# ELECTRON-DIFFRACTION REFINEMENT OF THE STRUCTURE OF MUSCOVITE

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On the basis of electron-diffraction data from texture patterns a refinement of the structure of muscovite has been carried out with the use of Fourier syntheses. It has been established that Al may replace Si only in the half of the tetrahedra which are joined to the oxygens next to the glide planes of the octahedral layer. The substitution of Al in a tetrahedron results mainly in a change in the oxygen position in the reflection plane of the tetrahedral layer, and, as a result, in a shift of K, and this leads to a slight increase in $\beta$ over the theoretical value.

In the crystal chemistry and structural mineralogy of layer silicates the structure of muscovite $KAl_2(AlSi_3O_{10})(OH)_2$ is of particular significance. In it the repetition of layers with a two layer period is found in its neatest form. This two-layer period is, in one way or another, characteristic of the most varied types of these minerals. The structure may be harmonized as discovered by N. V. Belov with other types of repeats, in accordance with the twinning of micas and micaceous minerals [1]. Hence, such periodicity can exist both in entirely regular structures, and also in disordered structures, in which the repeat period of the layers change statistically and one cannot determine a strict period $\underline{c}$.

Within the limits of an idealized model, the structure of muscovite was determined in 1930 [2]. The most profound crystal chemical discussion of the structure is found in Belov's work [1]. An analysis of the positions in the interlayer holes of the K cations as a function of the configuration of the tetrahedral nets was given by Yamzin [3]. Finally, Gatineau and Mering [4] from a one-dimensional projection found a new $\underline{z}$ coordinate, which in particular leads to differences from the assumed positions in one plane of the atoms $O_{oct}$, Si, and $Al_{tetr}$.

However, in spite of all this, there remain in the structure of muscovite many vague features which may be explained only after a complete determination of the structure with the use of Fourier-analysis methods. In the present work the electron-diffraction method of structure analysis was used for the solution of this problem; this method has been used with good results in the determination of structures of finely dispersed lamellar silicates [5-7].

The structural type of muscovite is best shown on the electron diffraction photographs of several sericites, which, obviously, may be thought of as thin-scaled and finely dispersed forms of muscovite. The texture electron diffraction photographs (Fig. 1) were notable for their clarity and contrast, low background, and high resolution. In particular, the usually overlapping reflections $\overset{\pm}{2}0l$, $\overset{\pm}{1}3l$ were resolved.

From the texture electron-diffraction photographs the following unit cell data are obtained: a = 5.18, b = 8.96, c = 20.1 A, $\beta$ = 95° 40'; the x-ray results [2] are: a = 5.18, b = 9.02, c = 20 A, $\beta$ = 95° 30'.

The presence of a two-layer period, and the condition of homogeneity and nonpolarity in the structure of muscovite lead most naturally to three-storied layers, in which the symmetry planes of the upper and lower tetrahedral (Si, Al) – 0 nets are displaced relative to the symmetry planes of the octahedral Al – O, OH nets by an amount $\Delta y$, which is 1/3, – 1/3 for the one layer and –1/3, 1/3 for the other, which adjoins the first.

