

A neutron-diffraction study of hemimorphite

By **RODERICK J. HILL**, **GERALD V. GIBBS**, **JAMES R. CRAIG**

Department of Geological Sciences, Virginia Polytechnic Institute
and State University, Blacksburg, Virginia

FRED K. ROSS

Department of Chemistry, Virginia Polytechnic Institute and State University,
Blacksburg, Virginia

and **JACK M. WILLIAMS**

Chemistry Division, Argonne National Laboratory, Argonne, Illinois

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Abstract

The hydrogen atoms in hemimorphite, $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$, have been located and its crystal structure refined using 415 three-dimensional single-crystal neutron-diffraction data. The mineral is orthorhombic, space group *Imm2*, with $a = 8.367(5)$, $b = 10.730(6)$, $c = 5.115(3)$ Å, and $Z = 2$. The structure consists of three-membered rings of corner-sharing $\text{Zn}(\text{OH})\text{O}_3$ ($\times 2$) and SiO_4 tetrahedra arranged in compact sheets parallel to (010). Three oxygen atoms in each tetrahedron are bonded to two zinc atoms and one silicon atom, while a fourth oxygen atom forms a bridging bond to an equivalent cation in an adjacent sheet. The water molecules are oriented parallel to (010) inside large cavities between the tetrahedral sheets and are held in place by hydrogen bonds to and from the hydroxyl groups of the $\text{Zn}-\text{OH}-\text{Zn}$ bridging linkages. Mulliken population analyses calculated using constant bond lengths and the observed angles within and between the tetrahedra allow a rationalization of the bond-length variations in the SiO_4 group, but are less successful in the case of $\text{Zn}(\text{OH})\text{O}_3$. Detailed analysis of observed bond length and calculated overlap-population variations in a variety of tetrahedral oxyanions suggests that the poorer agreement in the case of the Zn tetrahedron is more a function of the larger overall size of the group than of the relative ionic character of the bonds.

Introduction

The crystal structure of hemimorphite has been of interest following the discovery by ZAMBONINI (1908), and later confirmed by FAUST (1951), ROY and MUMPTON (1956) and TAYLOR (1962), that the mineral

dehydrates in two stages. Crystal-structure analyses by ITO and WEST (1932), BARCLAY and COX (1960) and McDONALD and CRUICKSHANK (1967) have served to rationalize these dehydration properties by establishing the presence of hydroxyl groups strongly bonded to two zinc atoms, and water molecules located in a series of interconnected cavities parallel to the c axis.

The release of water over the temperature range 400–650°C (FAUST, 1951), without disruption of the structure, represents the loss of the H₂O molecules, whereas the breakdown of the structure to β Zn₂SiO₄ at about 740°C is a result of the expulsion of the hydroxyl groups (FAUST, 1951; TAYLOR, 1962).

Although the positions of the non-hydrogen atoms in hemimorphite are known with moderate precision (McDONALD and CRUICKSHANK, 1967), the exact location of the hydroxyl and water oxygen atoms, and of course the protons, remains in some doubt. Indeed, McDONALD and CRUICKSHANK have suggested that the water molecule may be rather free to move inside the cavity and to form hydrogen bonds to a variety of neighbouring oxygen atoms. Since the channels containing the water (and hydroxyl) are parallel to the polar c axis of the cell, a study of the mechanism of dehydration of this mineral is of particular interest. Moreover, TAYLOR (1962) has indicated that the product of complete dehydration of hemimorphite shows a marked preferred orientation with preservation of the repeat distance in the c -axis direction. The present neutron-diffraction study was initiated in order to locate the protons associated with the water molecule and hydroxyl group as a preliminary to a detailed x-ray study of the structure as a function of temperature. We also plan to undertake an analysis and comparison of the experimental charge-deformation distribution with theoretical electron-density maps obtained from accurate molecular-orbital theory.

Experimental

The sample selected for data collection was a 31 mg transparent fragment of hemimorphite from Chihuahua, Mexico, displaying well-developed {010} faces, and having approximate dimensions 1.6 × 2.6 × 2.1 mm. The crystal was oriented with the c axis parallel to the ϕ axis of a fully automated Electronics and Alloys four-circle diffractometer at the CP-5 reactor at Argonne National Laboratory. The unit-cell parameters were refined by least-squares methods to give the best

fit between calculated and observed angles 2θ , χ and φ (measured¹ at $22 \pm 2^\circ\text{C}$ with $\lambda = 1.142(1) \text{ \AA}$) for 29 automatically centered reflections in the range $2\theta = 33\text{--}63^\circ$. The resulting cell dimensions ($a = 8.367(5)$, $b = 10.730(6)$, $c = 5.115(3) \text{ \AA}$) and unit cell volume [$459.2(4) \text{ \AA}^3$] agree well with values reported previously by McDONALD and CRUICKSKANK (1967)

