THE CRYSTAL STRUCTURE OF BERYLLONITE ($NaBePO_4$)

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The crystal structure of beryllonite ($NaBePO_4$) has been determined. A model of the structure has been found by analyzing the three-dimensional functions of interatomic vectors, as a result of which approximate coordinates were obtained for the P and Na atoms and also approximate positions of a large part of the O atoms in the xz projection. The model was refined by a series of successive approximations of the electron density projections ρ (xz) and ρ (yz).

Beryllonite ($NaBePO_4$) was first described by Dana [1] and they by Dana and Wells [2] in 1888-1889. On the basis of its optical properties it was assigned to the orthorhombic system. As regards its external appearance the authors noticed that the zone of the b axis hardly differed from the zone of a hexagonal prism and the zone of the a axis also had a pseudohexagonal character. In 1934 Gossner and Besslein [3] used x-ray methods to show that the symmetry of beryllonite is monoclinic with the space group $C_{2h}^5 = P2_1/n$. They determined the parameters of the unit cell a = 8.13, b = 7.76, c = 14.17 A and $\beta \approx 90°$ which corresponds to 12 formula units in the cell. In 1954 Wehrenberg [4] corrected the parameters to a = 8.16, b = 7.79, c = 14.08, c = 14.08 A and $\beta \approx 90°$.

Our beryllonite specimens were from the deposit under Stoneham (Maine, USA), obtained from the Mineralogical Museum of the Academy of Sciences, USSR. The Laue diffraction patterns confirmed that beryllonite belonged to the monoclinic system. The unit cell parameters were not determined precisely but the parameters a, b, and c, obtained from the usual rotating-crystal x-ray photographs agreed within the limits of error with those given by Wehrenberg.

The work on beryllonite started in 1951-1952, when Mo-radiation was not yet widely used in our structural laboratories and for this reason the beryllonite photographs were taken with Cu-radiation. With the Weissenberg goniometer we obtained 17 scannings of the layer lines along the a, b, and c axes. Later scannings were taken of the zero layer lines along the a and b axes with Mo-radiation, which made it possible to obtain a complete set of $0kl$ and $h0l$ reflections up to the boundary determined by their thermal damping at $\sin\theta/\lambda \approx 1.2\ A^{-1}$.

The intensities of the reflections were measured visually using standards and the squares of the structural factors F_{hkl}^2 obtained from them were reduced to a single scale by comparing the same reflections from different scannings. In Cu-radiation a total of 1253 independent reflections were recorded, the experimental intensities of which were not equal to zero, with $h_{max} = 9$, $k_{max} = 8$, $l_{max} = 17$. With Mo-radiation 337 nonzero independent reflections were obtained of the $h0l$ plane and 253 reflections of $0kl$.

On the scannings of the layer lines reflections of the type $h0l$ with an uneven sum of indices and reflections of 0k0 with uneven k are systematically absent. This uniquely confirms the Fedorov group $C_{2h}^5 = P2_1/n$, established by Gossner and Besslein. The scanning of the zero layer line along the b axis has a clearly expressed pseudohexagonal character, which is predetermined by the fact that $\beta = 90°$, that the ratio of the a and c axes of the beryllionite cell is very close to $1 : \sqrt{3}$, and the projection of the structure on the xz plane is centered due to the glide-plane n. In this projection it is, therefore, possible to select a cell which coincides in shape with the hexagonal form, which also determines the hexagonal geometry of scanning. The intensities of reflections connected by a pseudo sixfold axis of symmetry, are, in the overwhelming majority of cases, close, but do not completely coincide, i.e., there is not strict hexagonal symmetry in the projection.

