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The crystal structure of macallisterite, $Mg_2[B_6O_7(OH)_6]_2$-$9H_2O$

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Cristallografia. — *The crystal structure of macallisterite,* $Mg_2[B_6O_7(OH)_6]_2 \cdot 9\,H_2O$ (*). Nota di ALBERTO DAL NEGRO, CESARE SABELLI e LUCIANO UNGARETTI, presentata (**) dal Socio G. CAROBBI.

RIASSUNTO. — La macallisterite è un borato idrato di magnesio di formula $2\,MgO \cdot 6\,B_2O_3 \cdot 15\,H_2O$. È stato descritto come minerale da Shaller, Vlisidis e Mrose nel 1965; lo stesso Shaller ha preparato sinteticamente un composto avente gli stessi dati strutturali di quello naturale. Il campione usato nel presente lavoro è di origine sintetica. Le costanti reticolari sono le seguenti: $a = 11.549$, $c = 35.567$ Å; nella cella elementare sono presenti sei unità stechiometriche e il gruppo spaziale è $R\bar{3}c$. Sono stati ripresi fotogrammi di Weissemberg e con le 987 riflessioni indipendenti è stata effettuata una sintesi di Patterson tridimensionale; in base alla sua interpretazione sono state eseguite delle sintesi di Fourier tridimensionali mediante le quali è stato possibile individuare tutti gli atomi presenti nella cella elementare. È stato portato a termine un raffinamento con il metodo dei minimi quadrati applicando alla fine fattori termici anisotropi a tutti gli atomi. Il fattore di discordanza finale per i riflessi osservati è 0.048. Nella struttura della macallisterite si possono individuare unità monomere costituite da un ottaedro magnesio–ossigeno, tre tetraedri e tre triangoli boro–ossigeno. In base a ciò la formula della macallisterite può essere più convenientemente scritta $Mg_2[B_6O_7(OH)_6]_2 \cdot 9\,H_2O$. Le unità monomere si collegano fra loro mediante una fitta rete di legami a idrogeno.

INTRODUCTION.

Macallisterite is a hydrous magnesium borate with formula $2\,MgO \cdot 6\,B_2O_3 \cdot 15\,H_2O$, described as new mineral by Shaller, Vlisidis and Mrose [1]. This mineral was found for the first time in the Death Valley region by James F. McAllister in 1954. It is possible to obtain this compound synthetically and both synthetic and natural material show the same crystallographic data [1].

Its occurrence and properties are fully described by Aristarain and Hurlbut [2]; we shall report here only the features necessary for the successive discussion.

The space group is $R\bar{3}c$ and the lattice parameters for the synthetic macallisterite are:

$a = 11.549 \pm 0.002$ Å
$c = 35.567 \pm 0.008$ Å
specific gravity calc. $= 1.864\,g \cdot cm^{-3}$
specific gravity meas. $= 1.868\,g \cdot cm^{-3}$.

Each unit cell contains six stoichiometric units:

$$2\,MgO \cdot 6\,B_2O_3 \cdot 15\,H_2O.$$

(*) Paper presented at the Congress of Associazione Italiana di Cristallografia, Torino, Italy, September 24–26, 1969.

This work was performed in the Sezione di Pavia (A. Dal Negro and L. Ungaretti, Istituto di Mineralogia, Università di Pavia) and Sezione di Firenze (C. Sabelli, Istituto di Mineralogia, Università di Firenze) del Centro Nazionale di Cristallografia del C.N.R.

(**) Nella seduta del 15 novembre 1969.

EXPERIMENTAL.

The specimen. Neither chemical analysis nor redetermination of the unit cell parameters were made on the sample used for this investigation. The crystal chosen for the structure determination was supplied by the Smithsonian Institution United States National Museum (no. 120873); the specimen was obtained synthetically by Shaller and it is a colorless prismatic fragment.

Recording and measurement of the intensities. The crystal was rotated about the *a* axis and Weissemberg equi-inclination photographs were obtained of the reciprocal levels with *h* from zero to 9 by using nickel filtered copper radiation and the multiple-film technique. A total of 987 independent reflexions out of the 1316 present in the CuK_α limiting sphere (about 75 %) were inspected; the intensities of 461 of them were measured with Nonius microdensitometer; the remaining 526 spots were too weak to be observed or accurately measured.

Correction and scaling of the intensities. The intensities were corrected for the Lorentz-polarization effect and for the incomplete $\alpha_1 - \alpha_2$ spot doubling. This correction is consistent with the application of the integration technique, that complicates the splitting-effect for its diagonal direction with respect to the sides of the film. No correction for the absorption was made because of the low value of the linear absorption coefficient.

Because of the particular crystallographic direction (*a* axis) assumed as rotation axis, in each *h k l* Weissemberg photograph ($h = 0$ to $h = 9$) there are reflexions equivalent for symmetry to reflexions present in different pictures. This fact allowed the reduction of all the measured intensities (2270) to a common relative scale, through an auto-scaling process accomplished according to the method of Hamilton *et al.* [3]. The calculation was carried out by means of the FILTRO computer program compiled in the Institute of Mineralogy of Pavia; with the same program the scaled intensities of the equivalent spots have been averaged in one value, which was assigned to all equivalent reflexions; consequently the 2270 reflexions photometrically measured reduced to 987 independent reflexions.

STRUCTURE ANALYSIS.

A three-dimensional Patterson synthesis was first computed. On this was derived information on the coordinates of the magnesium atoms on three-fold axes and of the oxygens linked to them octahedrically. With the coordinates of these atoms some consecutive three-dimensional Fourier syntheses were carried out; on them it was possible to locate the remaining atoms present in the unit cell with the obvious exclusion of hydrogens. A structure factors calculation with the coordinates so obtained gave an overall disagreement index $R = 0.118$.

TABLE I.

Structure factors of macallisterite.

Reflexions marked with a (*) were unobservably weak; in this case F_o derives from $0.5 \cdot I_{min}$.

