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The Crystal Structure of $Li_2SO_4 . H_2O$. A Three-Dimensional Refinement*

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The structure of $Li_2SO_4 . H_2O$ has been refined by the method of least squares with three-dimensional X-ray diffraction data measured by counter techniques from an approximately spherical crystal. Unit-cell dimensions are $a=5{\cdot}454$, $b=4{\cdot}857$, $c=8{\cdot}173$ Å, and $\beta=107°22'$, and the space group is $P2_1$. Although a final R of 3·8% was achieved, the data were not accurate enough to locate the hydrogen atoms. Several recently determined sulfate structures are compared and some conclusions drawn.

Introduction

The structure of $Li_2SO_4 . H_2O$ was originally determined by Ziegler (1934). This structure was further refined by Larson & Helmholz (1954) who used a limited set of data obtained from oscillation photographs. The author now has modern computing facilities and experimental equipment available to him, and, because of continued interest in the compound by other workers (*e.g.* MacGrath, Silvidi & Carroll, 1959; Hirahara & Murakami, 1956), thought it desirable to refine the structure further. Furthermore, this is a nearly ideal compound for the accurate determination of the size and configuration of the sulfate group. This group represents 75% of the scattering matter in the unit cell, and with Mo $K\alpha$ radiation μ is $\sim 6{\cdot}0$ cm^{-1}. The small size of the lithium ions may allow them to get close enough to the oxygen atoms to distort the sulfate group; if so, this should give some indication of the maximum distortion to be anticipated in the sulfate group in an ionic crystal.

Experimental

An approximately spherical crystal having an average radius of 0·008 cm was used in collecting intensity data with the single-crystal orienter and Mo $K\alpha$ radiation. The tube was operated at 35 kV and the reflected beam was filtered with 0·006 in. Zr foil. Lattice constants were remeasured and found to be $a=5{\cdot}454$, $b=4{\cdot}857$, $c=8{\cdot}173$ Å, all $\pm 0{\cdot}002$ Å and $\beta=107°22' \pm 2'$ (λ Mo $K\alpha_1=0{\cdot}70926$ Å). The only extinctions are $0k0$ with k odd. These, together with other experimental data (Ziegler, 1934), indicate that the space group is $P2_1$. Reflections with $\theta_{\text{Mo}} \leq 37{\cdot}5°$ were examined with a krypton-filled proportional counter, and of 1191 non-extinguished reflections within this hemisphere, 1155 were observed. Lp corrections were applied but because of the nearly spherical shape and low absorption ($\mu R=0{\cdot}05$) no absorption corrections were necessary. Background corrections were assumed to be dependent on θ only, except for reflections having a higher or lower order within the sphere of measurement. For these reflections an empirical correction was applied, as described in the Appendix, to account for the white radiation.

Refinement of the structure

The structure was refined by full-matrix least-squares minimizing $\Sigma w(|F_o|-|F_c|)^2$ with $w=1{\cdot}0$ for all observed reflections and $w=0{\cdot}0$ for all unobserved reflections. Starting parameters were those of Larson & Helmholz (1954) corrected to eliminate the several typographical errors. Form factors were used in exponential form

$$f=\sum_{i=1}^{2} a_i \exp(-b_i s)+c,$$

where $s=\sin^2\theta/\lambda^2$, with the parameters given by Forsyth & Wells (1959). After a few cycles with isotropic temperature factors the reliability index,

$$R=\Sigma w||F_o|-|F_c||/\Sigma w|F_o| ,$$

Table 1. *Parameters in* $Li_2SO_4 . H_2O$ *after isotropic least-squares refinement*

Atom	x	y	z	B
S	0·2936 ± 0·0001	0	0·2084 ± 0·0001	0·73 ± 0·01 Å^2
O(1)	0·0207 ± 0·0006	0·0692 ± 0·0007	0·1692 ± 0·0004	1·48 ± 0·04 Å^2
O(2)	0·4364 ± 0·0006	0·1128 ± 0·0007	0·3789 ± 0·0004	1·23 ± 0·04 Å^2
O(3)	0·4008 ± 0·0006	0·1231 ± 0·0007	0·0787 ± 0·0004	1·29 ± 0·04 Å^2
O(4)	0·3301 ± 0·0006	0·7008 ± 0·0007	0·2101 ± 0·0004	1·30 ± 0·04 Å^2
O(w)	0·9104 ± 0·0007	0·4708 ± 0·0011	0·3945 ± 0·0005	2·62 ± 0·07 Å^2
Li(1)	0·3049 ± 0·0013	0·4935 ± 0·0025	0·9940 ± 0·0009	1·45 ± 0·09 Å^2
Li(2)	0·5621 ± 0·0013	0·4862 ± 0·0025	0·3945 ± 0·0009	1·46 ± 0·10 Å^2

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Table 2. *Calculated and observed structure factors for* $Li_2SO_4 . H_2O$

All *F*'s have been multiplied by 10. Minus signs on F_{obs} should be interpreted as 'less than'. The column headings are *h*, $\lvert F_{obs}\rvert$, $\lvert F_{calc}\rvert$, α.