From the squares of the structural amplitudes calculations were made of the Patterson projections for three coordinate planes and also Harker sections P (x0z) and P ($x\,{}^1/_2\,z$). The P (xz) projection is shown in Fig. 1. The large peaks on it are situated at the apices of regular triangles filling the whole plane. Smaller peaks can be seen roughly at the centers of these triangles. In the Harker section P (x0z) the peaks designated in Fig. 1 by the Figs. 1 and 3 are absent, on the other hand the peaks 2 are very strong. In the section P($x\,{}^1/_2\,z$) there are peaks 1 and the much weaker peaks 3, however, the peaks 2

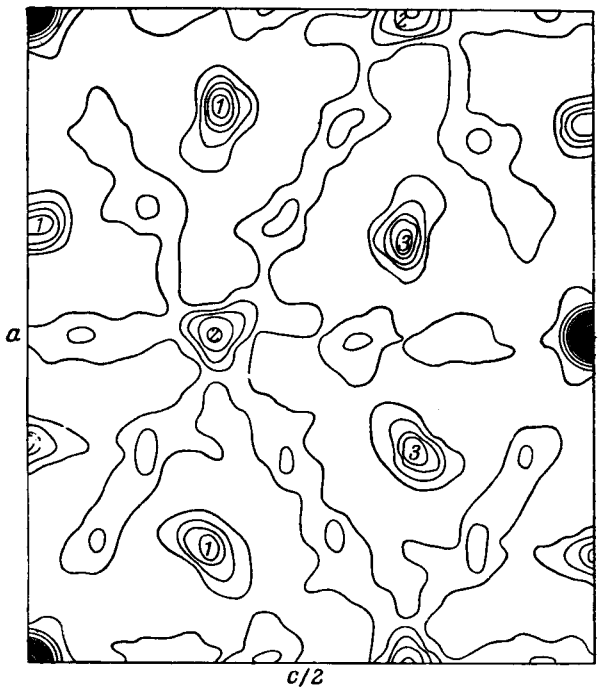

Fig. 1. Projection of the Patterson function P (xz).

are also present, although they are smaller in height than the peaks 1. This system of peaks with certain deviations (extra peaks 2 in the section P ($x\,^1/_2\,z$) and extremely high peaks 2 in the section P (x0z)) belongs to the scheme of the Belov-Butuzov theorem [5], applied to the case of the sixfold screw axis 6_3. According to this theorem the peaks 1 should coincide with the actual position of six atoms connected by a sixfold axis of symmetry and caused by interatomic vectors connecting the neighboring atoms of the six, the peaks 2 correspond to interatomic vectors connecting the atoms of the six through one, and the peaks 3 by vectors connecting the atoms of the six through two, i.e., atoms which are opposite with respect to the sixfold axis of symmetry. Deviations from the scheme can be explained by the superimposition of other interatomic vectors. In our case (6_3 axis) the six atoms are split up into two triplets, which are placed on two levels differing by a half of the parameter b. In the projections P(xy) and P (yz) appear all peaks corresponding to atoms of the described set of six. It was natural to take these six atoms, giving the strongest peaks to be P atoms.

In the projection P (zy) along the line $z = {}^1/_2$, where the peaks are concentrated—the ends of the vectors between the atoms connected by the glide-plane n, the strongest of the peaks has a coordinate y close to $^3/_{48}$. In the projection P (xy) for the strongest peak on the line $x = {}^1/_2$ the coordinate y is close to $^1/_{48}$, which makes probable the position of atoms in the described set of six, near the glide-planes, with coordinates y close to $^1/_4$ and $^3/_4$. At the same time this was an indication that a strong set of six is placed about the axis 2_1 and not about the center of symmetry, since in the latter case the atoms would be atomic in the glide-planes.

The P atom with atomic number 15 cannot play the role of a "heavy" atom since the Na and O atoms differ too little from it, especially if we consider the ionized state of all the atoms. Nevertheless, an attempt was made to use the P atoms to find the signs of the structural factors F_{h0l}, however, it did not give satisfactory placing of the other atoms.

Difficulties were also encountered in the attempt to determine the signs of the structural factors using the Harker-Kasper method of inequalities [6] and the Rumanova comparison method [7], developed in detail in our laboratory. However, the strong unitary structural factors were not sufficient for the successful use of inequalities. The comparison method for the structural factors F_{h0l} gave an obviously incorrect result, for the structural factors F_{0kl} several variants of signs were obtained, since it was not possible to establish all connections between the letters which represented signs during their determination. In the calculated six variants of the electron density projection ρ (yz) the P atoms "appeared" at the expected points, although the corresponding peaks had very widely differing heights. From the very large number of other peaks it was not possible to make any definite selection, especially when trying to "average" all these projections by simply combining them and by plotting the ρ (yz) projections for those structural factors whose signs were the same in all variants. As explained later, some of the peaks of these projections corresponded to the actual positions of the Na and O atoms, however, these peaks were lost in the large number of other, false peaks and all attempts to sort these peaks by plotting the appropriate syntheses were unsuccessful. In work with direct methods Mo-reflections of the h0l and 0kl planes were used and also almost the whole totality of Cu-reflections.

