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The Crystal Structures of $ZnAl_2S_4$

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Accurate X-ray powder diffraction data have confirmed that the low-temperature form of $ZnAl_2S_4$ possesses a normal spinel type of structure, the cubic unit cell having $a = 10{\cdot}00_5$ Å. Single-crystal and powder diffraction data have shown that the high-temperature form of $ZnAl_2S_4$ possesses a layered structure of the type *–A–C–B–C–A–*, each of the three components having an orthorhombic cell with $a = 12{\cdot}82_5$, $b = 7{\cdot}50_0$, $c = 6{\cdot}09_9$ Å, containing 4 formula units and belonging to the space group $Pna2_1$ (C_{2v}^9).

Introduction

The crystal structures of $ZnAl_2S_4$ were examined by Hahn & Frank (1952), using an X-ray powder diffraction technique. In addition to the previously recorded low-temperature spinel form of the material they obtained another modification by quenching the material from a high temperature. The low-temperature form of $ZnAl_2S_4$ was reported as being based on the normal spinel structure, the cubic cell having $a = 9{\cdot}96_8 \pm 0{\cdot}008$ Å. For the high-temperature form they proposed a wurtzite type of structure which was deficient in cations, the parameters of the hexagonal cell being $a = 3{\cdot}75_6 \pm 0{\cdot}005$ Å, $c = 6{\cdot}13_0 \pm 0{\cdot}007$ Å. The sulphur atoms were considered to be in a hexagonal close-packed array with the zinc and aluminum atoms randomly distributed amongst three-quarters of the tetrahedral sites normally occupied in wurtzite.

High-resolution X-ray powder data obtained by the present author have confirmed that the low-temperature form possesses a spinel type of structure. Powder and single-crystal data obtained from a specimen of the high-temperature form have revealed many previously unrecorded reflexions which can only be reconciled by the unit cell having orthorhombic symmetry.

In accordance with common practice, the low-temperature form of the material will be referred to as α-$ZnAl_2S_4$ and the high-temperature form as β-$ZnAl_2S_4$.

α-$ZnAl_2S_4$

Preparation of the material and its X-ray powder data

Appropriate amounts of ZnS, aluminum powder and sulphur were sealed in an evacuated quartz tube and heated at 600 °C for 15 hours. Following the preliminary heating the temperature was raised and maintained at 900 °C for a further 15 hours. The sample was then water quenched and yielded α-$ZnAl_2S_4$ as a white powder.

X-ray powder photographs of the material were taken with crystal monochromatized Cu $K\alpha$ radiation, using a de Wolff focusing camera of 22·9 cm effective diameter. Camera calibration was accomplished by the addition of aluminum powder to the sample being X-rayed. To reduce background fog to a minimum the camera was continuously evacuated during the exposure. The integrated intensities of lines in the X-ray powder pattern were measured by means of a Joyce–Loebl double beam recording microdensitometer.

Structural considerations

High resolution X-ray powder data have confirmed the cubic cell and spinel structure proposed by Hahn & Frank. The powder pattern has been indexed on a cubic cell having $a = 10{\cdot}00_5$ Å, and the observed and calculated spacings are compared in columns (i) and (ii) of Table 2. Assuming 8 molecular units per cell the calculated density 3·29 g.cm^{-3} is in good agreement with the measured value of 3·30 g.cm^{-3} obtained by Hahn & Frank. Preliminary calculations assuming the structure to be of the ideal normal spinel type [belonging to the space group $Fd3m$ (O_h^7)] revealed that the 111 reflexion should be relatively intense ($I_c = 50$ on the scale of Table 2) but no definite record of this reflexion was obtained on long-exposure powder photographs. This allowed the sulphur parameters in the structure to be determined since the 32 sulphur atoms in the unit cell are located at the special equivalent positions (x,x,x) in the centred version of the space group. The cations, on the other hand, are located at the equivalent positions (0,0,0) and $(\frac{3}{8},\frac{3}{8},\frac{3}{8})$ and are fixed by the symmetry requirements.