h	$\lvert F_{obs}\rvert$	$\lvert F_{calc}\rvert$	α
K= 0	L= 0		
1	170	187	180
2	42	17	0
3	278	270	0
4	31	25	0
5	94	92	180
6	-17	13	180
7	100	102	0
8	54	52	180
K= 0	L= 1		
-9	46	43	180
-8	73	75	0
-7	87	86	0
-6	33	31	180
-5	25	32	0
-4	159	158	0
-3	104	100	0
-2	426	451	180
-1	344	370	0
0	93	105	0
1	444	443	180
2	187	183	0
3	209	210	0
4	103	98	180
5	27	27	180
6	107	108	0
7	40	31	180
8	51	55	180
K= 0	L= 2		
-9	-18	2	180
-8	66	63	0
-7	51	52	180
-6	68	68	180
-5	117	118	0
-4	65	61	0
-3	129	127	180
-2	161	159	0
-1	264	275	0
0	268	259	180
1	264	256	180
2	150	157	0
3	181	178	180
4	194	195	180
5	79	78	0
6	31	29	180
7	67	64	180
8	-17	6	180
K= 0	L= 3		
-9	45	45	0
-8	-16	1	0
-7	65	88	180
-6	26	23	0
-5	56	53	0
-4	298	305	180
-3	85	83	180
-2	37	39	0
-1	274	286	180
0	167	173	180
1	86	84	0
2	122	115	0
3	243	247	180
4	82	83	0
5	46	45	0
6	107	111	180
7	16	9	180
8	-18	17	0
K= 0	L= 4		
-9	20	12	180
-8	55	60	180
-7	58	58	180
-6	147	148	0
-5	113	112	180
-4	133	132	180
-3	278	283	0
-2	199	192	180
-1	189	189	180
0	87	82	180
1	145	141	0
2	254	262	180
3	31	28	180
4	162	166	0
5	71	70	180
6	29	20	180
7	63	59	0
K= 0	L= 5		
-9	26	25	180
-8	62	59	180
-7	61	57	0
-6	16	8	180
-5	193	198	180
-4	104	103	0
-3	128	131	0
-2	150	142	180
-1	41	36	0
0	358	361	0
1	88	89	180
2	46	43	180
3	153	153	0
4	31	29	0
5	76	76	180
6	34	35	0
7	71	68	0
K= 0	L= 6		
-9	27	27	180
-8	59	64	0
-7	66	62	0
-6	31	30	180
-5	12	6	0
-4	169	175	0
-3	41	31	180
-2	190	192	180
-1	272	281	0
0	31	33	180
1	103	98	180
2	125	127	0
3	87	92	0
4	34	32	180
5	23	15	180
6	93	93	0
K= 0	L= 7		
-9	24	26	0
-8	46	47	0
-7	53	54	180
-6	-16	4	0
-5	88	87	0
-4	83	89	0
-3	112	108	180
-2	148	147	0
-1	163	165	0
0	190	194	180
1	70	72	0
2	71	66	0
3	65	62	180
4	56	57	180
5	50	52	0
6	17	4	0
K= 0	L= 8		
-8	32	30	180
-7	26	28	180
-6	54	55	0
-5	13	16	0
-4	113	114	180
-3	54	52	180
-2	152	160	0
-1	168	170	180
0	47	46	180
1	118	121	0
2	33	35	180
3	96	98	180
4	45	43	0
5	23	15	0
K= 0	L= 9		
-8	67	67	180
-7	15	18	0
-6	68	73	0
-5	88	86	180
-4	50	52	180
-3	124	119	0
-2	68	70	180
-1	130	129	180
0	28	27	0
1	62	62	0
2	155	161	180
3	22	13	0
4	62	62	0
5	50	64	180
K= 0	L= 10		
-8	48	48	180
-7	62	61	0
-6	55	55	180
-5	109	111	180
-4	83	86	0
-3	19	7	180
-2	74	71	180
-1	33	22	180
0	127	125	0
1	72	75	180
2	61	59	180
3	96	102	0
4	38	33	180
K= 0	L= 11		
-7	44	40	0
-6	85	87	180
-5	52	48	0
-4	63	58	0
-3	74	74	180
-2	34	23	180
-1	80	78	0
0	-22	5	0
1	79	76	180
2	74	77	0
3	38	32	0
K= 0	L= 12		
-6	-21	10	180
-5	95	91	0
-4	30	21	180
-3	40	38	180
-2	91	87	0
-1	45	37	0
0	66	71	180
1	49	46	0
2	45	45	0
K= 0	L= 13		
-5	26	28	0
-4	74	72	180
-3	32	28	0
-2	80	83	0
-1	97	92	180
0	19	20	0
K= 1	L= 0		
1	367	367	86
2	103	103	290
3	157	145	129
4	115	108	42
5	106	111	117
6	80	79	262
7	25	23	63
8	63	66	112
K= 1	L= 1		
-9	32	30	278
-8	60	61	277
-7	96	99	107
-6	49	50	358
-5	55	53	217
-4	87	91	98
-3	242	240	72
-2	133	124	183
-1	83	76	259
0	329	346	98
1	118	101	252
2	182	177	221
3	91	86	80
4	119	119	101
5	77	74	237
6	37	35	75
7	88	90	95
8	16	13	161
K= 1	L= 2		
-9	38	40	276
-8	47	52	115
-7	78	78	91
-6	94	95	267
-5	67	65	197
-4	163	159	88
-3	26	29	253
-2	155	145	193
-1	323	316	83
0	340	323	82
1	170	158	187
2	98	93	38
3	224	224	96
4	102	100	259
5	65	64	267
6	76	71	89
7	-16	4	234
8	47	47	259
K= 1	L= 3		
-9	17	14	153
-8	83	84	91
-7	14	9	126
-6	48	45	267
-5	150	151	102
-4	99	95	66
-3	197	192	260
-2	140	134	153
-1	219	200	354
0	239	233	207
1	221	217	283
2	133	128	66
3	68	66	127
4	166	167	282
5	83	81	88
6	39	39	57
7	63	61	263
8	24	30	304
K= 1	L= 4		
-9	24	28	83
-8	-16	4	226
-7	85	85	266
-6	22	17	279
-5	113	114	95
-4	192	193	291
-3	113	103	146
-2	171	167	33
-1	42	43	332
0	134	124	234
1	164	160	334
2	88	87	108
3	211	212	272
4	41	42	302
5	45	44	75
6	53	50	266
7	54	54	283
K= 1	L= 5		
-9	26	23	42
-8	44	47	270
-7	27	30	297
-6	84	82	85
-5	122	126	284
-4	125	127	264
-3	26	17	48
-2	115	106	312
-1	204	200	254
0	45	41	7
1	112	105	58
2	96	93	256
3	22	21	304
4	68	64	55
5	38	30	144
6	74	77	278
7	26	27	81
K= 1	L= 6		
-9	52	57	282
-8	44	47	265
-7	60	62	85
-6	30	34	337
-5	77	76	256
-4	64	62	64
-3	142	143	79
-2	156	156	267
-1	25	24	262
0	146	142	88
1	112	113	279
2	84	84	217
3	68	67	48
4	66	67	112
5	59	58	250
6	26	22	34
K= 1	L= 7		
-9	49	49	282
-8	53	57	114
-7	39	35	37
-6	89	88	255
-5	28	29	212
-4	105	101	72
-3	55	53	185
-2	110	110	276
-1	205	212	99
0	75	78	67
1	99	99	240
2	80	82	90
3	87	85	79
4	53	53	211
5	38	37	294
6	68	68	99
K= 1	L= 8		
-8	73	75	94
-7	32	35	297
-6	44	44	158
-5	85	82	74
-4	65	69	101
-3	103	108	255
-2	48	47	101
-1	107	110	90
0	105	106	254
1	18	19	204
2	88	94	79
3	34	26	159
4	61	62	271
5	54	53	84
K= 1	L= 9		
-8	23	16	281
-7	56	50	258
-6	48	50	111
-5	56	55	75
-4	77	76	261
-3	46	45	122
-2	89	89	62
-1	28	27	209
0	63	65	265
1	54	53	57
2	41	41	115
3	103	106	275
4	26	22	88
K= 1	L= 10		
-8	40	42	273
-7	-17	6	64
-6	74	72	96
-5	105	105	286
-4	47	44	219
-3	54	48	60
-2	45	40	302
-1	83	83	240
0	52	51	358
1	64	69	100
2	85	89	275
3	23	14	305
4	41	40	78
K= 1	L= 11		
-7	54	56	95
-6	32	26	304
-5	78	78	276
-4	73	72	101
-3	52	49	10
-2	82	82	249
-1	27	24	315
0	59	59	73
1	47	47	255
2	52	55	276
3	45	47	80
K= 1	L= 12		
-6	76	76	275
-5	20	11	143
-4	57	55	76
-3	55	51	279
-2	41	37	254
-1	74	74	82
0	20	6	47
1	52	53	251
2	38	33	70
K= 1	L= 13		
-5	49	48	78
-4	26	17	127
-3	67	65	272
-2	59	58	102
-1	39	33	74
0	50	51	255
K= 2	L= 0		
0	466	478	40
1	166	156	293
2	105	100	109
3	129	124	35
4	79	79	353
5	121	120	150
6	18	15	184
7	85	86	20
8	16	31	189
K= 2	L= 1		
-8	62	66	19
-7	59	57	10
