Acta Cryst. (1967). **23**, 255

The Crystal Structure of Leucophanite*

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(*Received* 14 *November* 1966)

Leucophanite is a silicate of general formula $CaNaBeSi_2O_6F$. The space group assumed for this work is $P2_12_12_1$ with $a=7{\cdot}401$, $b=7{\cdot}420$, $c=9{\cdot}939$ Å, $Z=4$. The true space group is probably $P1$. The crystal structure has been solved, on the basis of its analogy with that of another silicate, melilite, from a three-dimensional Patterson synthesis. The final bond distances and angles are obtained from coordinates refined by the least-squares method applied to three-dimensional orthorhombic data (final R value: 9·4%). Triclinic refinement is in progress. The crystal structure consists of infinite sheets of BeO_4 and SiO_4 tetrahedra between which Ca and Na atoms are arranged. The relationships between the crystal structures of melilite and leucophanite are described and a hypothesis is advanced to explain the differences between them.

Introduction

Leucophanite is a late-magmatic silicate containing Ca, Na, Be and F. Its chemical and crystallographic data, cited by Strunz (1966) in the last edition of *Mineralogische Tabellen*, are derived from two papers by Zachariasen (1930, 1931) on leucophanite and meliphanite (another silicate closely related to leucophanite). According to Zachariasen these minerals could both be derived from the 'ideal' compound $Ca_2BeSi_2O_7$. The former would be obtained by replacing $\frac{1}{2}$Ca with Na and $\frac{1}{7}$O with F, the latter by replacing $\frac{1}{3}$Ca with Na, $\frac{1}{9}$Si with Al and an appropriate amount of O with F.

Zachariasen also considered that meliphanite, being only a little different from the ideal compound, would probably have a crystal structure very near to that of melilite $Ca_2MgSi_2O_7$ (Warren, 1930), because of the similar properties of Be and Mg. In fact both minerals are tetragonal and have almost identical cell parameters (taking into account the different orientation and the doubling of c in meliphanite). On the other hand, the replacement of O by F in leucophanite would exceed the threshold at which a distortion in the structure would occur producing a lower symmetry, in this case orthorhombic.

The structural model proposed by Warren was successively confirmed and refined by Smith (1953). The crystal structures of both meliphanite (Dal Negro, Rossi & Ungaretti, 1967) and leucophanite have been analysed in our laboratory.

Experimental

For the present work natural crystals from Brevig (Norway) were used. Two chemical analyses carried out by us are in substantial agreement with the published formula: $CaNaBeSi_2O_6F$.

The lattice parameters were determined at room temperature by measuring with a single-crystal diffractometer the 2θ values of appropriate reflexions and extrapolating the corresponding interplanar spacings, plotted against $\frac{1}{2}(\cos^2\theta/\sin\theta+\cos^2\theta/\theta)$, to $2\theta=180°$. The values so obtained are: $a=7{\cdot}401\pm0{\cdot}008$, $b=7{\cdot}420\pm0{\cdot}008$, $c=9{\cdot}939\pm0{\cdot}005$ Å.

The theoretical specific gravity computed on the basis of these cell parameters for $Z=4$ is 2·961, whereas the experimental one is 2·959 g.cm^{-3}.

The space group used for this work is $P2_12_12_1$ according to the following systematic absences: $h00$ with $h=2n+1$, $0k0$ with $k=2n+1$, $00l$ with $l=2n+1$ and to Zachariasen's considerations. Actually not only three $h00$ reflexions with $h=2n+1$ were detected, but a careful inspection of the X-ray pictures revealed slight differences in the intensities of hkl, $\bar{h}kl$, $hk\bar{l}$ and $\bar{h}k\bar{l}$ reflexions. These differences are significantly larger than the errors in measuring the intensities. So the true space group would be $P1$. However, it has been thought that the differences mentioned above are due to such small displacements from the orthorhombic symmetry as to be not essential in the determination of the crystal structure. For this reason the intensities of only one octant of the reciprocal sphere were measured. Of course the question must be reconsidered in the refinement.

A cylindrical specimen of leucophanite was used for recording intensities. The axis of the cylinder was parallel to the b axis and the radius was 0·016 cm. Weissenberg equi-inclination photographs of hkl (k from 0 to 6) reflexions were taken with nickel-filtered copper radiation, using the multiple film technique. A total of 628 independent reflexions in the space group $P2_12_12_1$ was inspected; 42 of them did not give any observable blackening on the films.

The intensities were measured with a Nonius microdensitometer and corrected for α_1–α_2 spot doubling and for Lorentz–polarization and absorption factors. The linear absorption coefficient is $\mu=147$ cm^{-1} for Cu $K\alpha$ radiation and the absorption factors $A^*=A^{-1}$ ranged

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* Paper presented at the VII Congress of the International Union of Crystallography, Moscow, USSR, July 1966.

from 7·5 to 51·5. A secondary extinction correction was applied during refinement.

