compounds having an orthorhomic lattice with periods similar to $R_3'R_2''X_3$ are formed at a composition $Hf_3Ni_2Si_3$ (Table II). Study of $Hf_3Ni_2Si_3$ single crystals showed that their structure, although having a disposition of the atoms and coordination characteristics similar to $Hf_3Ni_2Si_3$, belonged to the Pnm*a* space group, obtained from Cmcm by slight displacements of the atoms (the additional reflections determining the ascription to the Pnm*a* group are weak). For the other compounds (only studied by the powder method) one of these two space groups is also feasible.

1) R', R", and X are atoms with different coordination $CN_{R'} > CN_{R''} > CN_X$. Apart from this $r_{R'} > r_X$ and $r_{R''} > r_X$ (r is the radius of the atom).

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Determination of the crystal structures of chapmanite and bismuthoferrite by high-voltage electron diffraction

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The crystal structures of chapmanite and bismuthoferrite are determined from three-dimensional Patterson functions, these being analyzed by the rhombs-of-peaks method. The parameters of the monoclinic cells are $a = 5.19$, $b = 8.99$, $c = 7.70$ *A*, $\beta = 100^\circ\ 40'$ and $a = 5.21$, $b = 9.02$, $c = 7.74$ *A*, $\beta = 100^\circ\ 40'$ respectively, $Z = 2$, space group Cm. Chapmanite and bismuthoferrite consist of two-stage kaolinite-like layers of composition $Fe_2Si_2O_8$ (OH) in the sequence $\sigma_6\tau_0\sigma_6$. The contiguous plane lattice of neighboring layers in normal projection on the *ab* plane lie in such a way that the empty octahedron of the layer lies over the hexagonal loop of Si tetrahedra. The Sb(Bi) atoms lie in the interlayer space, adjacent to the bases of the empty octahedra, as the fourth vertex of a triangular pyramid. The structures of chapmanite and bismuthoferrite are unique examples of the realization of layer-like silicates comprising kaolinite-like layers with Fe^{3+} cations in the octahedra.

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Chapmanite $SbFe_2Si_2O_8OH$ and bismuthoferrite $BiFe_2Si_2O_8OH$ are rare minerals encountered in nature in the form of fine-granular precipitates,[1] which makes their x-ray analysis rather difficult. As regards chemical composition these minerals were earlier ascribed to silicates with isolated SiO_4 tetrahedra.[1] The lattice constants of chapmanite and bismuthoferrite ($a = 11.65$ and 11.61, $b = 9.00$ and 9.02, $c = 15.26$ and 15.22 Å, $Z = 4$) were derived from x-ray powder photographs,[2] allowing for optical data relating to chapmanite,[3] indicating orthorhomic symmetry.

In the present investigation we applied high-voltage (350 kV) electron diffraction to chapmanite from the Smil-

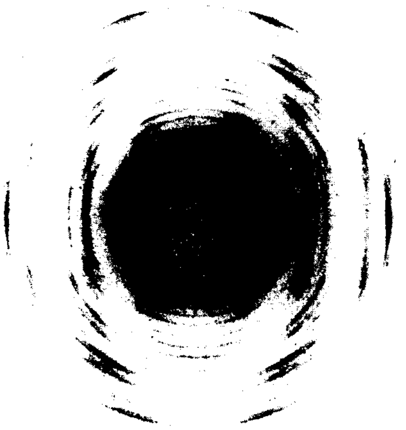

FIG. 1. Oblique-texture electron-diffraction pattern of chapmanite $\varphi = 60°$.