H K	E	10Fo	10Fc
H K 0			
0 3*	105	-141	
-2 4	1729	-1603	
-1 5	1105	1188	
0 6	2965	3138	
-3 6	1603	3507	
-2 7	615	650	
-1 8	2353	2390	
-4 8*	233	-252	
0 9	2354	2388	
-3 9	883	613	
-2 10*	254	223	
-5 10	869	808	
-1 11*	237	-283	
-4 11*	289	350	
0 12*	187	252	
-3 12*	231	30	
-6 12	1427	1310	
-2 13	578	640	
-5 13	597	505	
-4 14	968	958	
-7 14	495	492	
H K 1			
1 -3	791	-947	
-1 4	1022	1086	
1 -6	712	739	
-2 6	1120	-1157	
-1 7	1356	1416	
3 -7	426	457	
2 -8*	196	63	
-3 8*	227	290	
1 -9	1233	1330	
-2 9	1308	1261	
4 -9	664	558	
-1 10	944	919	
3 -10*	229	-151	
-4 10*	353	-376	
2 -11*	238	-232	
-3 11*	237	-142	
5 -11	691	-649	
1 -12*	163	-50	
-2 12*	258	-280	
4 -12*	232	-144	
-5 12	861	-842	
3 -13*	189	-103	
-4 13*	218	-140	
6 -13*	211	-265	
5 -14*	134	-56	
-6 14*	137	14	
H K 2			
0 1	1986	2324	
0 -2	776	-780	
-1 3*	229	-293	
0 4*	184	-243	
1 -4	469	-480	
0 -5	1815	-1818	
-2 5	3045	2906	
-1 6	432	-444	
2 -6	1085	1009	
0 7	500	-588	
1 -7	727	-678	
-3 7*	394	454	
0 -8	1487	1567	
-2 8	409	-431	
3 -8*	195	-34	
-1 9	1381	1423	
2 -9	661	688	
-4 9*	215	-142	
1 -10*	217	-135	
1 -10*	207	-148	
4 -10*	258	275	
0 -11	938	-933	
-2 11*	238	19	
3 -11*	237	-34	
-5 11*	202	187	
-1 12*	199	169	
2 -12*	257	-217	
-4 12*	260	-136	
5 -12	768	739	
-3 13*	188	30	
4 -13*	218	175	
-6 13	384	-367	
-5 14*	133	-114	
6 -14*	148	-183	
H K 3			
-1 2*	75	53	
-2 4	3618	-3596	
-1 5	1170	-1105	
1 -5*	130	-144	
-2 7	616	-593	
2 -7	462	-461	
-1 8	444	456	
1 -8*	193	38	
-3 9*	225	21	
3 -9	667	-643	
-2 10*	254	152	
2 -10	761	778	
-5 10	532	462	
-1 11*	236	-153	
1 -11*	193	-32	
-4 11*	265	-231	
4 -11	511	-527	
-3 12*	230	-107	
3 -12*	230	132	
-6 12*	183	-109	
-2 13*	186	-293	
2 -13*	160	90	
-5 13*	181	32	
5 -13	516	449	
-4 14*	152	58	
4 -14*	152	292	
-7 14*	164	-168	
H K 4			
-1 1	1581	-1530	
0 2	2631	-2578	
-2 3	1832	-1849	
0 -4*	191	-233	
-1 4	613	776	
0 5	293	-322	
-3 5*	124	-97	
1 -6	1295	-1292	
-2 6	273	221	
0 -7	1069	-1166	
-1 7	1697	-1761	
-4 7	650	-598	
0 8	875	-915	
2 -8	1315	-1377	
-3 8	1634	-1673	
1 -9	403	-414	
-2 9	751	-778	
-5 9*	216	150	
0 -10*	216	-50	
-1 10	398	416	
3 -10*	230	-39	
-4 10*	407	-296	
0 11*	192	-153	
2 -11	607	-612	
-3 11	913	-886	
-6 11*	247	296	
1 -12	445	-438	
-2 12*	208	-34	
4 -12*	230	-83	
-5 12	557	-502	
3 -13*	228	-270	
-4 13	651	-623	
-1 13	412	-421	
5 -14	353	-407	
-6 14	634	-694	
H K 5			
-1 3	977	932	
-3 4	570	-529	
-2 5	1778	-1800	
-1 6	319	-322	
4 -6	362	-306	
1 -7	520	-466	
-3 7	1186	-1153	
2 -8*	249	-22	
-5 8	995	911	
1 -9*	207	67	
2 -9	846	-915	
-4 9	530	511	
1 -10	654	678	
-3 10*	336	-360	
5 -10*	236	-156	
-2 11*	290	-360	
3 -11*	289	421	
-5 11	441	381	
-1 12	1127	1127	
2 -12*	207	62	
-4 12*	230	83	
-7 12*	202	38	
3 -13*	184	-218	
-4 13	469	-480	
-6 13*	169	127	
5 -14*	129	148	
-8 14*	275	-201	
H K 6			
0 0	1334	-1483	
-1 2	509	-462	
0 3	1384	1347	
-1 3	2747	2684	
-2 4*	216	-188	
1 5	677	-605	
-4 5*	165	-203	
0 6	338	372	
-8 13*	210	-138	
-7 14*	148	216	
H K 10			
-1 1	3738	-3711	
2 1*	426	477	
-2 3*	126	-137	
-1 4	747	-778	
-4 4	1310	-1268	
3 4*	1798	-1798	
-3 5	3949	-3936	
-2 6	1944	-1932	
0 6	479	-534	
-1 7	846	-353	
-4 7	616	-567	
-7 7	397	418	
0 8	2141	-2270	
-1 8*	253	-217	
0 12	333	335	
-2 9*	332	-391	
-5 9	944	-852	
-8 9	1752	-1870	
0 -10	530	-612	
-1 10	795	-797	
-4 10	977	-920	
-7 10*	232	105	
0 11	403	-355	
-3 11	473	-447	
-6 11	1786	-1667	
-9 11	429	-436	
1 -12	361	-417	
-2 12*	196	-39	
-5 12	850	-851	