In order to account for the 111 reflexion being below the detection limit the sulphur atoms were moved from the ideal equivalent position $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ to the position

Table 1. α-$ZnAl_2S_4$.
Fractional atomic coordinates

Origin at centre ($\bar{3}m$)

	Equipoint	$x(y)(z)$
Zn^{2+}	8(*b*)	$\frac{3}{8}$
Al^{3+}	16(*c*)	0
S^{2-}	32(*e*)	$0{\cdot}235 \pm 0{\cdot}003$

Interatomic distances

Zn–S (tetrahedral bonding) $2{\cdot}43 \pm 0{\cdot}05$ Å
Al–S (octahedral bonding) $2{\cdot}36 \pm 0{\cdot}03$

Table 2. α-$ZnAl_2S_4$.
Observed and calculated powder data

(i)		(ii)		(iii)		
d_o (Å)	I	d_c (Å)	hkl	I_c		I_o
—	—	5·776	111	0·1		—
—	—	5·002	200	0		—
3·539	*s*	3·538	220	205		163
3·018	*vs*	3·017	311	223		220
2·889	*ms*	2·888	222	77		97
2·502	*ms*	2·501	400	67		99
2·295	*wm*	2·295	331	56		34
—	—	2·237	420	0		—
2·042	*m*	2·042	422	69		58
1·925	*ms*	1·926	511	171	175	134
			333	4		
1·769	*vs*	1·769	440	249		277
—	—	1·691	531	1		—
—	—	1·668	442	2	2	—
			600	0		
1·582	*wm*	1·582	620	25		28
1·526	*wm*	1·526	533	34		28
1·508	*w*	1·508	622	11		23
1·444	*w*	1·444	444	12		23
1·406	*vw*	1·406	551	4	15	9
			711	11		
—	—	1·387	640	0		—
1·336	*wm*	1·337	642	53		44
1·306	*m*	1·303	553	39	46	49
			731	7		
1·250	*m*	1·251	800	33		54
1·222	*w*	1·222	733	21		16
—	—	1·213	644	1	1	—
			820	0		
1·178	*w*	1·179	660	2	15	21
			822	13		

In column (iii) $I_c=|F_c|^2pf_1(\theta)\times10^{-5}$, where p is the multiplicity and $f_1(\theta)$ is the angular term defined by Goodyear & Duffin (1957). The absorption factor was almost constant for all reflexions, and so no correction has been made for this.

indicated in Table 1, thus reducing the calculated intensity of the 111 reflexion below the observational limit. Table 1 lists the final coordinates of the atoms in the structure together with the interatomic distances. Table 2, column (iii), compares the observed and calculated intensities of lines in the powder pattern calculated from these coordinates, assuming an overall temperature factor of 1·0 Å^2. In assessing the powder data the reliability index has been taken to be $R=\Sigma\,||\sqrt{I_o}|-|\sqrt{I_c}||/\Sigma\,|\sqrt{I_o}|$ which calculated at 0·125. For reflexions 222 and 444 (to which the sulphur atoms make large contributions in the calculated structure factors) the errors between the observed and calculated intensities may be explained by a slight preferred orientation in the powder specimen; these planes lying parallel to the close-packed layers of sulphur atoms.

β-$ZnAl_2S_4$

Preparation of the material

Attempts at preparing β-$ZnAl_2S_4$ by a similar method to that employed in the preparation of the α form, by heating the sample above 1050°C, were only partially successful. The material was, however, successfully produced by using α-$ZnAl_2S_4$ as a starting point. A sample of α-$ZnAl_2S_4$ was sealed in an evacuated quartz tube and initially heated at 950°C for 43 hours, then the temperature was increased to 1050°C and held constant for a further 24 hours. The specimen was then water quenched, yielding β-$ZnAl_2S_4$ as a white polycrystalline mass containing some crystals large enough for single-crystal X-ray study.

X-ray data

X-ray powder photographs of the material were taken, using the same technique outlined above. The powder data were indexed on the basis of an orthorhombic unit cell having

$$a=12{\cdot}82_5,\ b=7{\cdot}50_0,\ c=6{\cdot}09_9\ \text{Å}\,,$$

giving calculated spacings which are compared with the observed data in columns (iii) and (ii) of Table 6. The chief differences between the data observed by the present author and those derived from the hexagonal unit cell reported by Hahn & Frank, given in column (i) of Table 6, lie in the observation of numerous weak reflexions and the splitting of some of the stronger lines in the pattern into close doublets. The relationships between the orthorhombic unit cell and the previously proposed hexagonal unit cell are:

$$a_o\simeq2\sqrt{3}a_h;\ a_o<\sqrt{3}b_o;\ b_o\simeq2a_h;\ c_o\simeq c_h;\ V_o\simeq8V_h\,.$$

Since Hahn & Frank, using a non-focusing powder camera, failed to record these extra lines the possibility exists that the difference between the two sets of data is simply one of technique.

