REDESCRIPTION OF THE SINGLE LAYER STRUCTURE OF THE MICAS

A. PABST, *University of California, Berkeley 4, California.*

ABSTRACT

It can be shown that the structure of single layer micas described by Hendricks (1939) as "monoclinic hemihedral," space group C_s^3-Cm, is very nearly holohedral. By adjustments in the x coordinates of some of the atoms not exceeding 0.005 and a new choice of origin at a center of symmetry all atomic coordinates can be brought into conformity with the conventional description of structures in the space group C_{2h}^3-C2/m. It is suggested that this description is preferable since no evidence is known requiring the lower symmetry previously assigned.

INTRODUCTION

In his well-known paper on polymorphism of the micas, Hendricks (1939) described what he referred to as "THE SINGLE LAYER STRUCTURE OF THE MICAS (MONOCLINIC HEMIHEDRAL)." In the summary of the paper this was again referred to as "Single layer monoclinic hemihedral" and was reported to occur with far greater frequency than any of the other six types described.

Since much emphasis is placed on the "hemihedral" character of this most frequent of mica structures it is of interest to examine the basis for assignment of the space group. On this point Hendricks made the following statement (1939, p. 734):

> "There is only one way in which the simplest unit of structure can contain a portion of one mica layer. Atomic coordinates of this arrangement having the orientation b_1 of Fig. 1*a* are given in Table I. The structure is isomorphous with the monoclinic hemihedral point group C_s-m, the space group being C_s^3-Cm."

TABLE I. ATOMIC COORDINATES FOR THE SINGLE LAYER STRUCTURE. SPACE GROUP C_s^3-Cm, $\beta=100°$

General Positions				Special Positions			
	x	y	z		x	y	z
4 O	.25	.25	.00	2 O	.00	.50	.00
4 Si	.02	.33	.06				
4 O	.08	.33	.22	2 (OH)	.08	.00	.22
4 Mg	.44	.33	.34	2 Mg	.44	.00	.34
4 O	.32	.17	.46	2 (OH)	.32	.50	.46
4 Si	.37	.17	.62				
4 O	.14	.25	.68	2 O	.39	.00	.68
				2 K	.45	.50	.84

Reproduced in facsimile from Hendricks, (1939, p. 735). The same figures are given in a table in *Strukturbericht VII*, p. 170.

TABLE 2. SINGLE LAYER MICA STRUCTURE

A. Atomic coordinates of Hendricks "expanded" in accordance with conventional description in space groups C_s^3–Cm. The boldface coordinates are those taken from table I. x coordinates in brackets are adjusted as described in text.

Positions													Positions						
4	b	x	y	z	x	$\bar{y}$	z	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z	$\frac{1}{2}+x$	$\frac{1}{2}-y$	z	2	a	x	O	z	$\frac{1}{2}+x$	$\frac{1}{2}$	z
4	O	**.25**	**.25**	**.00**	.25	.75	.00	.75	.75	.00	.75	.25	.00	2	O	.50	.00	.00	**.00**	**.50**	**.00**
4	Si, Al	**.02**	**.33**	**.06**	.02	.67	.06	.52	.83	.06	.52	.17	.06								
4	O	**.08** (.075)	**.33**	**.22**	.08 (.075)	.67	.22	.58 (.575)	.83	.22	.58 (.575)	.17	.22	2	(OH)	**.08** (.075)	**.00**	**.22**	.58 (.575)	.50	.22
4	Mg	**.44** (.445)	**.33**	**.34**	.44 (.445)	.67	.34	.94 (.945)	.83	.34	.94 (.945)	.17	.34	2	Mg	**.44** (.445)	**.00**	**.34**	.94 (.945)	.50	.34
4	O	**.32** (.315)	**.17**	**.46**	.32 (.315)	.83	.46	.82 (.815)	.67	.46	.82 (.815)	.33	.46	2	(OH)	.82 (.815)	.00	.46	**.32** (.315)	**.50**	**.46**
4	Si, Al	**.37**	**.17**	**.62**	.37	.83	.62	.87	.67	.62	.87	.33	.62								
4	O	**.14**	**.25**	**.68**	.14	.75	.68	.64	.75	.68	.64	.25	.68	2	O	**.39**	**.00**	**.68**	.89	.50	.68
														2	K	.95 (.945)	.00	.84	**.45** (.445)	**.50**	**.84**

