blocks. The limits to extension fo the library are quite high (up to $10^4$-$3 \cdot 10^4$ statements), since magnetic tape can be used for storage of the library. One section of the operative memory and three sections of the magnetic drum are used when the minimum set of "Refleks-2" as described in the present paper is operated. The computation rate depends on the procedures used for evaluating the set of reflections and on the length of the latter set. If the block of information input, the block for averaging equivalent reflections, the editing block, and the output block (the blocks which take the longest computation time) are included in the list of blocks to be used, evaluation of a set of data on 1500 reflections takes from 40 min to 3/2 h.

The program "Refleks-2" can be used for evaluating the information from any single-crystal diffractometer. The program blocks are described and instructions for their operation are given in ref. 10.

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1) If the printing block is indicated in the list of blocks to be used.
2) For this purpose the corresponding entering blocks for "Rentgen" or

"Kristall" should be indicated in the list of blocks to be used.

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Translated by Simon Kruyer

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# Crystal structure of strontioborite Sr[B₈O₁₁(OH)₄]

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The crystal structure of strontioborite ($a = 9.909 \pm 0.005$, $b = 8.130 \pm 0.010$, $c = 7.623 \pm 0.001$ Å, $\beta = 108.4 \pm 0.2^0$, space group $p2_1$, $Z = 2$) is solved by the heavy-atom method and refined to $R = 0.11$ by sucessive electron-density syntheses and the method of least squares. The structure contains a new boron-oxygen radical $[B_8O_{11}(OH)_4]^{2-}$. The composition established in the course of the solution corresponds to the formula $Sr[B_8O_{11}(OH)_4] = SrO \cdot 4B_2O_3 \cdot 2H_2O$ and differs considerably from that obtained earlier.

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Strontioborite was discovered and described by V. V. Lobanova[1] as the first magnesio–strontium borate of composition $4(Sr_{0.75}Ca_{0.25}) O \cdot 2MgO \cdot 12B_2O_3 \cdot 9H_2O$. Later the dimensions of the unit cell ($a = 9.80 \pm 0.03$, $b = 8.22 \pm 0.02$, $c = 7.55 \pm 0.2$ Å, $\beta = 107°46' \pm 10'$, space group $P2_1$) obtained by V. V. Kondrat'eva cast doubt on the chemical formula of the mineral.[2]

In an x-ray analysis of crystals with the composition $CaO \cdot 4B_2O_3 \cdot 2H_2O$ (synthesis and properties described in ref. 3) we found all the signs to indicate that this crystal might be isostructural with strontioborite. The coincidence of the space group ($P2_1$), the similarity between the lattice constants ($a = 9.88$, $b = 8.28$, $c = 7.43$ Å, $\beta = 108°$), the x-ray powder photographs, and the intensities of the reflections in the x-ray goniometrical scans of the synthetic and natural borates led us to assign a composition of $Sr, Ca, Mg) O \cdot 4B_2O_3 \cdot 2H_2O$ to strontioborite when solving its structure.

The strontioborite sample was kindly presented to us by I. I. Khalturina. The small amount of the mineral available prevented us from making a complete chemical analysis. The lattice constants refined in the DRON-1 diffrac-

tometer were $a = 9.909 \pm 0.005$, $b = 8.130 \pm 0.010$, $c = 7.623 \pm 0.001$ Å, $\beta = 108.4 \pm 0.2°$, $d_{meas} = 2.40$ g/cm³.

In order to record the diffraction pattern we selected a lamellar type of crystal with dimensions of $0.4 \times 0.3 \times 0.1$ mm. The experimental material included the intensities of 722 independent, nonzero reflections of the kh0 − hk4 type (equiinclinational Weissenberg goniometer, Cu $K\alpha$ radiation). The intensities were estimated visually by reference to a standard $\sqrt[4]{2}$ photometric density scale. In converting the intensities to $|F_e|$ we introduced corrections for the polarization and Lorentz factors but made no allowance for absorption and extinction.