-6	43	42	171
-5	49	51	59
-4	125	135	352
-3	157	155	109
-2	153	148	207
-1	180	181	63
0	97	97	45
1	129	124	216
2	98	98	101
3	185	182	350
4	46	44	204
5	52	54	188
6	90	90	357
7	24	20	266
8	61	59	179
K= 2	L= 2		
-8	46	50	29
-7	57	60	177
-6	46	43	164
-5	99	101	358
-4	21	18	121
-3	59	63	240
-2	107	104	346
-1	95	98	337
0	83	82	210
1	150	143	213
2	45	46	29
3	74	68	201
4	134	139	202
5	39	39	64
6	65	64	302
7	66	65	179
8	20	16	234
K= 2	L= 3		
-9	55	56	346
-8	22	23	170
-7	66	65	195
-6	67	67	332
-5	38	43	114
-4	182	181	209
-3	69	68	142
-2	82	76	292
-1	170	165	195
0	69	66	217
1	154	147	299
2	59	58	52
3	158	157	238
4	31	30	96
5	71	71	337
6	76	70	201
7	41	42	158
K= 2	L= 4		
-9	17	15	255
-8	71	75	171
-7	61	62	282
-6	86	87	14
-5	97	102	213
-4	69	72	240
-3	156	155	9
-2	148	144	234
-1	141	137	157
0	84	78	260
1	77	75	50
2	137	137	190
3	39	36	186
4	102	107	17
5	34	27	240
6	48	47	161
7	47	45	5
K= 2	L= 5		
-9	38	40	171
-8	39	35	204
-7	69	69	352
-6	61	61	147
-5	114	113	199
-4	83	84	25
-3	59	58	9
-2	69	66	192
-1	25	23	14
0	209	205	9
1	34	34	207
2	61	56	154
3	95	89	17
4	45	44	17
5	79	74	164
6	22	16	43
7	61	63	20
K= 2	L= 6		
-8	67	66	359
-7	41	37	9
-6	51	48	164
-5	44	41	352
-4	101	103	18
-3	84	87	136
-2	76	74	211
-1	161	164	54
0	14	16	322
1	68	68	159
2	67	70	57
3	108	107	348
4	53	56	136
5	29	23	221
6	73	70	20
K= 2	L= 7		
-8	36	39	24
-7	60	58	171
-6	41	40	95
-5	106	106	344
-4	83	83	100
-3	52	55	252
-2	91	90	15
-1	80	82	39
0	94	97	226
1	70	72	101
2	76	75	338
3	44	43	157
4	56	54	186
5	36	37	4
6	17	16	349
K= 2	L= 8		
-8	34	30	209
-7	38	41	151
-6	70	68	350
-5	19	18	134
-4	100	101	169
-3	38	38	285
-2	76	79	37
-1	101	99	203
0	30	28	201
1	65	69	357
2	21	20	269
3	73	74	198
4	19	17	1
5	37	35	333
K= 2	L= 9		
-8	53	55	140
-7	28	29	347
-6	53	53	352
-5	76	76	195
-4	26	27	224
-3	97	93	349
-2	63	64	196
-1	77	80	189
0	38	38	308
1	40	38	32
2	94	96	205
3	22	13	157
4	49	53	360
K= 2	L= 10		
-7	46	44	13
-6	51	51	190
-5	71	68	201
-4	58	61	23
-3	47	45	285
-2	76	71	162
-1	41	40	284
0	76	77	8
1	44	45	186
2	43	44	215
3	60	60	33
K= 2	L= 11		
-7	24	23	79
-6	54	58	220
-5	43	38	34
-4	46	44	350
-3	57	57	179
-2	21	21	144
-1	58	60	357
0	34	28	106
1	39	42	203
2	40	43	38
K= 2	L= 12		
-6	16	10	340
-5	62	62	17
-4	27	25	167
-3	22	18	186
-2	59	58	15
-1	25	24	24
0	41	44	185
1	24	26	52
K= 2	L= 13		
-5	32	27	102
-4	46	45	188
-3	31	26	5
-2	56	49	35
-1	53	54	209
K= 3	L= 0		
1	199	191	115
2	112	108	349
3	104	102	235
4	148	151	85
5	20	18	148
6	87	83	260
7	38	38	120
8	29	29	128
K= 3	L= 1		
-8	39	38	287
-7	44	40	114
-6	64	67	76
-5	104	109	257
-4	61	59	60
-3	208	210	97
-2	167	172	249
-1	54	52	344
0	229	220	143
1	39	41	235
2	193	191	251
3	116	112	130
4	86	87	111
5	105	102	262
6	41	38	135
7	66	66	98
8	21	15	259
K= 3	L= 2		
-8	23	21	135
-7	70	70	107
-6	83	84	247
-5	80	79	247
-4	152	153	107
-3	74	75	206
-2	162	162	267
-1	200	200	107
0	184	181	96
1	203	201	264
2	95	95	81
3	142	140	117
4	90	87	286
5	63	64	249
6	69	68	108
7	20	17	19
K= 3	L= 3		
-8	70	69	93
-7	34	33	214
-6	50	47	292
-5	75	74	107
-4	103	100	106
-3	161	163	279
-2	99	105	219
-1	229	233	83
0	262	264	253
1	81	79	310
2	150	145	101
3	18	19	326
4	101	99	303
5	51	51	113
6	76	77	55
7	67	67	274
K= 3	L= 4		
-8	20	20	194
-7	75	76	268
-6	26	28	25
-5	75	76	124
-4	88	91	323
-3	84	83	274
-2	201	202	75
-1	52	54	359
0	178	174	286
1	128	128	67
2	31	28	98
3	147	146	294
4	-15	9	212
5	67	63	74
6	46	46	295
7	36	33	280
K= 3	L= 5		
-8	49	53	261
-7	46	45	360
-6	72	72	88
-5	63	60	283
-4	107	106	294
-3	47	48	93
-2	42	45	71
-1	187	186	283
0	54	55	64
1	127	128	86
2	110	113	298
3	22	20	280
4	95	92	78
5	28	23	279
6	52	50	279
K= 3	L= 6		
-8	44	44	285
-7	69	65	77
-6	26	26	65
-5	97	100	278
-4	95	94	59
-3	113	112	98
-2	132	131	281
-1	38	38	331
0	128	128	123
1	54	55	321
2	136	138	250
3	105	106	93
4	29	27	119
5	74	73	260
6	33	32	95
K= 3	L= 7		
-8	20	17	131
-7	65	64	83
-6	104	104	254
-5	27	25	259
-4	129	131	95
-3	104	103	231
-2	71	72	315
-1	125	126	129
0	93	91	82
1	130	134	266
2	58	60	125
3	96	96	91
4	89	87	256
5	16	9	219
K= 3	L= 8		
-8	56	56	101
-7	-17	10	263
-6	57	56	249
-5	102	102	84
-4	49	51	158
-3	112	113	273
-2	48	47	128
-1	96	96	117
0	103	102	269
1	38	38	234
2	100	103	101
3	26	23	272
4	56	52	271
K= 3	L= 9		
-7	54	54	259
-6	26	24	112
-5	66	65	107
-4	80	80	272
-3	-16	6	251
-2	113	114	88
-1	53	53	266
0	64	65	288
1	75	72	90
2	15	10	148
3	73	74	295
4	27	22	148
K= 3	L= 10		
-7	21	23	27
-6	48	44	113
-5	50	44	299
-4	69	70	269
-3	74	74	87
-2	18	15	17
-1	115	114	268
0	79	82	62
1	33	35	122
2	68	68	305
3	17	7	287
K= 3	L= 11		
-6	-18	5	330
-5	60	61	300
-4	35	33	97
-3	77	77	67
-2	105	107	270
-1	27	28	25
0	65	69	95
1	54	52	283
2	34	36	282
K= 3	L= 12		
-5	-17	4	350
-4	60	62	94
-3	46	41	271
-2	45	42	287
-1	71	73	102
0	20	14	44
K= 3	L= 13		
-3	50	47	294
-2	32	36	132
K= 4	L= 0		
0	120	121	349
1	41	39	57
2	160	159	162
3	96	97	356
4	65	64	34
5	140	140	164
6	28	26	7
7	44	42	23
K= 4	L= 1		
-7	48	47	0
-6	51	50	172
-5	64	64	143
-4	152	155	358
-3	112	116	161
-2	119	121	146
-1	83	79	14
0	24	23	57
1	130	133	152
2	18	16	244
3	152	153	352
4	77	81	168
5	34	36	226
6	79	77	352
7	16	5	220
K= 4	L= 2		
-8	26	28	25
-7	27	29	185
-6	75	71	157
-5	87	88	352
-4	21	21	303
-3	88	84	182
-2	61	60	338
-1	151	152	332
0	123	123	174
1	33	31	208
2	121	121	335
3	68	66	158
4	56	54	203
5	32	32	310
6	55	54	348
7	50	56	189
K= 4	L= 3		
-8	24	21	242
-7	47	49	184
-6	59	57	350
-5	29	24	302
-4	65	62	187
-3	76	75	169
-2	175	176	340
-1	91	91	188
0	92	88	183
1	208	213	335
2	40	39	205
3	43	37	218
4	38	37	284
