

Refinement of the crystal structure of hardystonite, $\text{Ca}_2\text{ZnSi}_2\text{O}_7$

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Auszug

Die Kristallstruktur von Hardystonit, $\text{Ca}_2\text{ZnSi}_2\text{O}_7$, wurde auf Grund von *hkl*-Interferenzen bis zum Wert $R = 5,3\%$ verfeinert. Die Bindungen Zn–O und Si–O sind vorwiegend kovalent. Benachbarte $[\text{ZnSi}_2\text{O}_7]^{4-}$ -Schichten werden durch Ca^{2+} -Ionen zusammengehalten; hierbei herrscht Ionenbindung vor.

Abstract

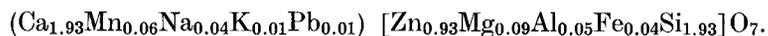
The structure of hardystonite, $\text{Ca}_2\text{ZnSi}_2\text{O}_7$, was refined to $R = 5.3\%$ from three-dimensional diffractometer data. The Zn–O and Si–O bonds are predominantly covalent, and the adjacent covalent sheets of $[\text{ZnSi}_2\text{O}_7]^{4-}$ are linked by Ca^{2+} ions, with the interlayer bonding being predominantly ionic in character.

1. Introduction

The crystal structure of hardystonite, $\text{Ca}_2\text{ZnSi}_2\text{O}_7$, was determined first by WARREN and TRAUTZ (1930). The reinvestigation was undertaken as part of a systematic structural study of various members of the melilite mineral group. Order-disorder of Mg, Al, Si among tetrahedral sites, and diadochy of Ca, Na, etc. in 8-coordination sites, are of principal interest in this group of minerals, as explained by SMITH (1953) when he reexamined the structure of a melilite. Reexamination of hardystonite structure was specifically chosen since each cation site is occupied by only one atomic species, and since an accurate determination of structural parameters of this crystal would assist in discussing problems concerning other chemically more complicated melilites.

2. Experiments

The specimen chosen for this study is from Franklin, N. J. Three chemical analyses of hardystonite from this locality are reported by PALACHE (1935). A mean of these three analyses yields the following formula when calculated on the basis of 7 oxygen atoms,



The ionic species within the parentheses tend to occur in the 8-coordination site, while those in square brackets tend to occur in the tetrahedral sites.

After collecting the intensity data for the crystal-structure analysis, the single crystal of hardystonite from which intensities were measured was chemically analyzed by the x-ray-emission microanalysis technique. Measurements were made at 15 kV and 0.5 μA . Standards used were Zn metal and ZnCO_3 for Zn, galena for Pb, and H39 clinopyroxene (SMITH, 1966) for other elements. The results of this analysis, corrected according to the procedure of SMITH (1965), are compared with those reported by PALACHE in Table 1. The microprobe analysis shows slightly more CaO and slightly less MnO and

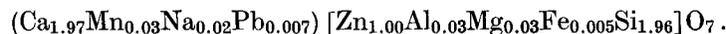
Table 1. *Hardystonite analyses*

Oxides	X-ray-emission microanalysis, S. J. LOUISNATHAN, analyst	Wet chemical analyses quoted by PALACHE (1935)		
	1	2	3	4
SiO ₂	36.80%	38.10%	37.78%	36.59%
Al ₂ O ₃	0.94	—	0.91	0.77
Fe ₂ O ₃	0.20*	0.57	0.43	—
FeO	—	—	—	0.42
ZnO	25.56	24.30	25.38	22.47
MnO	0.76	1.50	1.26	1.23
CaO	34.61**	33.85	34.22	35.16
MgO	0.39	1.62	0.26	1.47
K ₂ O	—	—	0.78	—
Na ₂ O	0.29	—	1.10	—
PbO	0.56	—	—	1.99
Ignition	—	0.52	0.34	—
Total	100.11	100.46	102.46	100.00

* The microprobe analysis does not distinguish ferrous from ferric iron.

** About 1.5% random variation within the grain was observed, average value is given above.

MgO. The formula of hardystonite according to the x-ray-emission analysis is,



This analysis also showed that the single crystal was chemically homogeneous within 1%. The atomic factors of the cation sites were assumed to be those for pure Ca, Si and Zn because of the trivial effects of the substitution by other ions.

