Table 1. *Atomic position parameters, with standard deviations*

Values are given as fractions, × 10^4, of the unit cell edge. The last two columns give the parameter B (together with its standard deviation) of the temperature factor $\exp\{-B(\sin\theta/\lambda)^2\}$.

	x/a	$\sigma_{x/a}$	y/b	$\sigma_{y/b}$	z/c	$\sigma_{z/c}$	B	σ_B
Mg	2487	7	2487	7	2290	24	0·64	0·10
B(1)	3883	18	3761	18	8738	34	0·21	0·24
B(2)	1119	22	1091	21	5830	40	0·95	0·31
O(1)	0000	—	0000	—	9841	36	0·85	0·22
O(2)	5000	—	5000	—	4512	31	0·65	0·23
O(3)	3352	14	2388	13	9916	27	0·84	0·22
O(4)	1598	15	2638	14	4709	28	0·95	0·21
O(5)	4795	11	2913	12	7300	30	0·32	0·17
O(6)	0176	13	1979	13	7183	29	0·88	0·20
O(7)	2450	12	4823	13	8028	24	0·54	0·19
O(8)	2704	13	0176	12	6387	23	0·43	0·18

factor as a consequence remained high. The final value of 22% left room for doubts about the essential correctness of the proposed structure. Moreover, no assessment of the accuracy of the atomic coordinates was possible under the circumstances. It was therefore considered worth while to attempt a least-squares refinement based on space group $P4_2$, utilizing the experimental data of Paton & MacDonald.

A modified version of the Busing, Martin & Levy (1962) least-squares refinement program was used. (The observed structure factors were weighted according to the scheme of Hughes, setting $2F_{\min} = 15$.) The atomic coordinates given by Paton & MacDonald served as a starting point (with the exception of the z parameter of Mg, which was eventually found to have an incorrect sign).

By initially refining a fraction of the atoms at a time, the parameters were found to converge, and the reliability factor came down from 22% to 15·7%. The parameters obtained in this way were not entirely satisfactory as far as the atoms O(1) and O(2) (in special positions) were concerned. The resulting z parameter of these two atoms led to differing boron–oxygen bond lengths (1·32 and 1·54 Å) for chemically equivalent bonds. By adjustment of these z parameters to give boron–oxygen bond distances of 1·47 Å and continuing the refinement process, the parameters converged to new values. The reliability factor remained at 15·7%, but less disparate values for the boron–oxygen bond lengths ensued.

Parameters, with their standard deviations, from the last refinement cycle are given in Table 1. The boron–oxygen bond lengths calculated from these parameters average 1·47 Å. This agrees with the accepted value for the boron–oxygen bond, when the boron atom is in fourfold coordination. The individual bond lengths fall within a range around the average value, corresponding to about ± 3 times the standard deviation (3 × 0·03 Å).

The structure contains an isolated borate polyanion, $(OH)_3B–O–B(OH)_3^{2-}$, roughly described as two BO_4 tetrahedra sharing a corner. The B–O–B bond angle, calculated from the original parameter values of Paton & MacDonald, was found to be 111·6°. As observed by Takeuchi (1958) and Krogh-Moe (1962), this value for the B–O–B angle is considerably smaller than the values usually reported for the B–O–B angle between planar BO_3 triangles sharing a corner. Thus the B–O–B angle of the $O_2B–O–BO_2^{4-}$ polyanion in magnesium pyroborate is 134·5°, with estimated standard deviation 1·3° (Block, Burley, Perloff & Mason, 1959). However, from the present refinement the values 120·5 and 127·0°, with estimated standard deviations 3·5°, are obtained for the two different B–O–B angles in pinnoite. Hence the experimental evidence for a more acute B–O–B bond angle in pinnoite than in magnesium pyroborate is not entirely conclusive.

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Six new zinc sulphide polytypes of the family 16*L*–48*R*.