TABLE 1

Experimental and Theoretical Values of Φ for the h0*l* and 0k*l* Reflections

| $hkl$ 1 | $\|\Phi_e\|^2$ | $\Phi_T$ 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 200 | 14.2 | 13.7 | $\bar{4}02$ | 13.8 | —13.0 | 020 | — | 0.6 | 060 | 14.7 | —18.2 | 081 | 2.2 | 2,7 |
| 202 | 7.2 | 7.1 | $\bar{4}04$ | 4.3 | —4.3 | 022 | 5 3 | 3.0 | 062 | 5.7 | —5.0 | 083 | 2.1 | —2.2 |
| 204 | 3.6 | —4.0 | $\bar{4}06$ | 4.3 | 3.4 | 024 | 14.0 | 12.2 | 064 | 1.2 | —1.8 | 085 | 0,7 | 0,5 |
| 206 | 10.0 | —7.7 | $\bar{4}08$ | 1.2 | 0.9 | 026 | 2.4 | —2.2 | 066 | 1.5 | 0.1 | 087 | 0.7 | 0.1 |
| 208 | 6.5 | 7.8 | $\bar{4}$.0.10 | 1.3 | —4.8 | 028 | 1.2 | 1.0 | 068 | 4.5 | —3.8 | 089 | 0.5 | —0.2 |
| 2.0.10 | 10.6 | —12.3 | $\bar{4}$.0.12 | 8.2 | 9.0 | 0.2.10 | 2.0 | 2.2 | 0.6.10 | 4.2 | 6.3 | 0.8.11 | 3.0 | —2.8 |
| 2.0.12 | 11.9 | —14.3 | $\bar{4}$.0.14 | 5.9 | 7.2 | 021 | 7.3 | 3.4 | 0.6.12 | 2.2 | 3.0 | 0.8.13 | 4.2 | 3,6 |
| 2.0.14 | 4.5 | —5.3 | $\bar{4}$.0.16 | 5.0 | 3.5 | 023 | 11.9 | 10.4 | 0.6.14 | 2.6 | —2.1 | 0.8.15 | 1.1 | —1,3 |
| 2.0.16 | 2.6 | 2.3 | 600 | 5.8 | —4.5 | 025 | 15.0 | —13.7 | 0.6.16 | 8.2 | —7.5 | 0.8.17 | 1.3 | —1.0 |
| 2.0.18 | 5.2 | —6.0 | 602 | 1.8 | 1.9 | 027 | 4.8 | 4.2 | 0.6.18 | 1.3 | —0.1 | 0.10.0 | 1,7 | —0.5 |
| $\bar{2}02$ | 17.0 | —17.6 | 604 | 0.7 | —0.3 | 029 | 3.8 | 3.2 | 0.6.20 | 5.5 | —4.3 | 0.10.2 | 0.9 | —0.7 |
| $\bar{2}04$ | 11.3 | —11.8 | 606 | 1.4 | —4.6 | 040 | 7.2 | —4.6 | 0.6.22 | 6.5 | —6.0 | 0.10.4 | 1.1 | 2.7 |
| $\bar{2}06$ | 16.8 | —14.2 | 608 | 2.8 | 6.1 | 042 | — | 1.8 | 061 | — | 1.0 | 0.10.6 | 1.2 | 1.3 |