With understandable reluctance we turned to the three-dimensional function of interatomic vectors P(xyz). Starting from preliminarily calculated arbitrary projections of P_N (xz) for N = 0,1 ..., 8 piercings were made in the direction of the b axis, in which the value of the functions P_N were used as coefficients of unidimensional series. At first the piercings were made at intervals of $^1/_{48}$ of the parameter c and $^1/_{24}$ of the parameter a, later the configuration of individual peaks was made more accurate by additional piercings.

In the function P (xyz) we found all peaks caused by interatomic vectors connecting the P atoms. However, in addition at the level $y = {}^1/_4\,({}^3/_4)$ we found fairly strong peaks at the points designated in the P (xz) projection (Fig. 1) by the numbers 1 and 3. They were interpreted as peaks corresponding to the vectors P—Na. The Na atoms should have been at the centers of hexagons formed by the P atoms and have had coordinates y close to 0 and $^1/_2$ (Fig. 2). In position 2 (Fig. 1) at a height

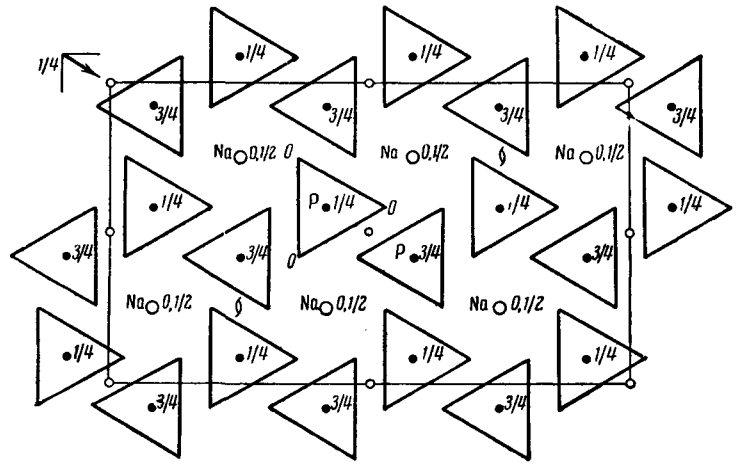

Fig. 2. Position of atoms obtained from an analysis of P (xyz). The numbers indicate the approximate height.

$y = {}^1/_2$ there is a relatively small peak corresponding to the Na–Na distances from different hexagons, confirming the assumption previously made. However, on the lines x = 0, z = 0 there should be a peak with a coordinate $y = {}^1/_2$, corresponding to vectors between those Na which are above one another in one hexagon. However, this peak was not found and on the line x = 0, z = 0 apart from the initial peak there was only a comparatively small peak with a coordinate y slightly exceeding $^1/_3$, which disproved the a priori assumed position of Na; however, after several attempts to interpret P (xyz) by other methods the absence of this peak had to be neglected and the initial interpretation used.

On the P (xz) (Fig. 1 there are weaker peaks in the centers of the triangles formed by the peaks 1, 2, 3. In the three-dimensional function each of them was split-up in the direction of the y axis into two or three with different heights. Since these peaks are not included in the system of interatomic vectors P–P, P–Na, Na–Na they could only be identified with the vectors P–O and Na–O. Although the coordinates of separate atoms could not be found, it nevertheless became apparent that the O atoms are in relation to the P atoms in positions close to those in which they are shown in Fig. 2.