A crystal of roughly square cross-section 0·05 mm × 0·05 mm and elongated parallel to the b axis was chosen for the single-crystal intensity measurements. Seven layer lines were recorded on equi-inclination Weissenberg photographs taken with Cu $K\alpha$ radiation. The X-ray reflexions recorded on these layer lines were indexed according to the orthorhombic cell calculated from the more accurate powder data. Systematic absences of the type $0kl$: $k+l=2n+1$, $h0l$: $h=2n+1$ indicated that the space group must be $Pna2_1$ (C^9_{2v}). The intensities of nearly 250 reflexions were estimated visually from multiple film exposures by means of a calibrated scale. The observed intensities were corrected for Lorentz and polarization factors and an allowance made for spot shape on the upper layer lines (Phillips, 1954). Absorption corrections were made by applying the correction factors given by Bond (1959), assuming the specimen to be cylindrical of average radius 0·024 mm and $\mu r=0{\cdot}5$.

In addition, precession photographs revealed that all the crystals examined were twinned; the reflexions with $h=2n$, $k=2n+1$ being split into three sets, centred on the origin of the reciprocal net and orientated at 120° to each other. All other recorded reflexions were single. This leads to the three orientations of the a^*b^* reciprocal net, shown in Fig. 1, required to index all the observed reflexions. As the intensities of the corresponding reflexion in each orientation of the reciprocal net were identical, the intensities of reflexions having $h=2n$, $k=2n+1$ were trebled to place them on the same relative scale as the intensities of the remaining reflexions.

Structural considerations

The shape and size of the unit cell immediately rules out any arrangement other than a hexagonal close-packed array of sulphur atoms. Therefore for initial structure factor calculations a wurtzite-type of structure with 4 formula units per cell was assumed, giving a calculated density of 2·83 g.cm^{-3}, which is in fair agreement with the density of 2·63 g.cm^{-3} measured by Hahn & Frank. Atomic scattering factors used in these calculations for Zn^{2+}, Al^{3+} and S^{2-} were taken from *International Tables for X-ray Crystallography* (1962).

With atoms located in idealized positions no single structure could be found giving calculated structure factors in agreement with the observed single-crystal data. The space group does, however, permit two different hexagonal close-packed ordered structures which will be referred to as components *A* and *B*. A least-squares refinement of the atomic coordinates and isotropic temperature factors for all atoms in the unit cell of each of these structures failed to converge, leading to inadmissible distortions from the model structures. The minimum value of the reliability index, $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$, could not be reduced below 0·30 with all the observed structure factor data on the same scale.

Table 3. β-$ZnAl_2S_4$.
Fractional atomic coordinates

Equipoints all 4(*a*)

Tetrahedral cation sites*

Equipoint x, y, z	Component *A*	Component *B*	Component *C*
$\frac{1}{6}, 0, \frac{5}{8}$	Zn^{2+}	$Al^{3+}(1)$	$(\frac{1}{2})Zn^{2+}$
$\frac{1}{6}, \frac{1}{2}, \frac{5}{8}$	*V*	$Al^{3+}(2)$	$(\frac{1}{2})Zn^{2+}$
$\frac{1}{12}, \frac{1}{4}, \frac{1}{8}$	$Al^{3+}(1)$	Zn^{2+}	$Al^{3+}(1)$
$\frac{1}{12}, \frac{3}{4}, \frac{1}{8}$	$Al^{3+}(2)$	*V*	$Al^{3+}(2)$

Hexagonal close-packed sulphur array
(common to all three components)

	x	*y*	*z*
$S^{2-}(1)$	$\frac{1}{6}$	0	0
$S^{2-}(2)$	$\frac{1}{6}$	$\frac{1}{2}$	0
$S^{2-}(3)$	$\frac{1}{12}$	$\frac{1}{4}$	$\frac{1}{2}$
$S^{2-}(4)$	$\frac{1}{12}$	$\frac{3}{4}$	$\frac{1}{2}$

Mean Zn(Al)–S interatomic distance 2·29 Å.

* *V* denotes a vacant site.

Table 4. β-$ZnAl_2S_4$. *Observed and calculated structure factors*

$|F_c|(A)$, $|F_c|(B)$ and $|F_c|(C)$ are the structure factors calculated for structures *A*, *B* and *C* respectively. $|F_c|$ are the structure factors calculated on the basis of the idealized layered structure, where

$$|F_c|=\{|F_c|(A)^2+|F_c|(C)^2+|F_c|(B)^2+|F_c|(C)^2\}^{\frac{1}{2}}.$$

Reflexions not listed (other than space group extinctions) have $|F_c|=0$ and $|F_o|$ below the observational limit.