5	66	67	348
6	45	46	177
K= 4	L= 4		
-8	63	64	189
-7	40	39	344
-6	63	64	334
-5	45	45	235
-4	47	47	186
-3	124	125	337
-2	63	60	320
-1	192	195	170
0	108	111	345
1	55	55	352
2	123	128	165
3	13	5	277
4	80	79	351
5	27	29	138
6	42	44	185
K= 4	L= 5		
-8	27	20	176
-7	65	67	1
-6	33	30	189
-5	74	72	165
-4	44	42	23
-3	93	94	345
-2	113	113	163
-1	15	11	160
0	157	160	351
1	68	70	160
2	86	85	164
3	87	89	356
4	28	26	83
5	83	82	161
6	32	24	358
K= 4	L= 6		
-8	40	39	8
-7	34	35	357
-6	64	64	177
-5	30	29	78
-4	94	93	355
-3	103	103	158
-2	66	66	139
-1	54	54	17
0	38	39	52
1	111	116	160
2	27	28	14
3	93	93	1
4	101	98	163
5	23	17	326
K= 4	L= 7		
-7	40	39	167
-6	65	63	150
-5	114	114	359
-4	57	57	171
-3	43	44	153
-2	59	58	353
-1	36	33	347
0	60	61	159
1	48	49	176
2	106	108	353
3	76	73	160
4	34	31	192
5	40	46	353
K= 4	L= 8		
-7	61	60	170
-6	59	56	0
-5	21	16	338
-4	94	107	172
-3	33	33	14
-2	64	65	339
-1	61	60	172
0	36	37	182
1	94	101	337
2	-16	7	165
3	49	54	194
4	38	37	330
K= 4	L= 9		
-7	-18	15	350
-6	62	61	341
-5	53	50	199
-4	30	31	189
-3	108	106	343
-2	36	33	221
-1	90	89	172
0	83	85	337
1	19	18	340
2	55	57	175
3	24	18	285
K= 4	L= 10		
-6	17	17	206
-5	43	44	179
-4	37	35	358
-3	71	72	340
-2	102	104	174
-1	42	43	344
0	74	72	343
1	49	60	168
2	-17	10	220
K= 4	L= 11		
-5	-18	7	118
-4	60	63	350
-3	57	56	168
-2	32	37	159
-1	77	80	356
0	40	37	157
1	34	36	158
K= 4	L= 12		
-3	38	39	161
-2	44	44	358
-1	17	16	17
K= 5	L= 0		
1	52	53	65
2	26	27	142
3	95	92	293
4	71	70	108
5	19	16	66
6	62	64	264
7	17	15	175
K= 5	L= 1		
-7	31	33	75
-6	33	31	120
-5	84	87	279
-4	50	52	95
-3	68	69	93
-2	106	107	272
-1	34	36	165
0	21	17	121
1	39	42	186
2	106	106	254
3	27	22	144
4	53	53	119
5	62	59	265
6	26	22	248
K= 5	L= 2		
-7	35	36	106
-6	78	77	254
-5	33	33	237
-4	74	74	107
-3	68	67	246
-2	68	70	266
-1	54	55	111
0	61	61	82
1	116	113	267
2	26	23	110
3	47	48	84
4	34	31	234
5	58	57	267
6	35	34	102
K= 5	L= 3		
-7	42	41	277
-6	31	30	252
-5	49	49	79
-4	20	15	121
-3	74	74	262
-2	33	30	274
-1	119	119	107
0	113	113	277
1	27	28	222
2	65	65	86
3	31	27	43
4	43	40	263
5	25	28	17
6	63	67	91
K= 5	L= 4		
-7	51	51	271
-6	42	41	103
-5	31	28	41
-4	22	26	247
-3	49	49	329
-2	100	101	83
-1	24	23	4
0	76	72	304
1	62	60	98
2	51	49	48
3	45	43	261
4	19	20	306
5	64	62	85
K= 5	L= 5		
-7	29	28	77
-6	49	51	73
-5	40	37	279
-4	25	24	278
-3	55	54	78
-2	21	22	100
-1	61	61	279
0	37	37	66
1	65	66	83
2	27	26	309
3	38	36	291
4	60	61	86
5	-19	8	2
K= 5	L= 6		
-7	55	56	87
-6	-17	7	40
-5	55	59	288
-4	72	70	91
-3	46	49	57
-2	71	70	262
-1	17	12	75
0	26	28	85
1	27	28	159
2	89	86	273
3	52	50	112
4	28	26	97
K= 5	L= 7		
-6	74	74	270
-5	19	17	171
-4	74	74	104
-3	77	75	273
-2	37	31	193
-1	23	25	59
0	45	44	109
1	77	77	265
2	15	4	324
3	56	58	110
4	51	50	274
K= 5	L= 8		
-6	34	39	285
-5	64	66	106
-4	22	25	275
-3	60	60	258
-2	24	23	144
-1	30	32	96
0	60	58	247
1	27	27	271
2	50	47	103
3	-18	4	264
K= 5	L= 9		
-6	29	27	94
-5	16	19	118
-4	48	48	272
-3	-17	7	357
-2	58	57	93
-1	33	35	291
0	34	31	271
1	40	38	84
2	-17	8	47
K= 5	L= 10		
-5	24	27	246
-4	26	31	301
-3	45	47	95
-2	-17	8	83
-1	54	59	283
0	48	52	95
1	21	25	37
K= 5	L= 11		
-3	40	42	95
-2	56	59	285
-1	17	17	89
K= 6	L= 0		
0	97	100	345
1	44	47	142
2	106	101	198
3	69	64	26
4	26	24	36
5	81	78	192
6	37	36	88
K= 6	L= 1		
-6	53	51	176
-5	37	36	225
-4	90	88	30
-3	59	57	196
-2	84	81	169
-1	68	65	19
0	27	27	33
1	103	101	184
2	22	17	21
3	83	81	7
4	64	59	205
5	20	20	164
K= 6	L= 2		
-6	42	46	198
-5	60	64	0
-4	14	13	99
-3	69	70	209
-2	41	37	342
-1	84	83	14
0	84	82	213
1	26	26	154
2	98	97	8
3	38	34	212
4	36	36	163
5	39	39	356
K= 6	L= 3		
-6	46	45	349
-5	37	32	4
-4	58	57	163
-3	42	39	265
-2	112	108	22
-1	40	39	200
0	63	65	224
1	118	113	21
2	55	53	285
3	50	47	176
4	25	25	343
5	48	49	355
K= 6	L= 4		
-6	51	61	342
-5	28	29	163
-4	43	39	217
-3	97	95	348
-2	42	41	79
-1	110	106	213
0	72	71	39
1	56	55	0
2	71	73	190
3	22	22	123
4	66	67	357
K= 6	L= 5		
-6	-18	11	141
-5	54	56	171
-4	43	40	348
-3	62	61	27
-2	91	87	192
-1	-15	6	239
0	86	84	10
1	52	47	192
2	61	64	188
3	57	58	26
4	-18	7	291
K= 6	L= 6		
-6	41	47	191
-5	-17	8	197
-4	66	64	20
-3	66	66	184
-2	53	53	162
-1	57	56	5
0	27	29	102
1	72	75	193
2	19	22	38
3	50	49	18
K= 6	L= 7		
-5	61	63	27
-4	30	27	209
-3	57	55	184
-2	38	39	360
-1	25	27	354
0	64	64	175
1	23	23	242
2	56	66	29
K= 6	L= 8		
-5	24	19	58
-4	60	62	196
-3	20	18	39
-2	59	60	359
-1	47	44	178
0	28	29	217
1	67	71	7
K= 6	L= 9		
-4	29	25	242
-3	70	65	6
-2	-18	6	181
-1	58	60	201
0	65	60	22
K= 7	L= 0		
1	92	92	73
2	58	68	247
3	42	39	317
4	39	42	101
K= 7	L= 1		
-4	16	10	173
-3	63	64	78
-2	58	56	275
-1	63	62	249
0	85	85	74
1	24	33	229
2	72	84	266
3	48	42	89
4	17	19	92
K= 7	L= 2		
-5	27	33	256
-4	59	57	90
-3	28	24	271
-2	79	78	263
-1	42	46	76
0	50	47	81
1	101	98	271
2	-17	8	138
3	64	67	73
4	52	56	251
K= 7	L= 3		
-5	38	42	78
-4	29	27	69
-3	83	81	258
-2	22	18	38
-1	69	70	105
0	54	52	281
1	47	48	247
2	68	80	83
3	-18	8	14
K= 7	L= 4		
-4	56	56	248
-3	26	24	331
-2	72	76	88
-1	16	9	304
0	52	51	277
1	44	47	99
2	43	51	73
3	65	66	252
K= 7	L= 5		
-4	44	44	260
-3	62	61	83
-2	32	28	95
-1	62	65	261
0	34	31	83
1	61	62	81
2	36	43	255
K= 7	L= 6		
-4	24	19	114
-3	70	66	74
-2	70	69	262
-1	20	18	234
0	74	73	73
1	47	44	229
K= 7	L= 7		
-3	17	24	305
-2	68	71	247
-1	63	68	67
0	-18	10	131
K= 8	L= 0		
0	75	72	337
1	37	38	166
2	34	34	187
K= 8	L= 1		
-2	49	49	158
-1	43	40	342
0	20	13	17
1	44	50	173
2	-18	11	340
K= 8	L= 2		
-2	21	24	343
-1	31	27	346
0	24	23	166
1	21	19	172
K= 8	L= 3		
-2	34	33	352
-1	17	19	147
0	-18	11	179