The signs of F_{h0l} were calculated, starting from the positions of the P and Na atoms and also the averaged (as they are shown in Fig. 2) positions of 9 (out of 12) O atoms. Since only the averaged coordinates of the O atoms were used in the calculation, for the first synthesis of the electron density 60 near in amplitudes of F_{h0l} were taken, because with inaccurate coordinates of the atoms it was not possible to guarantee the correctness of the signs of far out amplitudes. For these 60 reflections (without three O and three Be) the calculated coefficient of divergence $R = \frac{\sum ||F| - |F_0||}{\sum |F_0|}$ was found to be 37.8%. The first synthesis ρ (xz) gave a certain displacement of the O atoms from the given positions. In later approximations this displacement gradually increased. From the second synthesis ρ (xz) it was possible to establish the approximate position of the three missing O atoms. The coefficient R after the third approximation was 26.6%, but with the inclusion in the calculation of all reflections obtained with Cu-radiation it was raised to 34.6%. By subsequent approximations of ρ (xz) and two difference syntheses $\rho_e - \rho$, the coefficient R was reduced to 21.8%.

We then considered the ρ (yz) projection, the y coordinates for the P atoms being taken from the ρ (yz) projections obtained from the determination of the signs of F_{0kl} by direct methods, the y coordinates of the O atoms were obtained from their x, z coordinates and the assumed P–O distances and the Na atoms were placed at an equal distance from both levels occupied by the P atoms. We again started with 60 near in $0kl$ reflections, and for them the coefficient R was 61%! However, after two approximations of ρ (yz) it was reduced to 39.4% and after a fourth approximation it was reduced to 28.8%. The addition of all Cu-reflections, as in the case of the xz projection, increased R to 38.6%. After a seventh approximation, taking into account the Be atoms and the difference synthesis proceeding from them, $\rho_e - \rho$, we obtained R = 24.3%.

In addition to the displacement of the O atoms, in the process of approximations, it was found that those atoms Na (Na_2 and Na_3) which are not near the 2_1 axes, contrary to expectation, are separated in the direction of the y axis not by the distance b/2, but by a much smaller value. To a certain extent this justified the absence of a peak with coordinates (0, 1/2, 0) in P (xyz). This peak, caused by the Na–Na vectors, parallel to the b axis, should be weak and spread out. It total absence can presumably be explained by the inaccurate reduction to one scale of F^2_{hkl} from different layer lines for P (xyz) we mainly used layer lines of rotation about the b axis).

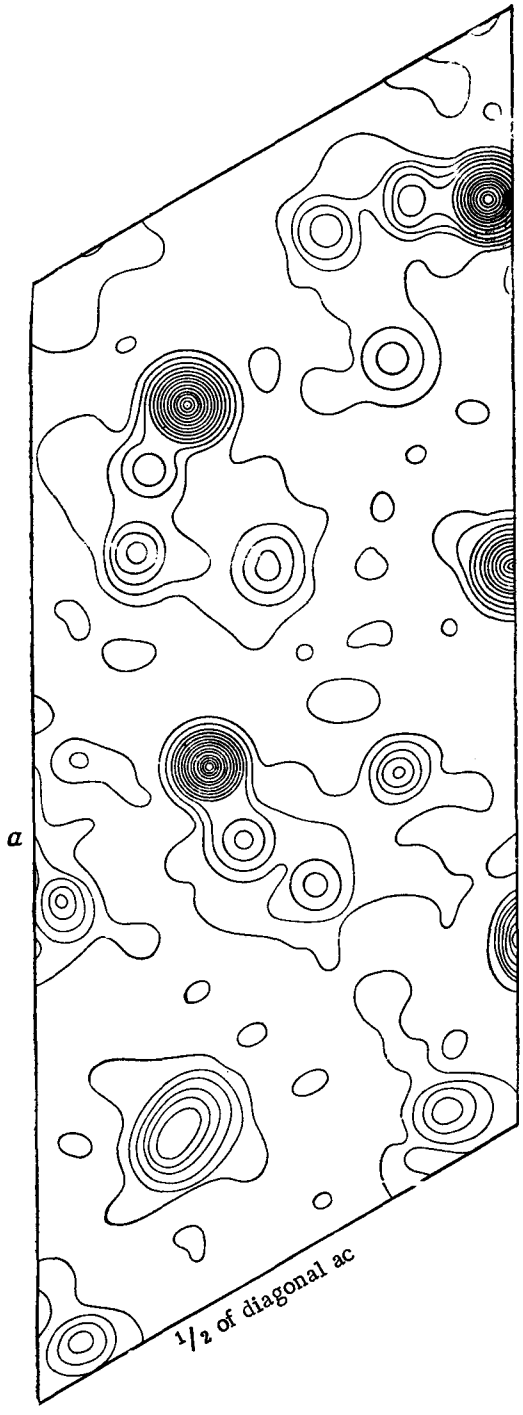

Fig. 3. Electron density projection ρ (xz) (half of reduced cell).