H	K	L	$|F_c|(A)$	$|F_c|(B)$	$|F_c|(C)$	$|F_c|$	$|F_o|$
0	0	2	254	254	254	508	496
0	0	4	6	6	6	12	54
0	0	6	118	118	118	236	279
2	0	0	15	15	15	31	44
2	0	1	25	25	25	50	76
2	0	2	13	13	13	25	56
2	0	3	17	17	17	35	55
2	0	4	8	8	8	16	36
2	0	5	10	10	10	21	49
2	0	6	5	5	5	9	19
4	0	0	183	183	183	367	314
4	0	1	115	115	115	231	239
4	0	2	108	108	108	216	254
4	0	3	209	209	209	419	419
4	0	4	1	1	1	3	18
4	0	5	152	152	152	303	284
4	0	6	55	55	55	111	113
4	0	7	43	43	43	85	84
6	0	0	22	22	22	43	67
6	0	2	18	18	18	37	70
6	0	4	13	13	13	25	44
6	0	6	8	8	8	17	18
8	0	0	125	125	125	251	239
8	0	1	81	81	81	163	143
8	0	2	81	81	81	163	157
8	0	3	167	167	167	334	309
8	0	4	3	3	3	6	21
8	0	5	125	125	125	251	183
8	0	6	46	46	46	93	71
10	0	0	7	7	7	13	38
10	0	1	11	11	11	22	48
10	0	2	6	6	6	12	21
12	0	0	177	177	177	353	266
12	0	2	117	117	117	233	190
14	0	0	4	4	4	8	18
14	0	1	7	7	7	14	18
16	0	0	58	58	58	116	58
16	0	1	39	39	39	77	41
0	1	1	0	106	0	106	103
0	1	3	0	83	0	83	74
0	1	5	0	55	0	55	57
1	1	1	91	0	0	91	87
1	1	2	48	0	0	48	63
1	1	3	71	0	0	71	69
1	1	4	34	0	0	34	51
1	1	5	48	0	0	48	68
2	1	0	0	92	0	92	86
2	1	1	0	52	0	52	57
2	1	2	0	81	0	81	86
2	1	3	0	41	0	41	31
2	1	4	0	58	0	58	51
3	1	0	102	0	0	102	91
3	1	2	91	0	0	91	102
3	1	4	65	0	0	65	76
4	1	0	0	84	0	84	74
4	1	1	0	47	0	47	26
4	1	2	0	75	0	75	80
4	1	3	0	38	0	38	34
5	1	0	46	0	0	46	53
5	1	1	77	0	0	77	81
5	1	2	41	0	0	41	43
5	1	3	62	0	0	62	58
6	1	1	0	83	0	83	74
6	1	3	0	67	0	67	37
7	1	0	39	0	0	39	38
7	1	1	66	0	0	66	61
7	1	2	35	0	0	35	51
7	1	3	54	0	0	54	56
8	1	0	0	62	0	62	86
8	1	1	0	35	0	35	37
8	1	2	0	56	0	56	37
9	1	0	65	0	0	65	69
9	1	2	59	0	0	59	66
0	2	0	28	28	28	56	83
0	2	2	23	23	23	46	99
0	2	4	15	15	15	30	69
0	2	6	9	9	9	18	21
2	2	0	184	184	184	368	312
2	2	1	116	116	116	232	237
2	2	2	108	108	108	216	239
2	2	3	210	210	210	420	403
2	2	4	1	1	1	3	20
2	2	5	152	152	152	304	291
2	2	6	56	56	56	111	137
2	2	7	43	43	43	85	99
4	2	0	12	12	12	24	48
4	2	1	19	19	19	39	74
4	2	2	10	10	10	20	51
4	2	3	14	14	14	29	59
4	2	4	7	7	7	13	21
4	2	5	9	9	9	18	54
4	2	6	4	4	4	9	20
4	2	7	6	6	6	12	39
6	2	0	275	275	275	550	403
6	2	2	176	176	176	352	333
6	2	4	3	3	3	7	23
6	2	6	98	98	98	197	200
8	2	0	8	8	8	15	20
8	2	1	13	13	13	26	39
8	2	2	7	7	7	14	42
8	2	3	10	10	10	21	54
8	2	4	5	5	5	10	32
8	2	5	7	8	7	15	20
10	2	0	101	101	101	202	176
10	2	1	66	66	66	131	131
10	2	2	66	66	66	133	125
10	2	3	137	137	137	274	198
10	2	4	5	5	5	10	21
10	2	5	105	105	105	209	132