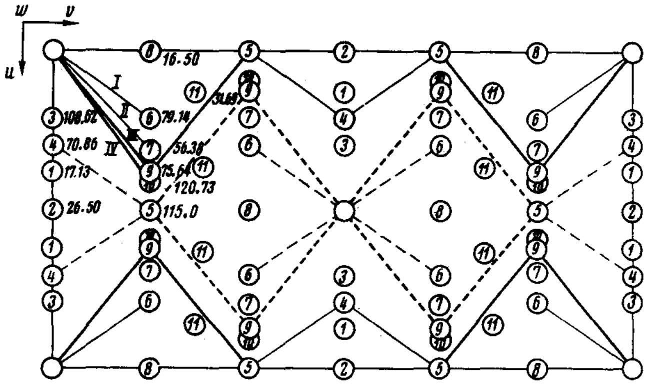

FIG. 2. Three-dimensional Patterson function of chapmanite in point form. The first figure by the circle is the peak intensity in relative units, the second is the height in hundredth parts of the w axis. For the original segments I (thin lines) and III (thick lines) the complete systems of rhombs are shown. The dashed lines in both cases denote the rhombs of peaks formed by a C translation.

kov site (Czechoslovakia)[4] and bismuthoferrite from Schneeberg (Saxony, East Germany),[5] samples of which were obtained from the Mineralogical Museum, Academy of Sciences of the USSR (museum numbers 65557 and 13067, respectively). Owing to the small amounts of material the chemical composition of the samples was not analyzed – published data for minerals from these sites were employed.[4,5]

Oblique-texture electron-diffraction patterns (Fig. 1) revealed the sharp structural similarity of chapmanite and bismuthoferrite to layer-like silicates and most of all to minerals with two-stage layers; they clearly indicated base-centered monoclinic cells: For chapmanite a = 5.19, b = 8.99, c = 7.70 Å, β = 100°40' and for bismuthoferrite a = 5.21, b = 9.02, c = 7.74 Å, β = 100°40', Z = 2 (Fig. 1).

The intensities of the reflections were estimated from oblique-texture electron-diffraction patterns recorded with multiple exposures. The most sharply distinguished reflections were measured in an MF-4 microphotometer. For structural analysis we used 180 and 156 independent reflections with maximum values of $3h^2 + k^2$ = 100 and 84 for chapmanite and bismuthoferrite, respectively, at a maximum value of l = 9.

Since the general characteristics of the intensity distribution failed to reflect any of the polytypic forms of kaolin and serpentine minerals, further investigation was based on the use of a three-dimensional Patterson function analyzed by the rhombs-of-peaks method.[6,7] Unfortunately the simultaneous study of both structures was impossible; they were considered successively, first chapmanite[8] and then bismuthoferrite, and this somewhat complicated the interpretation of the Patterson functions.

The projection of the Patterson function of chapmanite on the uv plane in the point approximation is shown in Fig. 2. In the Patterson synthesis attention is drawn to the regular disposition of the majority of the maxima, mainly with respect to planes perpendicular to the v axis at intervals of b/6. On this basis we might conclude that the segments between pairs of atoms in the structure (primarily between cations) had projections along the b axis multiple to b/6, as is characteristic of layerlike silicates.

In order to ease solution of the Patterson function we took space groups C2, Cm, and C2/m, compatible with the existence of extinctions for h + k ≠ 2n only, and plotted theoretical Patterson diagrams relating to those positions of the original segment with Δy = 1/6 relative to the symmetry elements in the basic system (b.s.) for which the foregoing peak distribution was obtained in the vector system (v.s.). Segments with projections b/3 were not considered, since for a base-centered lattice in addition to the original segment with Δy = 1/6 a segment with Δy = 1/3 also existed.