Table 2. *Lattice parameters of hardystonite*

Method	<i>a</i>	<i>c</i>	Reference
Rotation photograph Mo radiation	7.83 Å	4.99 Å	WARREN and TRAUTZ (1930)
Diffractometer data CuK α radiation	7.823	5.013	L.G. BERRY (PDF Card No. 12-453)
Powder photograph synthetic sample	7.75 (5)	5.01	SEGNET (1954)
Powder photograph FeK α radiation	7.8287 ± 0.0016	5.0140 ± 0.0004	This work
Diffractometer data CuK α radiation	7.8279 ± 0.0010	5.0138 ± 0.0006	This work

The lattice parameters of hardystonite as measured by different workers are given in Table 2. In the present study they were obtained from powder patterns using a diffractometer and a 114.6 mm Buerger-type camera, with a spectroscopically pure silicon as internal standard. Ni-filtered CuK α radiation was used for the diffractometer pattern, and Mn-filtered FeK α radiation for the powder pattern. Measured 2θ values were corrected using the known positions of the silicon lines. Of the 50 or so of the lines measured, 32 lines were used in the determination of cell parameters by least-squares techniques [SMITH (1956) and BURNHAM (1962)].

PALACHE (1935) reports a density range of 3.39 to 3.44 g/cm³ for hardystonites, which is consistent with density (3.42 g/cm³) calculated using x-ray-emission microanalysis data and the refined cell-dimension data. There are two formula units of hardystonite in the unit cell. The space group is $P\bar{4}2_1m$ or $P42_1$ as the only systematic extinctions

are $h00$ with h odd. WARREN and TRAUTZ (1930) discarded $P42_1$ as it was not possible to build a reasonable structure in this space group.

A grain of hardystonite free from zoning, twinning or inclusions was chosen and ground into a sphere of diameter 0.18 mm by the method of BOND (1951). Weissenberg and precession photographs were taken and the space-group extinction conditions were checked. Intensities were collected on a manual scintillation-counter diffractometer of Weissenberg geometry, using Zr-filtered $\text{MoK}\alpha$ radiation. For the layers $hk0$ through $hk4$, the symmetry-related reflections hkl and $h\bar{k}l$ were measured in addition to hkl . (It should be mentioned here, that for the space group $P\bar{4}2_1m$, $F(hkl)$ is not identical to $F(h\bar{k}l)$ when anomalous scattering is taken into consideration). For layers $hk5$ through $hk8$, only one set of intensities, namely hkl , was measured. Corrections for Lorentz and polarization factors were applied to the intensities using a program written by STEPHENSON and KNOWLES (private communication). No corrections for absorption were applied.

3. Refinement

The structure was refined with the SORFLS least-squares program written by R. B. K. DEWAR (private communication). This program is a local modified version of the ORFLS program of BUSING, MARTIN and LEVY (1962) which includes provision for anomalous dispersion and a correction for secondary extinction using ZACHARIASEN's (1963, 1967) formula for a sphere.

The atomic coordinates of WARREN and TRAUTZ (1930) yielded $R = 22\%$. Six refinement cycles with unit weights for all reflections and isotropic temperature factors, brought R to 15% . Introduction of individual scale factors to the different l layers during three cycles of refinement reduced R to 13% . Tests made to choose a proper weighting scheme showed that the errors in F_{obs} were neither dependent on $\sin\theta$ nor on the magnitudes of F_{obs} .

There were 151 reflections (or nearly half this number when only one set of symmetry-related reflections are taken into account) which showed rather significant differences in $|F_{\text{obs}} - F_{\text{calc}}|$. Of these, eighteen were very bad and were not used in subsequent refinements. A careful check of the rest revealed a difference of over 10% in the background counts on opposite sides of the peak. For such reflections, intensities were measured again, tracing the peak on a recorder during the second counting. Most of these peaks were weak, yielding