-1 12*	247	-153	
-4 13*	200	-2	
-7 13*	160	-34	
-10 13*	208	-199	
-4 14*	111	15	
-9 14	520	-499	
H K 11			
-1 2*	138	265	
-2 4	1482	-1460	
-1 9	1095	-1155	
-4 9	698	697	
-7 9*	225	253	
-3 10*	232	-86	
-6 10	855	-830	
-9 10*	248	357	
-2 11*	228	98	
-5 11	419	373	
-8 11*	231	-69	
-1 12*	381	134	
-4 12*	219	-159	
-7 12	558	-539	
-10 12*	192	33	
-3 13*	165	-17	
-6 13	412	-390	
-9 13*	260	146	
-5 14*	105	-189	
-8 14	295	361	
H K 12			
0 0	3414	-3391	
-1 2	670	688	
0 3	726	716	
-3 3	1226	-1193	
-2 4	1302	-1307	
-1 5	360	-421	
-4 5	574	-623	
0 6	900	866	
-3 6	2849	-2914	
-6 6	1251	1338	
-2 7*	241	284	
-5 7	443	385	
-1 8*	289	-371	
-4 8*	307	-296	
-7 8*	220	-239	
0 9	758	-738	
-3 9*	237	-147	
-6 9*	209	-139	
-9 9	1271	-1349	
-2 10*	333	-368	
-5 10	538	-522	
-8 10*	233	-97	
-1 11	391	356	
-4 11	569	-566	
-7 11*	230	-118	
-10 11*	179	42	
0 12*	124	64	
0 -12*	152	-225	
-3 12*	211	-99	
-6 12	520	-501	
-9 12*	259	-235	
-2 13	478	-544	
-5 13*	157	34	
-8 13*	162	-70	
-11 13*	128	-354	
-7 14*	190	239	
H K 13			
-2 3	1212	1241	
-1 4	699	664	
-3 5	783	801	
-6 5	521	540	
-5 6*	302	302	
-1 7	488	-498	
-4 7	385	-418	
-3 8*	214	-175	
-6 8*	186	-90	
-2 9*	227	-190	
-5 9	423	-393	
-8 9	923	1001	
-1 10*	245	-236	
-4 10*	215	-120	
-7 10*	232	-181	
-3 11*	278	334	
-6 11	639	-558	
-9 11*	273	262	
-12 11*	188	195	
-5 12*	213	264	
-8 12	410	-363	
-11 12*	169	131	
-4 13*	185	-85	
-7 13*	139	-175	
-10 13*	154	-7	
H K 14			
0 1	2746	-2541	
0 2	1691	1630	
-1 3	3133	3038	
0 4	822	832	
-3 4*	178	-141	
-2 5	1445	1413	
-5 5	492	616	
-1 6*	166	78	
-4 6	661	682	
0 6*	234	-213	
-3 6*	194	23	
-6 6	1371	-1407	
-2 7*	208	-35	
-5 7*	238	280	
-8 7	1122	1193	
-1 8*	178	-84	
-4 8*	755	844	
-7 8*	211	-165	
0 9*	810	776	
-3 9	1008	-957	
-6 9	835	-781	
-9 9*	211	10	
-2 10*	274	-325	
-5 10	431	-423	
-8 10*	224	-152	
-11 10	772	-821	
-4 11*	215	11	
-7 11	562	-548	
-10 11	670	-716	
-3 12	449	-434	
-6 12*	155	44	
-9 12	395	-425	
-5 13*	124	-83	
-8 13*	167	89	
H K 15			
-1 5*	209	246	
-4 5	679	676	
-3 6	513	491	
-6 6	728	-759	
-5 7*	225	-153	
-1 8	370	-375	
-4 8	638	578	
-7 8*	205	81	
-3 9*	212	-133	
-6 9*	212	-129	
-2 10*	282	-325	
-5 10*	237	22	
-8 10*	230	37	
-1 11*	170	37	
-4 11*	253	-331	
-7 11*	249	225	
-10 11*	170	-127	
-3 12*	243	234	
-6 12*	146	-31	
-9 12*	243	-277	
-5 13*	144	32	
-8 13*	157	10	
-11 13*	96	-81	
-7 14*	180	-43	
H K 16			
0 1	2021	1986	
0 2*	157	69	
-3 2*	160	212	
-1 4*	308	-224	
-4 4	842	808	
0 5*	205	31	
-3 5	349	321	
-2 6*	186	169	
-5 6	368	361	
-1 7	910	967	
-4 7	403	443	
-7 7	733	821	
0 8	579	592	
-3 8*	257	-264	
-6 8*	205	-24	
-2 9*	281	259	
-5 9*	264	-285	
-8 9	379	372	
-1 10*	193	136	
-4 10	836	762	
-7 10*	256	258	
-10 10	710	794	
0 11*	158	60	
-3 11*	219	1	
-9 11*	212	82	
-2 12*	207	-212	
-5 12*	219	260	
-8 12*	161	-443	
-11 12*	122	-110	
-4 13*	164	80	
-7 13*	213	207	
-10 13*	130	189	
H K 17			
-1 3*	166	-118	
-3 4	799	815	
-2 5	769	759	
-1 6	488	-471	
-4 6*	207	-209	
-3 7*	219	-172	
-6 7	358	-328	
-5 8	660	644	
-2 9*	227	-190	
-5 9	423	-393	
-8 9	923	1001	
-1 10*	245	-236	
-4 10*	215	-120	
-7 10*	232	-181	
-3 11*	278	334	
-6 11	639	-558	
-9 11*	273	262	
-12 11*	188	195	
-5 12*	213	264	
-8 12	410	-363	
-11 12*	169	131	
-4 13*	185	-85	
-7 13*	139	-175	
-10 13*	154	-7	
H K 18			
0 0	2267	2220	
-1 2	911	930	
0 3	3241	-3347	
-3 3	2244	-2329	
-2 4*	198	-138	
-5 4	602	-606	
0 8	1069	1097	
-3 8*	261	-311	
-6 8	458	-533	
-2 9*	222	-132	
-5 9*	280	300	