dropped to 6·8%, with unobserved reflections omitted. Hydrogen atoms were not included. The final parameters for the isotropic refinement are given in Table 1. Because the origin in the y direction in space group $P2_1$ is arbitrary, y_S was fixed at zero.

It had been hoped initially that the hydrogen atoms could be located. With this end in mind, anisotropic thermal parameters were introduced to account for as much of the electron density as possible before attempting to locate the hydrogen atoms. A few least-squares cycles, including anisotropic thermal parameters for all atoms except Li, were computed and R was reduced to 5·3%. At this point the reflections that had relatively large ΔF's were remeasured and an extinction correction was applied to all of the data. The extinction correction had the form

$$I_{\text{corr}} = \frac{I_{\text{obs}}}{1-gI_{\text{obs}}}\,,$$

where $g = 8{\cdot}0 \times 10^{-5}$. A few more least-squares cycles were calculated with anisotropic Li thermal parameters and Dawson's (1960) sulfur form factor in exponential form ($a_1 = 7{\cdot}698$, $b_1 = 1{\cdot}301$, $a_2 = 6{\cdot}820$, $b_2 = 25{\cdot}95$, $c = 1{\cdot}477$). The R index was reduced to 3·8%. The sum of the residuals squared was 179 electrons^2. Thus, $\sigma(\varrho_{\text{obs}}) = 0{\cdot}26$ e. Å^{-3} according to the formula of Cruickshank (1950). The final observed and calculated structure factors are given in Table 2. These structure factors were calculated by using the final parameters of Table 3. The experimental values have been corrected for extinction and for the white radiation streak. The ratio of the final changes to their standard deviations was less than 10^{-3} for all parameters.

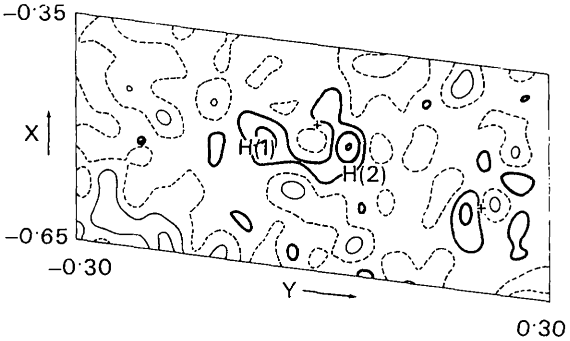

Fig. 1. Difference Fourier section through O(1)–O(w)–O(w)′. Contour interval is 0·2 e.Å^{-3}. Heavy lines are positive contours, the dashed line is the zero contour, and the light lines are negative contours. The unit cell here is obtained by the transformation matrix,

$$\begin{pmatrix} \bar{2} & \bar{1} & 0 \\ 0 & 2 & 1 \\ 0 & 0 & 1 \end{pmatrix}$$

and the section is at $z = 0{\cdot}389$ in this cell. + represents O(w) and ● represents O(1).

A three-dimensional ΔF Fourier synthesis was then computed. This showed no peak or hole greater than ±0·6 e. Å^{-3}. A section through the atoms participating in the probable hydrogen bonding is shown in Fig. 1. The hydrogen atom positions found by Smith (1960) are shown. H(1) is 0·2 Å below the section and H(2) is 0·1 Å below the section. The peaks near the hydrogen positions have values of 0·52 and 0·60 e. Å^{-3}, less than 3 times the estimated $\sigma(\varrho)$, and are only about 0·8 and 0·7 Å from the water oxygen atom. Other peaks and valleys of similar magnitude appeared in the sulfate group. It was concluded that the present set of data is not precise enough to locate the hydrogen atoms in the compound. The water oxygen has a relatively large thermal motion and the hydrogen bonds, as proposed by Larson & Helmholz (1954), are rather long. The hydrogen atoms can be expected to have rather large thermal parameters and thus should be quite difficult to locate by X-ray diffraction techniques.

All interatomic distances less than 3·5 Å (excluding S–O and S–Li distances >2·9 Å) are given in Table 4 along with bond angles about the sulfur atom and O(w). The standard deviations of these distances and angles were calculated using all of the terms from the

Table 3. *Position and thermal parameters*

Final least-squares position parameters

Atom	x	y	z
S	0·2938 ± 0·0001	0	0·2084 ± 0·0001
O(1)	0·0217 ± 0·0004	0·0701 ± 0·0006	0·1694 ± 0·0003
O(2)	0·4355 ± 0·0004	0·1129 ± 0·0005	0·3787 ± 0·0002
O(3)	0·4010 ± 0·0004	0·1230 ± 0·0005	0·0789 ± 0·0003
O(4)	0·3298 ± 0·0004	0·7008 ± 0·0005	0·2102 ± 0·0003
O(w)	0·9112 ± 0·0005	0·4718 ± 0·0009	0·3950 ± 0·0004
Li(1)	0·3053 ± 0·0009	0·4949 ± 0·0018	0·9938 ± 0·0006
Li(2)	0·5619 ± 0·0010	0·4878 ± 0·0018	0·3950 ± 0·0006

Final least-squares anisotropic thermal parameters x 10^4

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	84 ± 1	81 ± 2	28 ± 1	6 ± 4	25 ± 1	−3 ± 3
O(1)	82 ± 5	241 ± 10	67 ± 3	43 ± 11	29 ± 6	−35 ± 9
O(2)	150 ± 6	133 ± 7	36 ± 2	−49 ± 12	21 ± 6	−15 ± 8
O(3)	163 ± 7	142 ± 7	51 ± 3	55 ± 12	101 ± 7	48 ± 8
O(4)	182 ± 7	96 ± 7	50 ± 3	22 ± 12	28 ± 7	−1 ± 8
O(w)	190 ± 8	334 ± 17	152 ± 5	−63 ± 21	181 ± 10	−103 ± 17
Li(1)	155 ± 14	151 ± 17	60 ± 6	−33 ± 49	52 ± 15	39 ± 34
Li(2)	160 ± 14	156 ± 20	57 ± 6	71 ± 46	36 ± 15	11 ± 29

Table 4. *Interatomic distances in* $Li_2SO_4 . H_2O$

No corrections have been made for thermal vibration. Distances from the O(*w*) atoms at the edges of the Li(2) coordination tetrahedron are marked*.