TABLE 2—(*continued*)

B. Adjusted atomic coordinates modified by adding .555 to all x values and .16 to all z values. The resulting coordinates fit the conventional description of positions in space group C_{2h}^3-C2/m indicated in the table below.

Positions													Positions						
8	*j*	*x*	$\bar{y}$	*z*	*x*	$\bar{y}$	*z*	$\frac{1}{2}+x$	$\frac{1}{2}+y$	*z*	$\frac{1}{2}+x$	$\frac{1}{2}-y$	*z*	4	*i*	*x*	*O*	*z*	$\frac{1}{2}+x$	$\frac{1}{2}$	*z*
4	O_2	**.805**	**.25**	**.16**	.805	.75	.16	.305	.75	.16	.305	.25	.16	2	O_1	**.055**	**.00**	**.16**	.555	.50	.16
4	Si, Al	**.575**	**.33**	**.22**	.575	.67	.22	.075	.83	.22	.075	.17	.22								
4	O_3	**.63**	**.33**	**.38**	.63	.67	.38	.13	.83	.38	.13	.17	.38	2	(OH)	**.63**	**.00**	**.38**	.13	.50	.38
4	*h*	O	*y*	$\frac{1}{2}$	O	*y*	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}+y$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}-y$	$\frac{1}{2}$	2	*c*	O	O	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
4	Mg_2	**.00**	**.33**	**.50**	.00	.67	.50	.50	.83	.50	.50	.17	.50	2	Mg_1	**.00**	**.00**	**.50**	.50	.50	.50
		$\frac{1}{2}-x$	$\frac{1}{2}-y$	$\bar{z}$	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\bar{z}$	$\bar{x}$	$\bar{y}$	$\bar{z}$	$\bar{x}$	*y*	$\bar{z}$			$\bar{x}$	*O*	$\bar{z}$	$\frac{1}{2}-x$	$\frac{1}{2}$	*z*
4	O_3	.87	.17	.62	.87	.83	.62	.37	.67	.62	.37	.33	.62	2	(OH)	.37	.00	.62	.87	.50	.62
4	Si, Al	.925	.17	.78	.925	.83	.78	.425	.67	.78	.425	.33	.78								
4	O_2	.695	.25	.84	.695	.75	.84	.195	.75	.84	.194	.25	.84	2	O_1	.945	.00	.84	.445	.50	.84
														2	*b*	$\frac{1}{2}$	O	O	O	$\frac{1}{2}$	O
														2	K	.50	.00	.00	**.00**	**.50**	**.00**

The atomic coordinates for this structure given by Hendricks in his Table I are reproduced here in facsimile under the same number. They do indeed correspond to a structure in the space group *Cm*. However, in this space group, the choice of origin being taken in a plane of symmetry, its position in the x and z direction remains arbitrary. Hendricks so placed it that the base of the cell is at the level of the oxygens on the "outside" of the $(Si,Al)_4O_{10}$ sheet. Inspection of the z parameters in Table I will show that by moving the origin downward 0.16 the K atoms come to lie at the zero level, Mg's at half height and all other atoms at corresponding heights of plus and minus z.

Inspection of the x coordinates shows that an increase of 0.555 in these will bring the atoms very nearly, but not quite, into positions corresponding to the conventional description for a structure in the space group C_{2h}^3-C2/m. After this shift it is found that K atoms, Mg atoms, OH's and those O's adjacent to the Mg's depart only by plus or minus 0.005 from positions which would correspond to the higher symmetry. To the writer it seems that this slight departure from the higher symmetry arises simply from the way in which coordinates were given in the original description. They were given, as may be seen in Table I, to the nearest hundredth and so the small shift of parameters required to match the higher symmetry may be considered to be within the limits intended by Hendricks.