Table 3. Observed and calculated structure amplitudes in hardytonite

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
2	0	0	1060	1224	6	2	1	4331	4358	8	1	2	1033	1011	11	0	3	1193	1077	8	-8	3	1152	1221
4			2463	2180	-2			4185	4418	-1			1139	1052	1	1	3	4281	4302	1	0	4	931	976
6			7657	7646	7	2	1	1504	1908	9	1	2	2957	2888	-1			4309	4467	2			683	827
8			2438	2127	-2			1631	1854	-1			3000	2977	2	1	3	3528	3416	3			3354	3286
10			73	174	8	2	1	1432	1370	10	-1	2	1495	1420	-1			3478	3397	4			379	308
12			1635	1655	-2			1597	1494	10	-1	2	1419	1426	3	1	3	3169	3249	5			374	4
2	1	0	1545	1397	9	2	1	1204	1302	11	1	2	1058	1037	-1			3167	3321	6			4279	4399
3			6580	6642	-2			1534	1292	-1			967	1029	4	1	3	3921	3849	7			1567	1609
4			3643	3595	10	2	1	1489	1559	12	1	2	73	245	-1			3628	3785	8			415	580
5			3181	3196	-2			1245	1440	-1			726	232	5	-1	3	4602	4531	9			679	536
6			2483	2418	11	2	1	1441	1052	2	2	2	5764	5754	-1			4284	4283	10			694	627
7			688	532	-2			988	1034	-2			5676	5671	6	1	3	428	447	1	1	4	2129	2180
8			476	456	12	2	1	1978	1844	3	2	2	2274	2083	-1			342	446	-1			2055	2247
9			2222	2335	-2			2071	1930	-2			2186	2077	7	1	3	2483	2387	2	1	4	1279	1285
10			1978	1975	3	3	1	3602	3533	4	2	2	3769	3766	-1			2120	2331	-1			1335	1260
11			2111	2157	-3			5290	5406	-2			3754	3801	8	1	3	2314	2259	3	1	4	4237	4190
12			1114	1099	4	3	1	403	306	5	2	2	2086	1854	-1			1962	2207	-1			4151	4224
2	2	0	5076	5027	5	3	1	1202	953	-2			1899	1831	9	1	3	1861	1858	4	1	4	2808	2822
3			697	807	-3			521	766	6	2	2	1507	1390	-1			2192	2119	-1			2768	2880
4			6129	6259	6	4	1	936	777	5	1	3	1283	1174	-1			1150	1244	5	-1	4	2084	2413
5			1786	1655	7	3	1	2959	2898	7	2	2	2547	2519	-1			1150	1244	11	1	3	1497	1796
6			2138	2166	-3			2881	2989	-2			2441	2535	-1			1725	1735	-1			577	539
7			1473	1395	8	3	1	73	439	8	2	2	2468	2618	2	2	3	5450	5419	7	1	4	1058	1109
8			2109	2130	-3			73	424	-2			2197	2485	2	2	3	5072	5067	7	1	4	1058	1109
9			1861	1864	9	1		3366	3362	9	2	2	1876	1866	-1			1091	1059	-1			710	952
10			2413	2455	-3			3262	3303	-2			1157	1151	3	2	3	1114	995	8	1	4	1455	1237
11			782	701	10	3	1	573	505	10	2	2	2037	2120	-2			963	993	-1			1437	1287
3	3	0	4358	4219	-3			627	509	-2			1863	1948	4	2	3	1953	2097	9	1	4	2147	2340
4			73	112	11	3	1	545	398	11	-2	2	767	531	-2			2292	2364	-1			2520	2533
5			3607	3757	-3			579	562	5	3	2	2492	2338	4	3	3	3459	3538	10	1	4	1340	1352
6			2082	1975	4	4	1	5403	5239	-3			864	555	-2			2477	2539	-1			1457	1418
7			5432	5464	-4			5177	5073	4	3	2	2077	1967	6	2	3	3291	3127	2	2	4	4047	3961
8			1200	1065	5	4	1	3176	2996	-3			2111	1957	-2			3467	3379	-2			3650	3640
9			73	131	-4			2978	2961	5	3	2	4033	3956	7	2	3	1317	1190	3	2	4	73	78