In the presence of a two-fold axis the segment in the

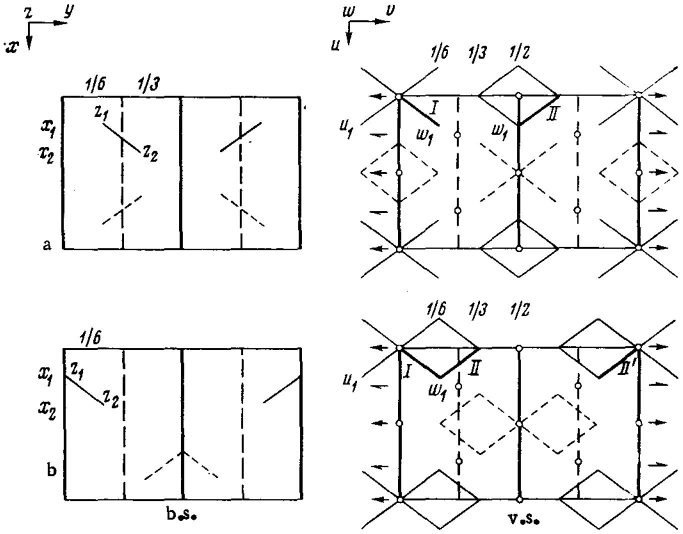

FIG. 3. Vector systems formed by a segment with $\Delta y = {}^1/_6$ in the basic system (space group Cm). a) Middle of the segment displaced relative to the m plane by $\Delta y = {}^1/_4$; b) one end of the segment in the m plane. The dashed lines show the v.s. and b.s. generated by a C translation.

TABLE I. Coordinates of the Atoms in the Chapmanite Structure

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
Sb	0.418(1)	0.5	0.743(1)	O_3	0.220(5)	0.173(3)	0.143(4)
Fe	0.500(2)	0.1655(1)	0.000(2)	OH	0.684(5)	0.0	0.144(4)
Si	0.301(4)	0.171(2)	0.375(3)	O_4	0.082(5)	0.254(3)	0.446(4)
O_1	0.289(5)	0.332(3)	−0.135(4)	O_5	0.336(5)	0.0	0.443(4)
O_2	0.296(5)	0.0	−0.135(4)				

b.s. may lie in a general position with one end on the axis (rhombs connected in pairs[9]) and parallel to the two-fold axis (rhombs degenerating into lines).

In the presence of an m plane the foregoing peak distribution in the v.s. is realized in two forms: a) the middle of the segment is displaced from the m plane by $\Delta y = 1/4$ (segment in the general position, two rhombs merge into one,[10]; b) one end of the segment lies in the m plane (rhombs linked in pairs) (Fig. 3). For the same direction of the original segment, as regards the geometry of the v.s. peak distribution, (a) is indistinguishable from a superposition of the v.s. (a) + (b). However, the versions are distinguished by the ratio of the interaction peak intensities $u_1 v_1 w_1$ and $u_1 1/2 w_1$; in case (a) the intensity ratio is 1 : 2 and in case (a) + (b) 3 : 2.

In the case of the C2/m space group, the v.s. is formed by the superposition of the v.s. generated by the m plane and two-fold axis, with the addition of rhombs degenerated into lines corresponding to an inversion center.

In the Patterson synthesis we located only the rhombs of peaks generated by an m plane and represented by the four systems I–IV: I–(a) + b); II–(a), III and IV–(b) (Fig. 2); we accordingly took the space group Cm for chapmanite.

Allowing for the multiplicities of the atoms, the interatomic distances, and the peak intensities, to each system of rhombs we referred the pair of atoms generating it. For a cation content of the unit cell $Sb_2Fe_4Si_4$, the Sb atoms can only occur on the m plane (system b) in the Cm space group, and then the two systems of rhombs (a) in the Patterson synthesis should relate to Fe and Si atoms in a general position. Under these conditions v.s. I may be formed by an Fe–O segment ~ 2.00 Å long, characteristic of Fe^{3+} octahedra, v.s. II by an Fe–Si pair, v.s. III and IV by Sb–Si and Sb–Fe pairs in accordance with the intensities of their peaks.

From v.s. II we found the coordinates ($0 ^1/_3 0$) and (0.31 1/6 0.38) for the pair of Fe, Si atoms relative to the m plane[7]; this only fixed the y coordinate, while x and z were valid apart from a constant factor. In order to be specific, let the first position refer to Fe and the second to Si. The Cm symmetry of each of the atoms is multiplied in the cell having $b = a\sqrt{3}$ with the formation of a hexagon. This is exactly how the Si atoms are disposed in all the layerlike silicates, and Fe in their dioctahedral varieties.

