

CRYSTAL STRUCTURE OF A TRIOCTAHEDRAL MICA:  
PHLOGOPITE<sup>1</sup>

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ABSTRACT

The crystal structure of an iron-rich phlogopite has been refined by Fourier projections and by a three-dimensional least-squares method. The structure is monoclinic,  $C2/m$ , with unit cell dimensions  $a=5.36 \text{ \AA}$ ,  $b=9.29 \text{ \AA}$ ,  $c=10.41 \text{ \AA}$ , and  $\beta=100^\circ 0'$ . There are two formula weights of composition  $(K_{0.9}Mn_{0.1})Mg_3(Si_3Fe_1)O_{10}(OH)_2$  in the unit cell. The iron is located in the tetrahedral sites, and the tetrahedra are rotated  $12^\circ$  about a normal to the base of the tetrahedron. The octahedral sites contain only magnesium, and the  $12^\circ$  rotation in the tetrahedral layer brings it into adjustment with the octahedral layer above it.

INTRODUCTION

In addition to their occurrence in igneous and metamorphic rocks, the members of the mica group of minerals are found widely disseminated in sediments and are considered to be important precursors of clay minerals. The hydrothermal stability range of the micas has been extensively investigated by Yoder and Eugster (1954, 1955), and the polymorphism existing among these minerals has been the subject of research by many investigators (Hendricks 1939; Levinson and Heinrich, 1954; Levinson, 1953; Smith and Yoder, 1956). The very extensive investigation on mica polymorphism by Smith and Yoder (1956) points out the pressing need for accurate determinations of atomic coordinates, ". . . in order that the structural controls (responsible for the polymorphism) can be more fully evaluated. From these determinations it should be possible to determine why muscovite adopts the 2M structure, and phlogopite and biotite tend to adopt the 1M structure." Again these authors point out that "detailed study of the ionic distribution in the mica structures is needed in order that accurate estimates of the structural forces can be made."

The recent determination of the crystal structure of muscovite (Radoslovich, 1960) supplied data towards the solution of some of these problems, and this investigation is similarly aimed towards a better understanding of the trioctahedral mica crystallizations.

DETERMINATION OF THE STRUCTURE

The specimen selected for investigation was obtained through the courtesy of Professor E. Wm. Heinrich of the University of Michigan

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and was described by him in "Studies in the Natural History of Micas," (1953) under number 1076 in the chapter on phlogopite. It is identical with a sample of manganophillite described by Jakob (1925), and his chemical analysis of this specimen is shown in Table 1.

This specimen was chosen for this investigation because of the high iron content, the absence of aluminum, and the presence of manganese in order to determine whether these ions are located in the octahedral or tetrahedral interstices of the silicate layer or whether they are also partly

TABLE 1. CHEMICAL ANALYSIS OF NO. 1076 PHLOGOPITE

SiO <sub>2</sub>	39.37%	MnO	4.52%
TiO <sub>2</sub>	0	MgO	26.79
Al <sub>2</sub> O <sub>3</sub>	0	CaO	0
Fe <sub>2</sub> O <sub>3</sub>	16.94	Na <sub>2</sub> O	0.49
FeO	0	K <sub>2</sub> O	8.67
Mn <sub>2</sub> O <sub>3</sub>	0	H <sub>2</sub> O(+150° C.)	3.32
		H <sub>2</sub> O(-150° C.)	0

in exchangeable positions. The chemical formula calculated from the analysis of Table 1 places the iron in the tetrahedral sites and requires that some manganese be between the silicate sheets together with potassium. The analysis actually affords slightly more than 16 cations per 24 oxygen units so that some manganese must presumably be with the Fe<sup>3+</sup> in tetrahedral positions. Idealized a formula may be quoted as (K<sub>0.9</sub>Mn<sub>0.1</sub>) Mg<sub>3</sub>Si<sub>3</sub>(Fe, Mn)<sub>1</sub> O<sub>10</sub>(OH)<sub>2</sub>. That the chemical analysis does not simultaneously afford both 16 cations and 24 oxygen atoms per cell indicates that some doubt exists as to the oxidation state of the manganese, but the allocation of approximately one heavy scatterer to a tetrahedral site cannot be questioned. If order on a unit cell scale exists among the tetrahedral ions in this crystal, it is clearly subject to demonstration by *x*-ray diffraction analysis. The reported density of 2.953 g/cc (Jakob, 1925) agrees with the value 2.95 g/cc obtained in this laboratory, and the calculated formula weight of 453.5 checks well with the weight of 448 calculated from the chemical analysis and based on 22 negative charges due to O<sub>10</sub>(OH)<sub>2</sub>.

