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The Crystal Structure of Ammonium Thiotungstate $(NH_4)_2WS_4$

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Ammonium thiotungstate crystallizes in the orthorhombic space group $Pnam\,(D_{2h}^{16})$. The unit-cell dimensions are: $a=9{\cdot}52$, $b=12{\cdot}33$, $c=7{\cdot}01$ Å, and $Z=4$.

The tungsten coordinates were obtained from two Patterson projections; the others were determined from electron-density projections and refined by differential Fourier synthesis.

The atomic arrangement is isostructural with β-K_2SO_4 as suggested by Gattow. The interatomic distances W–S are uniform with a mean value of 2·17 Å giving for W^{6+} the same ionic radius found in the $[WO_4]^{2-}$ ion. The structure shows a similarity to a distorted close packing.

Introduction

The compound $(NH_4)_2WS_4$ was first prepared by Berzelius (1826). Its exact chemical composition was determined later by Corleis (1886), and the first crystallographic examination was carried out by Vater (1883). Vater stated that the semi-transparent orange prismatic crystals belonged to the rhombic dipyramidal class. Gattow (1959) showed $(NH_4)_2MoS_4$ to be isostructural with β-K_2SO_4 and from the same investigation it seems probable that there are further isostructural compounds with the composition A_2BX_4, where $A^+=$K, Rb, Cs, Tl, NH_4; $B^{6+}=$Mo, W, Se and $X^{2-}=$O, S, Se. Recently Gattow (1962) stated that K, Rb and Cs selenate are also isostructural with β-K_2SO_4. In the present work a full structure determination of $(NH_4)_2WS_4$ was accomplished for the determination of W–S atomic distance in the $[WS_4]^{2-}$ ion.

Experimental

The first crystals used in the present examination were prepared at the High-Pressure Research Institute, Pét (Hungary). More suitable crystals for X-ray diffraction have been placed at our disposal by Dr Gattow (Göttingen, Germany). From this latter preparation very fine (0·05–0·1 mm thick and 1 mm long) prismatic needles could be selected. From bigger crystal specimens thin needles, elongated in the other two crystallographic directions, could be prepared; this was made easier by the perfect cleavage parallel to (010) and the definite cleavage parallel to (001). The crystals being very soft, the mechanical preparation of thin crystals of cylindrical or spherical habit proved to be very difficult. For this reason square-shaped crystals were used, except one sample which was spherical with a diameter of 0·3 mm.

The unit-cell dimensions, determined from oscillation photographs made in a camera 114·6 mm in diameter, with Cu $K\alpha$ radiation, are:

$$a=9{\cdot}52\pm0{\cdot}02,\ b=12{\cdot}33\pm0{\cdot}02,\ c=7{\cdot}01\pm0{\cdot}01\ \text{Å}\,.$$

The ratio of the axes $a:b:c=0{\cdot}7721:1:0{\cdot}5685$ is in good agreement with that obtained by Vater (1883) from morphological examinations, *viz.* 0·7783 : 1 : 0·5675.

From Laue photographs it was shown that there exists only one mirror plane perpendicular to the c axis. In the direction of [100] a threefold rotation axis can be recognized. This, however, is only a pseudo-axis; the unit cell is nearly orthohexagonal, with an axial ratio $b:c=1{\cdot}762\simeq\sqrt{3}$.

From the absences, $0kl$ with $k+l=2n+1$ and $h0l$ with $h=2n+1$, it follows that the space group is $Pnam\,(D_{2h}^{16})$, if the higher possible symmetry is assumed.

The density, determined pycnometrically, is 2·76 g.cm^{-3}; thus in the unit cell 4 molecules are present. The density calculated for four molecules per unit cell is 2·807 g.cm^{-3}. The absorption coefficient μ, calculated from the atomic mass absorption coefficients for Cu $K\alpha$ radiation, is 352·1 cm^{-1}.

The X-ray photographs for the determination of intensities were made in an integrating Weissenberg camera by the multiple film, equi-inclination technique. The intensities were estimated by visual comparison with a standard intensity scale in which the ratio of the intensities was known. From the possible 1047 reflexions the intensities of 803 were collected, and corrected for polarization and Lorentz factors. The scale and mean isotropic temperature factors were evaluated by Wilson's (1942) method from the $hk0$ reflexions; we found $B=1{\cdot}74$ Å^2. From the differential Fourier syntheses it was shown that the real temperature factor is somewhat smaller for W and bigger for S than the above mean value and not quite isotropic. A correction of this deviation as well as the absorption correction were omitted owing to temporary difficulties in performing the computations. The computation of the Patterson and Fourier function was carried out on Ural 1 and all other computations on IBM 628, our own programs being used for the first time.

