tex figures. If we confine ourselves to a coordination sphere radius of 3.0-3.16 Å, then the polyhedra reduce to seven- and eight-vertex figures. Note that the vertices of each polyhedron are occupied by five H_2O molecules in an independent part of the cell. The polyhedra are not discrete but are joined into a column parallel to [100] through a common $(H_2O)_5-O_{11}$ edge (this remains valid for the reduced polyhedra as well). For each cell there are two such isolated columns which are crystallographically linked by a single symmetry element, the 2_1 axis (Fig. 2). Parallel to these columns of "uniform" NH_4-polyhedra are corrugated mixed columns of (In + $2S_{3,4}$)-polyhedra composed of the same structural units as in Ref. 4, viz., block-bars of In-octahedra and two S_3- and S_4-tetrahedra arranged on the wings. The role of the S_1- and S_2-tetrahedra is different: They link together the In-octahedra of adjacent columns; a corrugated wall parallel to (010) is thus formed. The walls are isolated. The entire structure is combined into one whole by the NH_4-polyhedra unifying the vertices of the S_3- and S_4-tetrahedra into one wall, and the edges of the In-octahedra as well as the edges and vertices of the S_1- and S_2-tetrahedra into another. In fact, the large NH_4-polyhedron has only H_2O molecules (two in each polyhedron) as suspended vertices.

The participation of protons from the NH_4 group in the cementing of the structure is reflected in the less pronounced cleavage of ammonium sulfate in comparison with goldichite.[5]

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Hydrogen bonds in the crystal structure of nifontovite $Ca_2/B_5O_3(OH)_6/_2\cdot 2H_2O$

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The crystal structure of the caldium metaborate (Ca: B = 1: 2) nifontovite $Ca_3[B_3O_3(OH)_6]_2\cdot 2H_2O$ was deciphered by the present authors in 1973,[1] refined by the least-squares method in the isotropic approximation to R_{hkl} = 6.8% on the basis of experimental material obtained on a $P\bar{1}$ automatic diffractometer (Cu Kα radiation, 860 independent nonzero reflections, $\max \sin\theta/\lambda = 0.5$ Å^{-1}), has now been reanalyzed in order to localize the hydrogen atoms, to establish the hydrogen bonds, and to calculate their geometric characteristics.

The parameters of the monoclinic cell refined on the same automatic diffractometer a = 13.119(4), b = 13.445(5), c = 9.526(3) Å; γ = 118°.40(2), V = 1477.9(8) Å^3, Z = 4, d_x = 2.34, d_e = 2.36 g/cm^3, Fedorov group C_{2h}^6 = B2/b are in agreement within the limits of standard deviations with the values found earlier.[1]

The experimental material used in refining the nifontovite structure consisted of diffractometric data: 4009 independent nonzero ($I \geq 1.96\sigma I$) reflections [Mo Kα radiation, (2θ: θ) method, plane graphite monochromator, $\max \sin\theta/\lambda = 0.9$ Å^{-1}]. The conversion of I into $|F_{hkl}|$ without allowance for absorption ($\max \mu r = 0.89$) and all subsequent calculations were performed on an E-XTL Syntex special-purpose system for analyzing crystal structures.

During the reanalysis of the structure the initial coordinates of the Ca, B, and O basal atoms[1] were refined by the least-squares method to R_{hkl} = 5.3% in the full-matrix isotropic approximation and to 3.6% in the aniso-