12	2	0	10	10	10	20	32
12	2	2	9	9	9	18	47
14	2	0	69	69	69	138	116
14	2	1	46	46	46	92	80
14	2	2	46	46	46	92	75
14	2	3	95	95	95	191	98
0	3	1	0	90	0	90	89
0	3	3	0	72	0	72	75
0	3	5	0	49	0	49	43
1	3	1	77	0	0	77	92
1	3	2	41	0	0	41	58
1	3	3	62	0	0	62	60
1	3	4	30	0	0	30	35
1	3	5	42	0	0	42	57
2	3	0	0	78	0	78	86
2	3	1	0	44	0	44	61
2	3	2	0	70	0	70	75
2	3	3	0	35	0	35	55
2	3	4	0	51	0	51	43
3	3	0	87	0	0	87	77
3	3	2	78	0	0	78	88
3	3	4	58	0	0	58	61
4	3	0	0	72	0	72	63
4	3	1	0	41	0	41	32
4	3	2	0	65	0	65	35
4	3	3	0	33	0	33	40
5	3	0	39	0	0	39	49
5	3	1	66	0	0	66	63
5	3	2	35	0	0	35	43
5	3	3	54	0	0	54	47
6	3	1	0	72	0	72	37
7	3	0	34	0	0	34	22
7	3	1	58	0	0	58	57
7	3	2	31	0	0	31	23
0	4	0	277	277	277	553	430
0	4	2	177	177	177	353	348
0	4	4	3	3	3	7	35
0	4	6	99	99	99	197	185
2	4	0	9	9	9	19	53
2	4	1	16	16	16	32	67
2	4	2	8	8	8	16	51
2	4	3	12	12	12	24	51
2	4	4	6	6	6	12	35
2	4	5	8	8	8	16	24
2	4	6	4	4	4	8	40
4	4	0	126	126	126	252	236
4	4	1	82	82	82	163	193
4	4	2	82	82	82	164	202
4	4	3	168	168	168	335	281
4	4	4	3	3	3	5	24
4	4	5	126	126	126	252	212
4	4	6	47	47	47	93	101
6	4	0	15	15	15	30	63
6	4	2	13	13	13	26	75
6	4	4	10	10	10	20	48
8	4	0	101	101	101	203	167
8	4	1	66	66	66	132	135
8	4	2	67	67	67	133	127
8	4	3	138	138	138	275	225
8	4	4	5	5	5	10	22
8	4	5	105	105	105	210	165
10	4	0	5	5	5	10	24
10	4	1	9	9	9	17	35
10	4	2	5	5	5	9	24
12	4	0	147	147	147	295	223
12	4	2	98	98	98	195	149
14	4	0	4	3	4	7	16
0	5	1	0	67	0	67	83
0	5	3	0	56	0	56	57
1	5	1	58	0	0	58	52
1	5	2	31	0	0	31	45
1	5	3	48	0	0	48	33
1	5	4	24	0	0	24	24
2	5	0	0	58	0	58	52
2	5	1	0	33	0	33	39
2	5	2	0	53	0	53	39
2	5	3	0	27	0	27	41
2	5	4	0	40	0	40	41
3	5	0	66	0	0	66	54
3	5	2	60	0	0	60	61
3	5	4	46	0	0	46	33
4	5	0	0	55	0	55	54
4	5	1	0	31	0	31	39
4	5	2	0	50	0	50	41
5	5	0	30	0	0	30	46
5	5	1	51	0	0	51	52
5	5	2	27	0	0	27	34
6	5	1	0	55	0	55	41
7	5	0	27	0	0	27	34
7	5	1	45	0	0	45	42
0	6	2	11	11	11	23	78
0	6	4	9	9	9	19	58
0	6	6	7	7	7	14	14
2	6	0	102	102	102	204	217
2	6	1	66	66	66	133	177
2	6	2	67	67	67	134	168
2	6	3	138	138	138	277	230
2	6	4	5	5	5	10	29
2	6	5	106	106	106	211	138
4	6	0	6	6	6	12	45
4	6	1	10	10	10	20	55
4	6	2	5	5	5	11	31
4	6	3	8	8	8	17	31
4	6	4	4	4	4	8	27
6	6	0	179	179	179	357	257
6	6	2	118	118	118	236	193
8	6	0	5	5	5	9	29
8	6	1	8	8	8	16	29
8	6	2	4	4	4	9	29
8	6	3	7	7	7	14	25
10	6	0	70	70	70	140	115
10	6	1	46	46	46	92	88
10	6	2	46	46	46	93	76
10	6	3	96	96	96	192	107