Determination of the structure

As a starting point in the determination of atomic coordinates the heavy atom method was used. As the four W atoms in the unit cell must be in a fourfold position, in the general position with coordinates $(x, y, \frac{1}{4})$, the Patterson projection $P(uvp)$* (Fig. 1(*a*)) seemed to be satisfactory. In this projection three predominant peaks are revealed, with the coordinates $(0, \frac{1}{2})$, $(\frac{1}{2}, 0{\cdot}146)$ and $(\frac{1}{2}, 0{\cdot}354)$. In the fourfold position the interatomic vectors W–W are in this projection $(2x, 2y)$, $(\frac{1}{2}-2x, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}-2y)$. By comparing the related vectors it becomes obvious that from this projection only the x coordinate of W can be given and it is

$$x_{\mathrm{W}}=\tfrac{1}{4}\ .$$

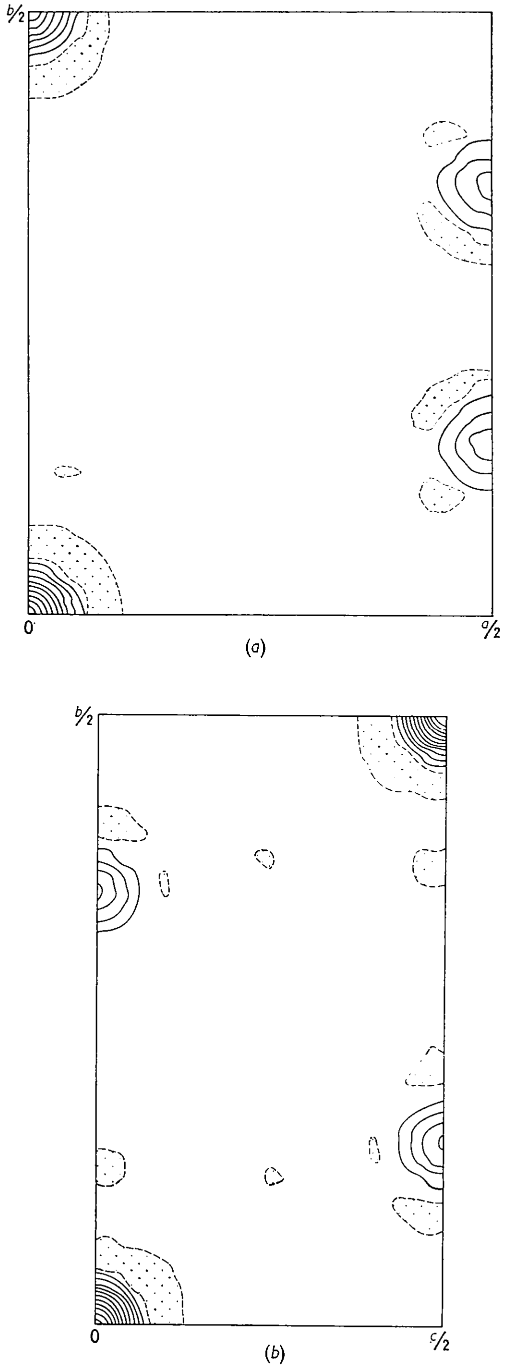

Fig. 1. (*a*) Patterson projection $P(uvp)$. (*b*) Patterson projection $P(pvw)$. Contours are at arbitrary intervals. Negative parts of the projection are dotted and encompassed by dashed lines.

Taking this x value, the second two vectors become $(\frac{1}{2}, 2y)$ and $(\frac{1}{2}, \frac{1}{2}-2y)$, from which an unambiguous determination of the y coordinate is impossible. In the projection $P(pvw)$ in Fig. 1(*b*) the coordinates of the three peaks are $(\frac{1}{2}, \frac{1}{2})$, $(0{\cdot}146, \frac{1}{2})$ and $(0{\cdot}354, 0)$. As the vectors of this Patterson projection are $(\frac{1}{2}, \frac{1}{2})$, $(2y, \frac{1}{2})$ and $(\frac{1}{2}-y, 0)$ the y coordinate of W can be determined and it is

$$y_{\mathrm{W}}=0{\cdot}073\ .$$

From the coordinates of W, the sign of 74 structure factors $F(hk0)$ could be determined. The two-dimensional space-group of this projection is *pgg*. The calculated electron-density projection gave a fairly good approximation of the S coordinates and from the same projection one could find out that while one set of S atoms is in an eightfold position the other two are in fourfold positions; that is, the latter two are on the mirror plane. The S atoms in the general position lie between two mirror planes with $z=\frac{1}{4}$ and $\frac{3}{4}$. Since the diameter of S^{2-} is almost $c/2$, the z coordinate of the S atom must be zero or nearly so, a fact supported by two three-dimensional Fourier sections at the heights $z=\pm 0{\cdot}033$ showing a symmetric decrease of electron density on both sides of $z=0$.

With the aid of the S atoms the signs of further structure factors were determined and after several Fourier and difference-Fourier syntheses the coordinates of the S atoms were refined.