| $\bar{2}08$ | 4.8 | —3.8 | 6.0.10 | 4.1 | 1.3 | 044 | 5.8 | —5.9 | 063 | 0 7 | 0.2 | 0.10.8 | 0.7 | 1.1 |
| $\bar{2}$.0.10 | 14.6 | —12.4 | 6.0.12 | 1.9 | —4.7 | 046 | 4.2 | —4.7 | 065 | 0.6 | —1.0 | 0.10.10 | 0.5 | 2,8 |
| $\bar{2}$.0.12 | 4.8 | —6.3 | $\bar{6}02$ | 5,8 | —8.2 | 048 | 1.6 | —0.9 | 067 | 0.7 | 0.5 | 0.10.12 | 2.6 | 3.8 |
| $\bar{2}$.0.14 | 2.5 | 2.6 | $\bar{6}04$ | 1.5 | —0.6 | 0.4.10 | 1.6 | —1.4 | 069 | 1.3 | 0.5 | 0.10.1 | 1.8 | 0.4 |
| $\bar{2}$.0.16 | 10.1 | 9.5 | $\bar{6}06$ | 4.6 | —3.5 | 0.4.12 | 10.5 | —7.7 | 0.6.11 | 0.6 | —2.1 | 0.10.3 | 0.4 | —1.8 |
| $\bar{2}$.0.18 | 8.0 | —5.8 | $\bar{6}08$ | 1.6 | 0.1 | 0.4.14 | 2.4 | 2 0 | 0.6.13 | 0.7 | —0.1 | 0.10.5 | 0.4 | 0.1 |
| 400 | 9.8 | 12.3 | $\bar{6}$.0.10 | 0 | —0.7 | 041 | 6.5 | —5.8 | 0.6.15 | 0.4 | 0.1 | 0.10.7 | 0.6 | —0.3 |
| 402 | 5.3 | 6.7 | $\bar{6}$.0.12 | 0 | 0.7 | 043 | 4.2 | 5.5 | 0.6.17 | 1.3 | 0.1 | 0.10.9 | 0.8 | —0.8 |
| 404 | 1.2 | 1.5 | $\bar{6}$.0.14 | 7.1 | 2.0 | 045 | 1.1 | —1.1 | 0.6.19 | 1.0 | —0.3 | 0.10.11 | 1.2 | —1.0 |
| 406 | 2.3 | 5.5 | $\bar{6}$.0.16 | 0.8 | 0.5 | 047 | 1.1 | —2.8 | 0.6.21 | 1.0 | —0.3 | 0.12.0 | 2.2 | 6.8 |
| 408 | 9.2 | 10.3 | $\bar{6}$.0.18 | 2.0 | 5.7 | 049 | 1.1 | 0.8 | 080 | 2.4 | —2.7 | | | |
| 4.0.10 | 2.9 | —2.9 | | | | 0.4.11 | 3.4 | 6.2 | 082 | — | —0.1 | | | |
| 4.0.12 | 2.9 | —6.3 | | | | 0.4.13 | 4.1 | —7.2 | 084 | 0.3 | —1.9 | | | |
| 4.0.14 | 4.1 | —2.1 | | | | | | | 086 | 0.5 | —0.2 | | | |
| | | | | | | | | | 088 | 0.5 | 0.9 | | | |
| | | | | | | | | | 0.8.10 | 2.0 | 1.7 | | | |
| | | | | | | | | | 0.8.12 | 1.1 | —1.6 | | | |
| | | | | | | | | | 0.8.14 | 1.1 | 1.1 | | | |
| | | | | | | | | | 0.8.16 | 1.1 | —0.1 | | | |