The intensities of the different levels were approximately on the same scale owing to the equal exposure times. After each structure factor calculation the scale was improved by the criterion $\Sigma F_o = \Sigma F_c$, applied separately to each level.

Structure analysis

Patterson sections normal to [010] were computed and the determination of the crystal structure was carried out on the basis of the following considerations: (1) A comparison of the intensities of melilite with those of leucophanite revealed some relevant correspondences. (2) The cell parameters of melilite are: $a = 7{\cdot}789$, $c = 5{\cdot}018$ Å; if these values are compared with those of leucophanite, one can see that *a* and *b* of this mineral are nearly identical with *a* of melilite while *c* has twice the length. (3) An arrangement of cations in positions analogous to those occupied by cations in melilite therefore appeared very probable, since these positions have a symmetry consistent also with the space group $P2_12_12_1$. Furthermore such positions should be occupied, at least to a certain degree, by different cations in the two halves into which the leucophanite cell may be divided (*c* of leucophanite is twice *c* of melilite) in order to account for its lower symmetry. (4) An analysis of the relative heights of the maxima of convenient Patterson sections should permit the determination of the differences in the arrangement of the atoms in the two halves of the cell and consequently the kinds of atoms occupying each position.

Some different arrangements derived from the Patterson sections were examined by means of their effects on calculated electron density projections on a plane normal to [010]. The correctness of the chosen hypothesis was verified by means of a three-dimensional electron density synthesis in which all the atoms were detected. At this stage the discrepancy factor computed on all the observed reflexions was 0·36.

Refinement

The method of least squares was applied in order to minimize the unweighted differences $F_o - F_c$. The calculations were carried out with a program which takes into account the full matrix (Sgarlata, 1965); the structure factors were derived from the atomic scattering factors obtained from Moore's (1963) constants considering all the atoms as half-ionized. At first three cycles were accomplished assuming an isotropic tem-

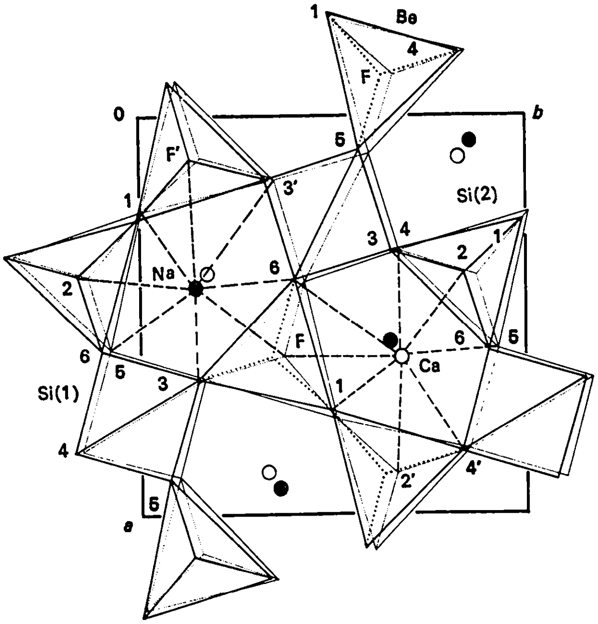

Fig. 1. Projection of the unit cell and key to the identification of the atoms and their coordination. The numbers without other specification refer to oxygen atoms.

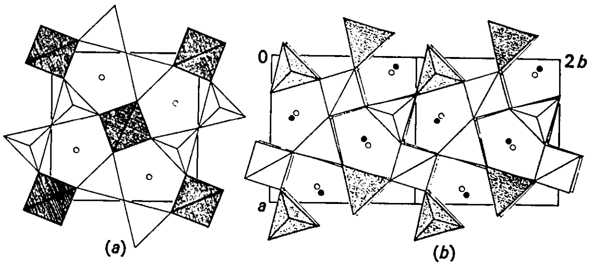

Fig. 2. (*a*) The crystal structure of melilite projected along [001]. (*b*) The crystal structure of leucophanite. Open circles: Ca; filled circles: Na; white tetrahedra: Si; hatched tetrahedra: Mg; dotted tetrahedra: Be.

Table 1. *Atomic coordinates and their estimated standard deviations* (*fractional* × 10⁴); *isotropic temperature factors*

	x/a	*y/b*	*z/c*	*B*
Ca	0·1050 (4)	0·8265 (5)	0·9894 (3)	1·23 Å²
Na	0·0670 (11)	0·8535 (13)	0·5059 (8)	2·33
Si(1)	0·7406 (5)	0·0132 (7)	0·2507 (4)	0·85
Si(2)	0·1080 (5)	0·1508 (7)	0·2265 (4)	0·71
Be	0·1091 (24)	0·1268 (50)	0·7174 (32)	1·84
O(1)	0·2421 (20)	0·0037 (23)	0·1623 (14)	1·38
O(2)	0·1052 (20)	0·1607 (29)	0·3829 (22)	1·46
O(3)	0·8382 (12)	0·8484 (21)	0·3381 (12)	1·28
O(4)	0·8383 (14)	0·8308 (20)	0·8476 (12)	1·33
O(5)	0·9130 (14)	0·0746 (19)	0·6574 (10)	1·46
O(6)	0·9087 (17)	0·1000 (18)	0·1627 (13)	1·35
F	0·1021 (13)	0·1315 (17)	0·8753 (9)	1·66