-8 9	703	749	
-1 10	403	470	
-4 10*	199	107	
-7 10*	260	318	
-10 10	352	-381	
0 11*	112	225	
-3 11*	189	192	
-6 11	880	798	
-9 11*	176	-138	
-2 12*	111	117	
-8 12*	297	256	
H K 19			
-2 3	413	-518	
-1 4	703	-693	
-3 5*	215	192	
-6 5	326	331	
-5 6	421	409	
-1 7*	231	-206	
-4 7*	227	-39	
-3 8*	267	-294	
-6 8	1286	-1327	
-2 9	952	931	
-5 9*	265	178	
-8 9*	222	-277	
-1 10*	183	141	
-4 10*	255	-331	
-7 10*	249	225	
-3 11*	207	102	
-6 11*	202	234	
-9 11*	196	-183	
-5 12*	199	-196	
-8 12	908	909	
11 12*	97	214	
-4 13*	130	-6	
-7 13*	117	-90	
H K 20			
0 1	1842	1905	
-2 2*	237	-314	
-1 3	775	-818	
0 4	954	1042	
-3 4	494	503	
-2 5	1906	1955	
-5 5	429	-401	
-1 6	414	659	
-4 6	1010	1097	
0 7	409	418	
-3 7	606	584	
-6 7	442	-529	
-2 8	983	-954	
-5 8	424	501	
-8 8	732	785	
-1 9	500	491	
-4 9*	232	-102	
-7 9*	278	345	
0 10	870	938	
-3 10*	220	105	
-6 10	996	959	
-9 10*	179	174	
-2 11*	190	40	
-5 11	1069	1003	
-8 11*	201	105	
-4 12*	198	-217	
-7 12*	194	230	
10 12*	138	-48	
-6 13*	103	-114	
H K 21			
-1 2	790	-822	
-2 4	1386	-1379	
-1 5	1241	-1260	
-4 5	529	-527	
-3 6	943	-1041	
-2 7*	266	-253	
-5 7	790	-759	
-1 8	739	783	
-4 8*	252	188	
-7 8*	226	-178	
-3 9	552	529	
-6 9	1015	1019	
-2 10*	242	283	
-5 10	604	556	
-8 10*	234	-243	
-1 11	365	-351	
-4 11	505	-529	
-7 11	470	400	
-3 12	611	-588	
-6 12*	139	-183	
-9 12	484	-489	
-5 13*	91	-173	
-8 13	255	-284	
H K 22			
-1 1	866	907	
0 2*	213	-266	
-2 3*	195	89	
1 4	648	655	
-4 4*	215	-151	
0 5	740	677	
-3 5	1687	1729	
-2 6	1000	1031	
-5 6	1366	-1394	
-1 7*	247	-278	
-4 7	860	912	
0 8	1069	1097	
-3 8*	261	-311	
-6 8	458	-533	
-2 9*	222	-132	
-5 9*	280	300	
-8 9	703	749	
-1 10	403	470	
-4 10*	199	107	
-7 10*	260	318	
-10 10	352	-381	
0 11*	112	225	
-3 11*	189	192	
-6 11	880	798	
-9 11*	176	-138	
-2 12*	111	117	
-8 12*	297	256	
H K 23			
-1 3	793	-797	
-3 4*	211	-22	
-2 5*	228	91	
-1 6	467	-514	
-4 6	587	611	
-3 7*	240	65	
-6 7*	299	332	
-5 8	457	-423	
-8 8	608	573	
-1 9*	195	88	
-4 9	604	-567	
-7 9*	268	-308	
-3 10*	207	-121	
-6 10	572	542	
-9 10*	163	-123	
-2 11*	168	107	
-5 11*	199	-250	
-8 11*	201	206	
-4 12*	142	132	
-7 12*	139	-169	
-10 12*	88	-37	
H K 24			
0 0	706	-775	
-1 2	1139	-1150	
0 3	1935	-2007	
-3 3	969	-1024	
-2 4*	286	-320	
-5 4*	228	187	
-4 5*	259	341	
0 6	1197	-1216	
-3 6	571	-565	
-6 6	1419	-1404	
-2 7*	256	224	
-5 7	741	-781	
-1 8	786	-778	
-4 8*	310	-378	
-7 8	855	-874	
0 9*	227	-226	
-3 9	853	-774	
-6 9	820	-779	
-9 9*	185	38	
-2 10*	303	-282	
-5 10*	232	257	
-8 10	511	-516	
-1 11	399	-383	
-4 11*	180	39	
-7 11	489	-475	
-10 11*	113	-26	
-3 12*	115	-413	
-6 12*	117	-107	
-9 12*	115	-477	
H K 25			
-2 3	1272	1289	
-1 4	977	1093	
-3 5	1041	1062	
-2 6	496	507	
-5 6	630	598	
-1 7*	203	-212	
-4 7*	243	-53	
-3 8	1055	-1016	
-6 8*	210	17	
-2 9*	210	50	
-5 9*	268	-201	
-8 9*	185	180	
-1 10*	150	192	
-4 10	718	-627	
-7 10*	195	104	
-3 11*	171	32	
-6 11*	255	-262	
-9 11*	148	-34	
-5 12*	376	386	
-8 12*	194	245	
H K 26			
0 1	1383	-1429	
-2 2	743	-772	
-1 3	607	-643	
0 4*	252	-291	
-3 4*	261	272	
-2 5*	694	-674	
-5 5*	265	-387	
-1 6	1133	-1140	
-4 6	538	-575	
0 7	755	-799	
-3 7*	243	10	
-6 7	806	-815	
-2 8*	373	-360	
-5 8	608	-562	
-8 8	507	-555	
-1 9	499	-494	
-4 9*	214	-16	
-7 9	630	-642	
0 10	448	-457	
-3 10*	226	264	
-6 10*	284	-428	
-9 10*	142	15	
-2 11*	165	-282	
-5 11	569	-507	
-8 11*	231	-393	
-4 12*	104	-76	
-7 12	494	-539	
H K 27			
-1 2	495	-534	
-2 4	649	673	