Three-dimensional *x*-ray diffraction data from a single crystal flake shaped like a very flat cylinder of 0.2 mm radius and 0.03 mm height were collected with both Weissenberg and precession cameras by using Cu K $\alpha$  and Mo K $\alpha$  radiation, respectively. Of the 629 independent reflections within the copper sphere, 392 were observed. No corrections for absorption were made on the data. The unit cell dimensions are  $a = 5.36 \pm 0.01 \text{ \AA}$ ,  $b = 9.29 \pm 0.02 \text{ \AA}$ ,  $c = 10.41 \pm 0.02 \text{ \AA}$ , and  $\beta = 100^\circ 0' \pm 10'$ . There are two

formula weights of the ideal composition in the unit cell. The diffraction symbol is  $2/mC$ , so that the space groups  $C2$ ,  $Cm$ , and  $C2/m$  had to be considered in the solution of the structure.

The chemical analysis indicated that all of the iron was located in the tetrahedral interstices, but in order to rule out iron in octahedral sites  $00l$  structure factors were computed with iron located in the octahedral and tetrahedral positions, respectively. The discrepancy coefficient

$$R = \frac{\sum | | F_o | - | F_c | |}{\sum | F_o |}$$

for the first case was 22 per cent and dropped to 16 per cent for the second alternative. Thus, the diffraction intensities confirmed the placement of the iron atoms indicated by the chemical analysis.

The space group of the single-layer structure of mica was given as  $Cm$  by Hendricks and Jefferson (1939), and Pabst (1955) showed that a very slight adjustment of the  $x$  parameters of some of the atoms, together with a new choice of origin, will bring all atomic parameters into a centro-symmetric space group  $C2/m$ . The correct choice of space group in these silicate minerals is complicated by the pseudohexagonal character of the structures, so that the statistical tests usually indicate only a hypersymmetric intensity distribution (Rogers and Wilson, 1953). It was therefore decided to initiate the structural investigation by deliberately choosing a noncentrosymmetric origin for the computation of phases and letting the successive electron-density maps show whether a centrosymmetric structure is justified. This mineral represents a particularly favorable case in which ordering in tetrahedral sites should be detectable from the structural analysis. In the case of aluminum substitution ordering manifests itself only by the increase in bond distance over the usual value of about  $1.62 \text{ \AA}$ , if silicon is the occupant. In this instance the heavy scatterer,  $\text{Fe}^{3+}$ , would show up unambiguously on the electron density maps. Furthermore, ordering of this ion would preclude the possibility of a centro-symmetric space group.

The initial (001) electron-density projections showed that the oxygen atoms of the structure were moving towards locations in the  $x, y$  plane which were related by a center of symmetry, although the positions were slightly rotated from the ideal centric structure, and electron-density difference maps confirmed the correctness of these new positions. The agreement between calculated and observed intensities showed a striking improvement with the assumption of the new centric coordinates; thus, the space group  $C2/m$  was considered correct, and refinement of the

structure was continued in that space group. The  $x$  and  $y$  parameters were refined by the usual projection methods and difference maps, and the  $z$  parameters were obtained from successive (100) projections. The final (001) and (100) electron-density maps are shown in Figs. 1a and 1b.