10			884	918	6	4	1	2547	2698	6	3	2	1742	1682	8	2	3	1091	1059	-2			75	92
11			509	560	-4			2635	2775	6	3	2	875	886	8	2	3	1992	1894	4	2	4	3248	3196
4	4	0	6641	6599	7	4	1	1552	1402	-3			1105	855	-2			1755	1647	-2			3266	3296
5			1060	773	-4			1500	1421	7	3	2	3792	3789	9	2	3	879	628	5	2	4	769	711
6			73	162	8	4	1	428	267	-3			3810	3821	-2			812	624	-2			728	752
7			1901	1936	-4			365	496	8	3	2	1742	1682	10	2	3	976	1107	6	2	4	1441	1532
8			1164	1354	9	4	1	965	644	9	3	2	451	308	-2			976	948	-2			1558	1758
9			1198	1077	-4			949	644	-3			681	573	11	2	3	1252	1017	7	2	4	1667	1422
10			2533	2490	10	4	1	2183	2314	10	3	2	728	846	-2			1141	1042	-2			1297	1367
11			785	636	-4			2335	2278	-3			855	826	3	3	3	5479	5400	8	2	4	2057	1864
6	5	0	1974	2020	11	4	1	834	1105	11	3	2	1594	1605	5	3	3	3459	3538	-2			1841	1737
7			1491	1555	-4			1227	1088	-3			1466	1610	4	3	3	2341	2363	9	2	4	485	381
8			73	53	5	5	1	2549	2441	4	4	2	3672	4001	-3			2353	2361	-2			570	394
9			2037	2045	-5			2359	2431	5	4	2	2012	2011	5	3	3	1382	1411	10	2	4	1922	1842
10			1633	1618	6	5	1	1206	1299	-4			1994	2060	-3			1033	1169	-2			1755	1842
11			347	386	-5			1392	1286	6	4	2	1105	1099	6	3	3	701	564	3	3	4	1283	1011
6	6	0	3824	3813	7	5	1	2811	4142	-4			970	914	-3			778	539	-3			1346	1246
7			494	417	-5			2734	3197	7	4	2	1545	1607	7	3	3	1879	1910	4	3	4	1721	1689
8			1800	1794	8	5	1	2052	2013	-4			1561	1668	-3			1883	1812	-3			1628	1691
9			1540	1455	-5			2086	2054	8	4	2	1791	1642	8	3	3	1125	1190	5	3	4	3490	3413
10			173	186	9	5	1	566	842	10	4	2	1683	1701	9	3	3	1017	1101	-2			1841	1737
8	7	0	1475	1329	-5			311	759	9	4	2	73	323	9	3	3	3131	3140	6	3	4	1458	177
9			1712	1731	6	6	1	73	553	-4			552	534	-3			3217	3302	-3			1265	1194
8	8	0	2159	2358	-6			73	502	10	4	2	1807	1932	10	3	3	1044	777	7	3	4	3133	3180
9			1218	1246	7	6	1	748	217	-3			1937	1956	-3			715	772	-3			3070	3100
1	0	1	158	1568	-6			277	221	11	4	2	1297	1216	11	3	3	73	561	8	3	4	751	968
2			7041	7094	8	6	1	3226	3170	-4			1340	1254	-3			358	358	-3			850	969
3			3370	3359	-6			3124	3125	5	5	2	2786	2828	4	4	3	2574	2520	9	3	4	823	689
4			3162	3354	9	6	1	850	626	-5			2883	2976	-3			2565	2619	-3			1053	937
5			1475	1484	-6			830	621	6	5	2	1202	1053	5	4	3	2332	2097	10	3	4	674	733
6			1412	1406	10	6	1	920	1370	-5			1085	1050	-4			2149	2037	-3			952	745
7			455	265	-6			1468	1364	7	5	2	1525	1747	6	4	3	2781	2754	4	4	4	3072	2962
8			4469	4605	7	7	1	426	401	-5			1743	1836	-4			2644	2585	-4			3084	3058
9			509	424	-7			347	344	8	5	2	974	466	7	4	3	2197	2313	5	4	4	1229	1258
10			1414	1395	8	7	1	1130	1110	-5			635	449	-4			2086	2249	-4			1100	1230
11			73	445	-7			1188	1087	9	5	2	2659	2592	8	4	3	523	389	6	4	4	1049	884