Table 2. *Structure factors of leucophanite* (× 10)

Reflexions marked with an asterisk were unobservably weak; in these cases F_o is derived from $\frac{1}{2}I_o$ min.

h 0 1

h	l	F_o	F_c	A	B
2	0	26*	20	20-	0
4	0	995	1018	1018-	0
6	0	940	965	965-	0
8	0	400	379	379+	0
1	1	222	165	0	165+
2	1	336	409	0	409+
3	1	94	91	0	91-
4	1	35*	6	0	6+
5	1	239	224	0	224-
6	1	316	309	0	309-
7	1	91	87	0	87+
8	1	215	201	0	201-
9	1	73	60	0	60+
0	2	490	505	505-	0
1	2	143	113	113-	0
2	2	700	755	755+	0
3	2	750	824	824+	0
4	2	300	307	307-	0
5	2	146	146	146+	0
6	2	122	94	94+	0
7	2	271	232	232-	0
8	2	256	231	231-	0
9	2	197	169	169-	0
1	3	327	373	0	373-
2	3	135	112	0	112+
3	3	106	105	0	105+
4	3	36*	64	0	64-
5	3	326	358	0	358+
6	3	259	250	0	250-
7	3	84	62	0	62-
8	3	98	89	0	89-
9	3	56	55	0	55-
0	4	364	348	348+	0
1	4	430	504	504+	0
2	4	65	48	48+	0
3	4	35*	45	45-	0
4	4	37*	43	43+	0
5	4	171	182	182-	0
6	4	433	449	449-	0
7	4	140	121	121-	0
8	4	241	233	233+	0
9	4	14*	79	79+	0
1	5	34*	33	0	33+
2	5	352	396	0	396+
3	5	37*	13	0	13+
4	5	38*	5	0	5-
5	5	153	153	0	153-
6	5	306	321	0	321-
7	5	108	98	0	98+
8	5	192	184	0	184-
0	6	718	731	731+	0
1	6	246	222	222-	0
2	6	310	321	321+	0
3	6	380	421	421-	0
4	6	387	448	448-	0
5	6	35*	25	25-	0
6	6	33*	20	20-	0
7	6	234	219	219+	0
8	6	185	155	155-	0
1	7	240	214	0	214-
2	7	54	39	0	39+
3	7	36*	11	0	11+
4	7	37*	27	0	27-
5	7	246	287	0	287+
6	7	92	83	0	83-
7	7	48	45	0	45-
0	8	853	874	874+	0
1	8	96	86	86+	0
2	8	38*	6	6+	0
3	8	441	487	487+	0
4	8	223	201	201-	0
5	8	32*	12	12+	0
6	8	379	401	401-	0
7	8	330	319	319-	0
1	9	224	185	0	185-
2	9	299	272	0	272+
3	9	100	91	0	91+
4	9	102	102	0	102+
5	9	78	65	0	65+
6	9	223	251	0	251-
0	10	133	141	141-	0
1	10	85	58	58+	0
2	10	362	332	332+	0
3	10	63	70	70-	0
4	10	270	249	249-	0
5	10	22*	31	31-	0
1	11	144	135	0	135-
2	11	68	50	0	50-
3	11	23*	32	0	32+
4	11	106	89	0	89-
0	12	372	379	379+	0
1	12	265	236	236+	0
2	12	141	139	139-	0
3	12	154	192	192+	0