Since the coefficients for the section P(0y0) are the sums F^2 over each of the rotation layer lines about the b axis, the errors in reducing these layer lines to a single scale are large, especially with a sharply cut off series.

The inclusion of all reflections obtained with Mo-radiation in the calculation of both projections again sharply increased the coefficients R: for the xz projection to 35.6%, for the yz projection to 34.5%. After eleven approximations for both projections (including the difference syntheses) for the structural factors F_{h0l}, taken to $\sin \theta/\lambda \approx 1.15$ A^{-1} (without experimental zeros) the number of which in the far out region of θ/λ considerably exceeds the number of visible reflections), the coefficient R was reduced to 19.8 and for F_{0kl} under the same conditions to 19.0%. During its calculation a temperature factor was introduced with B = 0.6. The x-ray patterns used in the work were obtained with a fairly large (about 0.5 mm in diameter) fragment of an irregularly shaped crystal. Absorption therefore played an important part. For almost all close in stronger reflections, the calculated values of F_{hkl} were much greater than the experimental values. If we exclude the three strongest near in reflections 020, 040, and 006 from the calculation of R_{0kl} then it is reduced from 19 to 15%. The exclusion of the six strongest reflections of h0l improves R correspondingly from 19.8 to 17%.

It therefore follows that the coefficient of divergence decreases considerably when the far out reflections are neglected; unfortunately, this cutting off of the series strongly affects the accuracy of the coordinates. The coordinates taken from the electron density projections plotted from the Cu-radiation reflections were used to calculate the P–O distances, which were found to be clearly unsatisfactory. Some were extremely high, reaching 1.7 A, others were too low—as low as 1.27 A, despite the fact that for one of the projections R was 21.8%, for the other 24.3%. When the electron density was computed from all reflections obtained with Mo-radiation the range of P–O distances was reduced to 1.48 - 1.56 A.

Figures 3 and 4 show the final projections of ρ (xz) and ρ (yz). Figure 3 shows a half of the primitive "hexagonal" cell, which can be selected for the xz projection. Figure 4 gives $^1/_4$ of the projection of the total cell on the yz plane.

The coordinates of the atoms obtained from these projections are given in the table. In the assymmetric unit there are 21 atoms in the general position, i.e., the structure is determined by 63 parameters with 84 atoms in the cell. The Be atoms, resolved in the yz projection, are overlapped in the xz projection by the P atoms and their x coordinates are obtained from elementary geometrical considerations. The x coordinates of the Na atoms are also approximate, since in the xz projection all Na combine in pairs. The series of combined peaks in the yz projection also affected the accuracy in determining the y coordinates of the individual atoms.

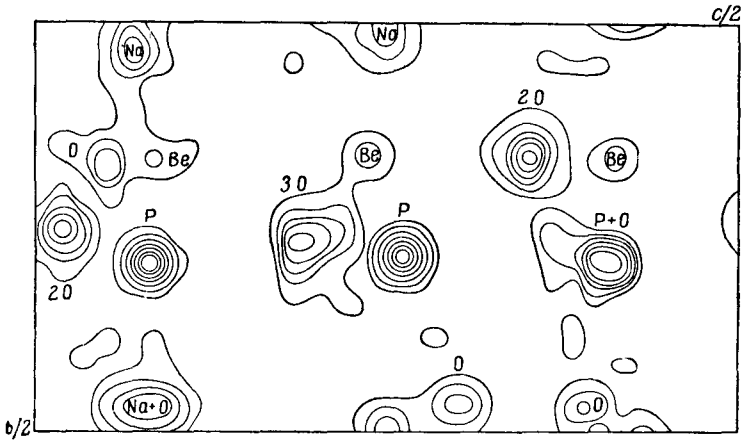

Fig. 4. Electron density projection ρ (yz).