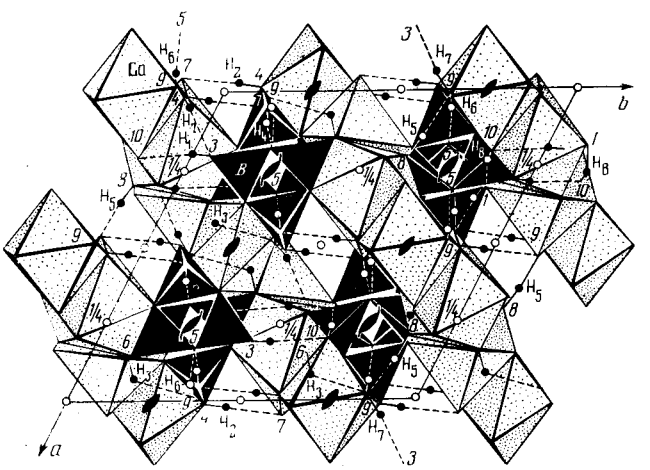

FIG. 1. Nifontovite $Ca_3[B_3O_3(OH)_6]_2\cdot 2H_2O$. xy projection. Solid lines indicate D = H bonds, dashed lines denote H = A bonds, and the numbers are the numbers of the O atoms.

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TABLE I. Nifontovite $Ca_3[B_3O_3(OH)_6]_2 \cdot 2H_2O$. Basal Atom Coordinates and Isotropic and Anisotropic Thermal Factors

Atom	x/a	y/b	z/c	B_j	Atom	x/a	y/b	z/c	B_j
Ca_1	0	0.25	0.24378(6)	0.51(1)	O_7*	0.4595(1)	0.3663(1)	0.1156(2)	0.74(2)
Ca_2	0.33830(3)	0.57045(3)	0.90893(4)	0.56(1)	O_8*	0.2037(1)	0.1187(1)	0.2046(2)	1.00(2)
B_1	0.2606(2)	0.1680(2)	0.3402(2)	0.59(3)	O_9**	0.0186(2)	0.1396(2)	0.0460(2)	1.22(3)
B_2	0.0916(2)	0.1577(2)	0.4734(2)	0.53(3)	O_{10}*	0.1994(1)	0.3514(1)	0.2061(2)	0.72(2)
B_3	0.2428(2)	0.3430(2)	0.3488(2)	0.54(3)	H_1	0.813(2)	0.006(2)	0.141(3)	6.6(9)
O_1	0.1782(1)	0.1193(1)	0.4581(2)	0.62(2)	H_2	0.977(2)	0.029(2)	0.376(3)	8.2(1.0)
O_2	0.1384(1)	0.2779(1)	0.4367(2)	0.54(2)	H_3	0.415(2)	0.172(2)	0.405(3)	9.8(1.1)
O_3*	0.3050(1)	0.4586(1)	0.4095(2)	0.72(2)	H_4	0.596(2)	0.171(2)	0.197(3)	5.9(9)
O_4*	0.0107(1)	0.4054(1)	0.3771(2)	0.74(2)	H_5	0.142(2)	0.130(2)	0.161(3)	9.1(1.0)
O_5	0.3180(1)	0.2910(1)	0.3440(2)	0.59(2)	H_6	0.554(2)	0.157(2)	0.471(3)	5.7(9)
O_6*	0.3435(1)	0.1230(1)	0.3425(2)	0.82(2)	H_7	0.964(2)	0.075(2)	0.032(3)	4.2(8)
					H_8	0.766(2)	0.150(2)	0.136(3)	8.8(1.0)

$$T=\exp[-1/4(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)]$$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca_1	0.42(1)	0.54(2)	0.56(2)	0.23(1)	0.00(0)	0.00(0)	O_4	0.77(5)	0.52(4)	0.91(5)	0.26(4)	0.28(4)	0.08(4)
Ca_2	0.57(1)	0.53(1)	0.65(1)	0.30(1)	—0.04(1)	—0.03(1)	O_5	0.46(4)	0.44(4)	0.90(5)	0.22(3)	0.11(3)	0.07(3)
B_1	0.61(6)	0.54(6)	0.68(6)	0.32(5)	0.05(5)	0.00(5)	O_6	0.90(5)	0.97(5)	1.00(5)	0.72(4)	0.02(4)	0.05(4)
B_2	0.52(6)	0.44(6)	0.60(6)	0.21(5)	0.03(5)	0.03(5)	O_7	0.62(4)	0.87(5)	0.59(4)	0.26(4)	—0.13(4)	—0.11(4)
B_3	0.54(6)	0.42(6)	0.67(6)	0.20(5)	—0.00(5)	0.03(5)	O_8	1.08(5)	1.35(6)	0.84(5)	0.76(5)	—0.22(4)	—0.45(4)
O_1	0.64(4)	0.55(4)	0.76(4)	0.34(4)	0.20(4)	0.21(3)	O_9	1.02(5)	1.13(6)	1.40(6)	0.34(5)	0.29(5)	—0.27(5)
O_2	0.50(4)	0.37(4)	0.76(4)	0.19(3)	0.14(3)	0.05(3)	O_{10}	0.72(4)	0.91(5)	0.59(4)	0.43(4)	—0.00(4)	0.07(4)
O_3	0.81(5)	0.37(4)	0.86(5)	0.14(4)	—0.06(4)	—0.05(4)							