h 1 1

h	l	F_o	F_c	A	B
1	0	21*	54	0	54+
2	0	242	230	230-	0
3	0	594	648	0	648+
4	0	446	463	463+	0
5	0	110	87	0	87-
6	0	154	161	161+	0
7	0	225	201	0	201-
8	0	185	115	115-	0
9	0	135	109	0	109-
0	1	261	275	0	275-
1	1	203	156	80+	134-
2	1	150	148	133-	67+
3	1	257	286	183-	221-
4	1	294	297	49+	293+
5	1	163	144	129-	65+
6	1	87	73	43-	60+
7	1	156	132	38+	127+
8	1	219	208	142+	152-
9	1	156	135	134+	23+
0	2	142	106	0	106+
1	2	572	603	200-	569+
2	2	986	1033	1033+	12-
3	2	257	271	261+	73+
4	2	330	388	331+	203+
5	2	291	302	48-	299+
6	2	364	364	286-	226-
7	2	188	141	51-	132-
8	2	262	228	228-	21+
9	2	75	68	55+	40+
0	3	376	414	0	414-
1	3	74	72	49-	54+
2	3	211	240	240+	3+
3	3	132	126	75-	102+
4	3	313	383	32+	382+
5	3	91	89	50-	74-
6	3	160	150	20-	149+
7	3	100	89	70+	55-
8	3	241	235	148-	183-
9	3	50	36	35+	11-
0	4	492	480	0	480-
1	4	329	374	372+	43-
2	4	565	680	678+	57-
3	4	694	857	231-	826+
4	4	189	184	151+	106+
5	4	285	305	114-	283-
6	4	299	295	82-	284+
7	4	66	66	14+	65+
8	4	107	103	42-	95-
0	5	55	18	0	18+
1	5	232	228	73+	217-
2	5	104	99	87-	48+
3	5	317	353	124-	331-
4	5	108	106	43+	97+
5	5	136	154	145-	54+
6	5	43	32	8+	31+
7	5	157	157	25+	155+
8	5	112	108	71+	82-
0	6	271	273	0	273+
1	6	434	440	360-	254+
2	6	493	539	536+	63+
3	6	385	452	147+	428-
4	6	447	522	482+	201-
5	6	433	519	365+	370+
6	6	198	192	188-	41-
7	6	169	176	14+	176-
8	6	352	316	314-	43+
0	7	308	287	0	287-
1	7	99	70	37-	60-
2	7	181	199	199+	4+
3	7	87	60	60-	10-
4	7	261	290	15+	290+
5	7	39*	26	0	26-
6	7	99	106	28-	103+
7	7	43	24	24+	1-
0	8	65	36	0	36-
1	8	123	97	93-	28-
2	8	134	74	73+	16-
3	8	544	566	117+	554+
4	8	215	215	76+	202+
5	8	176	172	23-	171-
6	8	100	106	9+	106-
7	8	36	25	16-	20-
0	9	42*	8	0	8-
1	9	137	126	105+	70-
2	9	58	42	17+	39+
3	9	204	197	95-	173-
4	9	111	97	83+	51+
5	9	124	134	134-	0
6	9	63	67	67-	3+
0	10	102	78	0	78-
1	10	368	324	79-	315+
2	10	245	219	219+	14+
3	10	136	95	50+	81+
4	10	40	27	13+	24-
5	10	174	167	137+	97+
0	11	209	185	0	185-
1	11	146	117	56-	103-
2	11	113	106	99+	40-
3	11	123	124	17+	123-
4	11	194	186	13+	186+
0	12	210	169	0	169-
1	12	191	181	83+	161-
2	12	253	223	218+	49-
3	12	56	65	58-	31+

h 2 1

h	l	F_o	F_c	A	B
1	0	247	230	0	230+
2	0	581	588	588-	0
3	0	78	64	0	64+
4	0	740	790	790+	0
5	0	416	424	0	424-
6	0	248	220	220-	0
7	0	61	51	0	51-
8	0	115	96	96+	0
9	0	243	225	0	225+
0	1	236	345	345-	0
1	1	219	201	127+	156-
2	1	134	139	0	139-
3	1	88	88	64+	61+
4	1	157	161	153+	53-
5	1	216	205	195-	64+
6	1	237	215	160+	145+
7	1	240	206	193-	73+
8	1	144	145	121-	80+
9	1	118	102	11-	102-
0	2	778	808	808-	0
1	2	1043	1003	31-	1003-
2	2	842	884	258+	846+
3	2	241	243	215+	114+
4	2	199	221	204-	87+
5	2	646	737	131-	726+
6	2	402	403	395+	80-
7	2	201	177	92+	152+
8	2	186	173	172-	25-
9	2	277	269	48-	265-
0	3	206	193	193+	0
1	3	206	237	213+	106+
2	3	291	291	12-	291-
3	3	233	232	205+	110-
4	3	95	91	85-	33-
5	3	161	161	161-	2+
6	3	155	149	114-	97+
7	3	278	281	273-	67-
8	3	140	132	83+	103+
9	3	113	107	29-	103+
0	4	154	116	116-	0
1	4	524	651	92-	645-
2	4	371	446	394-	210-
3	4	281	327	315-	91-
4	4	340	381	375+	69+
5	4	384	420	127+	401+
6	4	115	73	67+	30-
7	4	244	228	25+	227+
8	4	72	65	45+	47-
0	5	418	441	441-	0
1	5	107	84	79+	30+
2	5	257	278	63-	271-
3	5	73	87	14+	86+
4	5	189	214	201+	76-
5	5	175	176	127-	123-
6	5	234	239	171+	168+
7	5	119	104	91-	51+
8	5	156	138	89-	106+
0	6	352	322	322-	0
1	6	474	493	1-	493-
2	6	578	675	169+	654-
3	6	260	280	8+	280+
4	6	190	188	52-	181-
5	6	246	251	18+	251+
6	6	275	302	84+	291+
7	6	63	61	27-	55-
8	6	246	215	90-	196+
0	7	52*	2	2-	0
1	7	223	202	145+	142+
2	7	123	94	94-	0
3	7	212	198	170+	102-
4	7	51*	34	30+	18-
5	7	138	138	131-	44-
6	7	76	66	34+	57+
7	7	234	244	234-	71-
0	8	74	64	64-	0
1	8	153	111	55-	97-
2	8	443	451	264-	366+
3	8	68	47	23+	41-
4	8	308	325	322+	45+
5	8	58	57	46-	34+
6	8	95	83	10-	83-
7	8	147	136	120+	66+
0	9	240	222	222-	0
1	9	86	73	59-	44+
2	9	176	154	0	154-
3	9	117	80	80-	7-
4	9	99	99	91+	39-
5	9	91	81	29-	76-
6	9	130	108	74+	78+
0	10	361	350	350-	0
1	10	218	187	23-	186-
2	10	293	295	129+	266-
3	10	103	106	92-	54-
4	10	118	109	94-	57-
5	10	237	212	35+	210+
0	11	120	105	105-	0
1	11	197	196	185+	66+
2	11	94	73	62-	40-
3	11	201	207	205+	29-
4	11	107	105	105+	4-
0	12	131	125	125+	0
1	12	250	213	88-	195-
2	12	175	160	160-	2+