Coordinates of Atoms in the Crystal Structure of Beryllonite

Atom	x	y	z
P_1	0.921	0.788	0.238
P_2	0.106	0.291	0.081
P_3	0.432	0.790	0.092
Na_1	0.248	0.004	0.248
Na_2	0.747	0.472	0.084
Na_3	0.763	0.031	0.069
O_1	0.435	0.266	0.192
O_2	0.066	0.268	0.188
O_3	0.252	0.774	0.123
O_4	0.739	0.253	0.214
O_5	0.948	0.253	0.022
O_6	0.552	0.252	0.016
O_7	0.949	0.664	0.155
O_8	0.239	0.171	0.053
O_9	0.535	0.664	0.148
O_{10}	0.923	0.964	0.198
O_{11}	0.164	0.473	0.062
O_{12}	0.495	0.971	0.110
Be_1	0.917	0.161	0.239
Be_2	0.103	0.662	0.082
Be_3	0.431	0.165	0.090

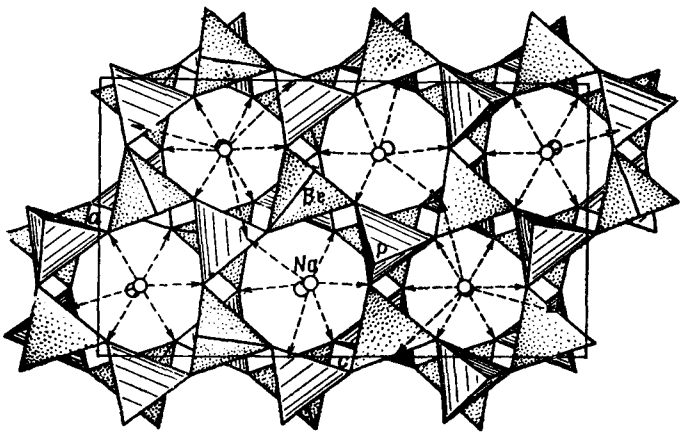

Fig. 5. Projection of the crystal structure of beryllonite onto the xz plane.

Some idea of the accuracy of the final electron density projections is given by a comparison of the values of z for those atoms which are resolved in both projections. Thus, the z coordinates of two of three P atoms differ by 0.001 of a parameter and for the third they coincide (with an accuracy of 0.0005 of a parameter). Of the three resolved O atoms for two $\delta z = 0.001$ of a parameter for the third $\delta z = 0.005$ of a parameter. Further improvement in the accuracy of the coordinates would be desirable after preliminary improvement of the experimental material, i.e., the maximum exclusion of the absorption effect.

Figures 5 and 6 show the xz and yz projections of the beryllonite structure. About the two screw axes 2_1 (Fig. 5) there are six PO_4 tetrahedra and six BeO_4 tetrahedra combined in pairs in the direction of the b axis by common apices. Six such P–Be pairs are situated at two levels according to the law of a sixfold screw axis 6_3 and are joined to one another by O atoms at the bases of the tetrahedra. The infinite sixfold "tubes" obtained are connected to one another in the direction of the a edge of the cell by the screw axes 2_1 and in the direction of the projection diagonals by the centers of symmetry, and in both cases they are connected by the common apices of the tetrahedra in a three-dimensional framework, in which each P-tetrahedron is surrounded by four Be-tetrahedra and vice versa. In the intervals between the "tubes" channels are formed having a less regular form, but also surrounded in the projection by six pairs of tetrahedra. Within the tubes and in the channels between them there are Na atoms. The Na_1 atoms are very close to the 2_1 axes, playing the part of pseudoaxes. Each of them is surrounded by nine O atoms; the nine pointed figures touch one another at common

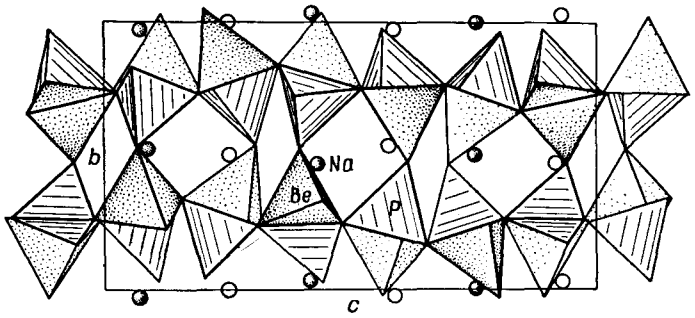

Fig. 6. Projection of the crystal structure of beryllonite onto the yz plane.