S–O(1)	1·462 ± 0·002 Å	
O(2)	1·482 ± 0·002	
O(3)	1·479 ± 0·002	
O(4)	1·466 ± 0·002	
O(1)–O(2)	2·400 ± 0·003	
O(3)	2·409 ± 0·003	
O(4)	2·412 ± 0·003	
O(2)–O(3)	2·401 ± 0·003	
O(4)	2·400 ± 0·003	
O(3)–O(4)	2·399 ± 0·004	
Li(1)–O(1)	1·917 ± 0·005	
O(3)	1·950 ± 0·008	
O(3)	1·969 ± 0·006	
O(4)	2·001 ± 0·007	
O(1)–O(3)	3·252 ± 0·003	
O(3)	3·370 ± 0·003	
O(4)	3·187 ± 0·003	
O(3)–O(3)	3·092 ± 0·002	
O(4)	3·070 ± 0·003	
O(4)	3·155 ± 0·003	
O(1)–S–O(2)	109·2 ± 0·1°	
O(3)	110·0 ± 0·1	
O(4)	110·9 ± 0·1	
O(2)–S–O(3)	108·4 ± 0·1	
O(4)	109·1 ± 0·1	
O(3)–S–O(4)	109·1 ± 0·1	
O(1)–O(*w*)–O(2)	44·2 ± 0·2	
O(4)	68·1 ± 0·2	
Li(2)	115·4 ± 0·4	
O(4)–O(*w*)–Li(2)	144·9 ± 0·4	
Li(2)–O(*w*)	1·907 ± 0·006 Å	
O(2)	1·937 ± 0·009	
O(2)	1·942 ± 0·006	
O(4)	1·953 ± 0·006	
O(*w*)–O(2)	3·091 ± 0·003	
O(2)	3·095 ± 0·004	
O(4)	3·274 ± 0·004	
O(2)–O(2)	3·081 ± 0·002	
O(4)	3·148 ± 0·003	
O(4)	3·247 ± 0·003	
O(*w*)–O(*w*)(2)	2·964 ± 0·003	
O(1)	2·869 ± 0·004	
O(2)	3·091 ± 0·003	*
O(2)	3·095 ± 0·004	*
O(2)	3·385 ± 0·004	
O(4)	3·274 ± 0·004	*
O(4)	3·285 ± 0·004	
Li(2)	1·907 ± 0·006	
O(1)–O(4)	3·462 ± 0·003	
O(*w*)–O(*w*)–O(*w*)	110·0 ± 0·2°	
O(1)	73·7 ± 0·2	
O(1)	146·5 ± 0·2	
O(2)	57·8 ± 0·1	
O(2)	108·1 ± 0·2	
O(4)	80·6 ± 0·2	
O(4)	113·1 ± 0·2	
Li(2)	96·9 ± 0·3	
Li(2)	100·8 ± 0·3	
O(2)–O(*w*)–O(4)	56·3 ± 0·1	
Li(2)	151·3 ± 0·4	

Table 5. *Analysis of anisotropic thermal parameters*

The angles are given with respect to the real lattice vectors

Atom	Axis	Root mean square amplitude	B_i	*a*	*b*	*c*
S	1	0·109 Å	0·94 ± 0·02	12·0 ± 6·3°	78·0 ± 6·3°	107·4 ± 2·5°
	2	0·098	0·76 ± 0·02	101·7 ± 6·4	17·9 ± 9·2	99·2 ± 12·3
	3	0·092	0·67 ± 0·02	92·3 ± 3·0	76·8 ± 12·3	19·9 ± 7·0
O(1)	1	0·104	0·86 ± 0·05	18·2 ± 2·8	99·2 ± 2·6	91·5 ± 3·6
	2	0·177	2·47 ± 0·09	75·3 ± 2·1	26·3 ± 4·2	115·0 ± 4·6
	3	0·140	1·55 ± 0·06	100·6 ± 4·0	65·6 ± 4·6	25·1 ± 4·6
O(2)	1	0·153	1·84 ± 0·06	20·6 ± 5·6	110·4 ± 5·8	109·1 ± 3·5
	2	0·125	1·22 ± 0·06	72·1 ± 5·8	28·5 ± 7·3	116·0 ± 7·8
	3	0·101	0·81 ± 0·05	80·2 ± 3·7	71·0 ± 7·2	33·2 ± 6·4
O(3)	1	0·161	2·06 ± 0·06	48·2 ± 3·8	62·7 ± 3·6	68·8 ± 2·9
	2	0·125	1·23 ± 0·05	127·6 ± 6·0	37·9 ± 6·7	75·4 ± 7·6
	3	0·102	0·81 ± 0·05	115·5 ± 5·6	114·1 ± 7·5	26·2 ± 5·5
O(4)	1	0·166	2·17 ± 0·08	10·0 ± 3·3	84·6 ± 2·8	115·6 ± 3·5
	2	0·106	0·89 ± 0·06	95·6 ± 3·5	5·6 ± 4·5	89·1 ± 9·1
	3	0·123	1·19 ± 0·06	81·7 ± 3·6	88·4 ± 10·4	25·7 ± 3·5
O(*w*)	1	0·141	1·58 ± 0·07	11·5 ± 3·5	92·3 ± 4·8	118·6 ± 2·8
	2	0·182	2·62 ± 0·11	81·8 ± 5·1	34·4 ± 4·4	61·3 ± 5·2
	3	0·233	4·30 ± 0·12	82·0 ± 2·0	124·3 ± 4·5	42·7 ± 3·7
Li(1)	1	0·141	1·57 ± 0·12	50·4 ± 25·1	72·9 ± 19·9	60·7 ± 22·6
	2	0·117	1·09 ± 0·14	72·4 ± 12·3	41·0 ± 14·9	130·3 ± 16·4
	3	0·157	1·94 ± 0·16	135·1 ± 26·2	54·1 ± 17·8	54·2 ± 12·9
Li(2)	1	0·162	2·06 ± 0·17	30·6 ± 15·6	59·9 ± 17·3	110·2 ± 16·3
	2	0·122	1·17 ± 0·13	117·6 ± 14·6	46·2 ± 24·6	113·0 ± 31·3
	3	0·136	1·47 ± 0·15	102·3 ± 26·6	58·7 ± 25·3	31·4 ± 23·7

Table 6. *Translational and torsional vibration matrices for the sulfate group relative to the axes a, b, c.*

The r.m.s. $\Delta U_{ij} = 0.0015$ Å^2.

$$\tau = \begin{pmatrix} 0{\cdot}0116 & 0{\cdot}0005 & -0{\cdot}0004 \\ & 0{\cdot}0108 & -0{\cdot}0001 \\ & & 0{\cdot}0099 \end{pmatrix} \text{Å}^2 \qquad \omega = \begin{pmatrix} 8{\cdot}7 & -2{\cdot}8 & -2{\cdot}2 \\ & 18{\cdot}4 & 0{\cdot}7 \\ & & 25{\cdot}7 \end{pmatrix} \text{deg}^2$$

$$\sigma\tau = \begin{pmatrix} 0{\cdot}0009 & 0{\cdot}0008 & 0{\cdot}0008 \\ & 0{\cdot}0009 & 0{\cdot}0008 \\ & & 0{\cdot}0005 \end{pmatrix} \text{Å}^2 \qquad \sigma\omega = \begin{pmatrix} 2{\cdot}3 & 2{\cdot}3 & 2{\cdot}0 \\ & 2{\cdot}3 & 2{\cdot}1 \\ & & 2{\cdot}3 \end{pmatrix} \text{deg}^2$$

variance-covariance matrix from the least-squares calculation and neglecting unit-cell errors. Inclusion of unit-cell errors increases these standard deviations by about 20 to 50% depending on the length of the bond.

The anisotropic thermal parameters were analyzed to find the axes of the ellipsoids and their orientation in the unit cell. These results are presented in Table 5. The standard deviations presented in Table 5 were computed using numerical derivatives and the complete variance–covariance matrix. The minor axes of the oxygen make angles of 5·5°, 4·9°, 12·5° and 2·0° with the S–O bonds. Rigid body analysis of the sulfate group was carried out by the method of Cruickshank (1956*a*) using a code supplied by Trueblood (1962). The τ and ω matrices given in Table 6 were calculated with a weight of two for the sulfur atom and one for each of the oxygen atoms. The thermal vibration of the oxygen atoms independent of the sulfur atom was computed from the matrices $\mathbf{B}_{\mathrm{O}i} - \mathbf{B}_{\mathrm{S}}$ (essentially the in phase assumption of Busing & Levy (1964)). These matrices were diagonalized and the angle of the smallest axis of each with the S–O bond was calculated. These angles were 5·8°, 3·7°, 6·0° and 3·6°. The residual mean square amplitudes along the bonds are −0·0006, 0·0015, 0·0003, and 0·0017 Å^2. None of these values is significantly different from zero as is anticipated for a tightly bound group such as the sulfate ion. Corrections to the bond lengths due to thermal motion in the sulfate group were calculated by the method of Cruickshank (1956*b*; 1961) and by the assumption of in phase motion (Busing & Levy, 1964). The results were almost identical and the values from the in phase assumption are presented in Table 7. Also listed in Table 7 are the Li–O distances corrected for this lengthening of the S–O distances*.