-1 5*	219	-27	
-4 5	778	-732	
-3 6*	245	199	
-6 6*	189	-172	
-2 7	645	617	
-5 7*	241	208	
-1 8*	232	-262	
-4 8*	246	43	
-7 8	421	-452	
-3 9*	190	-43	
-6 9*	233	-229	
-2 10*	172	-142	
-5 10*	171	45	
-8 10*	189	-151	
-4 11*	152	-30	
-7 11	341	-323	
-6 12*	73	90	
H K 28			
-1 1	1378	1480	
0 2	1163	1178	
-2 3*	236	22	
-1 4*	230	-250	
-4 4*	290	213	
0 5	1075	1010	
-3 5	809	-807	
-6 5*	258	-276	
-5 6	1425	1358	
-2 6*	200	171	
-7 6*	409	-499	
-4 7	869	941	
-1 7	464	431	
-7 7*	218	-44	
-3 8	1109	1000	
-6 8	621	569	
-2 9	442	411	
-5 9*	248	205	
-8 9*	203	213	
-1 10*	123	-36	
-4 10*	200	-238	
-7 10*	192	-251	
-10 10*	101	18	
-3 11*	131	111	
-6 11*	118	-81	
H K 29			
0 0	700	743	
-3 4*	232	125	
-2 5*	256	224	
-5 5*	257	-276	
-1 6	571	575	
-4 6	703	-672	
-7 6*	256	194	
-3 7	193	67	
-2 8*	339	316	
-5 8*	238	-260	
-1 9*	158	98	
-4 9*	223	196	
-7 9*	183	-65	
-3 10*	161	68	
-6 10	372	-342	
-9 10*	110	266	
-5 11*	107	-92	
-8 11*	198	-252	
H K 30			
0 0	627	-705	
-1 2	408	382	
-4 8*	189	194	
-3 3*	267	31	
0 3	1224	1282	
-2 4*	311	-276	
-5 4*	220	-191	
-4 5*	269	-325	
0 6*	198	22	
-3 6	821	-811	
-6 6	1194	1112	
-2 7	457	473	
-5 7*	211	82	
-1 8*	219	200	
-4 8*	282	312	
-7 8*	219	229	
-3 9*	133	-202	
-6 9*	169	175	
-9 9*	163	-276	
-2 10*	139	71	
-5 10	551	-491	
H K 31			
-2 3*	230	-60	
-1 4*	183	-61	
-3 5	667	-630	
-2 6*	217	-113	
-5 6*	210	-226	
-1 7*	183	8	
-4 7*	227	71	
-3 8*	236	288	
-6 8*	192	182	
-2 9	439	-411	
-5 9*	177	104	
-8 9*	149	220	
-1 10*	64	-36	
-4 10	409	394	
-7 10*	222	-219	
-6 11*	62	-234	
H K 32			
0 1	1211	-1255	
-2 2	552	-560	
-1 3*	401	451	
0 4	489	547	
-3 4*	269	-306	
-6 4	572	-611	
0 5*	134	13	
-5 5*	169	44	
-2 6*	131	116	
-5 6	393	-393	
-1 7*	119	-42	
H K 33			
0 0*	162	-34	
-1 2*	178	-195	
-2 3*	213	137	
-3 4	635	637	
-6 4	455	452	
-1 5*	108	35	
-4 5*	109	55	
H K 34			
0 1*	139	229	
-2 2*	125	53	
-1 3*	196	-317	
-3 4*	78	116	
-4 4*	226	-61	
0 5*	197	-46	
-3 5*	260	125	
-2 6*	200	171	
-5 6	482	454	
-1 7	464	431	
-4 7*	218	-44	
-7 7	384	389	
0 8*	128	146	
-3 8	654	677	
-6 8	348	348	
-2 9	402	408	
-5 9*	167	11	
-4 10*	79	-84	
H K 35			
-1 3*	244	299	
-3 4*	231	231	
-2 5*	214	121	
-1 6*	171	143	
-4 6*	222	254	
-3 7*	193	70	
-6 7*	151	-56	
-2 8	387	-366	
-5 8	466	-392	
-4 9*	125	8	
H K 36			
0 0	764	694	
-1 2*	309	339	
0 3	493	546	
-3 3	885	865	
-2 4*	329	416	
-1 5*	233	254	
-4 5	526	417	
0 6	742	719	
-3 6	834	870	
-6 6	712	668	
-2 7	436	419	
-5 7*	337	319	
-1 8*	194	210	
-4 8*	189	194	
-7 8*	104	64	
H K 37			
-2 3*	208	76	
-1 4*	203	109	
-3 5*	228	225	
-2 6*	247	-260	
-5 6*	152	-102	
-1 7*	196	265	
-4 7*	183	-203	
-3 8*	126	131	
-6 8*	98	12	
H K 38			
0 1	402	-371	
-2 2*	207	-110	
-1 3*	345	-323	
0 4	567	-610	
-3 4*	194	-152	
-5 5*	227	294	
-4 5	1015	-994	
-1 6*	530	-537	
-4 6*	161	185	
-2 7*	120	-142	
-3 7*	153	1	
-6 7	262	-262	
-2 8*	84	-360	
H K 39			
-1 2*	349	-341	
-2 4	734	-747	
-4 5*	159	75	
-3 6*	149	17	
-2 7*	116	130	
-4 8*	58	230	
H K 40			
-1 1*	177	163	
0 2	652	-620	
-3 3	465	-426	
-1 4	544	-519	
-4 4	572	-611	
0 5*	134	13	
-5 5*	169	44	
-2 6*	131	116	
-5 6	393	-393	
-1 7*	119	-42	
H K 41			
-1 3*	167	5	
-3 4*	191	275	
-2 5*	176	226	
-1 6*	88	-22	
H K 42			
-1 1*	177	163	
0 2	652	-620	
-3 3	465	-426	
-1 4	544	-519	
-4 4	572	-611	
0 5*	134	13	
-5 5*	169	44	
-2 6*	131	116	
-5 6	393	-393	
-1 7*	119	-42	
H K 43			
-2 3*	220	-267	
-1 4*	118	-2	
H K 44			
-1 3*	139	229	
-2 4*	125	53	
-1 5*	196	-317	
-3 6*	78	116	