h 3 1

h	l	F_o	F_c	A	B
1	0	661	687	0	687-
2	0	38*	11	11-	0
3	0	998	993	0	993-
4	0	190	170	170+	0
5	0	316	296	0	296-
6	0	148	120	120+	0
7	0	689	721	0	721+
8	0	35*	14	14+	0
9	0	18*	87	0	87+
0	1	258	314	0	314+
1	1	254	236	231-	50+
2	1	130	125	98+	78+
3	1	213	248	244+	48-
4	1	159	159	115+	111-
5	1	301	303	295+	72+
6	1	246	230	219-	73-
7	1	111	77	58-	52-
8	1	31*	14	14+	4+
0	2	899	815	0	815+
1	2	236	210	190-	91-
2	2	239	222	39+	219-
3	2	483	543	31+	543-
4	2	152	168	11-	168-
5	2	173	144	89+	114+
6	2	46*	12	12+	2+
7	2	163	146	52+	137-
8	2	39	40	1-	40+
0	3	38*	6	0	6-
1	3	39*	17	12+	13-
2	3	248	272	259-	86+
3	3	217	235	178+	154+
4	3	198	211	209-	32+
5	3	137	103	74+	72-
6	3	222	213	209+	43-
7	3	59	58	55-	19-
8	3	77	71	65+	29-
0	4	42*	3	0	3-
1	4	771	932	289+	887-
2	4	251	270	113-	246+
3	4	231	200	78-	185-
4	4	232	235	43-	232-
5	4	234	246	176-	172-
6	4	196	178	58+	169-
7	4	337	368	53-	365+
8	4	159	123	91+	84+
0	5	147	124	0	124+
1	5	271	248	243-	54+
2	5	90	81	68+	45+
3	5	231	246	206+	135-
4	5	77	85	76+	40-
5	5	272	343	341+	42+
6	5	117	109	102-	39-
7	5	54	43	41-	15+
0	6	475	448	0	448-
1	6	396	411	74-	405+
2	6	222	222	220+	34-
3	6	414	497	55+	494-
4	6	235	278	166+	223+
5	6	92	89	74+	51+
6	6	86	92	5-	92+
7	6	69	64	16-	62-
0	7	169	113	0	113+
1	7	78	72	20-	70-
2	7	300	306	306-	21+
3	7	109	104	83+	64+
4	7	155	159	156-	33-
5	7	105	84	70+	47-
6	7	164	178	177+	20-
7	7	45	30	30-	1+
0	8	508	523	0	523+
1	8	552	559	42-	558-
2	8	141	136	102-	91-
3	8	271	257	8-	257-
4	8	209	249	26-	248-
5	8	159	161	10+	161-
6	8	110	96	54+	80-
0	9	119	88	0	88+
1	9	200	180	176-	41+
2	9	168	133	121-	56+
3	9	173	173	168+	43-
4	9	88	77	56-	53-
5	9	178	199	198+	25+
6	9	66	59	8-	59-
0	10	71	64	0	64-
1	10	162	121	62+	105-
2	10	110	97	69-	69+
3	10	316	335	5-	335-
4	10	88	74	61-	42-
5	10	154	147	38-	143+
0	11	29*	7	0	7+
1	11	81	66	66+	2+
2	11	88	82	82-	8+
3	11	63	63	21-	60+
0	12	206	204	0	204+
1	12	112	106	92+	54-

