⁵I. A. Dan'kov, O. V. Zvereva, V. I. Ivannikov, et al., *Kristallografiya* **36**, 504 (1991) [Sov. Phys. Crystallogr. **36**, 277 (1991)].

⁶O. Yu. Rekhlova and V. I. Andrianov, Kristallografiya 36, 1097 (1991) [Sov. Phys. Crystallogr. 36, 618 (1991)].

⁷V. I. Andrianov, T. A. Shibanova, and V. I. Simonov, *Kristallografiya* **32**, 41 (1987) [*Sov. Phys. Crystallogr.* **32**, 20 (1987)].

⁸N. Walker and D. Stuart, Acta Cryst. A39, 158 (1983).

- ⁹V. I. Andrianov, Kristallografiya **32**, 228 (1987) [Sov. Phys. Crystallogr. **32**, 130 (1987)].
- ¹⁰I. D. Brown, Acta Cryst. B41, 244 (1985).
- ¹¹F. Menil, J. Phys. Chem. Solids 46, 763 (1985).

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Crystal structure of revdite Na₁₆[Si₄O₆(OH)₅]₂[Si₈O₁₅(OH)₆](OH)₁₀ \cdot 28H₂O

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The authors have determined the crystal structure of revdite (Enraf-Nonius autodiffractometer, MoK α radiation, 1785 reflections). The parameters of the monoclinic unit cell are: a=53.83(4), b=9.972(9), c=6.907(4) Å, $\beta=96.78(1)^\circ$, space group C2. All the calculations were made by means of the AREN program system. Refinement of the model in the anisotropic approximation led to $R_{hkl}=0.084$. In the structure of revdite we distinguish two types of silicon-oxygen bands, not joined together. The first type consists of bands [Si₄O₆(OH)₅], geometrically close to the bands of the synthetic crystals Li₂Mg₂[Si₄O₁₁] and comparable to the bands of vlasovite. The second type of silicon-oxygen bands are a combination of two bands of the first type, displaced relative to one another. The combination of the above-mentioned (Si, O) bands in the framework of one structure is new in comparison with silicates and their analogs containing various tetrahedral complexes.

Revdite, a water-soluble sodium silicate with the empirical formula Na₂Si₂O₅·5H₂O, is a hydrated analog of natrosilite Na₂Si₂O₅ (Ref. 1). In 1976 for the first time revdite was established by A. P. Khomyakov in specimens of ussingite² in deep workings of the Lovozero alkali massif (Kola peninsula). It is represented by colorless isometric crystals measuring up to 2 mm and by dense granular aggregates with a dull or silky luster. The grains are easily split along cleavage planes into fine flexible fibers extending along [001]. The initial attempts to determine the crystal structure were unsuccessful owing to the poor quality of the crystals. Later, in fresh workings of the same massif, more perfect crystals of revdite were found. One fragment, measuring 0.40 × 0.20 × 0.15 mm, served as a material for monocrystalline surveying and determination of the crystal structure of revdite.

The initial dimensions of the unit cell of revdite, determined on an Enraf-Nonius diffractometer, were: a = 13.685, b = 4.986, c = 6.907 Å, $\alpha = 90$, $\beta = 96.67$, $\gamma = 100.45^{\circ}$. However, x-ray data found by the photographic method² indicated a cell with doubled parameters a and b. The experimental material, obtained on the same autodiffractometer, in the framework of a triclinic cell with parameters a = 27.37(4), b = 9.972(9), c = 6.907(4) Å, $\alpha = 90.00(6)$, $\beta = 96.67(7)$, $\gamma = 100.45(9)^{\circ}$, V = 1840.6 Å³, comprised $3167|F| \ge 3\delta_F$ (MoK α radiation, $\theta_{max} = 27^{\circ}$, ω -scanning). After averaging of equivalent reflections the set contained 2928|F|, among which the strongest reflections had even indices h and k, indicating the presence of pseudotranslations a/2 and b/2.