After subtraction of the W and S atoms, the difference-Fourier projection in Fig. 2 gave the coordinates of the NH_4^+ ions, two of which are in fourfold positions. The final coordinates of the structure are given in Table 1. The final (001) projection is pictured in Fig. 3.

Table 1. *Final values of the atomic coordinates*

	x	y	z
W	0·250	0·073	$\frac{1}{4}$
S(1)	0·350	0·142	0
S(2)	0·283	−0·100	$\frac{1}{4}$
S(3)	0·025	0·104	$\frac{1}{4}$
$NH_4(1)$	0·162	0·392	$\frac{1}{4}$
$NH_4(2)$	−0·037	−0·150	$\frac{1}{4}$

A further refinement of the parameters of the NH_4^+ ions could be achieved with three-dimensional Fourier

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* The symbol p denotes the projection axis.

Table 2. *Observed and calculated structure factors*

h	k	ℓ	F_o	F_c
0	2	0	148	162
0	4	0	243	-271
0	6	0	185	-195
0	8	0	90	-77
0	10	0	0	-13
0	12	0	68	73
0	14	0	79	88
1	1	0	0	-1
1	2	0	216	-225
1	3	0	12	15
1	4	0	166	-156
1	5	0	0	-9
1	6	0	74	-55
1	7	0	26	-29
1	8	0	21	21
1	9	0	21	17
1	10	0	124	118
1	11	0	24	30
1	12	0	117	126
1	13	0	22	-16
1	14	0	0	-5
2	0	0	235	-268
2	1	0	30	24
2	2	0	175	-155
2	3	0	12	-20
2	4	0	74	70
2	5	0	55	-55
2	6	0	196	180
2	7	0	27	26
2	8	0	125	134
2	9	0	44	54
2	10	0	24	23
2	11	0	24	-26
2	12	0	82	-75
2	13	0	43	-36
2	14	0	85	-93
3	1	0	139	144
3	2	0	85	88
3	3	0	115	-115
3	4	0	198	191
3	5	0	76	-78
3	6	0	118	112
3	7	0	40	52
3	8	0	54	-64
3	9	0	23	26
3	10	0	127	-133
3	11	0	0	-14
3	12	0	80	-80
3	13	0	0	5
3	14	0	0	3
4	0	0	207	210
4	1	0	47	-35
4	2	0	152	150
4	3	0	0	-7
4	4	0	42	-42
4	5	0	53	43
4	6	0	196	-210
4	7	0	0	-10
4	8	0	144	-137
4	9	0	24	-34
4	10	0	24	39
4	11	0	0	12
4	12	0	77	80
4	13	0	18	18
4	14	0	46	40
5	1	0	0	-5
5	2	0	119	-110
5	3	0	0	-3
5	4	0	188	-193
5	5	0	0	7
5	6	0	92	-86
5	7	0	0	6
5	8	0	82	100
5	9	0	0	-4
5	10	0	107	122
5	11	0	0	-6
5	12	0	42	31
5	13	0	0	-1
5	14	0	0	-10
6	0	0	103	-107
6	1	0	69	-63
6	2	0	121	-109
6	3	0	58	-61
6	4	0	0	-12
6	5	0	44	34
6	6	0	131	145
6	7	0	48	36
6	8	0	128	133
6	9	0	0	-8
6	10	0	0	-6
6	11	0	22	-10
6	12	0	64	-67
6	13	0	0	-7
7	1	0	0	-4
7	2	0	77	76
7	3	0	32	31
7	4	0	139	132
7	5	0	24	-18
7	6	0	83	72
7	7	0	48	-45
7	8	0	58	-51
7	9	0	23	24
7	10	0	85	-98
7	11	0	38	39
7	12	0	54	-57
8	0	0	151	147
8	1	0	24	26
8	2	0	82	77
8	3	0	0	14
8	4	0	48	-45
8	5	0	34	-29
8	6	0	96	-98
8	7	0	0	1
8	8	0	76	-75
8	9	0	21	24
8	10	0	18	-15
8	11	0	0	-11
8	12	0	40	47
9	1	0	0	5
9	2	0	136	-144
9	3	0	0	-15
9	4	0	106	- 99
9	5	0	0	6
9	6	0	0	-1
9	7	0	21	21
9	8	0	47	40
9	9	0	0	-9
9	10	0	55	60
10	0	0	120	-126
10	1	0	32	-18
10	2	0	62	-49
10	3	0	31	-27