At this stage it was noted that whilst both the ideal structures of components *A* and *B*, given in Table 3, gave reasonable agreement over all reflexions having $k=2n$, component *A* accounted for reflexions having $h=2n+1$ and component *B* accounted for reflexions having $h=2n$ in the layers with $k=2n+1$. This immediately suggested that the material might possess a layered structure.

Preliminary structure factor calculations on a layered model of the type –*A*–*B*–*A*– revealed that whilst the agreement over each layer was reasonable the observed structure factor data from layers with $k=2n$ had to be placed on a different scale from that used for data from layers with $k=2n+1$. This indicated that a third component (*C* in Table 3) was probable, having an ordered array of aluminum atoms with the zinc atoms randomly distributed between the ideal sites occupied by zinc in the structures of *A* and *B* and the vacant cation sites. Structure factor calculations based on a layered structure of the type –*A*–*C*–*B*–*C*–*A*– gave immediate agreement with the observed data, with the measured structure factors from all seven layer lines on virtually the same scale. The observed and calculated structure factors are compared in Table 4. Idealized coordinates, given in Table 3, were used in the calculations together with an overall temperature factor of 1·15 Å^2 obtained from a Wilson plot. The overall reliability index, assuming ideal coordinates for the zinc, aluminum and sulphur atoms, is 0·224. Individual values of *R* for the various layer lines together with the final scale factors are given in Table 5.

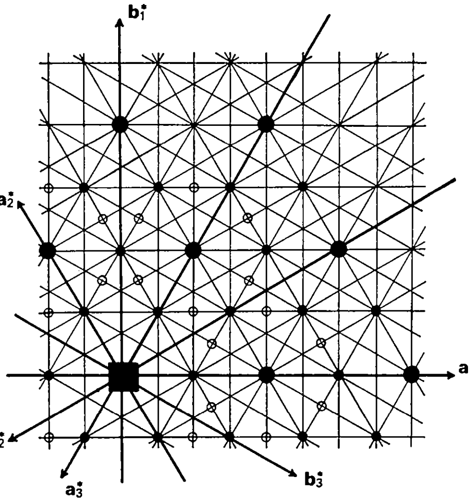

Fig. 1. Three orientations of the a^*b^* reciprocal net of β-ZnAl$_2$S$_4$ required to index all reflexions observed on single-crystal precession photographs. Large filled circles: strong reflexions; small filled circles: weak reflexions; small open circles: very weak reflexions.

Table 6 column (v) compares the intensities of lines in the powder pattern calculated from the model given above, with their measured values. As can be seen by comparing column (i) and $I_c(C)$ in column (iv) the powder pattern observed by Hahn & Frank can, if one regards the close doublets as being unresolved by a non-focusing camera, be accounted for by the type *C* structure.

No evidence has been found in the data from the samples of the completely disordered high-temperature form of ZnAl$_2$S$_4$ reported by Hahn & Frank. For an idealized structure of this type calculated structure factors account only for reflexions having $h+k=4n$ with $k=2n$ when indexed on the orthorhombic cell given above. This is not in agreement with the observed data.

Because of the observed twinning and in view of the overlap of many reflexions from the three structure types no refinement has been attempted.

Description of the structure

Fig. 2(*a*) shows the stacking sequence of blocks of *N* layers of unit cells of components *A*, *B* and *C* on

Table 5. *Individual R indices and scale factors*

Layer (*k*)	*R*	Final scale factor
0	0·188	0·897
1	0·142	1·075
2	0·245	0·981
3	0·181	1·087
4	0·246	1·049
5	0·178	0·975
6	0·351	1·273

Table 6. β-ZnAl$_2$S$_4$. *Observed and calculated powder data*

Column (i) Hahn & Frank.
Column (ii) Steigmann.
In column (iv) $I_c(A)$, $I_c(B)$ and $I_c(C)$ are the intensities calculated for structures *A*, *B* and *C* respectively; where $I_c(A)=|F_c|(A)^2pf_1(\theta)\times10^{-5}$ with similar expressions for structures *B* and *C*. The terms in these expressions are defined in Table 2. No absorption correction has been made (see Table 2).
In column (v) $I_c=I_c(A)+I_c(C)+I_c(B)+I_c(C)$.