In v.s. I(a), which together with I(b) composes the rhomb system I, for the pair of atoms (Fe and O) we obtain the coordinates (0 1/3 0) and (0.21 1/6 0.14) relative to the m plane. Since each of these positions may be referred to Fe, there are two centrosymmetrical solutions for the O atoms. Despite the symmetry of the Cm structure we have to use both solutions. The foregoing dispositions of the Fe atoms with respect to the vertices of the hexagon, in fact, the presence of Fe–O segments with O atoms in a general position ($y = 1/6$ and $1/3$) [according to v.s. (a)] and in the m plane [according to v.s. (b)], and the length of these segments ~2.00 Å are signs of a dioctahedral lattice of Fe^{3+} octahedra, centrosymmetrical in the ideal case. For the foregoing coordinates of the Fe from v.s. I(a) we obtain the coordinates (0.21 1/6 0.14) and (0.29 1/3 −0.14) for the oxygen atoms.

TABLE II. Interatomic Distances in the Chapmanite Structure (A)

		Fe-octahedron			
Fe–O_1	2.02(3)	O_1–O_1'	2.99(4)	O_1–O_3	2.66(4) [2]
Fe–O_1'	1.99(3)	O_1'–O_2	2.97(4)	O_2–OH	2.63(4)
Fe–O_2	1.99(2)	O_2–O_1	2.98(3)		
Fe–O_3	1.99(3)	O_3–O_3'	2.94(4)	O_1–O_3'	2.77(4)
Fe–O_3'	2.03(3)	O_3'–OH	2.95(3)	O_1'–OH	2.77(4)
Fe–OH	1.98(2)	OH–O_3	2.87(4)	O_2–O_3	2.74(4)
Av.(Fe–O)	2.00(1)	Av.(O–O)			2.83(2)
		Si-tetrahedron			
Si–O_3	1.69(4)	O_4–O_4'	2.59(4)		
Si–O_4	1.58(4)	O_4'–O_5	2.55(3)		
Si–O_4'	1.61(3)	O_5–O_4	2.64(3)		
Si–O_5	1.64(2)	O_3–O_4	2.68(5)		
Av.(Si–O)	$1.63(1_5)$	O_3–O_4'	2.76(4)		
		O_3–O_5	2.75(4)		
		Av.(O–O)	2.66(2)		
		Sb–O			
Sb–O_1	1.97(3) [2]	Sb–O_4	3.39(3) [2]		
Sb–O_2	2.00(3)	Sb–O_4'	3.46(3) [2]		
Av.(Sb–O_{oct}	1.98(2)	Sb–O_5	3.41(3)		
		Sb–O_5'	3.47(3)		
		Av.(Sb–O_{tetr})	3.43(2)		

Note: The prime indicates atoms related to the basic atoms by symmetry operations.

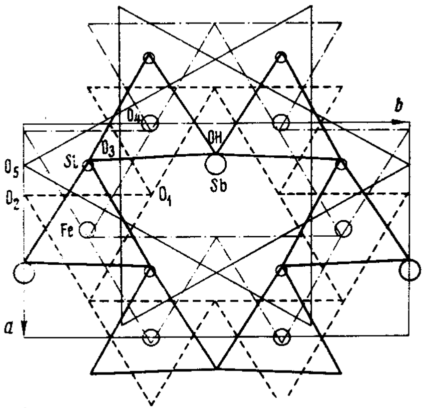

FIG.4. Structure of chapmanite in normal projection on the ab plane. The thick continuous lines are the upper bases of the octahedra, the thick broken lines the lower bases of the octahedra, the thin continuous lines the bases of the tetrahedra, the thin dotted and dashed lines the lower bases of the octahedra of the next layer.