10	4	0	59	48
10	5	0	0	3
10	6	0	65	55
10	7	0	24	22
10	8	0	49	50
10	9	0	0	10
11	1	0	19	16
11	2	0	75	80
11	3	0	0	-15
11	4	0	66	65
11	5	0	0	-11
11	6	0	26	17
11	7	0	0	10
12	0	0	49	66
12	1	0	17	-19
12	2	0	39	38
12	3	0	14	-13
0	0	2	280	-303
0	0	4	331	331
0	0	6	133	-137
0	0	8	137	144
2	0	1	0	-11
2	0	2	190	188
2	0	3	0	4
2	0	4	193	-189
2	0	5	0	-1
2	0	6	113	108
2	0	7	0	0
2	0	8	81	-90
4	0	1	22	-21
4	0	2	286	-302
4	0	3	33	23
4	0	4	153	152
4	0	5	29	-22
4	0	6	160	-170
4	0	7	27	17
4	0	8	62	75
6	0	1	0	14
6	0	2	191	187
6	0	3	0	-10
6	0	4	85	-83
6	0	5	0	7
6	0	6	104	115
6	0	7	0	-3
8	0	1	60	-43
8	0	2	120	-112
8	0	3	42	38
8	0	4	109	115
8	0	5	26	-29
8	0	6	59	-73
10	0	1	0	1
10	0	2	76	57
10	0	3	0	0
10	0	4	94	-99
10	0	5	0	0
12	0	1	14	-17
12	0	2	37	-49
0	1	1	109	-109
0	1	3	81	91
0	1	5	82	-68
0	1	7	72	46
0	1	9	33	-30
0	2	2	166	-183
0	2	4	116	113
0	2	6	117	-98
0	2	8	59	54
0	3	1	254	-253
0	3	3	197	204
0	3	5	161	-149
0	3	7	142	100
0	4	2	70	85
0	4	4	133	-155
0	4	6	27	34
0	4	8	75	-68
0	5	1	147	-169
0	5	3	129	139
0	5	5	114	-102
0	5	7	88	70
0	6	2	210	254
0	6	4	128	-144
0	6	6	146	148
0	6	8	75	-72
0	7	1	20	28
0	7	3	23	-21
0	7	5	0	14
0	7	7	0	-8
0	8	2	141	142
0	8	4	73	-60
0	8	6	101	88
0	9	1	128	126
0	9	3	97	-109
0	9	5	87	84
0	9	7	62	-60
0	10	2	37	-64
0	10	4	0	-10
0	10	6	19	-39
0	11	1	118	103
0	11	3	103	-91
0	11	5	95	75
0	12	2	87	-89
0	12	4	53	58
0	13	1	59	31
0	13	3	52	-28
0	13	5	34	23
0	14	2	39	-30
0	14	4	69	72
0	15	1	23	-37
1	1	1	259	-251
1	2	1	25	-10
1	3	1	59	-47
1	4	1	42	-35
1	5	1	174	167
1	6	1	22	14
1	7	1	192	191
1	8	1	19	34
1	9	1	71	63
1	10	1	0	-4
1	11	1	45	-57
1	12	1	22	-23
1	13	1	81	-84
1	14	1	0	-5
1	15	1	47	-48
2	0	1	0	-11
2	1	1	71	84
2	2	1	0	-8
2	3	1	159	165
2	4	1	0	7
2	5	1	154	141
2	6	1	0	8
2	7	1	60	40
2	8	1	0	-4
2	9	1	111	-93
2	10	1	0	-4
2	11	1	147	-137
2	12	1	0	3
2	13	1	68	-55
2	14	1	0	1
2	15	1	36	46
3	1	1	235	228
3	2	1	18	-19
3	3	1	38	26
3	4	1	15	-17
3	5	1	126	-140
3	6	1	17	12
3	7	1	167	-164
3	8	1	20	15
3	9	1	85	-73
3	10	1	0	-6
3	11	1	32	42
3	12	1	0	-10
3	13	1	85	87
3	14	1	0	2
3	15	1	38	54
4	0	1	20	-21
4	1	1	79	-81
4	2	1	15	-14
4	3	1	182	-187
4	4	1	16	20
4	5	1	143	-138
4	6	1	19	30
4	7	1	0	12
4	8	1	0	-8
4	9	1	107	107
4	10	1	22	-26
4	11	1	97	96
4	12	1	0	-4
4	13	1	41	27
4	14	1	14	15
5	1	1	202	-203
5	2	1	34	-38
5	3	1	17	-26
5	4	1	18	-25
5	5	1	147	147
5	6	1	20	22
5	7	1	145	152
5	8	1	22	32
5	9	1	44	38
5	10	1	0	-3
5	11	1	30	-49
5	12	1	19	-23
5	13	1	55	-67
5	14	1	0	-8
6	1	1	52	55
6	2	1	0	0
6	3	1	127	127
6	4	1	0	-8
6	5	1	117	112
6	6	1	0	-1
6	7	1	22	15
6	8	1	0	-1
6	9	1	76	-81
6	10	1	0	1