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Six hitherto unknown ZnS polytypes were found. Their unit cell and Zhdanov symbols are: 16*L* (14 2); 16*L* (5 3 3 5); 16*L* (3 3 2 2 3 3); 48*R* $(13\ 3)_3$; 48*R* $(8\ 4\ 2\ 2)_3$; and 48*R* $(10\ 6)_3$. X-ray oscillation photographs of their (10.*l*) column are shown; the calculated and observed intensities are compared.

The concept of polytype families has already been introduced in a previous publication (Mardix, Alexander, Brafman & Steinberger, 1967); five polytypes of the family 16*L*–48*R* were reported there. Six other polytypes of the same family were found in two vapour-phase-grown zinc sulphide crystals. The crystal 175 *S*23 contained polytype regions

Table 1. *Comparison of calculated and observed intensities for the six polytypes*

l	calc.	obs.	*l*	calc.	obs.	Further observed relations between intensities
16*L* (14 2)						
0	406	*vw*				
1	591	*w*	$\bar{1}$	220	*vw*	$5 \simeq 4 > 3 > 2 > 1$
2	731	*w*	$\bar{2}$	52	*vvw*	$0 > \bar{1}$
3	847	*w*	$\bar{3}$	23	*vvw*	
4	928	*w*	$\bar{4}$	928	*w*	
5	976	*w*	$\bar{5}$	36085	*vvs*	
6	1001	*w*	$\bar{6}$	13950	*vs*	
7	1026	*w*	$\bar{7}$	2722	*s*	
8	1114	*w*	$\bar{8}$	1114	*w*	
48*R* (10 6)$_3$						
2	239	*vw*	$\bar{1}$	68	*vvw*	$\bar{1}\bar{6} > 17 > 14$
5	505	*vw*	$\bar{4}$	539	*w*	$\bar{1}\bar{9} \simeq 13 > 20$
8	0	*a*	$\bar{7}$	112	*vvw*	$\bar{2}\bar{2} > \bar{4}$
11	1774	*s*	$\bar{1}\bar{0}$	747	*w*	$5 > 2$
14	6130	*vvs*	$\bar{1}\bar{3}$	4706	*vs*	$\bar{7} > \bar{1}$
17	7297	*vvs*	$\bar{1}\bar{6}$	21043	*vvs*	
20	3474	*vs*	$\bar{1}\bar{9}$	5020	*vs*	
23	213	*vw*	$\bar{2}\bar{2}$	894	*w*	
2	70	*vvw*	$\bar{1}$	18	*vvw*	$\bar{1}\bar{0} > \bar{7}$
5	410	*w*	$\bar{4}$	270	*vw*	$11 > 8 \simeq 23$
8	922	*s*	$\bar{7}$	741	*s*	$14 \simeq 17 > 20$
11	1437	*s*	$\bar{1}\bar{0}$	1275	*s*	$2 > \bar{1}$
14	1795	*vs*	$\bar{1}\bar{3}$	1702	*vs*	
17	1896	*vs*	$\bar{1}\bar{6}$	35564	*vvs*	
20	1733	*vs*	$\bar{1}\bar{9}$	1815	*vs*	
23	1403	*s*	$\bar{2}\bar{2}$	1526	*s*	
48*R* (8 4 2 2)$_3$						
2	239	*vw*	$\bar{1}$	1385	*s*	$\bar{1}\bar{6} > \bar{1}\bar{3} > \bar{1}\bar{9}$
5	738	*w*	$\bar{4}$	539	*w*	$14 > 11 \simeq 23 > 20$
8	0	*a*	$\bar{7}$	16	*vvw*	$\bar{1} > 17$
11	3646	*vs*	$\bar{1}\bar{0}$	747	*w*	$\bar{2}\bar{2} > 5$
14	6130	*vs*	$\bar{1}\bar{3}$	9668	*vvs*	
17	1075	*s*	$\bar{1}\bar{6}$	10942	*vvs*	
20	3474	*vs*	$\bar{1}\bar{9}$	7331	*vvs*	
23	4346	*vs*	$\bar{2}\bar{2}$	894	*w*	
16*L* (5 3 3 5)*						
0	406	*w*				$6 > 3 > 7$
1	190	*vvw*				$8 > 4 \simeq 2$
2	864	*s*				
3	4023	*vs*				
4	928	*s*				
5	12483	*vvs*				
6	5927	*vs*				
7	4072	*vs*				
8	2600	*s*				
16*L* (3 3 2 2 3 3)*						
0	406	*vw*				
1	528	*vw*				$6 > 2$
2	1809	*s*				$1 > 7 > 0$
3	5014	*vs*				
4	928	*w*				
5	10813	*vvs*				
6	2830	*s*				
7	534	*vw*				
8	11515	*vvs*				