TABLE III. Coordinates of the Atoms in the Structure of Bismuthoferrite

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
Bi	0.413(1)	0.5	0.716(1)	O_3	0.219(7)	0.170(4)	0.143(7)
Fe	0.500(3)	0.165(2)	0.000(3)	OH	0.684(7)	0.0	0.145(7)
Si	0.316(5)	0.166(3)	0.369(5)	O_4	0.081(7)	0.248(4)	0.448(7)
O_1	0.295(7)	0.328(4)	−0.144(7)	O_5	0.326(7)	0.0	0.429(7)
O_2	0.317(7)	0.0	−0.128(7)				

For the Fe−O pair v.s. I(b) gives a direct [Fe (0 1/6 0), O (0.21 0 0.14) and inverted [Fe (0.21 1/3 0.14, O (0 1/2 0] solution relative to the m plane, assuming the Fe must be in a general position. Both solutions are used on the same basis as in I(a). From these solutions, on moving the origins of the Fe−O vectors into the positions of the Fe atoms just selected, the coordinates (0.21 1/2 0.14) and (0.29 0 −0.14) are obtained for the O atoms in the structure.

The coordinates of the Sb atoms are established from v.s. III (Sb−Si) and IV (Sb−Fe), each giving two solutions relative to the m plane analogous to those considered for v.s. I(b). From v.s. III we have the atomic positions Si (0 1/6 0), Sb (0.38 0 0.64) and Si (0.38 1/3 0.64), Sb (0 1/2 0), and from v.s. IV Fe (0 1/6 0), Sb (0.41 0 0.73), and Fe (0.41 1/3 0.73), Sb (0 1/2 0). In the present case we only have to choose one solution. For the earlier obtained coordinates of the Fe and Si atoms, as a result of using the two v.s. (III and IV), the Sb atoms are uniquely assigned the coordinates (0.42 0.5 0.73$_5$), as referring to coincident solutions for systems III and IV.

As a result of the analysis of the Patterson function we determined the coordinates of all the cations and four octahedral O atoms. The remaining two O atoms were located by successively constructing Fourier-potential syntheses. The final refinement of the chapmanite structure was based on the method of least squares, giving an R factor of 11.2%. The coordinates of the atoms with the mean-square errors calculated on the B. K. Vainshtein principle[11] for B = 2.0 are given in Table I, the interatomic distances in Table II. The projection of the chapmanite structure on the *ab* plane is illustrated in Fig. 4.

In the Patterson synthesis of bismuthoferrite the system of rhombs of peaks formed by the Fe−O and Fe−Si pairs is similar to that of chapmanite. In a similar way we used v.s. II and I to obtain the coordinates of the Fe and Si and the octahedral O atoms. However, on the Patterson synthesis of bismuthoferrite, instead of two v.s. (II and IV in Fig. 2) we located only one "pure" system of rhombs (b) (III). This is also distinguished by a sharp rise in the peak intensities, which may be the result of not only the greater scattering power of Bi relative to Sb but also the superposition of the two v.s. corresponding to the pairs Bi−Fe and Bi−Si. For each of the positions of Fe (0 1/3 0) and Si (0.32 1/6 0.39) established from v.s. II, in actual fact, we obtained two solutions for the Bi coordinates from the system of rhombs III, one of these being common for both pairs of solutions and giving the Bi coordinates Bi (0.41 0.5 0.70$_5$) in the structure of bismuthoferrite. Further refinement of the structure by Fourier syntheses and the method of least squares yielded an R factor of 12.1%. The coordinates of the atoms with the mean-square deviations (B = 3.0) are given in Table III, the interatomic distances in Table IV, and the projection of the structure on the bc* plane in Fig. 5.

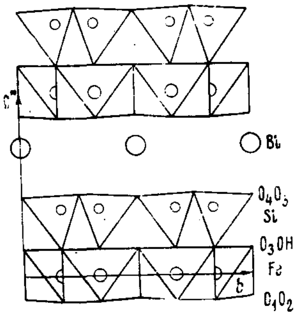

FIG.5. Structure of bismuthoferrite in projection on the bc plane.