Table 3. (Continued)

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
2	0	5	3634	3695	8	4	5	1252	1352	5	3	6	2495	2468	6	2	7	1997	1704	2	2	8	1069	1248
3			597	531	9			408	310	6			1058	1062	7			1035	788	3			701	359
4			3684	3665	5	5	5	1685	1548	7			656	652	8			1037	1248	4			1028	1136
5			965	1050	6			963	683	8			931	512	9			309	645	5			1333	1442
6			466	249	7			1446	1434	9			73	180	3	3	7	3808	3545	6			254	436
7			970	613	8			397	484	4	4	6	970	952	4			794	683	7			1055	795
8			1380	1457	9			918	999	5			1723	1570	5			897	706	8			1191	1023
9			173	140	6	6	5	726	696	6			1501	1271	6			855	688	3	3	8	466	375
10			2240	2196	7			73	73	7			1067	1141	7			75	294	4			489	400
1	1	5	3359	3426	7	7	5	1452	1553	8			2271	2187	8			618	504	5			1775	1870
2			1525	1500	1	0	6	1265	1429	9			318	452	9			1974	1754	6			694	235
3			518	487	2			1254	1232	5	5	6	1141	1016	4	4	7	584	472	7			769	958
4			1146	1202	3			954	1081	6			582	586	5			1073	863	8			315	239
5			2544	2537	4			2238	2238	8			1179	1209	6			2023	2151	4	4	8	814	604
6			333	350	5			1071	715	6	6	6	2556	2347	7			1213	1079	5			1206	1029
7			1822	1857	6			2409	2417	7			710	429	8			841	996	6			521	641
8			823	748	7			1175	1180	8			694	200	5	5	7	1928	1952	7			934	704
9			832	558	8			164	159	7	7	6	1671	1614	6			897	707	8			1547	1597
10			1107	1014	9			428	133	1	0	7	288	677	7			1087	1161	5	5	8	1186	1019
2	2	5	1782	2002	10			1173	1167	2			2389	2566	8			73	228	6			514	419
3			927	902	1	1	6	1701	1602	3			566	273	6	6	7	638	610	7			719	408
4			1543	1654	2			2777	2738	4			3172	3118	7			471	350	6	6	8	1656	1492
5			1031	1039	3			1955	1593	5			73	228	7	7	7	1270	1355	5	5	0	1773	605
6			3237	3155	4			1572	1716	6			888	659	1	0	8	252	217	7	7	0	868	264
7			1707	1754	5			658	743	7			1026	698	2			272	372	2	1	1	6444	6440
8			1491	1452	6			1085	1178	8			1265	1381	3			574	603	2	-1	1	6763	6422
9			784	702	7			1511	1646	9			859	381	4			859	1018	12	-1	1	1222	692
10			855	1007	8			1425	1392	1	1	7	1924	2204	5			557	667	4	-3	1	780	335
3	3	5	4451	4371	9			1218	1444	2			424	413	6			1554	1621	6	-3	1	542	834
4			688	601	10			455	421	3			442	321	7			620	301	9	8	1	73	435
5			1245	1257	2	2	6	2396	2519	4			1290	1516	8			405	210	10	0	2	195	222
6			381	370	3			859	849	5			1669	1712	9			645	307	11	0	2	1751	896
7			412	354	4			1847	1920	6			859	804	1	1	8	1042	1445	11	2	2	73	548
8			945	831	5			2298	2423	7			2003	1977	2			1543	1629	8	-3	2	73	714
9			2305	2254	6			1231	1128	8			1141	727	3			1664	1628	4	-4	2	2558	3740
10			189	276	7			710	870	9			915	667	4			1082	1128	9	0	3	792	26
4	4	5	1549	1406	8			1685	1759	2	2	7	2010	1888	5			620	668	8	3		1312	1344
5			1229	1299	9			922	716	3			306	304	6			647	416	9	4	4	73	445
6			2438	2488	3	3	6	706	698	4			902	766	7			1392	1218	7	-7	4	1799	1074
7			1416	1316	4			1087	1118	5			135	329	8			954	878	7	5	6	73	372