### THREE-DIMENSIONAL LEAST-SQUARES REFINEMENT

The coordinates obtained from the two-dimensional projections were used as starting values in a least-squares program. The program used evaluates first one temperature factor,  $A$ , parallel to the unique  $b$ -axis and then another temperature factor,  $B$ , in the plane perpendicular to the unique axis independent of the spatial coordinates of the atoms. Although the assumption that the vibrational modes of an atom can be described by

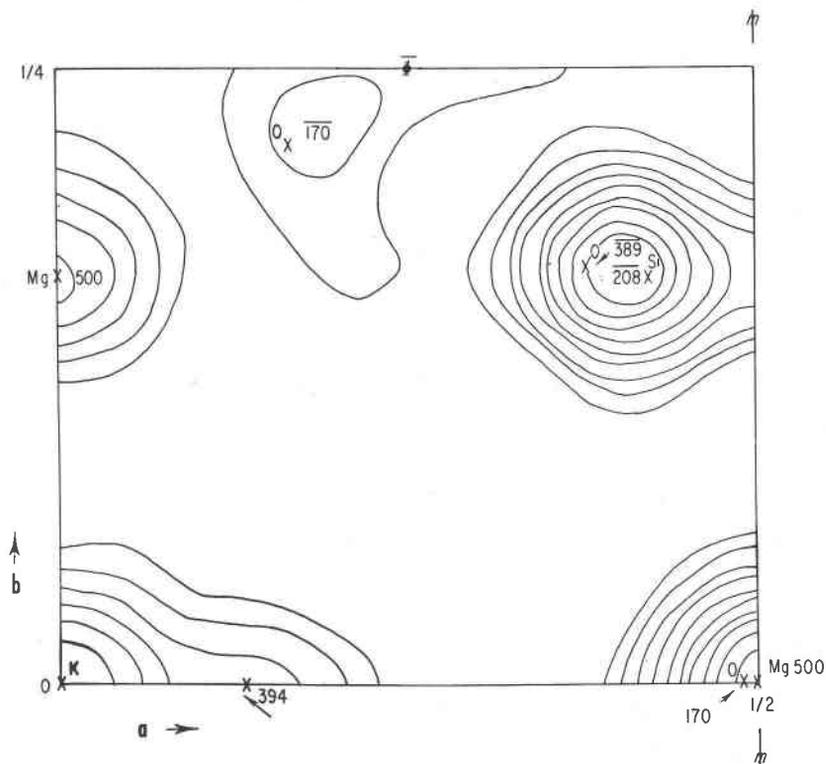


FIG. 1a. (001) Electron-density projection of phlogopite. Contours in intervals of about  $4e \text{ \AA}^{-2}$  beginning at  $8e \text{ \AA}^{-2}$ . The crosses mark the final location of the atoms, and the numbers indicate the  $z$  coordinates.