The structure was determined by the direct method on the basis of the AREN program system³ with the aid of an IBM PC/AT computer. Attempts to find a solution in the framework of the "large" triclinic unit cell, both in the centrosymmetric and in the acentric variant, were unsuccessful owing to the above-mentioned pseudoperiodicity: After normalization of the structural amplitudes, in the list of 450 greatest *E*, only two had an index $k \neq 2n$, and to the peaks of the *E*-syntheses there corresponded two or four equivalent ones, determining the translational pseudosymmetry. Therefore we used one of the devices suggested in Ref. 4: transition to a "small" cell, determined by the pseudotranslation vectors, with corresponding transformation of the indices of the reflections. Owing to the low quality of the experiment we did not succeed in obtaining, in the new cell, a model of



FIG. 1. Bands $[Si_4O_6(OH)_5]$ in (100) projection at level of about x/4.

Atom	x/a	y/b	z/c	B _{equ}
Sil	2025(1)	208(1)	680(1)	0,7(1)
Si2	2997(1)	492(1)	-10(1)	1,6(1)
Si3	2727(1)	498(1)	573(1)	1,6(1)
Si4	4522(1)	465(1)	680(1)	3,0(2)
Si5	4528(1)	28(1)	679(4)	2,6(2)
Si6	4528(1)	244(1)	8(2)	2,3(2)
Si7	2973(1)	282(1)	319(1)	1,2(1)
Si8	4741(1)	247(1)	430(2)	2,4(2)
Nal	3658(1)	489(2)	128(2)	3,1(2)
Na2	2082(1)	489(2)	957 (2)	2,8(2)
Na3	1302(1)	492(2)	833(1)	2,3(2)
Na4	3830(2)	250(2)	867 (2)	2,0(2)
Na5	463(2)	245(1)	14(2)	2,9(2)
Na6	5000	492(3)	0	1,9(5)
Na7	1175(2)	254(2)	134(2)	2,5(2)
Na8	5000	1(3)	0	1,3(5)
Na9	2507 (2)	265(2)	-5(2)	4,2(5)
01**	239(3)	252(2)	576(3)	1,3(3)
02*	2427 (2)	489(2)	502(2)	0,8(2)
03*	1727 (2)	235(2)	602(2)	1.9(3)
04**	2762(4)	153(3)	790(4)	2.5(5)
05*	1184(4)	505(4)	202(4)	1,9(5)
O6*	750 (2)	497 (3)	370(2)	2.5(2)
07*	2796(3)	146(2)	274(3)	1.3(3)
08	2920(2)	366(1)	105(2)	0,6(2)
09*	3813(4)	491 (3)	802(4)	2.0(5)
O10*	3661 (3)	256(2)	186(3)	1,7(4)
011*	1327(5)	252(3)	806(5)	2,2(5)
012*	4244(2)	493(3)	632(2)	1,9(2)
013	3265(2)	502(2)	948 (2)	1,4(2)
014**	4133(4)	496 (4)	216(3)	2,7(5)
015**	3510(3)	495(4)	448 (4)	3,1(4)
016	2081(3)	127(2)	852(3)	2,9(3)
O17**	1015(4)	258(2)	451 (4)	2,5(5)
O18**	1528(3)	489(3)	553(3)	2,9(4)
O19**	1602(4)	261 (4)	226(4)	3,0(5)
020	2776(2)	504(3)	810(2)	1,6(2)
021*	3258(3)	248(2)	382(3)	1,6(3)
022**	855(3)	505(3)	783(3)	1,6(3)
O23**	3401 (4)	261 (3)	777 (3)	1,5(4)
024**	4003(3)	252(2)	545(3)	2,3(3)
025	2863(3)	369(2)	486(4)	1,5(4)
O26**	1692(2)	512(2)	50(2)	1,8(2)
027	2127(4)	135(2)	506(4)	1,6(4)
028*	4211(4)	254(3)	46(4)	4,1 (5)
029	4593(3)	114(2)	885(3)	2,8(3)
O30	283(3)	398(2)	257(3)	2,9(3)
031*	2247 (3)	342(2)	194(3)	1,9(3)
032	4733(3)	238 (2)	197(3)	2,2(3)
033	2187(3)	339(2)	726(3)	1,3(3)
034	4598(3)	378(2)	888(3)	2,6(4)
035**	255(4)	394(3)	798(4)	3,8(4)
O36	4641 (3)	114(2)	496(3)	2,6(3)
037	4636(3)	382(2)	493(3)	2,5(3)
038**	260(4)	97 (3)	786(4)	4,0(4)
039*	282(3)	95(2)	257 (3)	3,6(4)
O40	5000	241 (3)	500	2,0(5)
041**	794(3)	248(2)	917(3)	2,6(3)

TABLE I. Revdite: Coordinates (for x, $\times 10^4$; for y and z, $\times 10^3$) of Basis Atoms and Equivalent Thermal Parameters

¹Values of anisotropic thermal factors may be obtained from the authors. *Hydroxyl atom.