The structure was solved by the heavy-atom method. Analysis of the peak distributions of the three-dimensional Patterson function enabled us unequivocally to select the $P2_1$ space group from the two possible groups ($P2_1$ and $P2_1/m$) indicated by the systematic extinctions, and also to determine the coordinates of the Sr atom. The Sr coordinates served as initial data for constructing the first electron-density synthesis. The uncertainty factor R at this stage was 0.33. Subsequently, by alternating successive Fourier syntheses with stages of refining the po-

TABLE 1. Coordinates of the Basic Atoms Together with Their Isotropic Temperature Factors (standard deviations in brackets)

| Atoms | $x/a$ | $y/b$ | $z/c$ | $B, Å^2$ |
|---|---|---|---|---|
| Sr | 0.2804(2) | 0.1000 | 0.1149(5) | 0.31(3) |
| O(1) | 0.759(2) | 0.123(5) | 0.027(3) | 0.3(3) |
| O(2) | 0.532(2) | 0.093(3) | 0.084(4) | 1.0(4) |
| O(3) | 0.600(2) | 0.347(3) | 0.009(4) | 0.6(4) |
| O(4) | 0.005(2) | 0.096(5) | 0.043(3) | 0.7(3) |
| O(5) | 0.335(2) | 0.580(3) | 0.293(4) | 1.0(3) |
| O(6) * | 0.212(2) | 0.077(2) | 0.424(4) | 1.1(4) |
| O(7) | 0.160(2) | 0.395(3) | 0.118(4) | 0.3(5) |
| O(8) | 0.580(2) | 0.615(2) | 0.314(3) | 0.5(4) |
| O(9) * | 0.489(2) | 0.149(3) | 0.424(4) | 0.9(4) |
| O(10) | 0.384(2) | 0.375(3) | 0.077(5) | 0.5(4) |
| O(11) | 0.715(2) | 0.214(2) | 0.209(4) | 0.6(4) |
| O(12) | 0.949(2) | 0.196(3) | 0.303(5) | 0.5(4) |
| O(13) * | 0.085(3) | 0.675(3) | 0.411(4) | 2.3(4) |
| O(14) * | 0.796(2) | 0.568(3) | 0.159(4) | 1.9(6) |
| O(15) | 0.907(2) | 0.358(3) | 0.031(4) | 0.4(4) |
| B(1) | 0.478(3) | 0.606(5) | 0.085(7) | 0.9(6) |
| B(2) | 0.018(4) | 0.437(4) | 0.024(8) | 0.4(6) |
| B(3) | 0.281(3) | 0.484(4) | 0.111(8) | 0.4(6) |
| B(4) | 0.484(4) | 0.436(4) | 0.014(8) | 0.2(6) |
| B(5) | 0.643(4) | 0.196(4) | 0.094(8) | 1.1(6) |
| B(6) | 0.910(4) | 0.188(5) | 0.104(8) | 0.1(5) |
| B(7) | 0.723(3) | 0.604(5) | 0.390(6) | 0.2(5) |
| B(8) | 0.861(3) | 0.197(4) | 0.411(7) | 0.2(5) |

Note: The asterisks in Tables 1-3 signify O atoms in OH groups.

sition parameters and difference syntheses, we located the light O and B atoms. All the calculations were carried out in accordance with the "Kristall" complex of programs devised for the 220M electronic computer.[4] We used the atomic scattering factors of the neutral atoms.[5]

At the same time as determining the structural motif we refined the chemical composition of the borate in question. Refinement of the Sr multiplicity factor indicated that the borate was purely a strontium compound. The number of light atoms located in the independent part of the cell was 23, including 15 O atoms and 8 B. The sample composition thus corresponds to the formula $SrO \cdot 4B_2O_3 \cdot 2H_2O$, $d_{calc} = 2.38$ g/cm$^3$ (close to the experimental density), with $Z = 2$. This composition differs considerably from that pro-posed by Lobanova; the difference is not due to the individual characteristics of the samples, since their powder patterns are identical.

Refinement of the structure by the method of least squares followed the program of ref. 6. The uncertainty factor amounted to 0.13 after refining the position parameters with $B_{gen} = 0.4$ A$^2$; refinement of B reduced the R factor to 0.11. The final set of coordinates and individual temperature factors is presented in Table 1 together with the standard deviations.