In support of his structure, which is truly hemihedral but nearly holohedral, Hendricks gave calculated and observed intensities for *h0l* and *0kl* reflections in his Tables II and III. There is good agreement of calculated intensities with observed intensities indicated qualitatively by the symbols vs, s, ms-s, ms, m, m-mw, mw, mw-w, w, vw and a. It seems unlikely that a change in coordinates of 0.005 for some of the atoms would modify calculated intensities to such an extent as to impair the agreement just mentioned. Under these circumstances it seems justified, in the absence of any observations requiring the lower symmetry, to describe the single layer mica structure in the space group C_{2h}^3-C2/m and to drop the designation "monoclinic hemihedral."

Analytical Demonstration

Detailed proof that the trifling shifts described above do indeed lead to a structure with the symmetry $C2/m$ may be given in tabular form. This has been done in Table 2. In the upper part of this table the coordinates given in Hendricks' Table I have been "expanded" in conformity with the requirements of space group C_s^3-Cm as described on page 87, vol. I, International Tables for X-Ray Crystallography, 1952. In brackets under some of these figures are entered x coordinates ad-

justed as follows: for Mg increased by 0.005, for K, OH and O's adjacent to Mg decreased by 0.005. In the lower part of the table the expanded and adjusted coordinates have been modified to correspond to a shift of origin by adding 0.555 to all x's and 0.16 to all z's. Also subscripts have been attached to the symbols of certain of the atoms for convenience in reference. It will be seen that the distribution of atoms now conforms to requirements for space group $C2/m$. Following the description on page 95 of the International Tables with origin at a center of symmetry, atomic coordinates as adjusted and modified are stated in the usual conventional fashion in Table 3. The coordinates there given correspond to those in bold face in the lower part of Table 2.

The parameter adjustments used are the smallest that can be made to

TABLE 3. ATOMIC COORDINATES FOR THE SINGLE LAYER MICA STRUCTURE IN SPACE GROUP C_{2h}^3–$C2/m$, STATED IN ACCORD WITH THE CONVENTIONS OF THE INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY

		x	y	z
2 K	in 2*b*	0, ½, 0		
2 Mg_1	in 2 *c*	0, 0, ½		
4 Mg_2	in 4 *h*	0, y, ½	.33	
4 OH	in 4 *i*	*x*, 0, *z*	.63	.38
4 O_1	in 4 *i*	*x*, 0, *z*	.055	.16
8 O_2	in 8 *j*	*x*, *y*, *z*	.805	.25 .16
8 O_3	in 8 *j*	*x*, *y*, *z*	.63	.33 .38
8 Si, Al	in 8 *j*	*x*, *y*, *z*	.575	.33 .22

bring atoms exactly into positions required for the higher symmetry. The shift of origin needed so that the origin will be at a center of symmetry as in the conventional description may be undertaken in various different ways since there are eight symmetry centers in the unit cell in the space group $C2/m$. An alternative shift would lead merely to an alternative description superposable by translation with that given in Table 3.

GRAPHICAL DEMONSTRATION

Finally it is possible to present the relation of the description of the single layer mica structure here proposed to that given by Hendricks in the form of a diagram. This has been done in Fig. 1. This figure shows three projections of the structure. At the right is shown the orthographic projection onto (010), at the upper left onto (001) and below this, designated (100)*, the projection onto (100) not orthographically but by lines parallel to a.