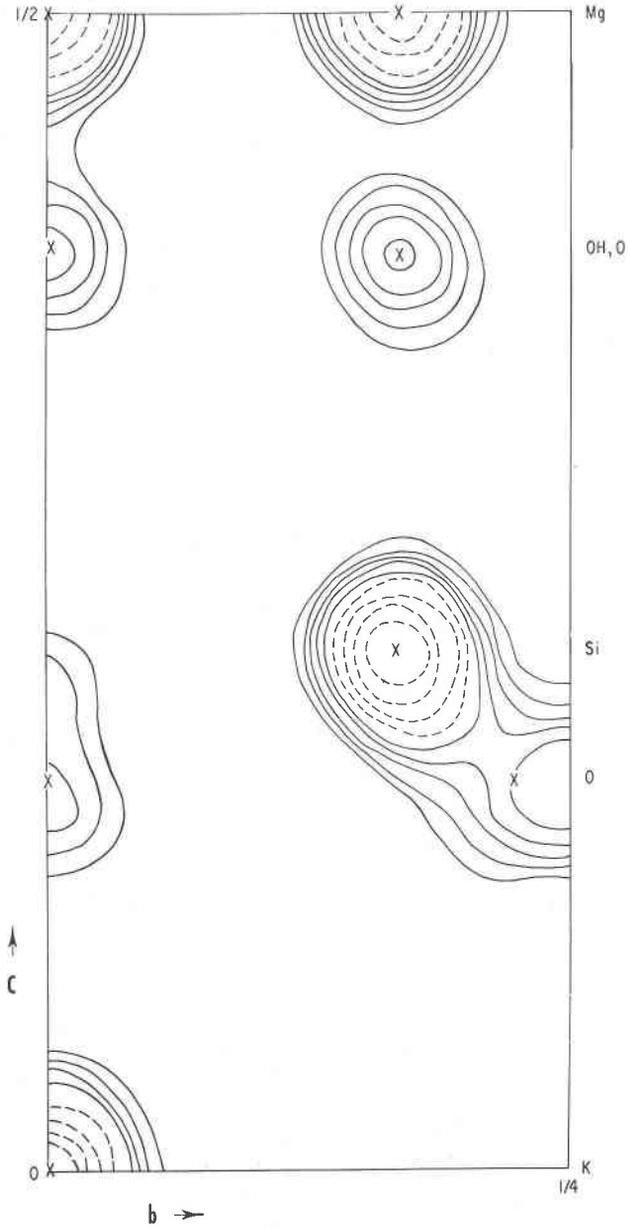


FIG. 1b. (100) Electron-density projection of phlogopite. Contours in intervals of  $2e \text{ \AA}^{-2}$  beginning at  $6e \text{ \AA}^{-2}$ . The dashed contours are in  $4e \text{ \AA}^{-2}$  intervals. The final coordinates are marked by crosses.

TABLE 2. FINAL COORDINATES

Atom	$\frac{x}{a}$	$\frac{y}{b}$	$\frac{z}{c}$	$A$ Å <sup>2</sup>	$B$ Å <sup>2</sup>	$\sigma(x)$ Å	$\sigma(y)$ Å	$\sigma(z)$ Å
K	0	0	0	2.91	2.22			
Mg <sub>1</sub>	0	.5000	.5000	1.16	1.39			
Mg <sub>2</sub>	0	.8333	.5000	1.16	1.39		.009	
Si <sub>0.75</sub>	.5766	.1679	.2261	2.16	2.42	.005	.005	.005
Fe <sub>0.25</sub>	.5766	.1679	.2261	1.84	2.73			
O <sub>1</sub>	.8338	.2229	.1692	3.62	2.79	.015	.017	.015
O <sub>3</sub>	.6273	.1682	.3900	3.62	2.79	.015	.016	.015
O <sub>2</sub>	.4963	0	.1700	3.62	2.79	.022		.023
OH	.1354	0	.3955	3.62	2.79	.022		.023

an ellipsoid of revolution which is oriented along a unique crystallographic direction is forced, it is to be preferred over the assumption of an identical isotropic temperature factor for all atoms of the structure. After three iterations of the temperature least-squares program, the anisotropic temperature factors and the coordinates obtained from the electron-density projections were used in a least-squares program for the correction of the atomic coordinates. Four iterations were carried out, and when the corrections became smaller than the standard deviations, the refinement was terminated. Table 2 lists the final coordinates, together with their standard deviations and temperature factors. The discrepancy coefficient R for the 392 observed independent reflections was 0.131. Table 4 lists the observed and calculated structure factors.

#### DISCUSSION OF STRUCTURE

The interatomic distances found in this structure are summarized in Table 3. The mean-value (Si,Fe)-O distance is 1.681 Å with a standard deviation of 0.02 Å. Smith (1954) has called attention to the lengthening of the Si-O bond when Al substitutes for Si, and, if a lengthening of the bond also occurs when Fe substitutes and it is assumed that the tetrahedral Fe-O distance is approximately 1.9 Å, then a 1.68-Å distance would correspond to approximately a 27-per cent Fe substitution, which is in good agreement with the 25-per cent substitution found analytically. The two crystallographically independent Si-O-Si angles in the Si-O net shown in Figure 2 are 134°. The mean value of the O-O lengths of the edges of the tetrahedron is 2.745 Å, with a standard deviation of 0.03 Å.