We thus find that the structures of chapmanite and bismuthoferrite comprise two-stage layers of $Fe_2Si_2O_8$-(OH) analogous to the kaolin layers $Al_2Si_2OH(OH)_4$ arranged successively and symbolically written $\sigma_6\tau_0\sigma_6$ (Ref. 12), never encountered before in kaolinite-like minerals. In these structures the hexagons of octahedral and tetrahedral cations of neighboring layers coincide in normal projection on the *ab* plane. In the interlayer gap separating these are Sb and Bi atoms adjacent to the bases of the empty octahedra, acting as the fourth vertices of triangular pyramids [the mean Sb(Bi)−O_{oct} and Sb(Bi)−O_{tetr} distances differ by more than a factor of 1.5]. Despite the difference in the dimensions of the Sb^{3+} and Bi^{3+} cations and their distances from O_{oct}, the thickness of the interlayer is the same in both structures (η = 3.17 and 3.18 Å). Here and subsequently when comparing structural data the first numbers will pertain to chapmanite and the second to bismuthoferrite.

TABLE IV. Interatomic Distances in the Structure of Bismuthoferrite (A)

Fe-octahedron

Fe−O_1	2.02(4)	O_1−O_1'	2.96(5)	O_1−O_3	2.73(6) [2]
Fe−O_1'	2.07(5)	O_1'−O_2	2.96(5)	O_2−OH	2.55(6)
Fe−O_2	1 93(3)	O_2−O_1	2.96(4)	O_1−O_3'	2.80(6)
Fe−O_3	2.01(5)	O_3−O_3'	2.98(5)	O_1'−OH	2.88(7)
Fe−O_3'	2.06(4)	O_3'−OH	2.98(4)	O_2−O_3	2.73(7)
Fe−OH	1.99(3)	OH−O_3	2.86(5)		
Av.(Fe−O)	2.01(1$_5$)	Av.(O−O)	2.84(2)		

Si-tetrahedron

Si−O_3	1.72(6)	O_4−O_4'	2.60(5)
Si−O_4	1.64(5)	O_4'−O_5	2.62(4)
Si−O_4'	1.59(5)	O_5−O_4	2.59(4)
Si−O_5	1.57(3)	O_3−O_4	2.70(7)
Av.(Si−O)	1.63(2)	O_3−O_4'	2.81(6)
		O_3−O_5	2.67(6)
		Av.(O−O)	2.67(2)

Bi−O

Bi−O_1	2.06(4) [2]	Bi−O_4	3.32(4) [2]
Bi−O_2	2.20(4)	Bi−O_4'	3.29(5) [2]
Av.(Bi−O_{oct}	2.11(2)	Bi−O_5	3.39(5)
		Bi−O_5'	3.40(4)
		Av.(Bi−O_{tetr})	3.35(3)

Note. The prime denotes atoms related to the basic atoms by symmetry operations.

In both structures the tetrahedra are severely drawn out along the normal to the layers while the edges of the bases are shortened. A result of this is the very small angles ψ of ditrigonal rotation of the bases of the tetrahedra relative to the hexagonal motif (30' and 20'). Whereas in chapmanite the bases of the tetrahedra practically lie in one plane, in bismuthoferrite they have deviations owing to the displacement of O_{base} in the m planes toward the octahedral lattice of the layer. The $Si-O_{vert}$ and $(Si-O_{base})_{av}$ distances are 1.69, 1.61 and 1.72, 1.60 Å for average Si–O values of 1.63 Å in both cases.

The octahedral plane lattices of chapmanite and bismuthoferrite are flattened, since their thickness is 2.10 and 2.14 Å instead of the ~2.30 Å in the case of regular octahedra with the same Fe–O distance. The bases of the octahedra of the inner O, OH surface of the layer are rotated relative to the ideal trigonal motif through angles φ of 2°50' and 2°20', while the bases of the outer O surface are rotated through φ of 30' and 1°40'. In both structures the Fe^{3+} cations are drawn close to the outer bases. The difference in bismuthoferrite relative to chapmanite lies in the inclinations of the bases of the octahedra in the layer, by virtue of which they do not lie in the same plane. The mean Fe–O distances are 2.00 and 2.01 Å in bismuthoferrite, individual distances showing a large scatter.