Table 7. *Interatomic distances corrected for thermal motion*

S–O(1)	1·473	O(2)–Li(2)	1·934
S–O(2)	1·487	O(3)–Li(1)	1·964
S–O(3)	1·486	O(3)–Li(1)	1·946
S–O(4)	1·473	O(4)–Li(1)	1·998
O(1)–Li(1)	1·908	O(4)–Li(2)	1·949
O(2)–Li(2)	1·939		

The residual oxygen thermal motion was analyzed as rigid body motion. The ω matrix was essentially identical with that from the complete set of data and the τ matrix was essentially zero. The r.m.s. $\Delta U_{i,j}$ was 0·0018 Å^2, indicating that the sulfate anion acts like a rigid body and that most of the residual motion of oxygen atoms is due torsional oscillation of the group about the sulfur.

Discussion

A careful analysis of the present data has not resulted in locating the hydrogen atoms in $Li_2SO_4 . H_2O$. The probable reason for this is the very high thermal motion of these atoms. Their location has been determined by Smith (1960) using neutron diffraction techniques. He found them to have thermal parameters of about 7·0. The positions are the same as proposed by Larson & Helmholz (1954). Other evidence of high thermal motion for the hydrogen atoms is given by the Raman spectra (Vassas-Dubuisson, 1953) from which it is found that the O–H stretching frequencies are nearly the same as in water vapor.

A projection of the structure on the *ac* plane is given in Fig. 2. It can be seen that the two Li ions have very similar environments. They both have four oxygen neighbours at an average distance of 1·947 Å uncorrected for the thermal motion of the sulfate ion and 1·943 Å corrected for the thermal motion. The range (corrected) is from 1·907 Å for O(*w*)–Li(2) to 1·998 Å for O(4)–Li(1). The two short distances are to the water oxygen and to O(1), the sulfate oxygen involved in the weak hydrogen bonding. The other six Li–O distances are to oxygen atoms which have two Li–O contacts as well as the S–O bond.

The crystal structures of several inorganic sulfate compounds have been determined with quite high precision during the last few years. Pertinent data relating to the sulfate group in several of these compounds are given in Table 8. All corrections to the S–O distances have been calculated in the same manner, *i.e.* that described above for $Li_2SO_4 . H_2O$. The average values of isotropic B_{O} were calculated from the anisotropic refinement (Hamilton, 1959). The average uncorrected S–O distances are nearly identical, all being within twice the estimated error of the most precisely known, $Li_2SO_4 . H_2O$. The average corrected distances are in two groups, neither of which is significantly different from the other, but this may be a real effect. We note that in the three compounds with the longer corrected distance the sulfate group is surrounded by hydrogen atoms only, and in the other two compounds the cations

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* The correction to the Li–O distance was computed from the equation $d_{\mathrm{cor}} = d_{\mathrm{obs}} + \Delta_{\mathrm{S-O}} \cos \alpha$, where $\Delta_{\mathrm{S-O}}$ is the change in the S–O bond length and α is the S–O–Li angle. This gives an estimate of the minimum possible length of this bond.

Table 8. *Data for sulfate groups*

		Individual S–O bond distances				Average S–O Distance	B_O	B_S	Reference
$Li_2SO_4 . H_2O$	uncorrected	1·462	1·466	1·479	1·482	1·472 ± 1	1·4	0·8	This work
	corrected	1·473	1·473	1·486	1·487	1·480			
	ligands	1 Li	2 Li	2 Li	2 Li				
	avg. lig. d.	1·917	1·977	1·960	1·940				
$MgSO_4 . 4H_2O$	uncorrected	1·466	1·468	1·478	1·480	1·473 ± 2	1·4	0·9	Baur (1964*a*)
	corrected	1·473	1·473	1·487	1·485	1·479			
	ligands	3 H	1 Mg	3 H	1 H+1 Mg				
	avg. lig. d.	1·97	2·08	1·83	1·85 and 2·08				
$FeSO_4 . 7H_2O$	uncorrected	1·462	1·466	1·481	1·488	1·474 ± 2	2·3	1·4	Baur (1964*b*)
	corrected	1·475	1·481	1·491	1·496	1·486			
	ligands	3 H	2 H	3 H	3 H				
	avg. lig. d.	1·92	1·82	1·86	1·85				
$MgSO_4 . 7H_2O$	uncorrected	1·460	1·469	1·473	1·482	1·471 ± 2	2·2	1·0	Baur (1964*c*)
	corrected	1·481	1·483	1·487	1·493	1·486			
	ligands	2 H	2 H	3 H	3 H				
	avg. lig. d.	1·73	1·73	1·82	1·93				
$Mg(NH_4)_2(SO_4)_2 . 6H_2O$	uncorrected	1·459	1·474	1·476	1·481	1·473 ± 2	3·1	2·1	Margulis & Templeton (1962)
	corrected	1·481	1·482	1·490	1·490	1·486			
	ligands	1 H	3 H	2 H	3 H				
	avg. lig. d.	1·79	1·90	2·00	1·95				

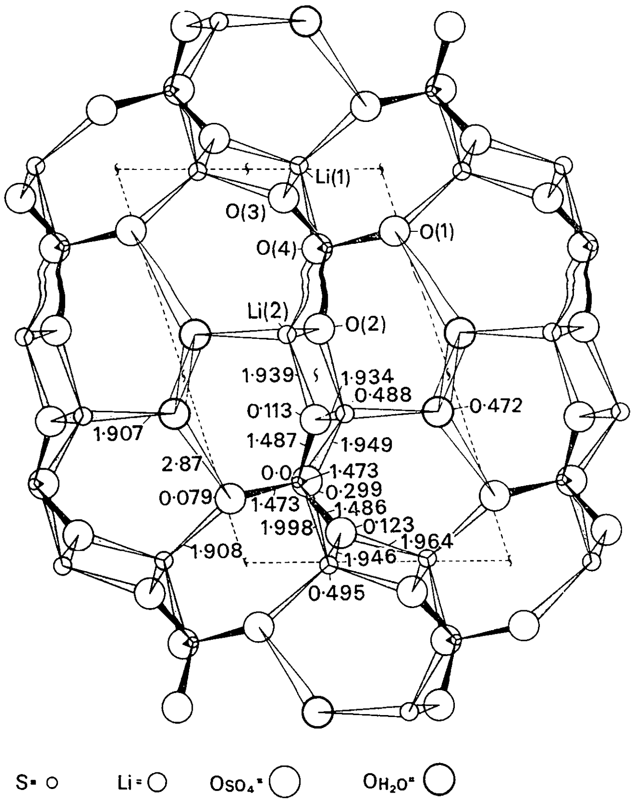

Fig. 2. Projection of $Li_2SO_4 . H_2O$ on the *a–c* plane.

are adjacent to at least two of the sulfate oxygen atoms. In all probability, the cations, being more highly charged and heavier, tie the sulfate group down more securely than do the hydrogen bonds and thus reduce the thermal vibration. This perhaps reduces the stretching of the S–O bond due to thermal vibration. The thermal parameters of the hydrogen bonded sulfate oxygen atoms are all significantly higher than those in the other two sulfate groups.

The list of distances in Table 8 seems to indicate that the sulfate group is slightly distorted by the surrounding ligands. For nearly all of the S–O distances listed we see that the shorter S–O bonds have either fewer ligands or the ligands are somewhat further away and thus have less influence on the S–O bond. Some of the hydrogen positions are perhaps quite poorly known, but the trend seems to be as one would anticipate. There also may be some secondary effects due to the repulsion of the sulfur atom by the cations. This effect may, in part, account for the shortness of the S–O(4) bond in $Li_2SO_4 . H_2O$.

APPENDIX

In recent years many structural determinations have been made with the use of quite accurate experimental data collected with proportional or scintillation counters. Spurious radiation has been corrected for in a variety of ways. The usual methods are to use crystal monochromatized radiation or balanced filters. However, one can correct for much of it by examining the white radiation streak near a strong reflection and obtaining an estimate of the ratio of the intensity at any point along this streak to the intensity of the reflection given by λ $K\alpha$. If one had a single, very strong reflection which had no higher or lower orders of any consequence, one could then measure the intensity of this reflection and the intensity in reciprocal space along this lattice row. These data could then be corrected for background, Lorentz, and polarization fac-

Table 9. *Comparison of* 00*l reflections with and without the streak correction*

Data have been corrected for extinction.