The table contains 715 reflections. The overall scale factor is 0.916×10^{-3} . Determination of absolute configuration requires that the signs on all hkl 's be reversed. The 18 reflections listed at the end of the table were not used in the least-squares refinements.

very jagged and irregular traces. All these 129 reflections were then uniformly weighted at half the weight assigned to the remaining 811 reflections. Such a weighting scheme appeared to be justifiable, since the quantity $g = \{[w(|F_{\text{obs}} - K_l F_{\text{calc}}|)^2]/(\text{NO} - \text{NV})\}^{1/2}$, (where NO is the number of observations, NV is the number of parameters varied, and K_l is the scale factor of the l th layer), was always close to unity (HAMILTON, 1964). Continuing the refinement under these conditions gave an R value of 9.9% and R' value of 9.5% after six

Table 4. Coordinates and thermal vibration
(Numbers in parentheses are the estimated standard deviations)

	x	y	z	β_{11}	β_{22}
Ca	0.3322 (01)	$\frac{1}{2}x$	0.5061 (03)	0.0055 (01)	β_{11}
Zn	0	0	0	0.0025 (01)	β_{11}
Si	0.1393 (02)	$\frac{1}{2}x$	0.9394 (03)	0.0020 (01)	β_{11}
O(1)	$\frac{1}{2}$	0	0.1771 (15)	0.0098 (10)	β_{11}
O(2)	0.1400 (05)	$\frac{1}{2}x$	0.2551 (11)	0.0055 (05)	β_{11}
O(3)	0.0818 (07)	0.1885 (05)	0.7847 (09)	0.0145 (09)	0.0017 (05)

* Since different scale factors were used for the different l layers, β_{33} of Zn tropic temperature factors.

cycles of refinement, where $R = \sum ||F_{\text{obs}}| - |K_i F_{\text{calc}}|| / \sum |F_{\text{obs}}|$, and $R' = [\sum w (F_{\text{obs}} - K_i F_{\text{calc}})^2]^{1/2} / [\sum w F_{\text{obs}}^2]^{1/2}$. Introduction of anomalous-dispersion corrections, with $f'_{\text{Zn}} = 0.30$, $f''_{\text{Zn}} = 1.50$, $f'_{\text{Ca}} = 0.20$, $f''_{\text{Ca}} = 0.35$, $f'_{\text{Si}} = 0.10$, and $f''_{\text{Si}} = 0.10$ (all values given are for $\theta = 0^\circ$, and were assumed to be constant for all values of θ) in four cycles of refinement gave $R = 8.7\%$ and $R' = 7.5\%$. Anisotropic temperature factors were introduced, and two parallel sets of refinements, one on hkl and $\bar{h}\bar{k}l$ data and other on $\bar{h}\bar{k}l$ and hkl data were done. After four cycles of refinement the set with hkl and $\bar{h}\bar{k}l$ gave $R = 8.1\%$ and $R' = 6.0\%$, while the set with $\bar{h}\bar{k}l$ and hkl gave $R = 6.7\%$ and $R' = 5.4\%$. Of the symmetry-related reflections, hkl and $kh\bar{l}$, the set that gave a better R value was retained and the other set removed, and this left 697 independent reflections for further refinements. In another four cycles, the refinement on positive l configuration converged to $R = 7.8\%$, and $R' = 5.8\%$, and that on negative l configuration converged to $R = 6.7\%$ and $R' = 5.3\%$. The quantity g at this final stage was 1.25. The differences in the z coordinates of the oxygen atoms relative to the Zn atom were of the order of 0.005 to 0.01 Å between the two configurations. These differences in R' and z coordinates are significant even at a confidence level of 0.1% (see HAMILTON'S, 1964, significance tests on R values). The final list of F_{obs} and F_{calc} are shown in Table 3. The final atomic coordinates and the thermal parameters of the atoms in hardystonite are given in Table 4.