TABLE 2

Atomic Coordinates in the Muscovite Structure

| Atoms (corresponding to Fig. 2) | x | y | z | Atoms (corresponding to Fig. 2) | x | y | z |
|---|---|---|---|---|---|---|---|
| $Al_{oct.}$ | 0.250 | 0.090 | 0.000 | $Si_2$ | 0.468 | 0.250 | 0.135 |
| $O_2$ | 0.417 | 0.250 | 0.053 | $O_5$ | 0.428 | 0.083 | 0.168 |
| $O_3H$ | —0.053 | 0.073 | 0.052 | $O_{5a}$ | 0.430 | 0.095 | 0.175 |
| $O_4$ | 0.447 | —0.073 | 0.052 | $O_6$ | 0.256 | —0.190 | 0.162 |
| $O_{4a}$ | 0.445 | —0.073 | 0.048 | $O_7$ | 0.756 | —0.143 | 0.162 |
| $Si_1$ | 0.468 | —0.083 | 0.135 | K | 0.000 | 0.083 | 0.250 |
| $Al_{tetr.}$ | 0.470 | —0.070 | 0.142 | | | | |

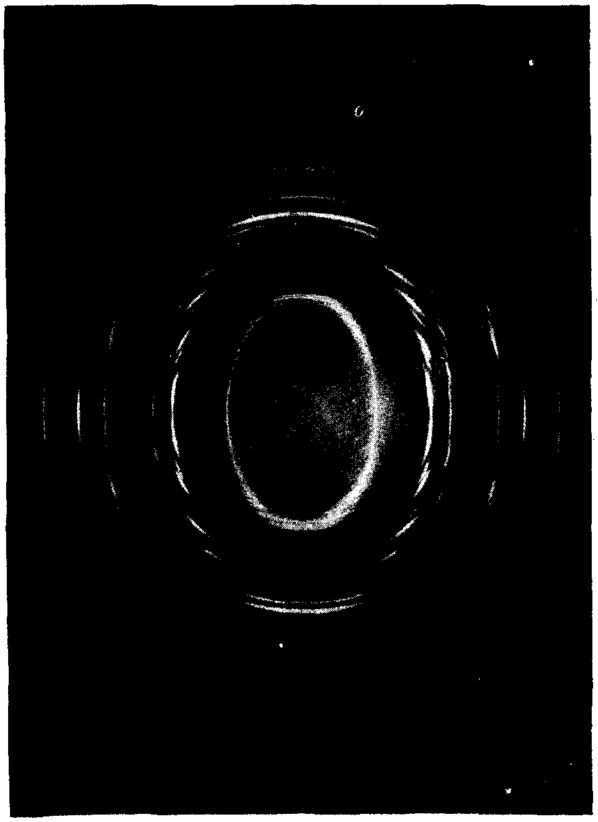

Fig. 1. Texture electron diffraction photograph of $W_2C$ ($\varphi \sim 50°$).

In view of the placement of potassium in interlayer holes (for this the tetrahedral meshes lie directly above one another to form the corresponding hole) the structure of muscovite and its unit cell, particularly the c axis direction, are determined automatically by the space group $C_{2h}^6 = C2/c$.

This idea of the muscovite structure is consistent with the results of [2] and coincides with the features of the electron diffraction photographs.

If we take the origin of coordinates at one of the centers of symmetry, which is also the center of the edge of the OH-OH octahedron, then the vectors a and c make an angle $\beta \sim 95°$.

If the origin is at one of the symmetry centers which is also the center of an octahedral void, then the vectors $\mathbf{a'} = -\mathbf{a}$ and $\mathbf{c'} = \mathbf{c} - \mathbf{a}$ make an angle $\beta \sim 100°$. It is easy to see that the planes of one cell are transformed into the planes n of the other, and vice versa.

For the construction of an initial model of the structure it was also assumed that the anions of the basic octahedra are close packed ($s = 0$) (for the parameter $\bar{s}$ see [6]), but for the basic tetrahedra the angle of rotation is $\psi = 12°$ ($s = 0.158$), corresponding to the equality $\cos\psi = a/2l_T$, where $l_T$ is the length of the tetrahedral edge. The $\underline{z}$ coordinates were taken from [4].

If one places the centers of the ditrigonal meshes of adjacent layers above one another, then, according to the equality $c \cos\beta = a/3$, one obtains the angle $\beta = 94°\ 55'$ (see also [1]). Corresponding to the experimental value of $\beta$, the K cation must be displaced approximately $\Delta x = -0.013$, and its octahedron (see [1]) is additionally slanted.

A comparison of experimental and calculated $\Phi$, calculated according to [5], once again shows, as in the case of kaolinite [6], that they are normalized differently as a function of the indices $hkl$.

Refinement of the structure of muscovite—sericite was carried out through projections of the structure onto the $x0z$ and $0yz$ planes; in view of the overlapping of several maxima, the corresponding difference syntheses were constructed.

The initial data for these syntheses are given in Table 1. The results obtained correspond to an R factor of 23% for the h0*l* and 0k*l* reflections (without 00*l* and some unreliable x-ray reflections with $\Phi_T > \Phi_e$).