h 4 1

h	l	F_o	F_c	A	B
1	0	433	499	0	499+
2	0	688	705	705-	0
3	0	202	178	0	178-
4	0	990	990	990+	0
5	0	218	179	0	179-
6	0	118	86	86+	0
7	0	79	39	0	39-
8	0	88	70	70+	0
0	1	247	243	243+	0
1	1	234	279	225-	165-
2	1	171	181	174+	52-
3	1	279	300	269-	135+
4	1	316	310	302-	71+
5	1	122	103	72+	75+
6	1	160	149	41-	144+
7	1	192	235	233+	36+
8	1	46	41	17+	38+
0	2	263	273	273-	0
1	2	407	464	180-	428+
2	2	238	230	228+	34-
3	2	184	167	125-	112-
4	2	419	472	426-	204+
5	2	405	401	175-	361-
6	2	244	220	220+	9-
7	2	199	195	183+	69-
8	2	143	131	46-	123-
0	3	168	131	131+	0
1	3	280	298	193-	228+
2	3	116	123	84-	91+
3	3	206	247	211-	130-
4	3	104	116	86+	79+
5	3	171	177	140+	109-
6	3	75	60	44-	42+
7	3	193	212	200+	72-
8	3	78	53	11+	52+
0	4	100	85	85+	0
1	4	160	170	58-	160+
2	4	259	311	309-	41-
3	4	176	165	155-	58+
4	4	243	270	213+	166-
5	4	231	276	186+	205-
6	4	35*	16	6+	15+
7	4	53	38	9+	37-
8	4	106	102	42+	94+
0	5	163	61	61+	0
1	5	83	86	68-	53-
2	5	112	132	117+	63-
3	5	97	88	45-	76+
4	5	159	187	177-	61+
5	5	54	54	54+	3+
6	5	127	141	37-	137+
7	5	88	101	83+	59+
0	6	427	412	412-	0
1	6	566	585	196+	552+
2	6	294	299	68+	292+
3	6	315	375	277+	254-
4	6	63	72	53-	49+
5	6	274	329	2+	329-
6	6	184	191	113+	154-
7	6	193	185	175-	62-
0	7	112	87	87+	0
1	7	219	202	188+	74+
2	7	101	84	39-	75+
3	7	257	272	269-	45-
4	7	96	85	50+	69+
5	7	43	53	50+	20-
6	7	84	71	66-	27+
0	8	185	144	144-	0
1	8	208	180	148-	103+
2	8	272	266	266-	10+
3	8	171	157	157-	8-
4	8	300	331	303+	135+
5	8	145	112	57-	97-
6	8	50	36	34+	14-
0	9	157	158	158+	0
1	9	76	55	37-	42+
2	9	170	169	96+	140-
3	9	76	49	47-	17+
4	9	173	193	187-	50-
5	9	77	73	37+	63-
0	10	231	213	213-	0
1	10	80	70	48+	52+
2	10	188	184	118+	142+
3	10	35	42	39+	17+
4	10	112	141	141-	8+
0	11	195	181	181+	0
1	11	175	161	131-	95+
2	11	90	97	9-	97+

h 5 1

h	l	F_o	F_c	A	B
1	0	24*	16	0	16+
2	0	355	365	365+	0
3	0	411	413	0	413+
4	0	131	94	94-	0
5	0	96	60	0	60-
6	0	223	222	222-	0
7	0	133	109	0	109-
8	0	13*	13	13+	0
0	1	21*	1	0	1-
1	1	260	282	159+	234+
2	1	208	221	205-	85-
3	1	101	106	89-	58+
4	1	132	126	38+	121-
5	1	103	104	104-	4-
6	1	45	20	16-	13-
7	1	179	170	9-	170-
8	1	142	148	91+	117+
0	2	139	149	0	149-
1	2	327	327	51-	323+
2	2	635	722	711-	131-
3	2	127	143	137-	43-
4	2	349	360	311-	183+
5	2	147	139	121+	70+
6	2	259	256	256+	7+
7	2	259	235	100+	213-
0	3	289	276	0	276+
1	3	292	308	225+	210-
2	3	34*	20	17+	12+
3	3	34*	48	37-	31-
4	3	259	286	34-	284-
5	3	233	242	241-	31-
6	3	121	117	41+	110-
7	3	165	143	29-	141+
0	4	65	48	0	48+
1	4	196	215	138-	165-
2	4	366	423	414-	90-
3	4	327	364	149+	333+
4	4	145	157	123-	99-
5	4	247	271	34+	259-
6	4	23*	14	6+	13+
7	4	109	87	59-	64+
0	5	135	105	0	105-
1	5	374	361	221+	286+
2	5	163	142	131+	56-
3	5	181	206	98-	182+
4	5	30*	51	50+	11-
5	5	185	195	183-	70+
6	5	109	90	90-	4+
7	5	206	213	19-	213-
0	6	109	86	0	86-
1	6	494	494	296+	396+
2	6	267	248	248-	11-
3	6	104	121	121+	3-
4	6	257	283	280-	44+
5	6	326	378	311-	215+
6	6	185	159	148+	59+
0	7	180	169	0	169+
1	7	171	119	88+	81-
2	7	134	104	102+	22-
3	7	88	78	57-	54+
4	7	163	194	19+	194-
5	7	72	78	51-	60-
6	7	73	73	22-	70-
0	8	131	129	0	129-
1	8	155	142	66-	126-
2	8	108	107	45-	98-
3	8	228	235	57-	229+
4	8	183	160	34-	157+
5	8	178	194	122+	151-
0	9	34	25	0	25-
1	9	145	145	87+	117+
2	9	49	31	19+	25-
3	9	44	43	19-	39+
4	9	74	72	69+	22-
0	10	57	60	0	60-
1	10	178	176	104+	143+
2	10	205	206	204-	34+
3	10	63	72	43-	58-