The potassium ion has six near neighbors at a distance of 2.95 Å. A triad of oxygen ions from the lower oxygen surface together with the

TABLE 3. INTERATOMIC DISTANCES  
 $\sigma \leq 0.02 \text{ \AA}$ 

(Si, Fe)—O <sub>1</sub>	1.673	Mg <sub>1</sub> —OH	1.975
(Si, Fe)—O <sub>1</sub> '	1.676	Mg <sub>1</sub> —O <sub>3</sub>	2.119
(Si, Fe)—O <sub>2</sub>	1.694		
(Si, Fe)—O <sub>3</sub>	1.679	Mg <sub>2</sub> —OH	2.094
		Mg <sub>2</sub> —O <sub>3</sub>	2.097
K—O <sub>1</sub>	3.441		
K—O <sub>1</sub> '	2.954		
K—O <sub>2</sub>	2.929		
K—O <sub>2</sub> '	3.475		

centrosymmetrically related triad of oxygens of the upper oxygen surface form an octahedral configuration around the central K<sup>+</sup>. Six additional oxygen ion—triads within the oxygen surfaces above and below the K<sup>+</sup>—are at a distance of 3.45 Å. Thus the potassium appears to be in 6 fold coordination and the bonding to the other six oxygen ions to complete the 12 fold coordination is very weak. The situation in this specimen of phlogopite is similar to that reported in muscovite (Radoslovich, 1960).

Figure 2 shows the projection on the *x, y* plane of a silicon ion surrounded by its three basal oxygen atoms in the locations determined in

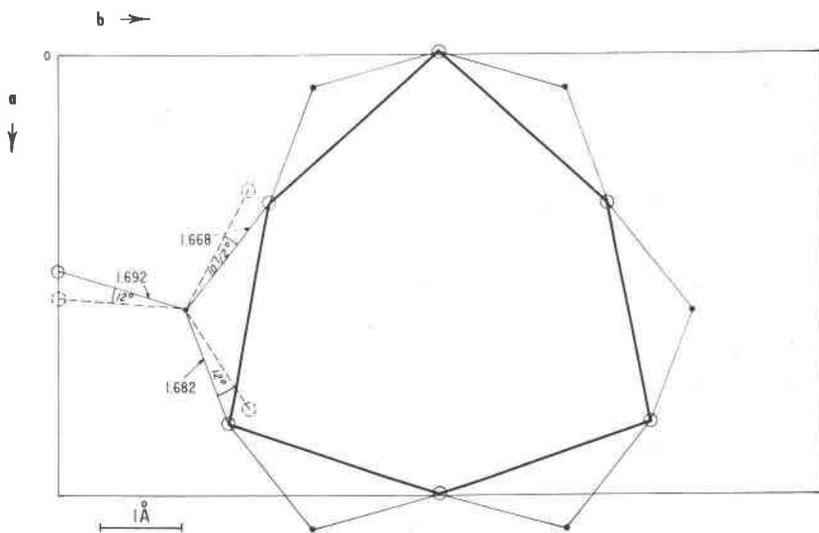


FIG. 2. Si—O net showing the distorted oxygen hexagon (heavy lines) and the rotation of the tetrahedra. The full circles are the locations of Si, and the open circles are oxygens. The circles formed by the dashed lines show the oxygen locations of the "ideal" structures as given by Hendricks (1939) and as modified by Pabst (1955).