**Water molecule.

Na-octahedra												
Nal - 013		2,32(1)	Na3 - 011*	2	,34(3)	N	Na4 — 028*	2,26(2)				
010*		2,36(2)	022**	2	,39(2)		023**	2,32(2)				
015*	*	2,43(2)	018**	2	,40(2)		09*	2,45(3)				
09*		2,49(3)	026**	2	,43(1)		O10*	2,47(2)				
014*	•	2,55(2)	010*	2	,64(2)		05*	2,48(3)				
011* 2,72(3)		05*	2	,70(3)		024**	2,51(2)					
(2,48)				(2,48)			(2,42)					
ł	Na	7 - 019**	2,31 (2)	İ	Na9 03	31*	2,20(2)	Í				
	041**		2,39(2)		04**		2.37(3)					
	017**]	08		2.47(1)					
011*			2,49(3)	1	033		2,48(2)					
	0.5*		2,55(3)		07*		2.61(2)					
	09*		2.65(3)		016		2.75(2)					
			(2,41)				(2,48)					
Na-antiprisms												
	Na	6 038**	2.39(3)	N	a8 — 03	5**	2.33(2)	<u> </u>				
	4	038**	2,39(3)	1	03	5**	2,33(2)					
		039*	2,42(2)		0	30	2,03(2)					
		039*	2.42(2)	ĺ	030		2.42(2)					
	034		2,48(2)		029		2.50(2)					
	034		2.48(2)		029		2,50(2)					
			(2.43)				(2.42)	[
l			Na-nyrami	ــــــ طو			1 (-1-4)	I				
<u> </u>	No	1 07644	2 27(1)		145 OA	1.8.9	1.07(2)					
		2,27(1)		035**		2,20(2)						
	031		2,29(2)	033**		2,29(2)						
	033		2,30(2)		030*		2,52(2)					
	0/		2,36(2)		039		2,52(2)					
	04		(2, 34)		030		(2 33)					
·												
Si-tetrahedra												
Si1 - 03*		1,65(1)	Si2 - 013	T	1,50(1)	T	Si3 — 025	1,62(2)				
016		1,44(2)	05*		1,57(1)	020		1,63(1)				
027		1,56(2)	020		1,61(1)		02*	1,63(1)				
033		1,57(2)	O16		1,81(2)		027	1,69(2)				
		(1,56)			(1,62)			(1,64)				
0-0 (2,54)		(2,54)	0 - 0		(2,64)		0 - 0	(2,68)				
Si4 — 012*		1,5,(1)	Si5 — O6*		1,52(1)		Si6 — O29	1,55(2)				
034		1,69(2)	029		1,66(2)		034	1,57(2)				
039*		1,69(2)	030		1,67(2)		032	1,68(2)				
037 1,70(2)		1,70(2)	036		1,69(2)		O28*	1,79(2)				
		(1,65)			(1,64)			(1,65)				
0 — 0		(2,68)	00		(2,66) 0 -		0 - 0	(2,70)				
Si7 — O21*		1,58(1)	Si8 — O40		1,42(1)							
025		1,60(2)	O36		1,52(2)							
07*		1,66(1)	037		1,54(2)							
08		1,69(1)	032		1,60(2)							
		(1,63)	1		(1,52)							
0 — 0		(2,65)	0-0		(2,48)	1						

the structure in the automatic mode, or a wide variation of the calculated parameters in the direct method. Therefore, in order to select the most reliably set of phases in the multivariant method we used⁵ the NQEST estimate, employing the ratios between the phases of four reflections (negative quartets). From the 398 strongest normalized structure amplitudes we generated 6000 triple products and in the automatic mode we compiled 46 negative quartets. After calculation of 64 phase variants, the multivariant method selected eight sets, having selected the second set as the best according to the ROC+NQEST criterion. The *E* synthesis constructed according to this set corresponded to $R_{hkl} = 0.188$. The method of successive approximations after four iterations reduced the value of the *R* index from 0.305 to 0.255 and revealed a fragment of the structure which, after the appropriate transition, served as the starting-point for correction of the phases in the complete cell in the acentric variant, and then in the space group $P\bar{1}$. The model of the structure obtained from 53