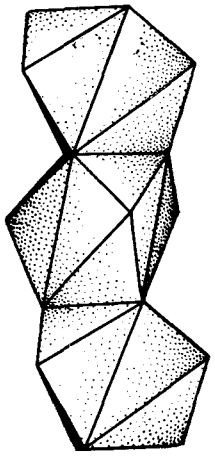

Fig. 7.

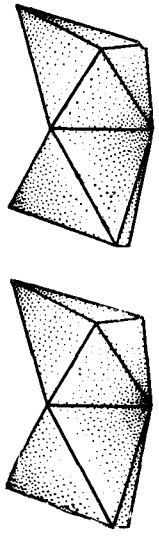

Fig. 8.

Fig. 7. Column of Na_1 "nonavertica."
Fig. 8. Pairs of Na_2 and Na_3 octahedra.

edges, forming infinite columns (Fig. 7). The Na_2 and Na_3 atoms are in distorted octahedra, joined by common edges in isolated pairs (Fig. 8), between which, in the direction of the b axis, there are discontinuities—unpopulated vacancies. The Na polyhedra are partially joined with the PO_4 and BeO_4-tetrahedra by common edges.

If the phosphorus-beryllium framework is split up into infinite lattices, parallel to the c axis of the cell, it is found that each such lattice consists of infinite chains connected to one another by 8-piece links, very similar to silicon-oxygen chains $[Si_6O_{17}]_\infty$ found by Memedov and Belov in the calcium silicate xonotlite [8]. These xonotlite chains are split up into more elementary units, sililar to the $[SiO_3]_\infty$ chains found by these authors in wollastonite [9]. The P—Be chains in beryllonite differ from the wollastonite and xonotlite chains by somewhat different rotations of the components of their tetrahedra. The whole framework can therefore be considered as being built up of the same chains stretched in the direction of the c axis.

The P—O distances vary between 1.48 and 1.56 A and the edges of the PO_4 tetrahedra are from 2.42 to 2.54 A. The Be—O distances vary between 1.58 and 1.66 A and the edges of the corresponding tetrahedra between 2.58 and 2.76 A. The Na_1—O distances (in the nine pointed figures) vary between 2.51 and 2.82 A, the greatest distances being from the Na_1 to the three side O atoms, converting the stretched octahedron into a "nonaverticon." In Na_2 and Na_3 octahedra the Na—O distances are within the limits 2.68 - 2.22 A the least (2.44 - 2.22 A) distances are from the Na atoms to the outer apices of a pair of octahedra, which is presumably due to the repulsion between a pair of Na atoms, separated only by a common face of the octahedra surrounding them. The edges of the Na polyhedra vary between 4.34 and 2.47 A, the small edges also being the edges of the neighboring BeO_4 and PO_4 tetrahedra.

The framework structure of beryllonite agrees with the considerable hardness of the mineral (5.5-6). Approximately the same (5-6) hardness is shown by framework silicates belonging to the sodalite and cancrinite groups. Parallel to the planes of the six-member rings of P—Be tetrahedra is a perfect cleavage surface of beryllonite: (010).

It has already been mentioned that beryllonite has the optical properties of an orthorhombic crystal; the plane of its optic axes keeps a constant position, coinciding with the (100) plane. This is presumably due to the strong pseudohexagonality of the crystal. The phosphorus-beryllium "tubes" (Fig. 5) have an almost perfect hexagonal structure. Taken separately, such an element of structure would be "uniaxial" with regard to light. The whole structure is made up of these hexagonal tubes, a half of which are rotated with respect to other centers of symmetry. However, these tubes taken as a whole as "uniaxial" elements of structure and also the Na atoms are connected in the xz projection by slip pseudoplanes of symmetry a and c. This presumably causes the orthorhombic character of the double refraction.

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