TABLE 4. THREE-DIMENSIONAL STRUCTURE FACTORS

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>
0	2	0	48	-58	4	0	1	61	-56	$\bar{5}$	3	2	21	25
0	4	0	35	28	4	2	1	49	51	6	0	2	29	25
0	6	0	163	144	4	4	1	23	22	$\bar{6}$	0	2	51	50
0	8	0	17	-9	4	6	1	30	-28	0	0	3	118	-120
0	12	0	56	40	4	8	1	17	18	0	2	3	61	58
1	1	0	31	-47	$\bar{4}$	0	1	53	54	0	4	3	6	-9
1	3	0	69	58	$\bar{4}$	2	1	11	-16	0	6	3	32	-35
1	5	0	18	-23	$\bar{4}$	6	1	23	22	0	8	3	11	9
1	7	0	29	-24	5	1	1	19	16	0	12	3	12	-15
1	9	0	33	23	5	3	1	16	16	1	1	3	32	32
1	11	0	12	-12	5	5	1	12	11	1	3	3	84	73
2	0	0	110	119	5	7	1	14	12	1	5	3	11	12
2	2	0	31	29	$\bar{5}$	3	1	36	39	1	7	3	18	19
2	6	0	84	83	6	2	1	9	8	1	9	3	24	23
3	3	0	41	-42	6	4	1	10	11	1	11	3	3	7
3	5	0	15	-12	$\bar{6}$	0	1	14	-11	$\bar{1}$	1	3	71	78
3	9	0	27	-23	0	0	2	35	-46	$\bar{1}$	3	3	87	80
4	2	0	36	35	0	2	2	76	84	$\bar{1}$	5	3	33	43
4	4	0	20	16	0	4	2	35	31	$\bar{1}$	7	3	33	39
4	8	0	13	12	0	8	2	23	26	$\bar{1}$	9	3	13	11
5	1	0	23	17	0	10	2	16	15	$\bar{1}$	11	3	13	17
5	3	0	71	-51	1	1	2	93	87	2	0	3	40	-38
5	5	0	20	16	1	3	2	56	-63	2	2	3	20	-29
5	7	0	10	7	1	5	2	67	62	2	4	3	4	-5
6	2	0	18	14	1	7	2	30	29	2	6	3	29	-25
6	4	0	24	21	1	9	2	32	-33	2	0	3	56	-60
0	0	1	46	-50	1	11	2	15	15	$\bar{2}$	2	3	19	21
0	2	1	11	4	$\bar{1}$	1	2	73	64	$\bar{2}$	4	3	32	42
0	4	1	33	33	$\bar{1}$	3	2	102	-97	$\bar{2}$	6	3	55	-62
0	6	1	42	-40	$\bar{1}$	5	2	24	28	$\bar{2}$	8	3	16	23
0	12	1	12	-10	$\bar{1}$	7	2	35	42	$\bar{2}$	10	3	12	13
1	1	1	30	35	$\bar{1}$	9	2	48	-53	3	3	3	66	61
1	3	1	43	-49	$\bar{1}$	11	2	15	18	3	5	3	8	7
1	5	1	34	40	2	0	2	101	84	3	7	3	9	-9
$\bar{1}$	1	1	13	-25	2	2	2	10	6	3	9	3	45	40
$\bar{1}$	3	1	126	121	2	4	2	52	49	$\bar{3}$	1	3	53	61
$\bar{1}$	5	1	17	-23	2	6	2	17	12	$\bar{3}$	5	3	34	51
$\bar{1}$	9	1	35	43	2	8	2	19	21	$\bar{3}$	7	3	15	18
2	0	1	93	-97	2	10	2	15	12	$\bar{3}$	9	3	7	7
2	2	1	32	41	$\bar{2}$	0	2	48	-49	4	0	3	23	17
2	4	1	46	55	$\bar{2}$	2	2	32	37	4	2	3	19	-21
2	6	1	70	-72	$\bar{2}$	4	2	9	6	4	4	3	10	-8
2	8	1	21	26	3	1	2	34	31	4	6	3	10	6
2	10	1	159	14	3	3	2	35	-31	4	8	3	8	-8
$\bar{2}$	0	1	57	57	3	5	2	25	26	$\bar{4}$	0	3	73	-68
$\bar{2}$	2	1	23	26	3	7	2	11	10	$\bar{4}$	2	3	12	12
$\bar{2}$	4	1	23	-28	3	9	2	15	-14	$\bar{4}$	4	3	16	20
$\bar{2}$	6	1	50	53	$\bar{3}$	1	2	16	20	$\bar{4}$	6	3	44	-50
3	1	1	38	38	$\bar{3}$	3	2	39	-39	$\bar{4}$	8	3	8	12
3	5	1	22	26	$\bar{3}$	5	2	10	17	5	3	3	73	57
3	7	1	26	25	$\bar{3}$	9	2	10	-10	5	5	3	7	-4
3	9	1	4	-5	4	0	2	24	23	$\bar{5}$	1	3	12	17
$\bar{3}$	1	1	16	-26	4	6	2	20	24	$\bar{5}$	7	3	8	11
$\bar{3}$	3	1	132	145	$\bar{4}$	0	2	78	83	6	0	3	12	3
$\bar{3}$	5	1	18	-25	$\bar{4}$	2	2	15	-23	$\bar{6}$	0	3	24	-24
$\bar{3}$	9	1	47	53	$\bar{4}$	6	2	29	40	0	0	4	62	57
$\bar{1}$	3	5	103	115	1	7	6	14	11	1	3	7	22	20
$\bar{1}$	7	5	21	-21	1	9	6	63	-40	1	5	7	26	25