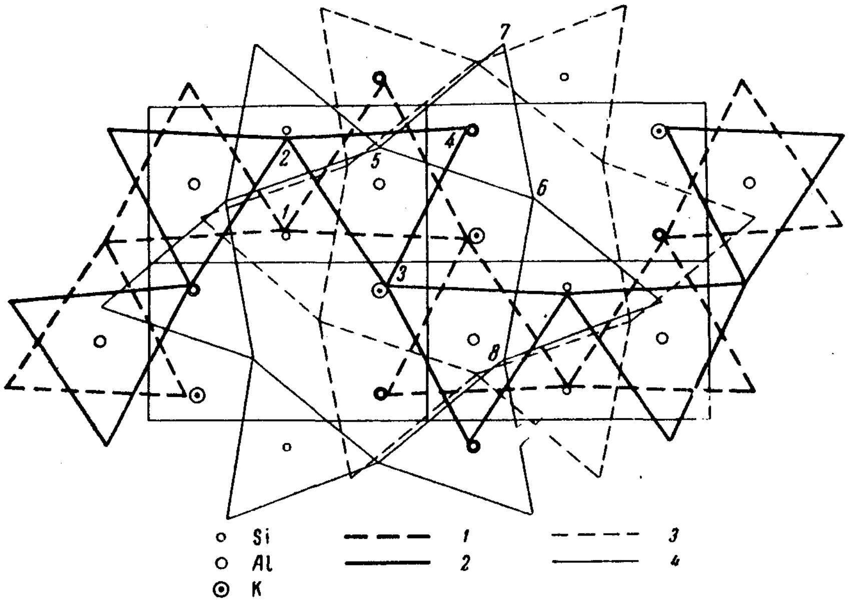

Fig. 2. Sketch of the muscovite structure as a normal projection onto the xy0 plane. 1) Lower bases of octahedra; 2) upper bases of octahedra; 3) bases of the lower tetrahedra; 4) bases of the upper tetrahedra.

The syntheses lead to refined coordinates of the atoms (Table 2), from which one calculates that the octahedral faces are rotated relative to one another about their normals through an angle $\phi \sim 3°$ ($s = 0.030$), and the tetrahedral faces are rotated through $\psi \sim 11°$ ($s = 0.168$). The accuracy of the coordinate determination, as calculated from Vainshtein's formula [5], is K – 0.02, Si, Al – 0.03, and 0-0.04 A. In Fig. 2 we depict a normal projection of one layer onto the xy0 plane in the form of a common motif of basic tetrahedra and octahedra, without showing the distortion connected with the substitution of Al for Si.

Gatineau and Mering [4] established that Al atoms which replace Si atoms have a somewhat larger coordinate and join by means of tetrahedra to the atom $O_{oct}$, which has a smaller z coordinate than in the case of Si atoms. However, there are initially four possibilities for the placement of such Al tetrahedra. In accordance with the projection of the structure onto the 0yz plane (Fig. 3) and the corresponding calculated synthesis, the Al tetrahedra adjoin only those O atoms which are situated near to the glide planes of the octahedral nets, whereas those O atoms situated on the mirror planes of these nets adjoin only Si tetrahedra (Fig. 2).

For every four atoms $O_{oct}$ there are two atoms of each kind. Yet, in the case of muscovite, there is only one Al tetrahedron. In accordance with the findings of N. V. Belov, the variability of degree of replacement of Si by Al in lamellar silicates is evidence for the complete statistical distribution of the Al atoms. Besides, if an Al tetrahedron adjoins some one given atom O, then this brings about a violation of the basal centering of the lattice and allows the appearance on electron diffraction photographs (particularly from single crystals) reflections with $h + k = 2n + 1$. However, this is not observed, for any of the lamellar silicates, for example, those studied by microdiffraction [8]. From the projections obtained it follows that statistical placement of Al tetr. atoms occurs in only two of the four possible positions.

The results obtained agree with the assertion of Loewstein [9] on the difference of charge on adjacent tetrahedra, and acquires a common value for all at least dioctahedral lamellar silicates. Thus, in montmorillonites, the majority of tetrahedra are filled by Si atoms; the Al tetr. atoms are distributed according to the laws of chance among that half of the tetrahedra which adjoin the $O_{oct}$ already mentioned. In the other limiting case – in dioctahedral brittle micas – in which the $O_{oct}$ situated on mirror planes of the octahedral net adjoin only

Si tetrahedra, but next to the $O_{oct}$ on glide planes are situated only Al tetrahedra. But in the trioctahedral xanthophyllites, in which for every three Al there is one Si [10], this rule, of necessity, is completely violated.