FIG. 2. Bands $[Si_8O_{15}(OH)_6]$ in (100) projection at level of about x/2.

electron density peaks, identified with the atoms Si, Na, and O, was refined in the isotropic approximation to $R_{hkl} = 0.23$. Analysis of the model revealed that the cause of its incompleteness and inaccuracy lies in the inaccurate choice of the unit cell and symmetry. The transition with the matrix 210/010/001 to the monoclinic cell with parameters a = 53.83(4), b = 9.972(9), c = 6.907(4) Å, $\beta = 96.78(1)^\circ$, V = 3680(8) Å³ enabled us to refine the structural fragment from 1785|F|, averaged in the space group C2, to $R_{hkl} = 0.16$ (in the space group C2/m the R index remained higher, about 0.20). From the F synthesis we located the missing atoms: one Si atom, three O atoms, and a water molecule. Refinement of the complete model reduced the R index to 0.132 in the isotropic approximation and 0.084 in the anisotropic one.

The final coordinates of the basis atoms and the interatomic distances are given in Tables I and II.

At this stage we formulated the crystal-chemical formula and determined the contents of the unit cell of revdite: Na₁₆[Si₄O₆(OH)₅]₂[Si₈O₁₅(OH)₆](OH)₁₀·28H₂O, Z = 2, $d_{exp} = 1.94$, $d_{calc} = 1.93$ g/cm³. In this formula, the O atoms, the OH groups, and the H₂O molecules are distinguished on the basis of a calculation of the local balance of valence forces on the anions.⁶

A characteristic feature of the structure of revdite is the presence of two different tetrahedral bands, not bound together. One of these is the band $[Si_4O_6(OH)_5]$ (Fig. 1), which geometrically resembles the bands of the synthetic crystals $Li_2Mg_2[Si_4O_{11}]$ (Ref. 7). The silicon-oxygen bands of both structures, constructed from fourfold tetrahedral rings, are readily compared with the more corrugated bands of vlasovite.⁸

The second silicon-oxygen complex of the revdite structure is unusual. This combination of two bands, lying at different levels along the x axis and mutually displaced, is of the first type (Fig. 2). The configuration of this complex (Si, O) anion with the formula $[Si_8O_{15}(OH)_6]$ is similar to the recently established tetrahedral group $[Si_8O_{21}]$ in the structure of the synthetic silicate $Cs_4(NbO)_2[Si_8O_{21}]$ (Ref. 9).

In the projections in Figs. 3 and 4 we clearly see the constitution of the whole structure, which can be described as an openwork framework of Na polyhedra, in the channels in



FIG. 3. Projection of revdite structure on (001) plane. Sodium polyhedra are marked by dots, (Si, O) tetrahedra by hachure, and water molecules by black circles.



FIG. 4. Projection of revdite structure on (010) plane. Notation: same as previous figure.

which there are single and double bands of Si tetrahedra, stretching along [001], and alternating along [100]. Of the nine independent Na atoms, five lie in octahedra, two in tetragonal pyramids, and two in trigonal antiprisms. The Na1, 3, 4, 7 polyhedra form columns parallel to [010] and joined by the Na2, 9 polyhedra, and also by the polyhedra Na5, 6, 8, which in turn form a hollow tube within which are the water molecules. The O1 atom of the H₂O molecule is not included in the Na5 polyhedron owing to the long distance Na5-O1 = 3.11 Å.

The combination of the above (Si, O) bands into a unified structure is new in respect of silicates and their analogs, characterized by the presence of different tetrahedral complexes.¹⁰ Apparently, the factor which reduces the stresses in this exceedingly unstable structure of revdite is the presence of "loose" low-discharge Na⁺ cations with fairly large coordination numbers, and also of easily polarized water molecules and (OH)⁻ groups.

¹I. M. Timoshenko, Yu. P. Men'shikov, L. F. Gannibal, and I. V. Bussen, Zap. Vsesoyuz. Mineral. Obshch., Pt. 103, No. 3, 317 (1975).