(Continued on next page)

TABLE 4 (Continued)

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>
1	9	5	62	59	1	1	6	8	7	1	7	7	9	6	2	8	8	6	-7
2	0	5	44	-44	1	3	6	46	-43	1	9	7	20	15	2	0	8	22	19
2	2	5	33	39	1	5	6	12	11	1	1	7	32	35	2	2	8	21	23
2	6	5	18	-13	1	9	6	19	-16	1	3	7	25	-25	2	4	8	12	12
2	8	5	10	8	2	0	6	28	-25	1	5	7	24	24	2	6	8	18	17
2	10	5	5	6	2	2	6	58	51	1	7	7	30	24	2	8	8	8	10
2	0	5	50	48	2	4	6	32	31	1	9	7	20	-12	3	1	8	30	31
2	2	5	13	-20	2	6	6	13	-8	2	0	7	13	11	3	3	8	52	-46
2	6	5	21	19	2	8	6	23	22	2	4	7	12	16	3	5	8	23	27
3	1	5	17	17	2	0	6	101	96	2	8	7	7	7	3	7	8	12	13
3	5	5	11	11	2	6	6	25	25	2	0	7	118	-112	4	0	8	34	27
3	7	5	16	14	2	6	6	71	67	2	2	7	58	53	4	4	8	5	-4
3	9	5	8	-2	3	1	6	21	19	2	4	7	23	19	4	0	8	12	-7
3	1	5	14	-18	3	3	6	55	-46	2	6	7	58	-53	4	2	8	12	11
3	3	5	59	59	3	5	6	12	12	2	8	7	18	18	4	4	8	21	22
3	5	5	15	-17	3	7	6	19	17	3	3	7	49	47	4	6	8	17	-12
3	9	5	25	28	3	1	6	17	-17	3	1	7	23	19	5	1	8	16	19
4	0	5	59	-52	3	3	6	45	34	3	3	7	7	0	5	3	8	36	-37
4	2	5	21	21	3	5	6	16	-19	3	5	7	12	14	5	5	8	15	16
4	4	5	24	22	3	9	6	11	4	3	7	7	13	14	6	0	8	6	-2
4	6	5	46	-39	4	0	6	19	19	3	9	7	6	0	6	2	8	5	10
4	0	5	30	-28	4	2	6	23	23	4	4	7	8	-7	0	4	9	23	-19
4	2	5	12	17	4	4	6	14	13	4	6	7	6	7	2	0	9	26	11
4	6	5	9	-4	4	6	6	18	17	4	0	7	13	-10	6	0	9	35	-28
5	1	5	18	17	4	0	6	88	82	4	4	7	11	14	0	0	10	38	34
5	3	5	20	-11	4	6	6	63	59	4	6	7	16	-15	0	6	10	33	26
5	5	5	15	17	4	8	6	6	-5	5	1	7	6	-6	2	0	10	56	54
5	3	5	18	20	5	1	6	11	-11	5	3	7	37	34	4	0	10	39	32
6	0	5	19	-17	5	3	6	12	5	5	0	7	22	15	6	0	10	24	20
6	0	5	12	-11	5	5	6	7	-7	0	0	8	62	59	0	0	11	44	-34
6	2	5	7	10	5	7	6	6	-8	0	4	8	9	-8	0	4	11	25	20
6	4	5	8	13	6	0	6	38	28	0	6	8	47	46	0	6	11	35	-29
0	0	6	34	31	6	0	6	37	37	1	3	8	14	12	2	0	11	38	-32
0	2	6	21	21	0	0	7	61	-59	1	7	8	7	-4	0	0	12	27	22
0	4	6	51	48	0	2	7	33	34	1	1	8	11	16	2	0	12	37	33
0	8	6	21	21	0	4	7	39	37	1	3	8	13	9	2	0	12	25	-8
0	10	6	15	12	0	6	7	56	-48	1	5	8	6	5	0	0	13	29	15
1	1	6	31	30	0	8	7	25	21	1	7	8	14	16	4	0	13	26	-18
1	3	6	118	-111	0	10	7	9	12	2	0	8	61	61	0	0	14	19	12
1	5	6	30	30	1	1	7	22	26	2	2	8	17	-23	2	0	14	34	26