The structure of strontioborite is of a layer-like character. The layers lie at a small angle to the (001) plane and consist of polymerized polyanions of composition $[B_8O_{11}(OH)_4]^{2-}$ and $Sr^{2+}$ cations. Each polyanion is connected to four similar polyanions by common vertices,
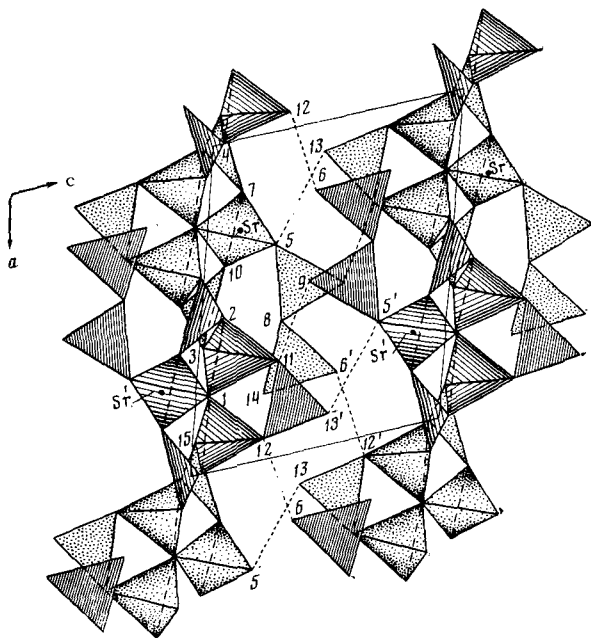


Fig. 1. Projection of the strontioborite structure along the b axis. The numbers denote the base atoms; the primes denote those related to the former by symmetry operations; the dashed lines indicate hydrogen bonds; the polyanions linked by a screw axis are distinguished by different shadings.
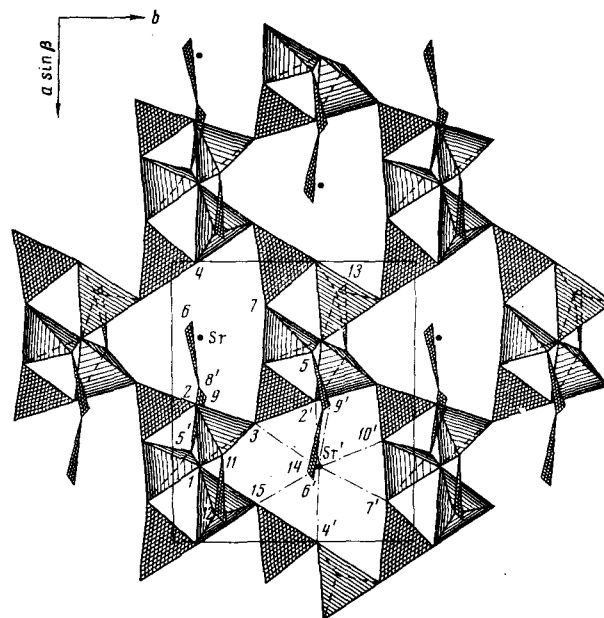


Fig. 2. Projection of the strontioborite structure along the c axis.

TABLE 2. Interatomic Distances Sr—O(OH) and Hydrogen Bonds (Å)

| Distances | | Hydrogen bonds | |
|---|---|---|---|
| Sr—O(10) | 2.52 | O(13)*—O(5) | 2.99 |
| Sr—O(2) | 2.58 | O(6)'*—O(12) | 2.66 |
| Sr—O(4) | 2.61 | O(9)*—O(11) | 2.70 |
| Sr—O(9)* | 2.62 | | |
| Sr—O(6)* | 2.66 | | |
| Sr—O(7) | 2.68 | | |
| Sr—O(3)' | 2.68 | | |
| Sr—O(15)' | 2.69 | | |
| Sr—O(14)'* | 2.72 | | |
| Av. | 2.64 | | |

Note: Here and in Table 3 the prime denotes atoms connected with the base atoms by symmetry operations.

with the formation of an infinite layer. The layered nature of the structure may readily be seen from the projection along the b axis (Fig. 1). The groups of four anions connected successively together form loops of triangular form with $Sr^{2+}$ cations in the centers (Fig. 2), as is characteristic of strontium borates. Around the cations is a polyhedron of nine O(OH) atoms. The lengths of the Sr—O(OH) bonds given in Table 2 fluctuate from 2.52 to 2.72 Å with an average of 2.64 Å (error ± 0.2 Å). The coordination sphere of Sr includes six O atoms of one layer and three (OH) groups, two of which belong to the neighboring layer.

The neutral layers of composition $Sr[B_8O_{11}(OH)_4]$ are joined to one another by the bonds linking the Sr atom with the hydroxyl groups and the hydrogen bonds of the (OH) groups as well as the O atoms of neighboring layers. The

lengths of the hydrogen bonds given in Table 2 lie in the range 2.66–2.99 Å and are similar to those usually obtained for borate structures. Separation of the OH groups is effected by analyzing the balance of valences. The structural characteristics offer an excellent explanation for the ideal cleavage of the crystal along the (001) plane.