Density measurements were made by the volume displacement method (in toluene) using six crystals in the range 21–58 mg and yielded a value of $3.475(10) \text{ g cm}^{-3}$; the calculated density based on the ideal formula $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ and $Z = 2$ is 3.484 g cm^{-3} . Several samples of hemimorphite with weights in the range 158–277 mg were held at a temperature of 800°C for several hours and yielded weight losses between 7.3 and 7.8% , again consistent with the presence of a single H_2O group in the ideal formula (theoretical weight loss = 7.48%).

Intensity data for the structure analysis were collected at $22 \pm 2^\circ\text{C}$ using a neutron wavelength $1.142(1) \text{ \AA}$ produced by diffraction from the (110) plane of a Be monochromator crystal². Each reflection was step-scanned using the $\theta\text{--}2\theta$ technique at 2θ intervals of 0.1° over a scan range of width $4.2\text{--}6.4^\circ$ in 2θ . Backgrounds were determined from stationary counts taken at both ends of the scan. A total of 818 reflections of the types hkl and $\bar{h}kl$, consistent with a body-centered lattice, were collected to a maximum $(\sin \theta)/\lambda = 0.72$. Two reflections were measured every 50 regular reflections in order to monitor crystal and instrument stability: their integrated intensities were observed to have a maximum random variation of 2.1% . The intensity of each reflection was corrected for background, Lorentz, polarization and absorption effects using a μ value of 0.913 cm^{-1} (the corresponding transmission factors ranged from 0.83 to 0.88). All data were placed on an absolute scale by calibration with a well-characterized NaCl crystal using a method described by PETERSEN *et al.* (1974). Multiply measured and symmetry-equivalent reflections (consistent with point group $mm2$) were averaged (using weights based on counting statistics) to yield a set of 433 unique structure factors, each with a standard deviation estimated from the equation $\sigma = [\sigma_I^2 + 0.03I^2]^{0.5}/2I^{0.5}$, where I is the corrected raw intensity and σ_I is derived from counting and averaging statistics. The “agreement factor” between

¹ Parenthesized figures here, and elsewhere in the text, represent the e.s.d. in terms of the least significant figure quoted.

² Further details are given by ROZIERE and WILLIAMS (1976).

Table 1. Observed (F_o) and calculated (F_c)