TABLE II.

Fractional atomic coordinates and isotropic thermal parameters (standard deviations in parentheses).

The sign (*) marks the oxygen atoms belonging to hydroxyls. The sign (**) marks those belonging to water molecules. B is the equivalent isotropic temperature factor after Hamilton [4].

ATOM	x	y	z	B (Å^2)
Mg	0.0000	0.0000	0.1409 (1)	1.38
O(1) (*)	0.6957 (2)	0.4917 (2)	0.9400 (1)	1.60
O(2) (**)	0.5241 (3)	0.3378 (3)	0.0085 (1)	2.51
O(3)	0.1033 (2)	0.2367 (2)	0.0463 (1)	1.61
O(4)	0.2388 (2)	0.1345 (2)	0.0517 (1)	1.61
O(5)(**)	0.0000	0.1950 (3)	0.2500	2.18
O(6)(*)	0.3217 (2)	0.3530 (2)	0.9741 (1)	2.27
O(7)	0.0000	0.0000	0.0584 (1)	1.40
B(1)	0.1222 (4)	0.1372 (4)	0.0659 (1)	1.57
B(2)	0.2157 (4)	0.2381 (4)	0.9591 (1)	1.71

TABLE III.

Fractional coordinates of hydrogen atoms deduced from the Fourier difference map.

The isotropic thermal factors have been taken equal to those of the oxygen atoms at which hydrogens are linked.

ATOM	x	y	z
H(O_1)	0.752	0.597	0.945
H(O_2)	0.492	0.354	0.035
H(O_2)'	0.460	0.350	0.990
H(O_5)	0.450	0.400	0.095

TABLE IV.

Final anisotropic thermal parameters ($\times 10^4$) *and their standard deviations (in parentheses).*

The anisotropic temperature factors are in the form:

$$\exp\left[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\right]$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mg . .	33 (1)	33 (1)	3 (0)	16 (0)	0	0
O(1) . .	53 (3)	33 (2)	3 (0)	25 (2)	0 (0)	0 (0)
O(2) . .	58 (3)	107 (4)	4 (0)	55 (3)	2 (0)	0 (0)
O(3) . .	34 (3)	34 (3)	4 (0)	17 (2)	—2 (1)	0 (0)
O(4) . .	31 (2)	36 (2)	4 (0)	15 (2)	1 (1)	—2 (1)
O(5) . .	63 (5)	54 (3)	4 (0)	31 (2)	4 (1)	2 (0)
O(6) . .	38 (3)	44 (3)	6 (0)	13 (2)	—5 (1)	—5 (1)
O(7) . .	35 (2)	35 (2)	3 (0)	17 (1)	0	0
B(1) . .	44 (5)	43 (4)	3 (0)	24 (4)	1 (1)	—2 (1)
B(2) . .	47 (5)	57 (5)	3 (1)	30 (4)	3 (1)	1 (1)

The least-squares method was used in order to refine the positional parameters and the individual temperature factors. At first two cycles with isotropic thermal parameters were carried out using the Busing and Levy modified program; at this stage the disagreement index was: $R_{obs} = 0.075$. Then two more cycles of least-squares were carried out taking into account anisotropic thermal parameters: the disagreement index dropped to 0.052 for the observed reflexions. At this point a three-dimensional difference Fourier synthesis was carried out and on it some maxima appeared which could be due reasonably to hydrogen atoms. With the coordinates so derived two more cycles of least-squares were undertaken using anisotropic thermal parameters for all the atoms but hydrogens: the temperature factors of the latter were taken equal to the equivalent temperature factors after Hamilton [4] of the oxygens bonded to them. The introduction of the hydrogen atoms in the calculation lowered both the R_{obs} factor, from 0.052 to 0.048, and the standard deviations for positional and thermal parameters of the remaining atoms. According to the Hamilton test [5] the observed decrease of the R-factor was considered significant with a very high level of probability ($> 99\,\%$).

TABLE V.

Analysis of the anisotropic thermal parameters.

(root mean square thermal vibrations along the ellipsoid axes (Å), magnitudes of the principal axes (Å^2) and angles (°) between the crystallographic axes and the principal axes of the vibration ellipsoids).

ATOM	r.m.s.	B	α	β	γ
Mg	0.13	1.32	—	—	90
	0.14	1.47	90	90	0
	0.13	1.32	—	—	90
O(1)	0.14	1.52	88	88	3
	0.16	2.13	25	95	93
	0.12	1.15	115	5	92
O(2)	0.16	2.14	52	109	38
	0.23	4.27	89	31	90
	0.13	1.29	38	114	128
O(3)	0.13	1.38	99	21	93
	0.16	2.11	109	81	19
	0.13	1.27	21	108	71
O(4)	0.13	1.37	100	29	67
	0.17	2.20	72	116	26
	0.12	1.22	21	103	103
O(5)	0.16	2.03	120	0	90
	0.19	2.92	44	90	56
	0.14	1.62	119	90	34
O(6)	0.17	2.28	143	24	87
	0.21	3.41	101	102	23
	0.11	1.05	56	70	67
O(7)	0.13	1.41	—	—	90
	0.13	1.42	90	90	0
	0.13	1.40	—	—	90
B(1)	0.15	1.80	36	85	82
	0.16	1.96	114	36	126
	0.11	1.02	116	54	37
B(2)	0.16	1.93	145	51	121
	0.17	2.33	79	42	81
	0.11	0.98	123	76	33

The observed and calculated structure factors are given in Table I.

Positional and thermal parameters with their standard deviations are listed in Tables II, III, IV. The analysis of the anisotropic thermal parameters is shown in Table V. Interatomic distances, angles and their standard deviations are listed in Tables VI, VII.

TABLE VI.

Interatomic distances (Å), *angles and their standard deviations* (*in parentheses*).

ATOMS	BOND LENGHTS	ATOMS	BOND ANGLES
Mg—O(1)	2.079 (2)	O(1)—Mg—O(2)	95° 54′ (6′)
Mg—O(2)	2.071 (4)	O(1)—Mg—O(2′)	86° 25′ (6′)
		O(1)—Mg—O(1′)	89° 16′ (12′)
		O(2)—Mg—O(2′)	88° 49′ (14′)
		O(1)—Mg—O(2″)	173° 12′ (9′)
B(1)—O(1)	1.469 (4)	O(1)—B(1)—O(3)	111° 9′ (23′)
B(1)—O(3)	1.450 (6)	O(1)—B(1)—O(4)	111° 49′ (21′)
B(1)—O(4)	1.454 (6)	O(1)—B(1)—O(7)	106° 55′ (16′)
B(1)—O(7)	1.528 (6)	O(3)—B(1)—O(4)	110° 58′ (17′)
		O(3)—B(1)—O(7)	108° 8′ (19′)
		O(4)—B(1)—O(7)	107° 36′ (20′)
B(2)—O(3)	1.360 (4)	O(6)—B(2)—O(3)	116° 9′ (26′)
B(2)—O(4)	1.346 (6)	O(6)—B(2)—O(4)	119° 29′ (17′)
B(2)—O(6)	1.386 (6)	O(4)—B(2)—O(3)	124° 10′ (25′)

TABLE VII.

Distances and angles related to the hydrogen bonds; standard deviations in parentheses.