Interatomic distances and bond angles together with their estimated standard deviations, taking into account both the errors in cell dimensions and in structural parameters, were calculated using the SORFFE program, a local modified version of the ORFFE written

parameters of atoms in hardystonite

in the last two decimal places of the preceding quantity)

β_{33}	β_{12}	β_{13}	β_{23}
0.0076 (04)	0.0025 (01)	0.0005 (02)	$-\beta_{13}$
0.0073*	0	0	0
0.0042 (06)	-0.0001 (02)	0.0003 (03)	$-\beta_{13}$
0.0044 (20)	-0.0050 (14)	0	0
0.0069 (16)	0.0028 (07)	-0.0004 (06)	$-\beta_{13}$
0.0124 (15)	-0.0016 (06)	0.0033 (08)	-0.0014 (07)

was not varied after converting the isotropic temperature factors into aniso-

Table 5. *Bond lengths and angles in hardystonite*
 The estimated standard deviations given in parentheses are $\times 10^4$ for
 bond lengths and $\times 10$ for bond angles

Bond lengths		Bond angles	
The ZnO_4 tetrahedron at point symmetry $\bar{4}$			
Zn—O(3) [4 ×]	1.937 (4) Å	O(3)—Zn—O(3') [2 ×]	112.3 (3)°
O(3)—O(3') [2 ×]	3.217 (8)	O(3)—Zn—O(3'') [4 ×]	108.1 (1)
O(3)—O(3'') [4 ×]	3.136 (8)		
The Si_2O_7 group at point symmetry $mm2$			
Si—O(1)	1.649 (3) Å	Si—O(1)—Si'	138.5 (3)°
Si—O(2)	1.583 (1)	O(1)—Si—O(2)	111.0 (2)
Si—O(3) [2 ×]	1.619 (4)	O(1)—Si—O(3) [2 ×]	101.4 (4)
O(1)—O(2)	2.664 (4)	O(3)—Si—O(3''')	103.5 (4)
O(1)—O(3) [2 ×]	2.529 (4)	O(3)—Si—O(2) [2 ×]	118.5 (2)
O(3)—O(3''')	2.543 (9)		
O(3)—O(2) [4 ×]	2.752 (4)		
The CaO_8 polyhedron at point symmetry m			
Ca—O(3) [2 ×]	2.412 (5)	O(2)—Ca—O(3) [2 ×]	66.8 (1)°
Ca—O(2)	2.472 (2)	O(3)—Ca—O(3')	63.6 (2)
Ca—O(1)	2.485 (4)	O(2)—Ca—O(2')	58.8 (2)
Ca—O(3''') [2 ×]	2.685 (5)	O(2)—Ca—O(3') [2 ×]	89.7 (1)
Ca—O(2') [2 ×]	2.700 (1)	O(2'')—Ca—O(3''') [2 ×]	84.7 (2)
O(1)—O(2'')	4.004 (1)	O(1)—Ca—O(3'') [2 ×]	58.4 (1)
O(3''')—O(3'')	5.043 (8)	O(1)—Ca—O(2'')	107.8 (2)
		O(3''')—Ca—O(3''')	139.8 (2)

by BUSING, MARTIN and LEVY (1964). The bond distances and bond angles in hardystonite (Table 5) do not include corrections for thermal movements.

4. Discussion

This study confirms the structure of hardystonite as obtained by WARREN and TRAUTZ (1930). The zinc tetrahedra are located at the corners and base-center of the primitive tetragonal lattice. All four tetrahedral oxygen atoms are shared by adjacent silicon tetrahedra, and the silicon tetrahedra are joined in pairs forming Si_2O_7 groups. The linkage of zinc and silicon tetrahedra results in an heterocyclic five-membered tetrahedral ring. The rings link together to form a corrugated sheet parallel to c (001), and the adjacent sheets are held together by Ca—O bonds.

The Zn—O bonding appears to have considerable covalent character. The mean Zn—O distance in zincite is 1.95 Å, and it varies from

2.08 to 1.96 Å for different zinc spinels (SLATER, 1965). The sum of tetrahedral covalent radii of oxygen and zinc is 1.97 Å (PAULING, 1960). In comparison, the distance of 1.937 Å in hardystonite is definitely shorter by a significant amount, and this distance compares well with the covalent Zn—O distance of 1.936 Å as obtained from the arithmetic mean of the shortest Zn—Zn distance (2.665 Å) in zinc metal and the O—O distance (1.207 Å) in the O₂ diatomic molecule. Using PAULING's (1960) arguments, this is a strong indication for the presence of covalent-bond character between zinc and oxygen. The bond angles (108° 5', four times; 112° 17', twice) within the ZnO₄ tetrahedron are almost regular, suggesting that zinc, using its *sp*³ hybrid orbitals, forms strong σ bonds with the oxygen atoms.