6	11	1	95	-98
6	12	1	0	4
6	13	1	33	-33
7	1	1	115	124
7	2	1	21	16
7	3	1	30	28
7	4	1	0	10
7	5	1	62	-72
7	6	1	0	-8
7	7	1	108	-109
7	8	1	0	-12
7	9	1	73	-66
7	10	1	0	-1
7	11	1	17	21
7	12	1	0	7
8	1	1	62	-62
8	2	1	0	-14
8	3	1	124	-128
8	4	1	31	33
8	5	1	88	-84
8	6	1	22	32
8	7	1	0	13
8	8	1	0	-13
8	9	1	64	76
8	10	1	17	-27
8	11	1	61	67
8	12	1	0	-3
9	1	1	108	-107
9	2	1	22	-24
9	3	1	22	-18
9	4	1	0	-11
9	5	1	73	76
9	6	1	20	13
9	7	1	76	91
9	8	1	17	16
9	9	1	30	34
9	10	1	0	-1
10	1	1	41	46
10	2	1	0	0
10	3	1	97	98
10	4	1	0	0
10	5	1	63	66
10	6	1	0	0
10	7	1	15	-12
10	8	1	0	-2
10	9	1	32	-60
11	1	1	47	55
11	2	1	0	11
11	3	1	22	22
11	4	1	0	7
11	5	1	27	-29
11	6	1	0	-6
12	1	1	28	-35
12	2	1	0	-5
1	1	2	64	-68
1	2	2	58	61
1	3	2	69	71
1	4	2	201	200
1	5	2	28	29
1	6	2	135	131
1	7	2	35	-39
1	8	2	77	-83
1	9	2	0	-7
1	10	2	150	-143
1	11	2	22	16
1	12	2	84	-61
1	13	2	0	-5
1	14	2	0	6
1	15	2	0	-2
2	1	2	93	105
2	2	2	137	149
2	3	2	69	76
2	4	2	27	-25
2	5	2	74	-70
2	6	2	182	-188
2	7	2	26	-27
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2	12	2	72	77
2	13	2	0	-13
2	14	2	77	72
2	15	2	0	14
3	1	2	17	-22
3	2	2	126	-133
3	3	2	20	-24
3	4	2	169	-157
3	5	2	32	40
3	6	2	87	-75
3	7	2	54	52
3	8	2	29	37
3	9	2	30	-38
3	10	2	124	113
3	11	2	43	-50
3	12	2	99	95
3	13	2	25	26
3	14	2	0	-2
4	1	2	41	-31
4	2	2	119	-115
4	3	2	31	-27
4	4	2	115	127
4	5	2	25	25
4	6	2	142	144
4	7	2	0	10
4	8	2	95	80
4	9	2	0	-17
4	10	2	0	17
4	11	2	0	4
4	12	2	54	-62
4	13	2	0	9
4	14	2	61	-77
5	1	2	0	4
5	2	2	205	218
5	3	2	0	1
5	4	2	127	134
5	5	2	0	-6
5	6	2	0	3
5	7	2	0	-6
5	8	2	31	-33
5	9	2	0	3
5	10	2	85	-81
5	11	2	0	5
5	12	2	79	-84
5	13	2	0	2
5	14	2	0	7
6	1	2	0	9
6	2	2	85	83
6	3	2	28	29
6	4	2	57	-62
6	5	2	29	20
6	6	2	96	-93
6	7	2	31	-33
6	8	2	98	-83
6	9	2	30	-33
6	10	2	40	-40
6	11	2	26	22
6	12	2	53	52
6	13	2	16	29
7	1	2	58	-53
7	2	2	103	-100
7	3	2	42	47
7	4	2	121	-112
7	5	2	44	37
7	6	2	62	-48
7	7	2	31	-28
7	8	2	30	32
7	9	2	0	-13
7	10	2	89	85
7	11	2	0	9
7	12	2	58	69
8	1	2	31	37
8	2	2	87	-77
8	3	2	22	20
8	4	2	31	21
8	5	2	31	-40
8	6	2	104	104
8	7	2	0	-2
8	8	2	86	83
8	9	2	25	35
8	10	2	0	0
8	11	2	0	-6
9	1	2	31	23
9	2	2	85	79
9	3	2	0	-22
9	4	2	110	117
9	5	2	28	-15
9	6	2	38	41
9	7	2	0	13
9	8	2	56	-71
9	9	2	0	4
9	10	2	59	-75
10	1	2	28	18
10	2	2	77	59
10	3	2	26	25
10	4	2	0	7
10	5	2	0	-2
10	6	2	69	-83
10	7	2	19	-22
10	8	2	67	-77
11	1	2	0	4
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3	9	5	61	-49
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2	7	8	0	7
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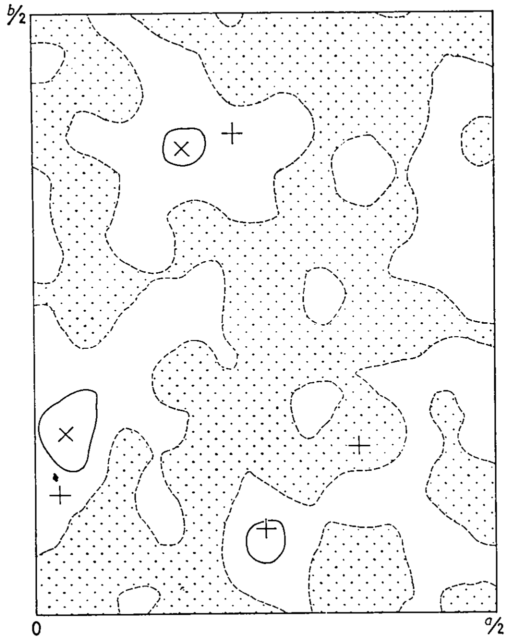