O(1)—O(3)	2.860 Å (3)
O(2)—O(5)	2.723 (2)
O(2)—O(6)	2.721 (5)
O(5)—O(4)	2.756 (3)
O(2)—O(6′)	3.153 (4)
O(2)—O(6″)	3.134 (4)
O(1)—H	1.068
O(2)—H	1.062
O(2)—H′	1.051
O(5)—H	1.010
H—O(2)—H	101° 36′
H—O(5)—H	102° 5′

Discussion.

The main feature of the crystal structure of macallisterite is the repeat of a unit formed by one Mg—O octahedron linked to a B—O polyanion (fig. 1). The latter is a $[B_6O_7(OH)_6]^{--}$ radical having an arrangement never found in other borates.

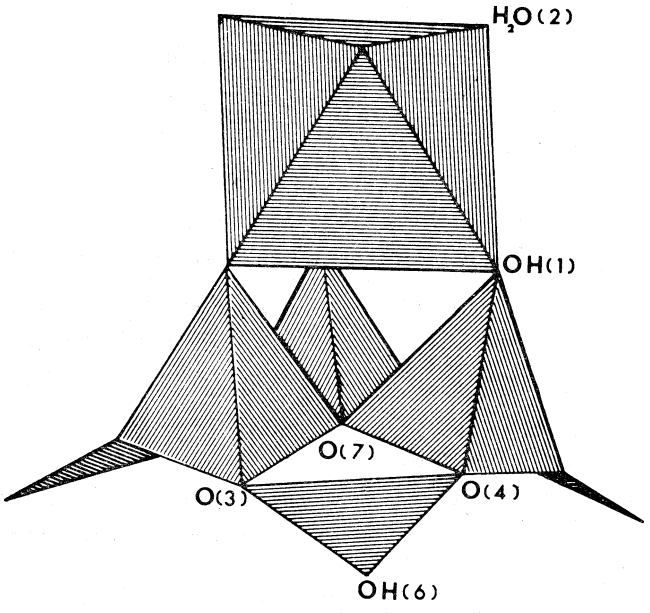

Fig. 1. – Clinographic projection of the monomeric Mg—O, B—O unit (with a rotation angle ϑ of 30° about the triad axis and an elevation angle φ of the same axis of 6° 20′).

Actually the polyanion (fig. 2) has a trigonal symmetry resulting from three B—O tetrahedra sharing a vertex and as many B—O triangles with two vertices common to different tetrahedra. The fourth vertex of tetrahedra, as well as the third of triangles, are occupied by hydroxyls, in agreement with the third Christ rule on the borates structure (hydroxyls occupy unshared vertices of B—O tetrahedra or triangles). This polyanion is the second example of a hydrated borate crystal structure with three borons linked to one oxygen. The first example of a similar arrangement has been found in tunellite [6].

As in other borates also in macallisterite it is possible to recognize six-membered boron-oxygen rings; each of them is formed by corner-sharing among two tetrahedra and one triangle. This six-membered B—O ring is not planar: its deviations from planarity are given in Table VIII. The

Mg—B—O units are aligned along the three-fold axes (fig. 3) and are repeated by two-fold axes or inversion centres. These units include all the oxygen atoms except one series of H_2O–oxygens, O(5), which are situated on two-fold axes and connect two Mg—O octahedra facing each other along a three-fold axis. The connection is made through hydrogen atoms of H_2O, O(2), molecules which are at the corners of the Mg—O octahedra. When the Mg—B—O units face with their B—O triangles, there is no strong direct

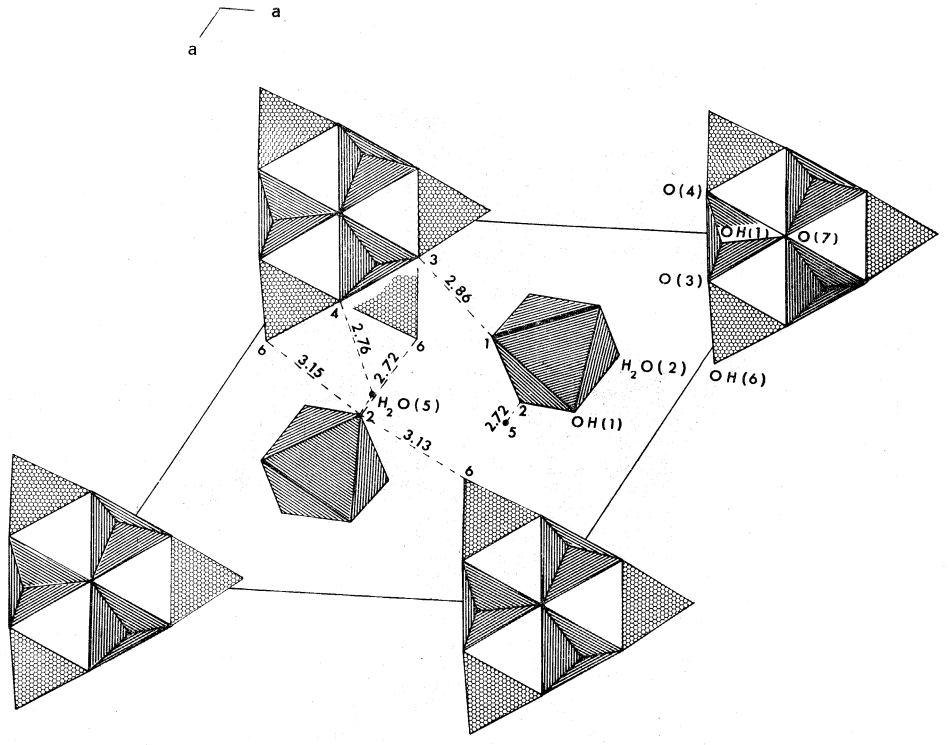

Fig. 2. – Projection of the cell slab with $-0.03 < z/c < 0.11$.

linkage between units lying on the same three-fold axes. The connection among units aligned along different three-fold axes is reached with a dense system of hydrogen bonds, which include bonds between O(6) hydroxyls and O(2) water molecules, O(1) hydroxyls and O(3) oxygens as well as between O(5) water molecules and O(4) oxygens.