		With streak correction		Without streak correction	
l	I$_{\mathrm{Meas}}$	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\lvert F_o\rvert$	$\lvert F_c\rvert$
1	1154	9·3	10·5	9·3	10·5
2	3965	26·8	25·9	26·2	25·6
3	1267	16·7	17·3	17·2	17·7
4	269	8·7	8·2	9·4	8·2
5	2819	35·8	36·1	35·2	35·9
6	103	3·1	3·3	6·9	3·6
7	629	19·0	19·4	19·4	19·7
8	63	4·7	4·6	6·5	4·9
9	25	2·8	2·7	4·3	2·8
10	174	12·7	12·5	12·9	12·8
11	10	< 2·2	0·5	3·0	0·8
12	40	6·6	7·1	6·9	7·1
13	7	1·9	2·0	2·6	2·4

tors, to give a measure of the effective diffracted power at each value of 2θ as seen through a window of width $\Delta(2\theta)$. Because the range of wave lengths seen through this window is a function of θ, we must correct for this by dividing the data by an effective window width parameter (csc θ). This gives a measure of the effective diffracted power of each wavelength seen by the counter system. By taking the ratio of the effective diffracted power at the $K\alpha$ line to that at any other point, one can determine how much intensity a reflection will contribute to the intensity at the other point along the lattice row. In order to obtain this information, one ordinarily must take lattice rows with several observed reflections. The choice of lattice rows to look at should be made from those in which the first line is the strongest and the second line quite a bit weaker, so that its contribution to the first line can be ignored. One then measures the intensity along the lattice row and processes it using equation (1) starting with the small 2θ values:

$$R\lambda = \frac{\dfrac{G(\theta)}{\csc\theta} - \sum_{k=2}^{K} \{G(k)\, R\lambda_k\}}{G(1)} \qquad (1)$$

where $G(\theta)$ is the intensity at θ divided by the Lorentz and polarization factors

$G(k)$ is $G(\theta)$ at the kth reflection

$R\lambda_k$ is the ratio of the effective diffracted power of the wave length λ_k which reflects at θ to the effective diffracted power at the kth reflection.

The apparent inconsistency at the first reflection, where $R\lambda_1$ should be equal to 1·0 rather than sin θ, is removed when one remembers that the csc θ term corrects for ranges of λ in the white radiation streak. In general the intensity of the $K\alpha$ line is many times stronger than the white radiation streak, and hence at the first reflection only one wave length ($K\alpha$) is seen rather than a range of wave lengths as at other points along the white radiation streak. The observed intensity data can then be processed with equation (2) to obtain a set of corrected relative $|F|^2$ values:

$$|F_{nH}|^2 = \{I_{nH} - [\sum_i (I_{iH} R\lambda_i)] \csc\theta\}/\mathrm{Lp} \qquad (2)$$

where I_{nH} is the observed intensity of the nth reflection along the lattice row H

$R\lambda_i$ is as defined in equation (1)

Lp is the Lorentz-polarization factor

$\sum_i$ denotes the sum over all reflections along the lattice row except the nth.

In $Li_2SO_4 . H_2O$ the 0k0 and h0h lattice rows fit the above conditions, and since the first reflections occur at quite different 2θ values (16·84° for 020 and 8·02° for $\bar{1}$01) it was felt that processing the two data sets would give a fairly good test of the correctness of the assumptions of equation (1). Values of $R\lambda$ obtained from both sets of data are presented in Fig. 3. The circles represent the 0k0 data and the crosses the h0h data. The intensity data for $Li_2SO_4 . H_2O$ were processed with and without the above correction. The

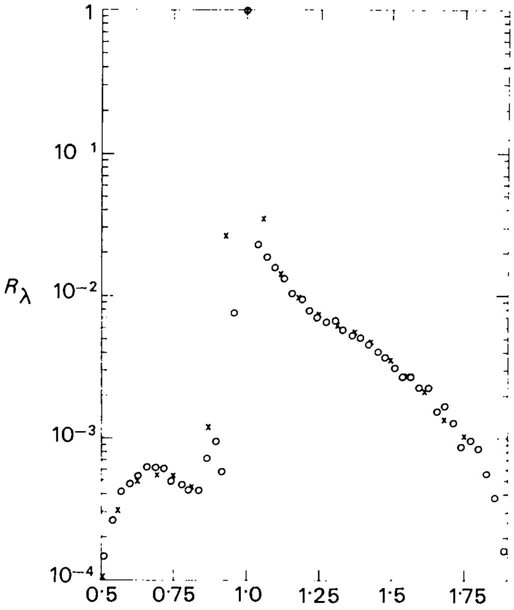

Fig. 3. Plot of $R\lambda$ *vs.* $\lambda/\lambda K\alpha$.

final *R* values were 4·0% and 4·5% respectively and the standard deviations of the S–O bonds were 0·002 Å and 0·003 Å (the value of *g* was $6{\cdot}4 \times 10^{-5}$). A perhaps more dramatic effect of this correction can be seen by examination of weak reflections along a lattice row containing some quite strong reflections. Table 9 presents the data for the 00*l* lattice row. The agreement of the 006 and 0011 reflections can be seen to be much improved after correcting for the white radiation.

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Mixed Oxides of Titanium and Niobium: The Crystal Structure of $TiNb_{24}O_{62}$ ($TiO_2 . 12\,Nb_2O_5$)

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$TiNb_{24}O_{62}$ is monoclinic, with $a = 29{\cdot}78$, $b = 3{\cdot}821$, $c = 21{\cdot}12$ Å, $\beta = 94{\cdot}9°$, space group *C*2. The structure, refined by two-dimensional Fourier methods, contains ReO_3-type blocks of metal–oxygen octahedra, 3 × 4 and infinite in extension along *b*. These join up in pairs, and the double blocks pack together by additional edge sharing, with metals in tetrahedral coordination at each of the junctions. The relationship to the structure of high-temperature Nb_2O_5, as well as to other known and hypothetical compounds formed from blocks of the same size, is examined.

Introduction

The phase equilibrium relations, and the crystal structures of the phases in the system TiO_2–Nb_2O_5, have been independently studied by the present authors (Roth & Coughanour, 1955; Wadsley, 1961*a*, *b*). Both of us concluded that only two compounds existed, $TiNb_2O_7$ ($TiO_2 . Nb_2O_5$) and a second identified by structure-analysis as $Ti_2Nb_{10}O_{29}$ ($2TiO_2 . 5Nb_2O_5$) occurring in two forms, orthorhombic and monoclinic. These are closely related to each other, and can be described as the members $n = 3$ and 4 of a 'homologous series' of oxides with the general formula $B_{3n}O_{8n-3}$, their structures being derived from that of a parent compound B_3O_8, at the time unknown, but now reported by Andersson (1964) for the oxyfluoride Nb_3O_7F. Attempts to prepare the additional homologue $n = 5$ ($TiNb_{14}O_{37}$, or $TiO_2 . 7Nb_2O_5$), and to identify the member $n = 6$ ($Nb_{18}O_{45}$) with one of the polymorphs of Nb_2O_5, were unsuccessful (Wadsley, 1961*b*). This particular series of oxides appeared to contain only the two compounds, unlike the reduced tungsten-molybdenum oxides $(W, Mo)_nO_{3n-1}$ (Magnéli, 1953) and the titanium oxides Ti_nO_{2n-1} (Andersson & Jahnberg, 1963) where both have six or more members each related by a common structural principle. Likewise Kihlborg (1963) found only three members of a series Mo_nO_{3n-m+1}.

The high temperature form of Nb_2O_5, and the reduced phase $Nb_{22}O_{54}$ found by Norin & Magnéli (1961), can be grouped together by another series-type general formula $B_{3n+1}O_{8n-2}$; Nb_2O_5 corresponds to $n = 9$ and $Nb_{22}O_{54}$ to $n = 7$ (Gatehouse & Wadsley, 1964). A new

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