K	FO	FC	AC	BC	K	FO	FC	AC	BC	K	FO	FC	AC	BC	K	FO	FC	AC	BC						
H= 0 L= 0					5	109	105	-105	0	H= 7 L= 1					5	149	143	-95	106						
2	573	578	-578	0	7	691	675	675	0	7	249	243	229	-81	7	372	389	-366	-131						
4	99	141	-141	0	7	397	407	-407	0	8	448	500	-498	49	11	201	199	-191	58						
6	1011	479	979	0	H= 10 L= 0					13	232	240	233	-57	13	232	240	233	-57						
8	177	161	-161	0	0	597	608	608	0	0	370	364	-294	215	H= 6 L= 2										
10	6	41	41	0	0	2	170	177	177	0	10	311	307	245	-185	0	731	744	190	719					
12	349	369	369	0	0	4	297	299	-299	0	12	281	287	-50	282	2	325	315	243	-201					
14	439	449	449	0	0	6	168	161	161	0	H= 8 L= 1					4	260	257	72	247					
H= 1 L= 0					8	203	197	197	0	1	440	450	-448	-48	6	369	372	172	330						
1	530	505	505	0	H= 11 L= 0					3	364	368	-20	-368	10	344	345	-11	345						
3	565	532	-532	0	0	1	118	123	123	0	7	505	511	-505	-77	12	127	119	101	-84					
5	472	495	495	0	0	5	48	72	72	0	11	260	262	-18	-261	H= 7 L= 2									
7	347	242	242	0	0	H= 12 L= 0				11	73	85	-81	26	1	256	297	-149	257						
9	89	115	-115	0	0	0	238	238	238	0	H= 9 L= 1					3	463	475	430	-202					
11	97	60	60	0	H= 0 L= 1					5	472	465	-185	427	7	37	62	-51	-35						
13	277	261	261	0	0	1	141	142	137	-38	6	211	217	145	162	9	435	430	386	190					
15	60	40	40	0	3	137	103	-103	-8	8	369	367	-274	-244	11	138	132	-92	95						
H= 2 L= 0					5	291	289	-24	-288	H= 8 L= 2					0	272	279	-272	59						
0	226	213	-213	0	7	543	547	465	287	2	128	119	117	-22	4	103	91	45	-79						
2	102	127	-127	0	9	598	607	-448	-410	6	287	295	-191	48	8	137	141	138	32						
4	123	101	-101	0	11	272	262	260	233	10	142	143	21	-142											
6	103	136	-136	0	13	365	348	334	95	H= 11 L= 1					H= 9 L= 2										
8	190	168	-168	0	15	509	536	-430	-319	3	252	239	201	129	5	426	423	187	379						
10	32	20	-20	0	H= 1 L= 1					5	436	433	348	258	9	159	164	-51	-156						
12	32	20	-20	0	0	219	215	-209	-47	7	115	109	3	-109	1	145	142	133	51						
14	46	27	-27	0	2	31	16	-10	-12	3	209	215	-202	73	1	145	142	133	51						
H= 3 L= 0					4	242	264	-143	-227	4	174	174	-105	-136	5	165	165	22	-163						
1	67	41	41	0	6	148	148	-49	139	H= 0 L= 2					7	426	423	187	379						
3	420	476	426	0	8	180	174	-171	-31	9	159	164	-51	-156	9	159	164	-51	-156						
5	281	276	-276	0	10	301	301	-199	-236	0	975	1047	804	670	H= 10 L= 2										
7	596	584	584	0	12	251	263	121	236	2	468	503	323	-385	0	485	485	485	-9						
9	43	27	27	0	14	388	388	-340	-187	4	210	192	31	189	4	121	119	-89	-76						
11	141	138	138	0	H= 2 L= 1					6	771	761	703	290	6	425	437	376	222						
13	313	314	314	0	0	562	560	-553	88	8	395	398	359	-172	H= 11 L= 2										
H= 4 L= 0					2	378	374	27	-373	10	404	415	-147	388	3	124	131	-24	100						
0	660	670	670	0	4	301	294	-244	163	12	479	479	473	-75	1	98	103	-22	100						
2	372	376	376	0	6	745	736	-727	-113	14	414	421	309	287	3	124	131	-24	100						
4	134	151	-151	0	8	119	123	-123	1	H= 1 L= 2					1	98	103	-22	100						
6	773	758	758	0	10	569	578	-572	-85	3	342	347	-119	326	1	145	142	133	51						
8	302	315	315	0	12	101	102	16	-101	5	293	294	-245	-162	1	145	142	133	51						
10	336	320	-320	0	H= 3 L= 1					7	474	483	-216	432	5	556	578	534	-223						
12	645	641	641	0	0	432	432	32	431	9	105	93	193	5	7	193	198	-115	162						
14	77	77	77	0	2	492	490	59	-486	11	216	215	-182	115	9	190	189	24	24						
H= 5 L= 0					4	566	542	540	-449	13	138	127	105	72	11	205	210	210	3						
1	177	167	167	0	6	357	358	-98	-361	H= 2 L= 2					13	144	140	126	61						
3	1207	1147	-1147	0	8	584	601	591	109	0	369	351	-348	-46	H= 1 L= 3										
5	114	125	125	0	10	369	366	-374	-150	2	187	194	183	64	1	223	236	219	-88						
7	224	220	220	0	12	44	58	45	37	4	227	223	184	-162	1	223	236	219	-88						
9	591	689	-689	0	H= 4 L= 1					6	432	436	-423	107	5	556	578	534	-223						
11	51	42	-42	0	0	179	189	-31	186	8	173	164	147	71	7	193	198	-115	162						
13	235	227	227	0	2	454	450	-331	-305	10	221	223	102	-198	9	190	189	24	24						
H= 6 L= 0					4	368	374	191	322	12	498	496	-440	229	11	205	210	210	3						
0	1139	1120	1120	0	6	236	213	-200	-72	14	147	144	127	-67	13	144	140	126	61						
2	195	206	-206	0	8	58	84	-83	-13	H= 3 L= 2					12	241	243	-216	-110						
4	174	172	172	0	10	56	89	73	50	1	92	93	18	91	H= 2 L= 3										
6	642	625	625	0	12	52	41	-38	16	3	542	552	469	291	1	680	663	-603	-277						
8	89	72	-72	0	H= 5 L= 1					5	212	204	33	-201	3	633	638	630	-190						
10	246	244	244	0	0	41	47	43	-19	7	556	559	23	559	5	514	494	-461	-177						
12	83	75	75	0	2	350	349	-319	-141	9	606	599	572	-181	5	575	556	-434	-348						
H= 7 L= 0					4	440	444	-400	-236	11	179	185	-39	181	13	453	447	-369	-252						
1	233	236	236	0	6	61	64	63	11	H= 4 L= 2					11	221	209	-73	-186						
3	38	8	8	0	8	405	398	-373	-138	13	453	447	-369	-252	13	453	447	-369	-252						
5	411	412	412	0	10	550	545	-475	-267	0	312	317	296	113	H= 3 L= 3										
7	27	50	-50	0	12	170	169	151	74	2	369	372	8	372	0	778	778	-757	178						
9	454	459	459	0	H= 6 L= 1					4	55	79	-79	-72	2	828	813	811	-55						
11	79	72	72	0	0	174	184	-166	-79	6	348	356	165	315	4	543	519	472	217						
H= 8 L= 0					2	152	161	153	-51	8	257	264	131	230	6	394	405	-406	-37						
0	63	44	-44	0	4	320	312	-189	-249	10	180	173	-142	-100	8	433	430	426	-56						
2	56	41	-41	0	6	285	281	109	259	12	405	407	21	407	10	373	369	275	245						
4</																									