h 6 1

h	l	F_o	F_c	A	B
1	0	182	218	0	218-
2	0	201	216	216-	0
3	0	186	151	0	151+
4	0	259	219	219-	0
5	0	250	240	0	240+
6	0	328	294	294-	0
7	0	19*	17	0	17+
0	1	91	76	76-	0
1	1	169	174	73+	158+
2	1	245	242	169+	174+
3	1	168	173	165+	53-
4	1	146	141	138-	30+
5	1	212	192	42+	188-
6	1	167	159	4-	159-
7	1	57	69	62-	31+
0	2	78	35	35-	0
1	2	284	279	229-	161+
2	2	362	394	376+	119-
3	2	44	20	1+	20-
4	2	268	269	268-	25-
5	2	98	81	4+	81-
6	2	65	31	21-	23+
7	2	68	60	11-	59-
0	3	46	34	34-	0
1	3	180	184	124+	136-
2	3	178	192	124-	147+
3	3	113	124	114+	50+
4	3	174	193	190+	39+
5	3	160	174	34+	171+
6	3	153	139	13-	139-
7	3	45	52	5-	52-
0	4	598	529	529+	0
1	4	282	316	316+	3-
2	4	98	100	63+	78-
3	4	168	206	183+	96+
4	4	132	136	123-	59-
5	4	34	37	34-	15+
6	4	356	376	373-	51+
0	5	32*	4	4+	0
1	5	42	41	40+	11-
2	5	290	341	70+	334-
3	5	83	97	97+	3+
4	5	116	153	128-	85+
5	5	57	57	23+	53-
6	5	185	233	71+	222-
0	6	103	61	61+	0
1	6	102	86	19-	84+
2	6	179	171	73+	155+
3	6	83	83	76-	35-
4	6	167	164	157-	50+
5	6	19*	5	4-	3+
0	7	70	62	62+	0
1	7	178	161	3-	161-
2	7	41	44	43-	11-
3	7	66	53	38+	37+
4	7	100	88	87+	14-
5	7	189	215	39+	212+
0	8	477	462	462+	0
1	8	100	85	44-	73-
2	8	160	165	13-	165-
3	8	130	138	113+	80+
4	8	102	129	121-	47-
0	9	94	82	82-	0
1	9	156	153	136+	71-
2	9	186	194	73+	180+
3	9	133	175	166+	57+

perature factor for each atom; the progress of refinement was indicated by a fall of the R value from 0·36 to 0·12.

Four more cycles with the attribution of anisotropic thermal factors to each atom followed by secondary extinction correction lowered R to 0·086. However this anisotropic refinement was not considered completely reliable because it was accomplished on data scaled by layers and only on the basis of the independent reflexions of the orthorhombic space group. Moreover the standard deviations of all the parameters are exceedingly high and thus seem to indicate that the parameters obtained for an atom (and its equivalents) in the space group $P2_12_12_1$ are an average of the independent values that could be obtained in the space group $P1$. However, these values would not be very different from those published here.

The anisotropic refinement will be carried out with all the independent triclinic reflexions. At the present time the refinement has been brought to completion as follows: a secondary extinction correction was calculated after the third isotropic least-squares cycle because a plot of ln I_c/I_o against I_c for the 104 most intense reflexions ($I_o > 1000$ on the absolute scale) indicated a conspicuous secondary extinction effect. A linear relation between $\ln I_c/I_o$ and I_c was assumed and a least-squares secondary extinction coefficient derived. This was applied as a correction to all the F_o's through the formula: $(F_o)_{\mathrm{corr}}=(F_o)_{\mathrm{ext}}\,.\,\exp(\frac{1}{2}\varepsilon I_c)$ where $\varepsilon=3{\cdot}739\,.\,10^{-5}$. The above correction lowered the R value to 0·097. After two more isotropic cycles, when the shifts were largely less than the standard deviations, the refinement was stopped.

The final R for 586 observed reflexions was 0·094 and 0·100 for all the 628 reflexions (giving to the unobserved ones a value half of the least observed intensity).

The atomic parameters, their standard deviations (Cruickshank, 1949) and the isotropic thermal parameters are shown in Table 1. The observed and calculated structure factors are presented in Table 2. Interatomic distances and angles are presented in Table 3 as well as their standard deviations (Ahmed & Cruickshank, 1953; Darlow, 1960). Reference should be made to Fig. 1 to identify the labelled atoms.