Note: One asterisk denotes oxygen of the OH-group and two asterisks, oxygen of the H_2O molecule.

TABLE II. Nifontovite $Ca_3[B_3O_3(OH)_6]_2 \cdot 2H_2O$. Interatomic Distances, Å

B-et B-tetrahedra

B_1-O_1	1.479(3)	B_3-O_2	1.483(3)	B_2-O_1	1.483(4)
O_5	1.456(3)	O_3	1.486(3)	O_2	1.472(3)
O_6	1.474(4)	O_5	1.457(3)	O_4	1.511(3)
O_8	1.481(3)	O_{10}	1.500(3)	O_7	1.479(3)
Cp.	1.472	Cp.	1.482	Cp.	1.481
O_1-O_5	2.418(2)	O_2-O_3	2.386(2) *	O_1-O_2	2.433(2)
O_6	2.411(3) *	O_5	2.443(2)	O_4	2.464(3)
O_8	2.438(2)	O_{10}	2.386(2) *	O_7	2.427(2)
O_5-O_6	2.436(2)	O_3-O_5	2.420(2)	O_2-O_4	2.374(2) *
O_8	2.465(2)	O_{10}	2.419(2)	O_7	2.438(2)
O_6-O_8	2.234(3)	O_5-O_{10}	2.452(2)	O_4-O_7	2.357(2) *
Mean	2.400		2.418		2.416

Ca-polyhedra

$Ca_1-O_2(2)$	2.484(2)	Ca_2-O_1	2.499(2)	O_2-O_3	2.386(2) *
$O_4(2)$	2.391(2)	O_2	2.413(2)	O_4	2.967(2) **
$O_9(2)$	2.481(2)	O_3	2.446(2)	O_6	4.059(2)
$O_{10}(2)$	2.332(2)	O_4	2.752(2)	O_7	3.533(2)
O_2-O_2'	3.342(2)	O_6	2.488(2)	O_8	3.162(2)
$O_4(2)$	2.967(2) **	O_6'	2.637(2)	O_3-O_4	3.590(3)
$O_4'(2)$	2.374(2) *	O_7	2.381(2)	O_6'	3.109(2)
$O_{10}(2)$	2.386(2) *	O_8	2.408(2)	O_8	2.980(2)
$O_4-O_9'(2)$	3.199(2)	O_1-O_3	3.528(2)	O_4-O_7	2.357(2) *
$O_{10}(2)$	3.319(2)	O_4	3.091(2)	O_6-O_6'	3.514(2) **
$O_{10}'(2)$	3.622(2)	O_6	4.243(2)	O_7	3.319(3)
O_9-O_9'	3.230(3)	O_6'	2.411(3) *	O_8	2.234(3) *
$O_{10}(2)$	3.104(2)	O_7	3.319(2)	$O_6'-O_8$	3.038(2)
$O_{10}'(2)$	3.293(3)				
Mean Ca_1-O	2.422	Ca_2-O	2.503	O-O	3.158
O-O	3.061				

Note: One asterisk denotes the common edges of B-tetrahedra and Ca-polyhedra and two asterisks denote the common edges of Ca-polyhedra.

tropic approximation. The eight basal hydrogen atoms were localized from the difference synthesis of the electron density (resolution 0.1 Å), constructed with allowance for the refined Ca, B, and O. The positions of the H atoms were refined in two stages: Only the positional parameters with fixed isotropic temperature factors B_j are refined in the first stage, and only the B_j in the second. The final coordinates of the basal atoms (R_{hkl} = 3.4%) and the corresponding interatomic distances are given in Tables I and II.