Chemical analyses of chapmanite[4] and bismuthoferrite[5] indicate a certain deficit of Sb and Bi and an excess of Fe compared with the ideal formulas, suggesting the partial isomorphic replacement of Sb by Fe in the chapmanite structure.[4] However, in the structural analysis of chapmanite and bismuthoferrite the Fourier-potential syntheses showed weak peaks in the center of the empty octahedron and also a certain reduction in the multiplicity of Sb and Bi according to least-squares data ($\mu \sim 1.90$). It is therefore more likely that some of the empty octahedra are occupied by excess Fe while the vertices of the adjacent pyramids are vacant; the formulas of chapmanite and bismuthoferrite are then $Sb_{0.93}Fe_{2.07}(Si_{1.98}Al_{0.02})O_8(OH)$ and $Bi_{0.92}(Fe^{3+}_{1.86}Fe^{2+}_{0.25}Al_{0.03})Si_2O_8(OH)$. This is reflected in the fall in R factors by 1.4 and 1.1%.

The specific structural characteristics of chapmanite and bismuthoferrite revealed by electron diffraction are largely due to the interlayer cations Sb and Bi (unusual for layerlike silicates) and the occupation of the octahedra by Fe^{3+} cations, which are incapable of replacing Al in the structures of kaolin minerals even to the slightest extent.

First of all the presence of Sb and Bi in the interlayer gaps produces a peculiar mutual disposition of the two-stage layers in the monoclinic single-layer structure 1M, with an electrostatically unfavorable superposition of Fe and Si cations in normal projection on the ab plane. The interlayer Sb and Bi cations adjacent to the outer surface of the octahedral lattice of the two-stage layers also counteract the attraction of the O atoms by the octahedral cations of the layer, so reducing the angle φ for the outer bases of the octahedra.

The occupation of octahedra larger than Al by Fe^{3+} cations, not accompanied by any increase in the height of the octahedra (impermissible owing to the necessity of screening the mutual repulsion of the octahedral cations by the common O–O edges of the octahedra), increased the a, b periods and reduced the density of disposition of O, OH in the median plane of the two-stage layer. However, there was also a reduction in the screening of the mutual repulsion of the octahedral and tetrahedral cations (Fe^{3+} and Si^{4+}), owing to which the distance between the atomic planes of these cations increased from ~2.70 Å in Al-layer silicates to 2.77 and 2.80 Å. The cations were correspondingly displaced toward the bases of the tetrahedra and the outer bases of the octahedra, although to a lesser degree than in the kaolin structures, owing to the counteraction of the interlayer cations. Another consequence of the increment in the distance between the tetrahedral and octahedral cations was a considerable lengthening of the tetrahedra, which could not be compensated by a limiting reduction of their bases to dimensions corresponding to the near-zero values of ψ. As a result the $(Si-O)_{av}$ distances increased to 1.63 Å. The minimum dimensions of the bases of the tetrahedra and the inadequate approach of the Si atoms to these arose from the necessity of weakening both the repulsion of Si and Sb (Bi), and also the earlier-mentioned effect of the superposition of Fe and Si atoms from neighboring layers in projection on the ab plane.

On lengthening the $Si-O_{ver}$ bonds the O_{ver} atoms saturate their valence to a lesser degree on account of the tetrahedral cations; this favors the partial occupation of the empty octahedra by Fe atoms.

The structural–mineralogical importance of chapmanite and bismuthoferrite lies in the fact that they represent unique examples of the realization of kaolinite-like layers with Fe cations instead of Al in the octahedra, and in a certain sense are opposed to other kaolin minerals, as are micas to pyrophyllites in the case of structures composing three-stage layers.

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