structure factors ($\times 100$) for hemimorphite

K	FO	FC	AC	BC	K	FO	FC	AC	BC	K	FO	FC	AC	BC
1	288	294	-246	-160	H= 4	L= 4	0	535	533	531	-49			
3	239	240	219	-98			2	245	236	-199	-127			
5	285	287	-286	-33	0	589	575	574	-19	4	119	113	-113	-7
7	278	273	44	-275	2	344	349	-334	160	6	481	478	457	-104
9	106	121	-96	-74	4	227	235	-146	185	8	293	292	-224	-171
11	156	138	76	-115	6	272	273	-253	-103					
13	148	147	-11	-147	8	181	179	-124	129	H= 6	L= 5			
					10	205	198	-123	155	1	127	135	133	26
H= 5	L= 3									3	231	228	-148	-173
0	400	405	164	-370	1	195	182	128	-129	5	411	417	228	257
2	142	142	-129	-53	3	588	585	-562	143	7	293	304	-66	-297
4	129	132	-15	-31	5	187	177	-104	-144	H= 7	L= 5			
6	327	331	107	-314	7	362	360	353	-71	0	231	234	-58	227
8	234	219	-200	-60	9	527	519	-507	109	2	170	155	123	-95
10	176	186	-12	-185	11	189	196	-165	-105	4	423	418	358	217
12	183	191	49	-185						H= 8	L= 5			
H= 6	L= 3				0	181	186	-132	-135	1	201	202	-136	-149
1	154	157	-34	-194	2	350	341	187	285	3	172	183	182	18
3	237	241	59	234	4	426	430	-307	134	H= 0	L= 6			
5	403	391	291	-261	6	119	111	102	-43	0	699	704	703	-35
7	389	401	-393	-85	8	194	292	182	229	2	472	492	-411	270
9	352	336	335	-24	10	434	435	-430	69	4	394	384	-350	-158
11	133	119	105	-56						6	483	492	449	201
H= 7	L= 3									8	259	254	-178	181
0	455	448	-356	-272	1	153	155	-155	-7	H= 1	L= 6			
2	196	203	140	145	3	426	430	313	295	1	161	165	162	-24
4	580	581	-34	-83	5	152	129	-81	100	3	487	491	-470	-142
6	540	525	-509	-130	7	178	171	125	117	5	164	160	51	-151
8	46	75	38	65	9	176	175	39	170	7	215	206	82	189
10	601	605	606	-82						H= 2	L= 6			
H= 8	L= 3				0	166	154	-79	-138	0	324	334	-160	293
1	405	407	-362	-137	2	106	103	-85	67	2	273	264	55	-258
3	503	510	504	-83	4	159	178	-129	-123	4	149	150	-55	-118
5	274	285	-291	-135	6	159	178	-129	-123	6	206	194	-148	133
7	417	413	-353	-215						8	234	209	54	-202
9	347	348	343	-57	H= 9	L= 4								
H= 9	L= 3				1	199	206	200	-52	H= 3	L= 6			
0	343	344	-344	-4	3	602	592	-585	93	1	229	245	-140	201
2	304	287	242	-153	5	247	255	254	-8	3	433	412	50	-409
4	77	62	-24	52						5	460	449	-270	383
6	179	160	-98	-126	H= 10	L= 4				7	129	137	58	-125
8	190	192	127	-144	0	709	708	705	67	H= 4	L= 6			
H= 10	L= 3									0	488	479	234	418
1	31	51	38	-34	1	310	316	298	106	2	240	234	-53	-273
3	178	173	173	-1	3	519	538	-520	-126	4	351	344	-344	12
5	105	88	-57	67	5	560	591	448	385	6	318	322	262	187
H= 0	L= 4				7	335	307	134	-277	H= 5	L= 6			
0	300	300	246	2	9	396	401	-276	241	1	207	211	204	-56
2	505	523	192	436	11	314	319	312	65	3	685	685	-651	-214
4	451	458	-475	293						5	195	192	76	-132
6	513	523	515	40	0	401	397	386	91	H= 6	L= 6			
8	431	416	199	366	2	169	164	-44	-163	1	381	377	371	-70
10	711	696	-671	187	4	185	183	117	99	2	274	275	-215	172
12	389	602	505	141	6	300	309	294	-94	4	222	229	-127	-190
H= 1	L= 4				8	260	169	-135	-146	H= 0	L= 7			
1	169	170	-71	-194	10	178	185	133	129	1	155	152	-38	147
3	342	346	-297	176						3	178	165	136	-94
5	361	348	-295	-184	1	274	277	-169	-220	H= 1	L= 7			
7	285	279	278	-13	3	346	339	335	48	1	217	209	-209	3
9	378	395	-380	178	5	283	272	-35	-270	3	422	429	422	-76
11	161	151	-137	-62	7	154	160	-156	-57	H= 3	L= 7			
H= 2	L= 4				9	243	225	194	-113	0	163	163	-112	118
0	137	121	-10	-120						2	133	138	-5	138
2	101	104	-77	71	H= 3	L= 5								
4	138	124	91	94	0	417	405	-258	-313	0	300	319	-246	203
6	260	270	-210	-170	2	519	523	325	410	2	238	259	257	-37
8	198	91	-58	70	4	248	257	257	-11	4	77	91	84	35
10	151	139	125	61	6	120	113	-112	-11	H= 2	L= 7			
12	444	440	-404	-170	8	265	270	123	241	1	217	209	-209	3
H= 3	L= 4				10	225	241	193	-144	3	422	429	422	-76
1	122	113	-18	111						H= 0	L= 7			
3	341	346	-216	270	1	175	182	127	-131	0	163	163	-112	118
5	262	269	267	172	3	198	204	-80	187	2	133	138	-5	138
7	376	377	-376	21	5	273	266	136	-229					
9	506	502	323	384	7	251	232	200	117					
11	146	152	-148	38	9	166	206	-183	-96					
					H= 5	L= 5								

