently good for one to conclude that Al_2Se_3 is isomorphous with α-Ga_2S_3. Although a refinement of the Al_2Se_3 structure has not been possible because single-crystal diffraction data have not been available, it is probable that similar distortions from idealized positions in the structure exist as were found in α-Ga_2S_3 by Goodyear & Steigmann.

References

Goodyear, J. & Duffin, W. J. (1957). *Acta Cryst.* **10**, 597.

Goodyear, J. & Steigmann, G. A. (1963). *Acta Cryst.* **16**, 946.

Schneider, A. & Gattow, G. (1954). *Z. anorg. allg. Chem.* **277**, 49.

Wilson, A. J. C. (1960). *X-ray Diffraction by Polycrystalline Materials.* London: Institute of Physics.