- ²A. P. Khomyakov, G. E. Cherepivskaya, T. A. Kurova, and V. P. Vlasyuk, Zap. Vsesoyuz. Mineral. Obshch., Pt. 109, No. 5, 566 (1980).
- ³V. I. Andrianov, Kristallografiya **32**, 228 (1987) [Sov. Phys. Crystallogr. **32**, 130 (1987)].
- ⁴V. I. Andrianov, Kristallografiya **32**, 1258 (1987) [Sov. Phys. Crystallogr. **32**, 742 (1987)].
- ⁵O. Yu. Rekhlova and V. I. Andrianov, Kristallografiya 36, 1097 (1991) [Sov. Phys. Crystallogr. 36, 618 (1991)].
- ⁶Yu. A. Pyatenko, Kristallografiya 17, 773 (1972) [Sov. Phys. Crystallogr. 17, 677 (1973)].
- ⁷W. V. Maresch and M. Czank, N. Jb. Miner. Mh. 7, 289 (1985).
- ⁸A. A. Voronkov, T. A. Zhdanov, Yu. A. Pyatenko, Kristallografiya 19, 252 (1974) [Sov. Phys. Crystallogr. 19, 152 (1974)].
- ⁹M. P. Crosnier, D. Guyomard, A. Verbaere, and Y. Piffard, Europ. J. Solid State Inorg. Chem. 27, 435 (1990).

¹⁰D. Yu. Pushcharovskii, Structural Mineralogy of the Silicates and Their Synthetic Analogs [in Russian], Nedra, Moscow (1986).

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X-ray structural investigation of the crystals of the monohydrate of *L*-arginine hydrobromide $C_6H_{14}O_2N_4HBr \cdot H_2O$

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By x-ray structural analysis the authors refine the crystal structure of L-arginine hydrobromide monohydrate $C_6H_{14}O_2N_4HBr \cdot H_2O$, the crystals of which were obtained from the system KBr-HBr-L-arginine-H₂O at pH=9 (molar ratio of KBr:L-arginine 1:1). The authors have made a comparative analysis of the structures of L-arginine hydrobromide monohydrate and the isostructural L-arginine hydrochloride monohydrate. On the basis of the revealed differences in the structures they explain the difference in the nonlinear optical properties of the crystals of these compounds.

INTRODUCTION

In contemporary technology increasing use is being made of new organic materials with high nonlinear characteristics. Some of them are crystals of salts of L-arginine. Among these compounds the leader is L-arginine phosphate monohydrate (LAP) and its deuterated analog (d-LAP) (Ref. 1). It is reckoned that the guanidine and carboxyl groups of L-arginine are "responsible" for the nonlinear-optical properties of these compounds. In the opinion of the same authors, the hydrogen bonds and anions in the structure do not in themselves have an appreciable influence on the nonlinear-optical properties of the materials, but only form the mutual arrangement of the carboxyl and guanidine groups of the different molecules. However, as shown by investigations on powders,² there is marked difference in the intensities of the second harmonics not only in LAP and L-arginine hydrobromide monohydrate (LAB), which belong to the same space group $P2_1$ but have different structures, 3,4 but also in the isostructural LAB and L-arginine hydrochloride monohydrate (LACh).⁵

1966 with poor accuracy (photographic method, R = 0.102), therefore for a detailed comparison of its geometrical parameters with the corresponding values for *LACh*, it appeared expedient to refine the structure of *LAB* from diffractometric data.

Note that, as shown by investigations of its physical properties, *LAB* is a good piezoelectric material.⁶ Its piezo-modulus d_{211} is three times as great as the d_{111} coefficient of quartz.

PREPARATION OF CRYSTALS

Crystals of *LAB* are, as a rule, obtained from solutions containing *L*-arginine and HBr at pH = 3.4 (Ref. 6). We studied the behavior of the system $C_6H_{14}O_2N_4$ -KBr-HBr- H_2O with a 1:1 molar ratio of *L*-arginine to KBr. At pH = 9we obtained single crystals by slow evaporation at room temperature. According to the chemical analysis data, the resulting single crystals contained 29.68% Br, 20.42% N, 17.21% O and 26.30% C. For the formula of *LAB* we calculated $C_6H_{14}O_2N_4$ HBr·H₂O: 29.25% Br, 20.51% N, 17.57%

Since the structure of LAB (Ref. 4) was determined in