(i)		(ii)		(iii)		(iv)			(v)		
d_c (Å)	*I*	d_o (Å)	*I*	d_c (Å)	*hkl*	$I_c(A)$	$I_c(B)$	$I_c(C)$	I_c		I_o
		6·42	*w*	6·47	110	17	0	0	17	19	9
				6·41	200	< 1	< 1	< 1	2		
		4·87	*w*	4·87	210	0	27	0	27		8
		4·73	*w*	4·73	011	0	32	0	32		14
		4·43	*w*+	4·44	111	39	0	0	39	44	21
				4·42	201	1	1	1	5		

Table 6 (*cont.*)

(i)		(ii)		(iii)		(iv)			(v)		
d_c (Å)	*I*	d_o (Å)	*I*	d_c (Å)	*hkl*	$I_c(A)$	$I_c(B)$	$I_c(C)$	I_c		I_o
		3·811	*vw*	3·808	211	0	9	0	9		4
		3·747	*w*	3·751	020	< 1	< 1	< 1	2	19	11
				3·715	310	17	0	0	17		
3·252	*ms*	3·240	*vs*	3·238	220	39	39	39	156	232	272
		3·208	*ms*	3·206	400	19	19	19	76		
3·066	*wm*	3·054	*s*	3·050	002	34	34	34	134		151
		2·947	*vw*	2·948	410	0	7	0	7		1
2·873	*m*	2·862	*s*	2·860	221	24	24	24	96	144	168
		2·840	*m*	2·838	401	12	12	12	48		
		2·755	*w*	2·762	112	4	0	0	4	5	2
				2·755	202	< 1	< 1	< 1	1		
		—	*tr*	2·654	411	0	3	0	3		1
		2·586	*w*	2·585	212	0	9	0	9		4
		2·436	*vw*	2·437	420	≪1	≪1	≪1	< 1	2	2
				2·427	510	1	0	0	1		
		2·366	*w*	2·366	022	< 1	< 1	< 1	1		7
		—	*tr*	2·357	312	9	0	0	9	12	2
				2·329	230	0	3	0	3		
		—	*tr*	2·313	031	0	5	0	5	12	1
				2·276	131	7	0	0	7		
		2·261	*w*	2·263	421	< 1	< 1	< 1	2	8	7
				2·255	511	6	0	0	6		
2·231	*m*	2·224 2·214	*ms*(*b*)	2·220	222	12	12	12	48	72	87
				2·210	402	6	6	6	24		
		—	—	2·176	231	0	2	0	2		—
		2·139	*vw*	2·158	330	4	0	0	4	4	2
				2·138	600	≪1	≪1	≪1	< 1		
		2·119	*vw*	2·120	412	0	5	0	5		3
		1·969	*tr*	1·971	430	0	2	0	2	5	1
				1·962	013	0	3	0	3		
		1·940	*w*(*b*)	1·948	611	0	6	0	6	11	4
				1·940	113	4	0	0	4		
				1·938	203	< 1	< 1	< 1	1		
		1·902	*vw*	1·912	132	1	0	0	1	3	4
				1·904	422	≪1	≪1	≪1	< 1		
				1·899	512	1	0	0	1		
1·877	*s*	1·871	*s*	1·876	213	0	1	0	1	62	137
				1·876	431	0	1	0	1		
				1·875	040	15	15	15	60		
		1·855	*ms*	1·857	620	27	27	27	108	112	63
				1·851	232	0	4	0	4		
		—	—	1·799	240	≪1	≪1	≪1	< 1	1	—
				1·790	530	< 1	0	0	< 1		
				1·780	710	< 1	0	0	< 1		
		1·749	*w*	1·762	332	4	0	0	4	4	4
				1·750	602	≪1	≪1	≪1	< 1		
1·730	*vs*	1·725	*s*	1·726	241	< 1	< 1	< 1	2	173	197
				1·722	223	28	28	28	112		
				1·718	531	3	0	0	3		
				1·717	403	14	14	14	56		
		—	—	1·709	711	3	0	0	3		—
		—	—	1·674	413	0	1	0	1		—
		—	—	1·656	432	0	3	0	3		—
1·626	*w*	1·619	*m*(*b*)	1·618	440	4	4	4	16	24	19
				1·603	800	2	2	2	8		
1·601	*s*	1·596	*ms*	1·597	042	8	8	8	32		78
		1·585	*m*	1·586	622	16	16	16	64		32
		—	—	1·577	033	0	1	0	1	3	—
				1·570	631	0	1	0	1		
				1·568	810	0	1	0	1		
		1·565	*m*	1·566	133	< 1	0	0	< 1	13	22
				1·564	441	3	3	3	12		
		—	—	1·561	423	≪1	≪1	≪1	< 1		—
		—	—	1·558	513	< 1	0	0	< 1		—
		1·551	*w*	1·550	801	2	2	2	8	8	3
				1·550	242	≪1	≪1	≪1	< 1		
		—	—	1·544	532	< 1	0	0	< 1		—