CRUICKSHANK (1961) has proposed the existence of π bonding in addition to σ bonding between Si and O atoms in silicates. For isolated Si₂O₇ groups he predicts distances of 1.656 Å to the bridging oxygen and 1.621 Å to the terminal oxygen atoms. In hardystonite the bridge-bond distance is 1.649 Å and there are two terminal-bond distances of 1.619 Å, which compare very well with predicted distances. The third terminal-bond distance of 1.583 Å is significantly shorter than the predicted distance.

Every oxygen atom in the structure has four nearest-neighbor cations in a distorted tetrahedral configuration, suggesting that every oxygen atom is in a state of partial *nonequivalent-sp*³ hybridization. This would increase the strength of σ bonds between oxygen and zinc, and of both σ and π bonds between oxygen and silicon. The terminal oxygen atom, O(3), is σ bonded both to silicon and zinc, indicating that the Si₂O₇ group in hardystonite cannot be considered as an isolated pyrosilicate ion. The effect of O(3) sharing its bonds between Si and Zn is to nearly equalize the Si—O(3) terminal bond and the Si—O(1) bridge bond, as for example, is found in hemimorphite, Zn₂Si₂O₇(OH)₂ · H₂O (McDONALD and CRUICKSHANK, 1967). This is not observed in hardystonite possibly because, the *nonequivalent-sp*³ hybridization of O(3) enhances the overlap between oxygen electrons and the *d* electrons of silicon, while the *d* electrons of zinc, buried in the ion core, do not take part in bonding. The apical oxygen atom, O(2), does not share its electrons in bonding with any other tetrahedral cations in the structure. SMITH and BAILEY (1963) observe that, for most corrugated Si₂O₅ sheets (which are comparable with the ZnSi₂O₇ sheet in hardystonite), the bond length to the unshared oxygen is

shorter than those to basal oxygen atoms. The short Si—O(2) distance in hardystonite is a result of double- to triple-bond character.

The CaO₈ polyhedron in hardystonite is a highly distorted square antiprism. The Ca—O distance for Ca in 8-coordination varies from 2.34 to 2.60 Å in different minerals. The bond distances and bond angles in the Ca polyhedron of hardystonite are given in Table 5. There is no evidence in these bond lengths for the presence of any significant covalent bonding. However, from the evidence that all oxygen atoms have some hybrid characteristics one may expect a certain amount of covalency in Ca—O bonds, especially in the Ca—O(3) and Ca—O(2) bonds. Using the argument of electrostatic-valence bond counts, SMITH (1953) has correlated the short Ca—O distances in melilite with the covalent character in these bonds. The distortion of the Ca polyhedron is more a consequence of bonding characteristics within the sheet than of any covalent bonding within the polyhedron. The mean of half of the bond angles (mean θ) at calcium is 57°21'. At such an angle, calculations of KEPERT (1965) show that the ligand-ligand repulsion energies tend to be minimal, thus enhancing the stability of the central ion in the polyhedron.

A consequence of such a description of bonding within the Si₂O₇ group in melilite-type structures is that, with different cation substitutions in the Zn or Ca sites, the dimensions of the Si₂O₇ group also vary. Specifically, with the increase in the covalency of bonding between oxygen atoms and cations other than Si, due to substitutions of different atomic species, there will be an increasing degree of equalization of bond lengths between the bridge bonds and terminal bonds of the pyrosilicate group.

Thus the structure of hardystonite can be summarized as consisting of [ZnSi₂O₇]⁻⁴ sheets within which the nature of bonding is dominantly covalent, the adjacent sheets being held together by Ca²⁺ ions with the interlayer bonding predominantly ionic in character.

Thus ZOLTAI'S (1960) classification of melilites as "two-dimensionally non-terminated, single-sheet, structure of tetrahedra" is more appropriate than the older description in terms of Si₂O₇ isolated sorosilicate groups.

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