Fig. 2. The electron-density projection on (001) with the W and S atoms subtracted. (+) shows the places of the subtracted atoms and (×) those of the remaining NH_4^+ ions. Contours are at arbitrary intervals. Negative parts of the projection are dotted and encompassed by broken lines.

sections at $z=\frac{1}{4}$ and $\frac{3}{4}$, by collection of the rest of the reflexions.

For the calculation of structure factors, the atomic scattering factors of W and S^{2-} were taken from *Internationale Tabellen* (1935) and that of NH_4^+ from Wyckoff & Armstrong (1930). The deduction of the scattering factor of the W^{6+} ion from that of the W atom was made by interpolation taking $f(W^{6+})=68$ at $\sin\theta/\lambda=0$ and $f(W^{6+})=f(W)$ at $\sin\theta/\lambda \geq 0{\cdot}4$.

Fig. 3. The final electron-density projection on (001). Contours are at arbitrary intervals. Negative parts of the projection are dotted and encompassed by broken lines.

Structure factors calculated from the parameters of Table 1 and corrected for temperature motion are compared with the observed structure factors in Table 2. The reliability factor $R(hkl)$ based on the values in Table 2 is 0·13; when, however, the reflexions with zero intensity are omitted, $R(hkl)=0{\cdot}10$.

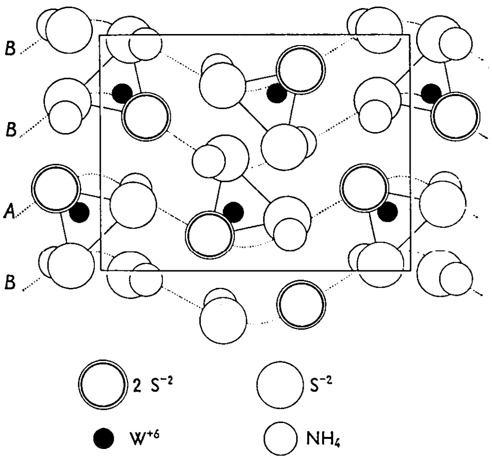


Fig. 4. Ammonium thiotungstate structure in (001) projection. Dotted lines show corrugated planes parallel to the plane (100) and built up of S^{2-} and NH_4^+ ions. The sequence of the planes *A* and *B* with different ionic arrangement in one period is *BABB*.

Discussion of the structure

The structure of ammonium thiotungstate, the projection of which can be seen in Fig. 4, is isostructural with β-K_2SO_4. This can be seen clearly by comparison of the parameters. After performing for the structure of β-K_2SO_4 a coordinate transformation

Table 3. *The parameters of* $(NH_4)_2WS_4$ and β-K_2SO_4

$(NH_4)_2WS_4$

$a=9{\cdot}52$; $b=12{\cdot}33$; $c=7{\cdot}01$ Å

W	0·250	0·073	0·250
S(1)	0·350	0·142	0
S(2)	0·283	−0·100	0·250
S(3)	0·025	0·104	0·250
$NH_4(1)$	0·162	0·392	0·250
$NH_4(2)$	−0·037	−0·150	0·250

β-K_2SO_4

$a=7{\cdot}46$; $b=10{\cdot}05$; $c=5{\cdot}76$ Å

S	0·250	0·083	0·250
O(1)	0·317	0·153	0·037
O(2)	0·317	−0·057	0·250
O(3)	0·048	0·083	0·250
K(1)	0·283	0·417	0·250
K(2)	0	−0·183	0·250