* The observed intensities are symmetrical with respect to the zero line.

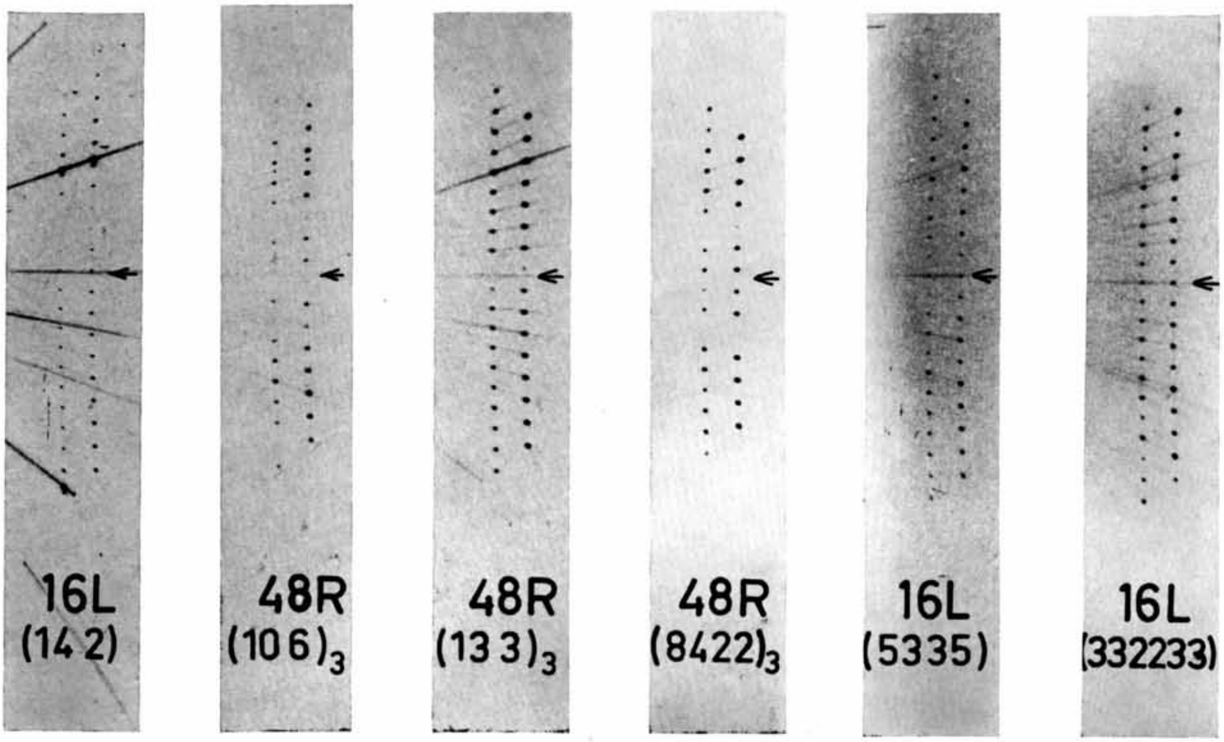

Fig.1. (10.l) column of an oscillation photograph about the c axis of the six polytypes (× 3). Cu K radiation, 60 mm diameter camera. The position of the zero line is indicated by an arrow.

of the structures: 16*L* (14 2); 48*R* (10 6)$_3$; 48*R* (13 3)$_3$; 48*R* (8 4 2 2)$_3$. The crystal 193 *S*61 contained the polytypes: 16*L* (5 3 3 5) and 16*L* (3 3 2 2 3 3).