The interatomic distances in the boron—oxygen tetrahedra and triangles are given in Table 3. The average bond lengths and interatomic distances agree with those found earlier in other borates,[7-11] namely: B—O distances in the triangles 1.37 and in the tetrahedra 1.46 Å; O—O distances in the triangles 2.37 and in the tetrahedra 2.39 Å. The accuracy of distance determination is B—O± 0.05 Å, O—O± 0.03 Å. The shortened edges O(4)—O(15) = 2.27 and and O(2)—O(3) = 2.30 Å are in common with the edges of the Sr polyhedron. For the triply-coordinated oxygen the three tetrahedral B=O distances equal 1.50, 1.52, and 1.52 Å. As in other borates with tunellite-like radicals, the average value of 1.51 Å is slightly greater than the ordinary value of 1.47 Å. The B—B distances in the polyanion vary over the range 2.42–2.65 Å with an average of 2.52 Å. The deviations of the atoms from the plane of the boron—oxygen triangles lie in the range 0.02–0.49 Å and are similar to those of structures with analogous polyanions. The O—B—O valence angles and the B—O—B angles at the oxygen atoms linked to three B atoms also lie within the range of values usually obtained.

The strontioborite polyanion $[B_3^t B_5^\Delta O_{11}(OH)_4]^{2-}$ consists of three $B(O, OH)_4$ tetrahedra and five plane $B(O, OH)_3$ triangles connected by common oxygen atoms.[1] The character of the spatial coupling between these groups (Fig. 3) enables us to distinguish the tunellite radical $[B_3^t B_3^\Delta (O,$

TABLE 3. Interatomic Distances (Å) in the Structure of Strontioborite

| B(3) tetrahedron | | B(5) tetrahedron | | B(6) tetrahedron | |
|---|---|---|---|---|---|
| B(3)—O(1)' | 1.50 | B(5)—O(1) | 1.52 | B(6)—O(1) | 1.52 |
| B(3)—O(5) | 1.53 | B(5)—O(2) | 1.36 | B(6)—O(4)' | 1.40 |
| B(3)—O(7) | 1.42 | B(5)—O(3) | 1.40 | B(6)—O(12) | 1.45 |
| B(3)—O(10) | 1.43 | B(5)—O(11) | 1.57 | B(6)—O(15) | 1.48 |
| Av. | 1.47 | Av. | 1.46 | Av. | 1.46 |
| O(1)'—O(5) | 2.34 | O(1)—O(2) | 2.44 | O(1)—O(4)' | 2.41 |
| O(1)'—O(7) | 2.42 | O(1)—O(3) | 2.39 | O(1)—O(12) | 2.41 |
| O(1)'—O(10) | 2.44 | O(1)—O(11) | 2.44 | O(1)—O(15) | 2.40 |
| O(5)—O(7) | 2.37 | O(2)—O(3) | 2.30 | O(12)—O(4)' | 2.37 |
| O(5)—O(10) | 2.49 | O(2)—O(11) | 2.29 | O(12)—O(15) | 2.39 |
| O(7)—O(10) | 2.34 | O(3)—O(11) | 2.46 | O(15)—O(4)' | 2.33 |
| Av. | 2.40 | Av. | 2.39 | Av. | 2.39 |

| B(1) triangle | | B(2) triangle | | B(4) triangle | |
|---|---|---|---|---|---|
| B(1)—O(5) | 1.38 | B(2)—O(4)' | 1.38 | B(4)—O(3) | 1.35 |
| B(1)—O(8) | 1.30 | B(2)—O(7) | 1.40 | B(4)—O(10) | 1.32 |
| B(1)—O(9)' | 1.43 | B(2)—O(15)' | 1.30 | B(4)—O(2)' | 1.46 |
| Cp. | 1.37 | Cp. | 1.36 | Cp. | 1.38 |
| O(5)—O(8) | 2.40 | O(4)'—O(7) | 2.36 | O(3)—O(10) | 2.37 |
| O(5)—O(9)' | 2.37 | O(4)'—O(15)' | 2.27 | O(3)—O(2)' | 2.37 |
| O(8)—O(9)' | 2.33 | O(7)—O(15)' | 2.40 | O(10)—O(2)' | 2.45 |
| Av. | 2.37 | Av. | 2.35 | Av. | 2.39 |