Location of hydrogen atoms and refinement

Refinement of the heavy-atom positions and isotropic temperature factors was initiated in space group *Imm2* using the atomic coordinates

Table 2. *Fractional atomic coordinates and temperature factor coefficients for hemimorphite**

Atom	x	y	z	β_{11}	
Zn	0.2047(1)	0.1613(1)	0	0.0029(1)	
Si	0	1465(2)	0.5076(5)	23(2)	
O(1)	1602(2)	2055(1)	6362(4)	38(1)	
O(2)	0	1669(2)	1938(4)	27(2)	
O(3)	3050(2)	0	410(6)	50(2)	
O(4)	0	0	5912(6)	54(3)	
O(5)	5000	0	5195(13)	164(10)	
H(35)	3740(8)	0	190(2)	154(9)	
H(53)	4256(14)	0	643(4)	247(21)	

Atom	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.0020(1)	0.0066(4)	-0.0005 5(1)	-0.0001 (2) 0.1(2)	0.0003 (2) 3(2)
Si	13(1)	45(6)	0	0	0(3)
O(1)	26(1)	70(4)	-17(1)	9(2)	9(2)
O(2)	33(1)	55(5)	0	0	4(2)
O(3)	18(1)	271(10)	0	-30(4)	0
O(4)	10(2)	124(9)	0	0	0
O(5)	227(12)	221(9)	0	0	0
H(35)	56(4)	692(41)	0	-224(18)	0
H(53)	247(18)	1163(101)	0	102(45)	0

* Parenthesized figures here and in all subsequent tables represent the e.s.d. in terms of the least significant figure to the left.