X-ray oscillation photographs about the *c* axis of the crystals were taken; Cu *K* radiation was used with a collimator diameter of 0·1 mm. The (10.*l*) columns of these photographs are shown in Fig. 1. The photographs labelled 16*L* (14 2) and 48*R* (10 6)$_3$ are of two nearby regions with a cubic region in between. This cubic region was also included in the two photographs and its characteristic spots are easily seen between those of the polytypes.

The identification of the polytypes was carried out by comparing the observed intensity order of the (10.*l*) spots with those calculated for all possible Zhdanov sequences of the family 16*L*–48*R*. A description of the procedure of identification is given in detail by Mardix *et al.* (1967). The observed and calculated spot intensities of the (10.*l*) column of the polytypes are given in Table 1.

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Unit-cell dimensions of ammonium cadmium chloride and potassium cadmium chloride.

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More accurate determinations of unit-cell dimensions of isomorphous $4NH_4Cl.CdCl_2$ and $4KCl.CdCl_2$, space group $R\bar{3}m$, gave $a=8\cdot842\pm0\cdot005$ Å, $\alpha=88°48'\pm10'$ and $a=8\cdot601\pm0\cdot001$ Å, $\alpha=89°57\pm5'$ respectively.

Ammonium cadmium chloride, $4NH_4Cl.CdCl_2$, and potassium cadmium chloride, $4KCl.CdCl_2$, are isomorphous and the unit-cell data for these rhombohedral crystals, space group $R\bar{3}m$, are given as in Table 1.

Table 1. *Unit-cell data*

	$4NH_4Cl.CdCl_2$*	$4KCl.CdCl_2$†
a	8·91 Å	8·57 Å
α	88° 54′	~90°
Density (calculated)	1·878 g.cm^{-3}	2·59 g.cm^{-3}
Density (measured)	1·930 ± 0·001 g.cm^{-3}	not stated

* *Structure Reports* (1947–1948).
† *Structure Reports* (1945–1946).

In these data, the *a* and α values had large and unstated margins of error. For the ammonium compound, it was mentioned that the value $a=8\cdot91$ Å was uncertain and that with the measured density the value of $a=8\cdot79$ Å was calculated.

As a consequence of our interest in the structure of such compounds, the unit-cell measurements were carried out by employing normal-beam, zero-layer, Weissenberg photographs about the *a* axis, using Cu *Kα* radiation. The camera had been calibrated by a sodium chloride powder pattern as a check of systematic errors. Utilizing about 15 high-angle reflexions, $\theta>63°$, which were all α doublets, starting values were obtained for the reciprocal quantities, a^* and α^*, by considering the relationships $(\sin^2\theta\pm\sin^2\bar{\theta})$, where θ and $\bar{\theta}$ refer to the reflexions $0kl$ and $0\bar{k}l$ respectively. With these starting values the corrections for random errors of measurements were obtained by a least-squares calculation (Whittaker & Robinson, 1929). The final lattice parameters together with their probable errors are given in Table 2.

Table 2. *Unit-cell data* (*present work*)

	$4NH_4Cl.CdCl_2$	$4KCl.CdCl_2$
a	8·842 ± 0·005 Å	8·601 ± 0·001 Å
α	88°48′ ± 10′	89°57′ ± 5′
Density (calculated)	1·923 g.cm^{-3}	2·581 g.cm^{-3}

The present values account for some of the high-angle reflexions which would not occur for the earlier unit-cell parameters and the density agreement is also improved.

Detailed structure investigations are likely to be very delayed. One of us (SKM) would like to acknowledge gratefully the award of a scholarship by the Government of India.

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