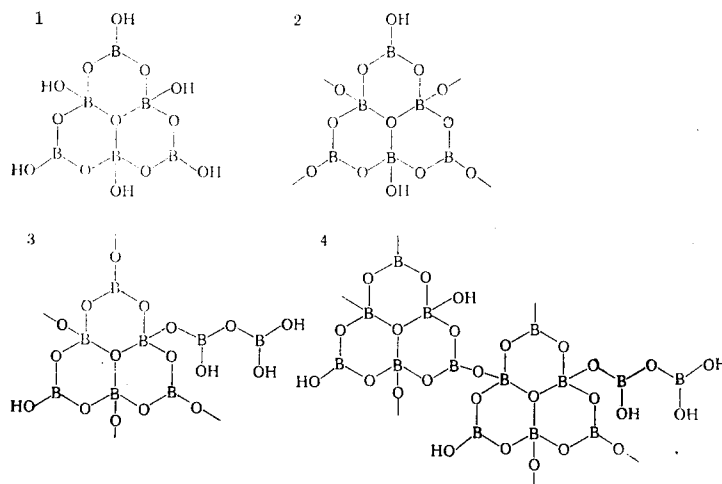| B(7) triangle | | B(8) triangle | |
|---|---|---|---|
| B(7)—O(8) | 1.35 | B(8)—O(11) | 1.41 |
| B(7)—O(6)' | 1.37 | B(8)—O(12) | 1.37 |
| B(7)—O(14) | 1.44 | B(8)—O(13)' | 1.30 |
| Av. | 1.39 | Av. | 1.36 |
| O(8)—O(6)' | 2.39 | O(11)—O(12) | 2.34 |
| O(8)—O(14) | 2.33 | O(11)—O(13)' | 2.43 |
| O(6)'—O(14) | 2.44 | O(12)—O(13)' | 2.31 |
| Av. | 2.39 | Av. | 2.36 |

Fig. 3. Schemes of boron—oxygen polyanions with tunellite-like radicals. 1) $[B_6O_7 \cdot (OH)_6]^{2-}$: $Mg_2[B_6O_7(OH)_6]_2 \cdot 9H_2O$ macallisterite, $Mg[B_6O_7(OH)_6] \cdot 2H_2O$ axaite, $Na_6Mg[B_6O_7(OH)_6]_4 \cdot 10H_2O$ rivadavite; 2) $[B_6O_9(OH)_2]^{2-}$: $Sr[B_6O_9(OH)_2] \cdot 3H_2O$ tunellite; $Ca[B_6O_9(OH)_2] \cdot 3H_2O$ noblite; 3) $[B_8O_{11}(OH)_4]^{2-}$: $Sr[B_8O_{11}(OH)_4]$ strontioborite, $Ca[B_8O_{11}(OH)_4]$; 4) $[B_{14}O_{20}(OH)_6]^{2-}$: $SrCa[B_{14}O_{20}(OH)_6] \cdot 5H_2O$ strontioginorite.

$OH)_{11}]^{2-}$ and the $[B_2^{\triangle}(O, OH)_5]$ radical (resembling swanite) connected to it by a common vertex quite clearly in the polyanion.

Of the boron—oxygen radicals so far discovered, only in tunellite do we encounter the foregoing abnormal surroundings of the oxygen atom, as characterized by the three boron atoms. In the ten years which have passed since the structure of tunellite was solved,[7] the polyanion $[B_3tB_3^{\triangle} \cdot (O,OH_{11})]^{2-}$ has been found in isolated and polymerized form in a number of natural[8-11] borates, and its existence has been proposed in certain synthetic compounds.[12] Figure 3 offers a schematic representation of certain known polyanions containing the tunellite radical. It is easy to see that the $[B_3{}^tB_5{}^{\triangle}O_{11}(OH)_4]^{2-}$ polyanion found in strontioborite enters as a constituent part into the polyanion of strontioginerite $[B_{14}O_{20}(OH)_6]^{4-}$.

The stability of the tunellite radical is no longer in any doubt. It is also undoubted that the possible ways of coupling the tunellite boron—oxygen radicals to each other and to other boron—oxygen radicals (polymerization) are by no means exhausted by the cases illustrated in Fig. 3.

The authors wish to thank I. M. Rumanov for consultation and help in executing this work and I. I. Khalturin

for presenting the samples studied.

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[1] $t$ = boron—oxygen tetrahedron; $\triangle$ = triangle.

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