of McDONALD and CRUICKSHANK (1967). As in the previous study, the unit-cell origin was defined by fixing the z coordinate of Zn at 0.0. Minimization of the function $\sum w(F_o - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors and $w = 1/\sigma^2$, resulted in convergence at a conventional R value of 0.123. The hydrogen atoms were then located from a Fourier difference map and the refinement was continued to convergence at $R = 0.081$. When the isotropic temperature-factor model was converted to an anisotropic model of the form $\exp[-\sum_{i=1}^3 \sum_{j=1}^3 \beta_{ij} h_i h_j]$ with the symmetry restrictions of

Table 3. *Magnitudes and orientations of the principal axes of thermal ellipsoids in hemimorphite*

Atom	Axis	Root-mean-square displacement	Angle to		
			+a	+b	+c
Zn	1	0.090(3) Å	46(20)°	52(7)°	112(37)°
	2	0.094(3)	113(28)	97(23)	156(34)
	3	0.116(2)	127(4)	39(4)	81(5)
Si	1	0.077(5)	90	89(29)	1(29)
	2	0.086(5)	90	179(29)	89(29)
	3	0.091(5)	0	90	90
O(1)	1	0.082(3)	43(5)	48(2)	95(14)
	2	0.092(3)	103(11)	84(9)	166(6)
	3	0.151(2)	130(1)	43(1)	77(2)
O(2)	1	0.085(4)	90	95(3)	5(3)
	2	0.098(3)	180	90	90
	3	0.139(3)	90	5(3)	85(3)
O(3)	1	0.104(4)	90	0	90
	2	0.125(4)	162(2)	90	108(2)
	3	0.195(3)	108(2)	90	18(2)
O(4)	1	0.076(6)	90	0	90
	2	0.128(5)	90	90	180
	3	0.138(4)	0	90	90
O(5)	1	0.171(7)	90	90	0
	2	0.241(7)	180	90	90
	3	0.364(9)	90	0	90
H(35)	1	0.146(9)	35(2)	90	55(2)
	2	0.181(6)	90	180	90
	3	0.354(10)	55(2)	90	145(2)
H(53)	1	0.285(13)	17(6)	90	107(6)
	2	0.379(14)	90	180	90
	3	0.401(18)	73(6)	90	17(6)

LEVY (1956), the R value dropped to 0.051. Further refinement with the inclusion of an isotropic extinction parameter (g), as defined and scaled by COPPENS and HAMILTON (1970), proceeded smoothly to convergence (parameter shifts in the final cycle were less than one

tenth of the corresponding e.s.d). The final values of R and R_w ³ were 0.028 and 0.035, respectively (0.031 and 0.035 for the entire data set of 433 structure factors), with the error in an observation of unit weight = 1.58. Although nearly one third of the data were affected more than 10% by extinction [$g = 0.61(4)$], only 5% of the reflections needed correction factors between 1.3 and the highest value of 2.2. The final scale factor was 0.989(7), close to the ideal value of unity expected for a data set placed on an absolute scale. The major positive and negative peaks in a Fourier difference synthesis were all located in the immediate environment of the water molecule but had maximum magnitudes somewhat less than 13% of the density of peaks corresponding to O and H atoms. The residual nuclear density may be a function of a small quantity of excess water present in a slightly different orientation within the channels, but could also be indicative of a minor amount of positional disorder in a single H₂O species.

Values for F_o and F_c ($\times 100$) are listed in Table 1. Atomic coordinates and thermal parameters along with their standard deviations estimated from the variance-covariance matrix are given in Table 2. The root-mean-square components of thermal displacement, and thermal-ellipsoid orientations appear in Table 3. The coherent neutron-scattering amplitudes used during least-squares refinement for Zn, Si, O and H were respectively 0.57, 0.42, 0.580 and -0.374 , all in units of 10^{-12} cm (BACON, 1972). Programs utilized for solution, refinement and geometry calculations were local modifications of DATALIB, DATASORT, FOURIER, ORFLS3, ORFFE3 and ORTEP⁴.

Discussion of the structure

Hemimorphite crystallizes with the topology displayed in Fig. 1 and the bonding dimensions summarized in Table 4. The framework consists of an assembly of three-membered rings of corner-sharing Zn(OH)O₃ ($\times 2$) and SiO₄ tetrahedra arranged in compact sheets parallel to (010). Three of the oxygen atoms in each tetrahedron are bonded to one silicon and two zinc atoms, while the fourth oxygen (or, in the case of the zinc polyhedron, the hydroxyl group) forms a bridging bond to an equivalent cation in an adjacent sheet. The cross-linking of the sheets produces additional rings of four, six and eight tetrahedra and forms a series of large cavities connected along the

³ $R_w = [\sum w(F_o - F_c)^2 / \sum w F_c^2]^{0.5}$.