which the structure factor calculations were based. As this sequence is idealized for the purpose of calculation one may assume that, in order to produce well defined diffraction spots, the crystal is built up of a number of layers of unit cells of a given component before a transition to the next component takes place. The number of layers of the three types of structure must, however, approximate to *N* layers of structure *A*, *N* layers of structure *B* and 2*N* layers of structure *C* in order to place the calculated and observed structure factors on the same scale. Fig. 2(*b*) depicts the arrangement of occupied and vacant tetrahedral sites in the unit cells of the structures of components *A*, *B* and *C* immediately above the close-packed sulphur layer, lying parallel to the (001) cell face, at $Z=0$. As can be seen from the diagrams, the *B* type structure is derived from the structure of type *A* by displacing each alternate row of –Zn–V–Zn–, running parallel to the [010] direction ,by $\frac{1}{2}b$. The distribution of Al remains the same in both cases, the origin of the unit cell being moved to $(\frac{1}{4},\frac{1}{4},0)$ in order to satisfy the symmetry requirements of the space group. The structure of component *C* represents a disordering of the Zn and the vacant tetrahedral sites, the arrangement of Al being the same as that in the structures of components *A* and *B*. In the structures of types *A* and *B* and, on the average, in type *C* each sulphur atom is surrounded by Zn, 2Al and one vacant tetrahedral site.

This type of layered structure also accounts for the observed twinning. As the close-packed sulphur layers possess threefold symmetry about a direction parallel to the *c* axis of the unit cell, the observed splitting of the reflexions having $h=2n$ and $k=2n+1$ may be explained by the rotation through ±120° of the cation arrangement of component *B* relative to component *C* across the transition boundary, the distribution of sulphur atoms being the same in both cases. Similar twinning may occur at the transition boundary between components *A* and *C* but this would be difficult to detect because, as is seen by reference to Table 4 and Fig. 1, all the reflexions accounted for by the structure of component *A* are common to all three orientations of the a^*b^* reciprocal net.

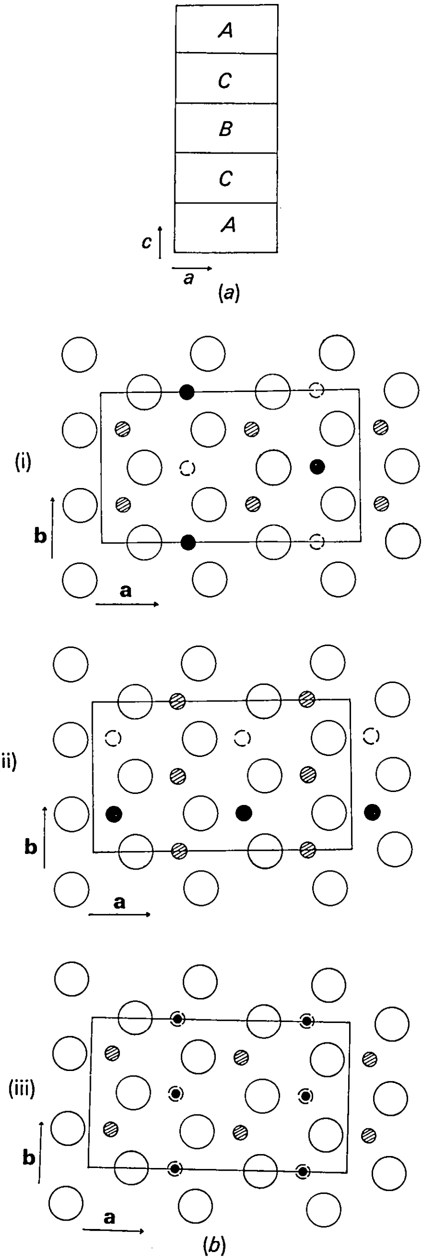

Fig. 2. (*a*) Idealized stacking sequence of components *A*, *B* and *C* parallel to the *c* axis of the unit cell of β-$ZnAl_2S_4$. (*b*) Atomic arrangement at $Z=0$ and $Z=c/8$ in the unit cell of (i) component *A*, (ii) component *B* and (iii) component *C* projected onto the (001) face of the cell (solid line). At $Z=c/8$ in (i) and (ii) filled circles represent zinc atoms and broken circles represent vacant tetrahedral sites in structures *A* and *B*; in (iii) solid circles ringed by broken circles represent zinc atoms and vacant tetrahedral sites randomly distributed in structure *C*. In each case aluminum atoms in the layer at $Z=c/8$ are denoted by shaded circles, and in the layer at $Z=0$ sulphur atoms are represented by large open circles.

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