this study and also in the positions given by Hendricks (1939) and as modified by Pabst (1955), which can be designated as the "ideal" mica structure. The silicon has remained essentially in its "ideal" location, but the tetrahedron has been rotated approximately  $12^\circ$  about an axis normal to the plane of the basal oxygens, passing through the silicon. The observed (Si,Fe)-O distance of  $1.68 \text{ \AA}$  in the tetrahedral layer corresponds to a calculated *b*-axis of  $9.5 \text{ \AA}$  and the angle by which the tetrahedra must be rotated to reduce *b* to the observed value of  $9.29 \text{ \AA}$  is  $12^\circ$ , in excellent agreement with the angle of rotation observed in the structure. The rota-

tion of the  $\text{SiO}_4$  tetrahedron found in the amesite structure (Steinfink and Brunton, 1955) is approximately  $11\frac{1}{2}^\circ$ , the same as in this structure. Although the two structures are different, one finds that in each a tetrahedral layer must articulate with an octahedral brucite type layer, and this is achieved by the rotation of the  $\text{SiO}_4$  tetrahedra.

The similar structural distortions observed in phlogopite and in muscovite indicate that the production of polytypes is not exclusively controlled by the distortions existing within the tetrahedral layer. The suggestion advanced by Bradley (1957) that ordering of Al and Si in tetrahedral sites may be the determining factor in the crystallization of the dioctahedral micas seems to be supported by the results of the investigations on muscovite and phlogopite. The randomness existing within the tetrahedral layer of phlogopite implies low structural control. It would be desirable to check this point further by additional structural investigations of biotites. Ordering of the tetrahedral ions in the 1M type would manifest itself by the appearance of lower symmetry and in such specimens one polytype should be overwhelmingly predominant.

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#### REFERENCES

- BRADLEY, W. F. (1957), Current Progress in Silicate Structures. *Proc. 6th Natl., Conf. Clays and Clay Minerals*, Pergamon Press.
- HEINRICH, E. WM., A. A. LEVINSON, D. W. LEVANDOWSKI AND C. H. HEWITT (1953), Studies in the Natural History of Micas, Univ. of Michigan.
- HENDRICKS, S. B., (1939), Polymorphism of the micas. *Am. Mineral.*, **24**, 729-771.
- JAKOB, J. (1925), The chemical constitution of the micas, I. Swedish manganophyllite. *Zeit. Krist.*, **61**, 155-163.
- LEVINSON, A. A. (1953), Studies in the mica group; relationship between polymorphism and composition in the muscovite-lepidolite series. *Am. Mineral.*, **38**, 88-107.
- AND E. WM. HEINRICH (1954), Studies in the mica group; single crystal data on phlogopites, biotites and manganophyllites. *Am. Mineral.*, **39**, 937-945.
- PABST, A. (1955), Redescription of the single-layer structure of the micas. *Am. Mineral.*, **40**, 967-974.
- RADOSLOVICH, E. W. (1960), The structure of muscovite,  $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ . *Acta Cryst.* **13**, 919.
- ROGERS, D. AND A. J. C. WILSON (1953), The probability distribution of x-ray intensities. *Acta Cryst.*, **6**, 439-449.

- SMITH, J. V. (1954), A review of the Al—O and Si—O distances. *Acta Cryst.*, **7**, 479-481.
- AND H. S. YODER (1956), Experimental and theoretical studies of the mica polymorphs. *Mineral. Mag.*, **31**, 209-235.
- STEINFINK, H. AND G. BRUNTON (1955), The crystal structure of amesite. *Acta Cryst.*, **9**, 487.
- YODER, H. S. AND H. P. EUGSTER (1954), Phlogopite synthesis and stability range. *Geochim. Cosmochim. Acta*, **6**, 157-185.
- , (1955), Synthetic and natural muscovites, *Geochim. Cosmochim. Acta*, **8**, 225-280.

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