⁴ All programs are listed in the *World list of crystallographic computer programs* (3rd ed. and supplements).

Table 4. Interatomic distances and angles in hemimorphite*

SiO ₄ tetrahedron:								
Si—O(2)	1.620(3) Å	O(2) ··· O(1) (× 2)	2.662(2) Å	∠O(2)—Si—O(1) (× 2)	110.4(1)°			
O(1) (× 2)	1.622(2)	O(4)	2.709(3)	O(4)	113.0(2)			
O(4)	1.629(2)	O(1) ··· O(1) ⁱ	2.681(3)	O(1)—Si—O(1) ⁱ	111.5(2)			
<Si—O>	1.623(2)	O(4) (× 2)	2.591(2)	O(4) (× 2)	105.7(1)			
		<O ··· O>	2.649(2)	<∠O—Si—O>	109.5(1)			
ZnO ₄ tetrahedron:								
Zn—O(3)	1.935(2) Å	O(3) ··· O(1) ⁱⁱ	3.211(2) Å	∠O(3)—Zn—O(1) ⁱⁱ	111.4(1)°			
O(1) ⁱⁱ	1.951(2)	O(1) ⁱⁱⁱ	3.259(3)	O(1) ⁱⁱⁱ	113.7(1)			
O(1) ⁱⁱⁱ	1.956(2)	O(2)	3.214(3)	O(2)	110.4(1)			
O(2)	1.980(2)	O(1) ⁱⁱ ··· O(1) ⁱⁱⁱ	3.116(2)	O(1) ⁱⁱ —Zn—O(1) ⁱⁱⁱ	105.82(7)			
<Zn—O>	1.956(1)	O(2)	3.169(2)	O(2)	107.47(9)			
		O(1) ⁱⁱⁱ ··· O(2)	3.179(3)	O(1) ⁱⁱⁱ —Zn—O(2)	107.71(8)			
		<O ··· O>	3.191(2)	<∠O—Zn—O>	109.4(1)			
Framework anions:								
∠Zn ^{iv} —O(1)—Zn ^v	114.01(7) Å	∠Zn—O(2)—Zn ⁱ	119.8(1)°	∠Zn—O(3)—Zn ^{vi}	126.9(1)°	∠Si—O(4)—Si ^{vii}	149.5(2)	
Zn ^{iv} —O(1)—Si	116.7(1)	Zn—O(2)—Si (× 2)	119.47(6)	Zn—O(3)—H(35) (× 2)	110.4(2)			
Zn ^v —O(1)—Si	128.3(1)							
Water molecule and hydroxyl group:								
O _a	H	O _a	O _a —H	H ··· O _a	O _a ··· O _a	∠O _a —H ··· O _a	H ··· H	∠H—O _a —H
O(3)	H(35)	O(5)	0.957(7)	1.986(8)	2.941(6)	175.0(8)	—	—
O(5)	H(35) × 2	O(3) ^{iv}	0.888(17)	2.271(19)	3.127(6)	161.8(15)	1.25(2)	89(2)

* Symmetry transformations for atoms outside the asymmetric unit:

17 *i.* $-x, y, z$ *ii.* $0.5-x, 0.5-y, -0.5+z$ *iii.* $x, y, z-1.0$ *iv.* $x, y, 1.0+z$ *v.* $0.5-x, 0.5-y, 0.5+z$ *vi.* $x, -y, z$ *vii.* $-x, -y, z$