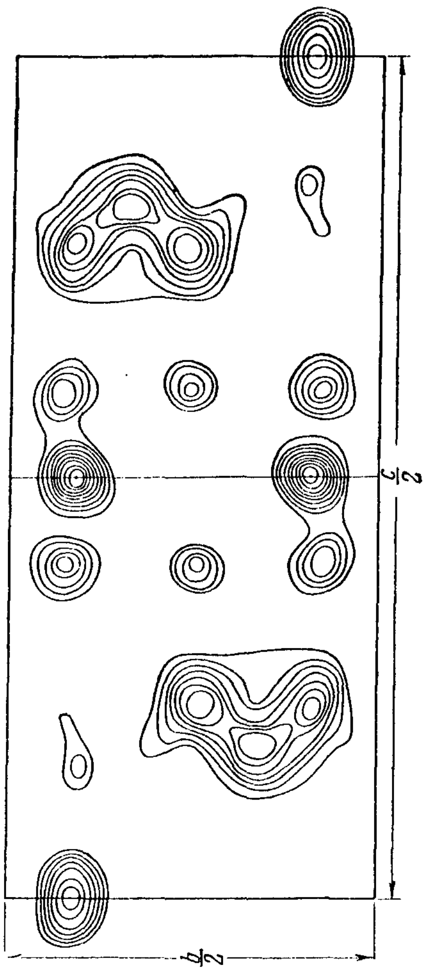

Fig. 3. Projection of the muscovite structure onto the 0yz plane.

TABLE 3

Interatomic Distances in the Muscovite Structure (atoms are designated in accordance with Fig. 2).

| | | | |
|---|---|---|---|
| $O_2 - O_1$ | 2.60 | $O_2 - Al$ | 1.92 |
| $O_3 - O_1$ | 2.86 | $O_3 - Al$ | 1.97 |
| $O_2 - O_3$ | 2.90 | $O_4 - Al$ | 2.00 |
| $O_6 - O_4$ | 2.71 | $Si - O_4$ | 1.66 |
| $O_6 - O_{4a}$ | 2.76 | $Al_T - O_{4a}$ | 1.88 |
| $O_5 - O_4$ | 2.90 | $O_5 - Si_1$ | 1.65 |
| $O_{5a} - O_{4a}$ | 2.97 | $O_{5a} - Al_T$ | 1.64 |
| $O_5 - O_6$ | 2.60 | $O_6 - Si_1$ | 1.56 |
| $O_{5a} - O_6$ | 2.71 | $O_6 - Al_T$ | 1.60 |
| $O_5 - O_7$ | 2.66 | $O_{5a} - Si_2$ | 1.63 |
| $O_{5a} - O_7$ | 2.76 | $K - O_8$ | 2.90 |
| $O_7 - O_6$ | 2.62 | $K - O_5$ | 2.98 |
| | | $K - O_{5a}$ | 2.90 |

In Table 2 are given the coordinates which depend on the substitution of Al for Si. These are marked in two ways, with those corresponding to the substitution of Al for Si by the subscript a. The z coordinates on the whole correspond to the values of [4], but are refined for $O_{tetr}$, and differ somwehat only for $O_{oct}$; they do not confirm the lowering of the coordinate z for OH.

In Table 3 we give the interatomic distances, including those which depend upon the replacement of Si by Al.

From a consideration of the data obtained, the mechanism of the substitution of Al for Si is clearly established. The placement of Al, for example, in the tetrahedron $O_4O_5O_6O_7$ (Fig. 3) is effected mainly by the removal to the left and up of $O_{5a}$, some lowering of $O_4$, and no change in the positions of $O_6$ and $O_7$. The Al is moved up and to the left in comparison with the analogous Si, and the noted movement of $O_5$ forces the movement of K by $\Delta x = -0.013$, which also causes the additional rotation of the K octahedra noted above, and the increase of $\beta$ by approximately 1° in comparison with its theoretical value.

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