$$x' = z,\ y' = \tfrac{1}{2} - y,\ z' = x$$

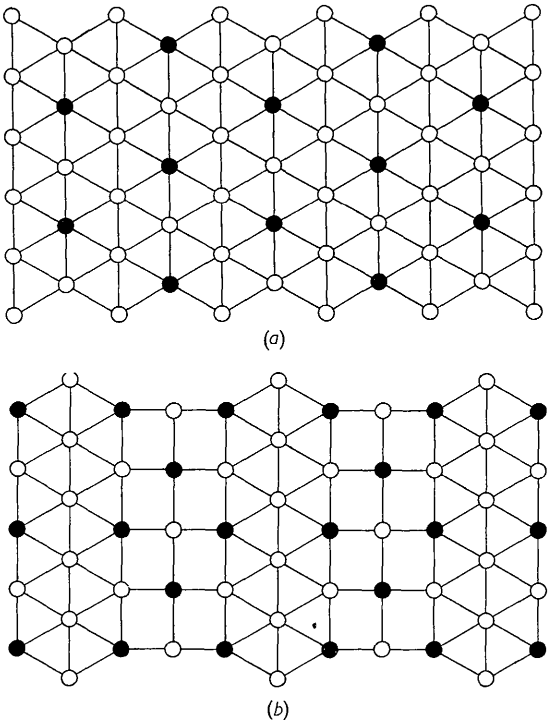
the related parameters of the two structures are as in Table 3.

According to the (x, y) projection (Fig. 4) the structure of $(NH_4)_2WS_4$ is built up of WS_4 tetrahedra. These complex $[WS_4]^{2-}$ ions are arranged in such a way that every tetrahedron is linked by two of its S^{2-} ions through an NH_4^+ ion to four neighbouring tetrahedra. By this linking, infinite $-S-NH_4-S-$ chains are built up parallel to the [001] direction. With this atomic arrangement Pauling's electrostatic valency rule is completely satisfied for every tetrahedron.

Table 4. *Interatomic distances**

W–S(1)	2·165 Å	S(1)–S(1′)	3·505 Å
W–S(1′)	2·165	S(1)–S(2)	3·53
W–S(2)	2·155	S(1)–S(3)	3·585
W–S(3)	2·176	S(2)–S(3)	3·52
Mean	2·165 Å	Mean	3·546 Å
N(1)–S(**1**)	3·67 Å	N(2)–S(**1**)	3·565 Å
N(1)–S(**2**)	3·67	N(2)–S(**2**)	3·565
N(1)–S(**3**)	3·475	N(2)–S(**3**)	3·47
N(1)–S(**4**)	3·475	N(2)–S(**4**)	3·47
N(1)–S(**5**)	3·545	N(2)–S(**5**)	3·18
N(1)–S(**6**)	3·545	N(2)–S(**6**)	3·10
N(1)–S(**7**)	3·47	N(2)–S(**7**)	3·575
N(1)–S(**8**)	3·96	N(2)–S(**8**)	3·575
N(1)–S(**9**)	3·96	N(2)–S(**9**)	3·52
N(1)–S(**10**)	3·78		
Mean	3·655 Å	Mean	3·447 Å

* The numbers in bold type refer to the nearest anions around the cations NH_4^+ denoted by N(1) or N(2); the other numbers in parentheses are the numbers of the symmetry positions of the atoms.


(a)

(b)

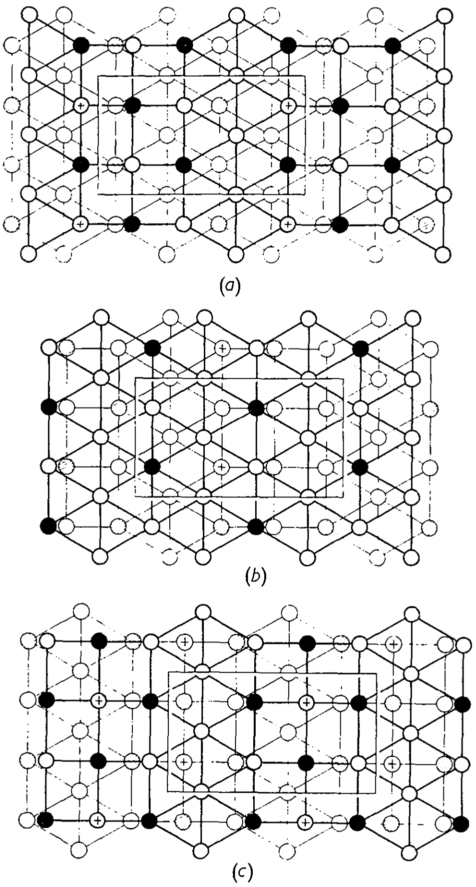
Fig. 5. The corrugated ionic planes (*a*) type *A* and (*b*) type *B*, with different ionic arrangement of S^{2-} (○) and NH_4^+ (●) ions in the structure of ammonium thiotungstate without distortion.

Table 5. *Interatomic distances and cationic radii in* AWO_4 *structures* (Å)

Compound	W–O	r (Å⁻²)	r (W⁶⁺)
$CaWO_4$	1·75	0·99	0·43
$PbWO_4$	1·78	1·20	0·46
$SrWO_4$	1·79	1·12	0·47
$BaWO_4$	1·81	1·34	0·49

The atomic distances in the WS_4 tetrahedron (Table 4) are quite similar so that a distortion of the tetrahedron can be scarcely detected. The S–S distance agrees fairly well with the twofold ionic radius S^{2-} (3·48 Å) given by Goldschmidt (1926).