Some very weak hydrogen bonds (3.15 Å) could be also possible among O(6) hydroxyls and O(2) water molecules, different from those mentioned above, but this fact would ask for a statistical distribution of a hydrogen between different positions. It may be worthy to remark that it was impossible to locate the hydrogen atom of O(6) hydroxyl in the difference synthesis.

In macallisterite the B—O distances and O—B—O angles agree with those known for both B—O tetrahedra and triangles. Also in macallisterite,

as happens in other borates [6, 7], the B—O(7) distance, concerning an oxygen atom linked to three different B atoms, is significantly larger then the remaining B—O lengths.

Mg—O octahedron is practically regular with an average distance Mg—O = 2.075 Å.

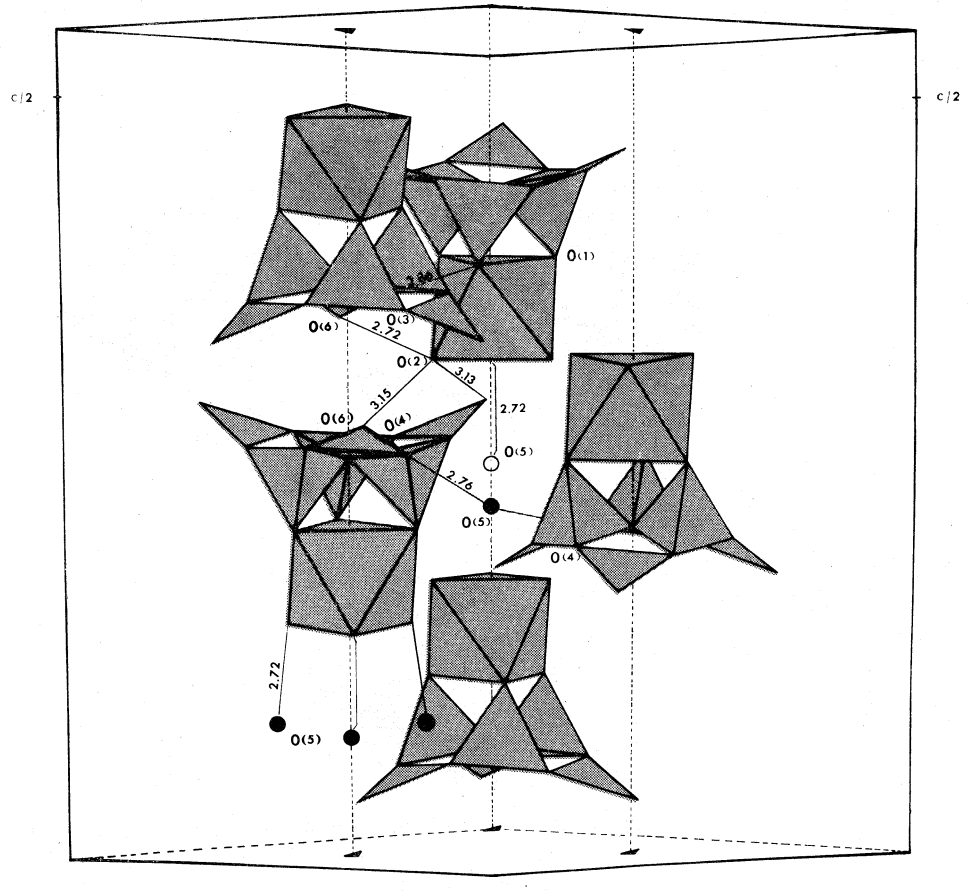

Fig. 3. – Clinographic projection of the half cell showing the arrangement of some monomeric unit (with a rotation angle ϑ of 30° about the triad axis and an elevation angle φ of the same axis of 6° 20′).

All hydrogen bonds, but the weak ones between O(6) and O(2), are comprised within generally accepted limits (Table VII). The distances between oxygens linked to the same magnesium are listed in Table IX, as well as those between oxygens belonging the same boron. The latter are not different from those found in other borates. The distance between boron atoms of two tetrahedra is 2.606 ± 0.004 Å and is slightly longer then analogous distances found in other borates but similar to those listed by Clark in tunellite for boron-boron distances around the triply linked oxygen. The distance between triangular and tetrahedral boron is 2.470 ± 0.004 Å.

TABLE VIII.

Ring angles, planes and deviations from planarity.

RING ATOMS	B—O—B angles (*)
B(1)—O(7)—B(1′)—O(3′)—B(2)—O(4)	B(1)—O(7)—B(1′) 117° B(1′)—O(3′)—B(2) 120° B(2)—O(4)—B(1) 124°

Equation, $0.9327\,x - 0.8015\,y + 17.1262\,z = 1$, of plane through the oxygens:

	x	y	z
O(3′)	0.1334	—0.1033	0.0463
O(4)	0.2388	0.1345	0.0517
O(7)	0.0000	0.0000	0.0584

ATOM	Distance from plane (**)
B(1)	+ 0.27 Å
B(1′)	+ 0.49
B(2)	— 0.19
O(6)	— 0.51

(*) The standard deviations are ± 25′.
(**) The standard deviations are ± 0.01 Å.

TABLE IX.

Oxygen-oxygen distances within the magnesium-oxygen and boron-oxygen polyhedra.

Octahedron around Mg		Tetrahedron around B(1)	
O(1)—O(2)	3.082 Å	O(1)—O(3)	2.408 Å
O(1)—O(1′)	2.921	O(1)—O(4)	2.420
O(1)—O(2′)	2.839	O(1)—O(7)	2.407
O(1)—O(2″)	4.141	O(3)—O(4)	2.393
O(2)—O(2′)	2.899	O(3)—O(7)	2.412
		O(4)—O(7)	2.407
		average	2.408
stand. dev.	± .004 Å	stand. dev.	± .003

Triangle around B(2)

O(3′)—O(4)	2.391 Å
O(3′)—O(6)	2.330
O(4)—O(6)	2.358
average	2.360
stand. dev.	± .004

The $[B_6O_7(OH)_6]^{--}$ polyanion in macallisterite is of the same kind as that described by Clark [6] in tunellite; in the latter case however, the polyanions are not in the monomeric form, but are polymerized in sheets according to the following reaction:

$$n\,[B_6O_7(OH)_6]^{--} \longrightarrow n\,[B_6O_9(OH)_2]^{--} + 2\,n\,H_2O.$$

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