Discussion

The crystal structure of leucophanite is closely related to that of melilite. The two crystal structures are compared in Fig. 2. In melilite Si_2O_7 groups are present and are connected by MgO_4 tetrahedra to form sheets between which the calcium atoms are arranged. The sites occupied by Ca in the melilite structure are split in leucophanite into two series of positions occupied by Ca and Na respectively. Beryllium does not occur in the Mg site but in one of the Si sites, and one Si occupies the Mg site while the other lies in the same position as in melilite. So no Si_2O_7 group is present in

Table 3. *Interatomic distances, angles, and their standard deviations (in brackets)*

	Bond length	Mean
Si(1)O(5)	1·605 (11) Å	
O(4)	1·615 (14)	
O(6)	1·651 (13)	
O(3)	1·664 (14)	1·634 Å
Si(2)O(2)	1·556 (22)	
O(1)	1·607 (16)	
O(3)	1·649 (15)	
O(6)	1·649 (13)	1·615
BeO(1)	1·565 (32)	
F	1·570 (33)	
O(5)	1·616 (24)	
O(4)	1·691 (38)	1·610
CaO(2)	2·354 (19)	
O(5)	2·374 (13)	
O(1)	2·389 (15)	
O(2′)	2·393 (16)	
O(4)	2·425 (11)	
F	2·531 (12)	
O(4′)	2·639 (12)	
O(6)	3·032 (13)	
NaO(1)	2·352 (17)	
O(3)	2·377 (13)	
F	2·381 (14)	
O(5)	2·501 (14)	
O(6)	2·525 (15)	
O(2)	2·601 (23)	
F′	2·773 (12)	
O(3′)	2·945 (14)	

	Bond angle	Mean
O(5)Si(1)O(4)	112·3 (6)°	
O(6)	112·7 (6)	
O(3)	108·1 (7)	
O(4)Si(1)O(6)	108·0 (7)	
O(3)	111·8 (7)	
O(6)Si(1)O(3)	103·6 (6)	109·4°
O(2)Si(2)O(1)	115·9 (9)	
O(3)	110·5 (9)	
O(6)	112·5 (7)	
O(1)Si(2)O(3)	107·5 (7)	
O(6)	104·1 (7)	
O(3)Si(2)O(6)	105·6 (6)	109·3
O(1)BeF	112·7 (1·9)	
O(5)	110·8 (2·2)	
O(4)	104·9 (1·6)	
FBeO(5)	110·1 (1·5)	
O(4)	111·7 (2·1)	
O(5)BeO(4)	106·3 (2·0)	109·4

leucophanite, but zigzag chains of SiO_4 tetrahedra are formed and are nearly parallel to [010]. These chains are connected by BeO_4 tetrahedra to form sheets between which the atoms of Ca and Na lie. If, as Zoltai (1960) correctly suggests, no distinction is made between SiO_4, BeO_4 and MgO_4 tetrahedra, leucophanite can be classified as a single sheet silicate together with melilite (and meliphanite). The above mentioned chains could justify the $\{100\}$ and $\{101\}$ cleavages while the $\{001\}$ cleavage is due to the presence of the sheets.

The differences between the crystal structures of melilite and leucophanite can be due, according to Zachariasen, to the presence of fluorine in the latter. In fact in synthetic Be-akermanite (Goria, 1953) and gugiaite $Ca_2BeSi_2O_7$ (Peng, Tsao & Chou, 1962) there is a complete replacement of Mg by Be and presumably Be occupies the position of Mg and is connected with four Si atoms. The tetragonal symmetry is not modified: the space group of Be-akermanite and gugiaite is $P\bar{4}2_1m$; the cell parameters of the former are $a=7{\cdot}501$, $c=4{\cdot}931$ Å and of the latter $a=7{\cdot}48$, $c=5{\cdot}04$ Å. But if in leucophanite Be were to remain in the positions of Mg in melilite, fluorine would be connected with Si, and this does not generally happen in natural silicates.

The bond distances and angles of the tetrahedral cations are quite regular and comparable to those found in other silicates.

The bond distances of Ca and Na are listed in Table 3 in order of increasing length. It is rather difficult to decide what is the coordination number of these cations on the basis of these bond distances. Smith describes the coordination polyhedron of Ca in melilite as an archimedean antiprism built up by four atoms at about 2·44 Å and four at about 2·70 Å, but the resulting electrostatic equilibrium is unsatisfactory however one computes it. In the present case one can reject the eight-coordination for Ca and, perhaps, the seven-coordination for Na, because some distances are surely too long. Moreover a careful analysis shows that the interaction between Ca and Na and the seventh atom must be very little because in both cases this atom is nearly completely screened by other oxygen atoms. The sixfold coordination for both the cations gives also the least discrepancies in the electrostatic equilibrium. The sixfold coordination polyhedron of Ca is not an octahedron but resembles a trigonal prism; the length of its sides ranges from 2·65 to 3·65 Å. The sixfold coordination polyhedron of Na is a very distorted octahedron (sides ranging from 2·62 to 4·54 Å, O–Na–O angles ranging from 58 to 157°). For these reasons leucophanite does not seem to be referable to Belov's (1961) 'second chapter' silicates. However, no conclusive statement can be made before the triclinic refinement of the crystal structure.

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