From the mean ionic distance W–S = 2·165 Å the ionic radius of $W^{6+} \simeq 0{\cdot}43$ Å. This value differs significantly from the ionic radius $W^{6+} = 0{\cdot}62$ Å given


(a)

(b)

(c)

Fig. 6. The fitting of two-two neighbouring ionic planes in one period of the lattice of ammonium thiotungstate without distortion. (*a*) The fitting of *BA*, (*b*) the fitting of *AB* and (*c*) the fitting of *BB* ionic planes of Fig. 5. In all three cases the unit cell is drawn and the places of W atoms are marked with crosses (+).

by Ahrens (1952), but is in fairly good agreement with the values in Table 5 derived from the ionic distances W–O known in the $[WO_4]^{2-}$ ion of the structures AWO_4 (A = Ba, Ca, Pb or Sr) given by Sillén & Nylander (1943).

Table 5 shows also the change of the ionic distances in the tetrahedral coordination with the radii, or with the polarization effect of the A cations. Also the NH_4^+ ion must have such an effect complicated to some extent by the protons around the N atom. The reduced ionic distance of W–O, as well as that of W–S can be attributed most probably to a partially covalent bond in the tetrahedron.

According to Fig. 4 and Table 4 the NH_4^+ ions have 9 and 10 nearest neighbours respectively, with distances ranging from 3·10 to 3·96 Å. The arrangement of the S^{2-} ions around NH_4^+ is rather irregular.

Although the structure of ammonium thiotungstate cannot be regarded as a close-packed one, a similarity to close packing can be detected. Parallel to the plane (100) corrugated ionic planes can be seen (broken lines show these planes for one period in Fig. 4), built up of S^{2-} and NH_4^+ ions and appearing with two different ionic arrangements given without distortion in Fig. 5. These two kinds of ionic plane A and B alternate in the crystal lattice according to the scheme ..*ABBABBA*... In Fig. 4 the period *BABB* is given. The fitting of any two neighbouring ionic planes is pictured in Fig. 6(*a*), (*b*), (*c*) in which the distortion of the lattice is omitted. As the ionic planes are built up of S^{2-} anions and NH_4^+ cations in one (*a*, *b*) period of the unit cell, by fitting the *AB* and *BA* planes, only one tetrahedron and by fitting the *BB* planes, two tetrahedra are built with only S^{2-} ions at the corners. Every other polyhedron of this ionic arrangement has at its corners different kinds of ions. If we put W atoms in the cavities surrounded only by S^{2-} ions and make a distortion by corrugating the related ionic planes which is necessary in order to separate from each other the atoms that are too near to one another in the undistorted arrangement, we come to the structure of ammonium thiotungstate.

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References

Ahrens, L. H. (1952). *Geochimica et Cosmochimica Acta*, **2**, 155.
Berzelius, J. J. (1826). *Ann. Phys. Lpz.* **8**, 277.
Corleis, E. (1886). *Liebigs Ann.* **232**, 268.
Gattow, G. (1959). *Naturwissenschaften*, **46**, 425.
Gattow, G. (1962). *Acta Cryst.* **15**, 419.
Goldschmidt, V. M. (1926). *Geochemische Verteilungsgesetze der Elemente*, **VII**.
Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Berlin: Borntraeger.
Sillén, L. G. & Nylander, A. (1943). *Ark. Kemi Min. Geol.* A, **17**, (4), 1.
Vater, H. (1883). *Z. Kristallogr.* **10**, 392.
Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 152.
Wyckoff, R. W. G. & Armstrong, Alice H. (1930). *Z. Kristallogr.* **72**, 319.

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Order in Binary σ-Phases

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The atomic order in two σ-phase Re–Mo alloys has been determined using powder photographs and X-ray diffractometry. The proposed order schemes support the same correlation between the position of the element in the periodic table and the lattice site as that obeyed by σ-phases formed by elements of the first long period. Rhenium is similar to manganese in its ordering behaviour.

Introduction

The existence of the σ-phase in many binary and ternary alloys of the transition elements has been reported in recent years (Greenfield & Beck, 1956; Knapton, 1957; Nevitt & Downey, 1957) and the detailed structure of this phase has been carefully determined for several representative alloys (Bergman & Shoemaker, 1954; Kasper, Decker & Belanger, 1952; Dickins, Douglas & Taylor, 1956). The existence of order in the σ-phase structure has been established in a number of alloys (Decker, Waterstrat & Kasper, 1954; Kasper & Waterstrat, 1956; Ageev & Shekhtman, 1959, 1960; Brown & Forsyth, 1961; Wilson &