In the nifontovite structure two species of Ca atoms are present in the eightfold surrounding that is usual for calcium metaborates,[2] Thomson cubes (Ca_1) and deltadodecahedra (Ca_2), which are bound into zigzag chains, their general direction being along the diagonal **a** + **b**. Their (2 + 4)-term link (as in norbergite) overlaps deeply into the translationally identical neighboring links with a pitch of 13.552 Å. The anion surrounding of the Ca atoms differs: Two vertices of each Ca-polyhedron are represented by O atoms, for Ca_1 four vertices are occupied by OH-

TABLE III. Geometrical Characteristics of Hydrogen Bonds in the Structure of Nifontovite $Ca_3[B_3O_3(OH)_6]_2 \cdot 2H_2O$

D–H...A	D–H(Å)	H...A(Å)	D—A(Å)	Angle DHA	D–H...A	D–H(Å)	H...A(Å)	D—A(Å)	Angle DHA
O_3–H_1...O_{10}	0.77	2.08	2.808	155°.9	O_8–H_5...O_9	1.00	2.00	2.985	171.2
O_4–H_2...O_7	0.82	2.09	2.905	174.2	O_9–H_6...O_5	0.83	1.91	2.695	158.9
O_6–H_3...O_9	1.03	2.10	2.932	135.4	O_9–H_7...O_3	0.83	2.01	2.732	146.0
O_7–H_4...O_5	1.02	1.72	2.723	169.0	O_{10}–H_8...O_4	0.81	1.98	2.777	167.0

Note: The angle H_6–O_9–H_7 = 104.°4.

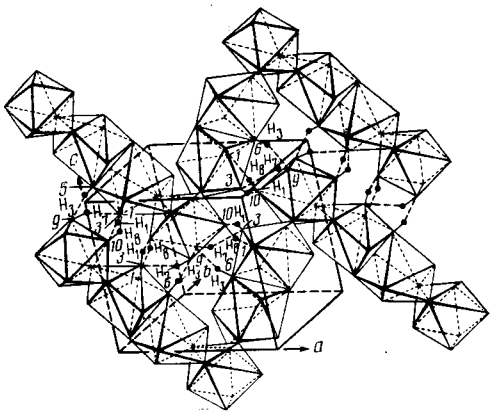

FIG. 2. Nifontovite. Wall of Ca-polyhedra in axonometric view. Intralayer hydrogen bonds are shown.

groups and two by H_2O particles, and for Ca_2 the remaining six vertices are occupied by OH-groups; the H_2O particles are arranged at the "free" vertices of the Ca_1-polyhedra, i.e., do not participate in the formation of other Ca-polyhedra and B-tetrahedra.

The layered character of the structure appears distinctly in Fig. 1. It must be specified that the layers are not continuous but are formed of chains of Ca-polyhedra joined in the direction of the c axis only by hydrogen bonds (Fig. 2). Individual walls separated from each other by 2.86 Å are cemented together by ternary two-sided $[B_2O_3 \cdot (OH)_6]$ rings (two tetrahedra are pointed in one direction; the angles are B_1–O_1–B_2 = 116°.49, B_2–O_2–B_3 = 124°.63, B_1–O_5–B_3 = 116°.30); and hydrogen bonds. Two forms of hydrogen bond, intralayer and interlayer, can be isolated in the nifontovite structure, with the latter playing a major role in the formation of the skeleton of the mineral.

Reanalysis of the nifontovite structure confirmed the correctness of the differentiation of the anion part into O, OH, and H_2O, which has been done earlier[1] only on the basis of the balance of the valence forces on the anions, and specified the hydrogen bonds. The localization of the H atoms made it possible to obtain the geometrical characteristics of the hydrogen bonds (given in Table III and Figs. 1 and 2) and especially their "corner" configuration.

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