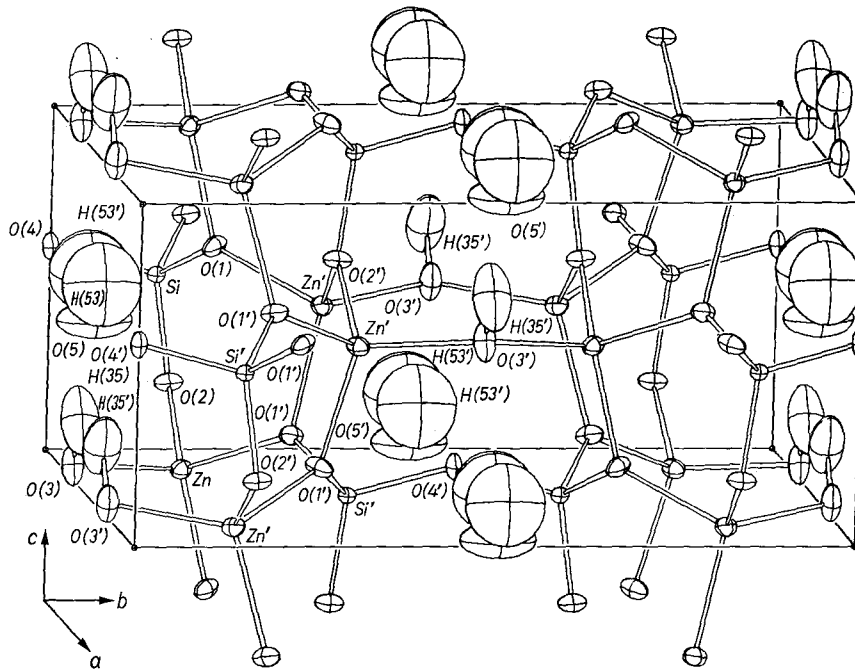


Fig. 1. Unit-cell diagram of the hemimorphite crystal structure. Thermal ellipsoids for all atoms represent 50% probability surfaces. Atoms outside the asymmetric unit are labelled with superscript primes

c axis. The water molecules near the centers of these cavities (in the plane of the eight fold rings), are orientated parallel to (010), and are held in place by hydrogen bonds to the hydroxyl groups (Fig. 2). On heating, it is apparent that the H₂O molecule is able to pass through the 6-membered ring (possibly by a process of proton exchange with the hydroxyl group) into an adjacent (vacated) cavity above or below it in the *c*-axis direction without disruption of the structure.

Although the nuclear coordinates determined in the present study (Table 2) for the atoms not involved in bonds to hydrogen are similar to the values derived by x-ray diffraction as reported by McDONALD and CRUICKSHANK (1967), the positions of the oxygen atoms of the hydroxyl group, O(3), and water molecule, O(5), differ by 0.03 and 0.07 Å, respectively. The significance of these differences is, of course, markedly reduced by the large e.s.d.'s associated with the atomic coordinates in the earlier study, but it is interesting to note that in the

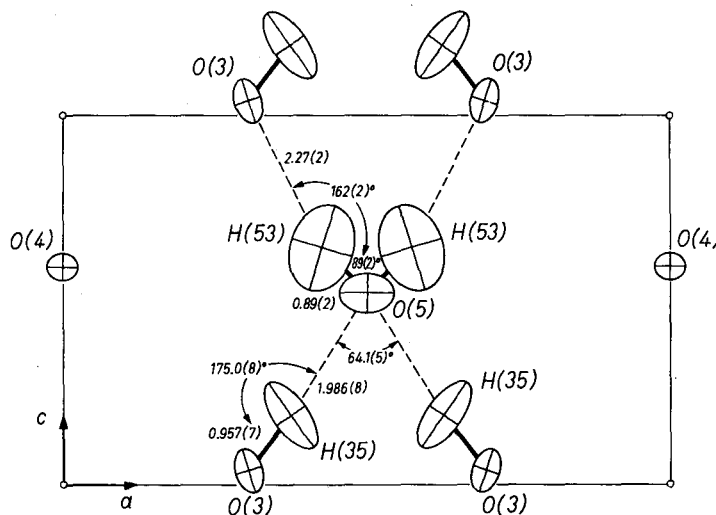


Fig. 2. Section through the cavity at $y = 0$ in the hemimorphite unit cell. Thermal ellipses for all atoms represent 50% probability surfaces. Hydrogen bonds are indicated by dashed lines

case of O(3) and O(5) the oxygen position in the x-ray study is displaced, relative to the neutron diffraction position, toward the region of space expected to be occupied by the oxygen lone pair electrons. Similar shifts due to asphericity of the electron distribution, as determined in the x-ray study, have been reported in a number of other structures containing terminal O, N and H atoms (see, for example, COPPENS, 1977), but the magnitudes of the nonhydrogen-atom displacements in these instances are only about 0.01 Å. We are at present collecting a set of room-temperature x-ray data in an attempt to verify the apparently larger shift observed for the more isolated water-molecule oxygen atom in hemimorphite.

The O(5) atom lies slightly below the center of a rectangle of nearest-neighbor O(3) atoms in the plane at $y = 0$ (Fig. 2). Based on the relative sizes of the angles subtended by the O(3) atom pairs above and below O(5), McDONALD and CRUICKSHANK (1967) inferred that the water-molecule protons are directed towards the O(3) atoms below O(5) in the unit cell but in positions considerably displaced from the O(5)—O(3) lines. In fact, the present study indicates that the H₂O group is oriented in the reverse direction, and although the O(5)—H(53) ··· O(3) angle does deviate significantly from 180° (Table 4),