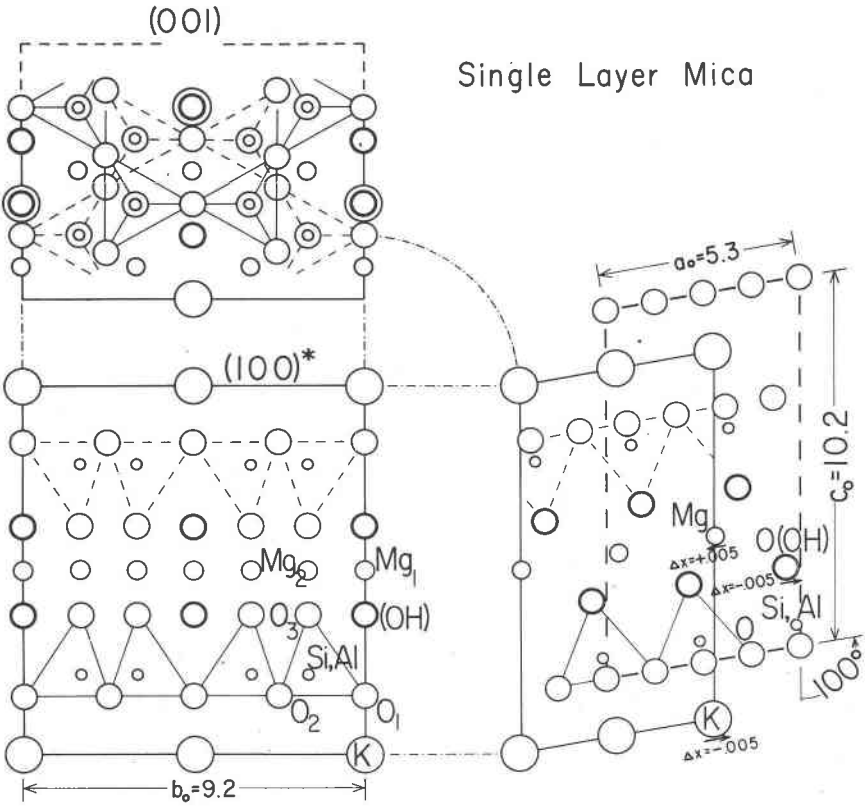

FIG. 1. Three projections to show that the single layer mica structure has the symmetry $C2/m$ after the small parameter adjustments for certain atoms shown at lower right.

At the right of the (010) projection a dimensioned cell is indicated by heavy dashed lines. Within this the atoms are plotted from the coordinates of Hendricks, the K atoms being at $z=0.84$ in this cell as given in Table I. Superposed on this is drawn the outline of a cell with the origin shifted so as to increase each x by 0.555 and each y by 0.16. The adjustments of parameter required for some of the atoms are too small to be directly discernible in the drawing. The direction and amount of these adjustments is indicated by suitable symbols under one each of the circles representing K, Mg and O(OH) in the (010) projection.

Comparison of the several projections will reveal that the K's and Mg_1's lie at points with the symmetry $2/m$ and the Mg_2's on two-fold axes, the entire array being in the space group $C2/m$.

(After reading the foregoing Dr. Hendricks, in a letter to Pabst dated

September 13, 1954, wrote in part as follows:—"Your analysis of the single layer mica structure is surely sound. . . . The small shift of parameters is entirely permissible within the limits of precision of our work.")

Reference

Hendricks, Sterling B. (1939), Polymorphism of the micas (with optical measurements by Merrill E. Jefferson): *Am. Mineral.*, **24**, 729–771.

Addendum, written May 12, 1955

Drs. J. A. Kohn and R. A. Hatch kindly furnished an excellent specimen of the synthetic fluorphlogopite which they recently described (*Am. Mineral.*, **40**, 10–21, 1955). The composition of this material is certainly known. The octahedral positions are fully occupied by magnesium with no substitutions. It is a single layer mica. This, if any, should be a suit-

Table 4. Calculated Structure Factors (F's) for the Single Layer Mica Structure for Those Orders of (*h*00) Observable with MoKα Rays

(*h*00)	Hendricks' parameters	Modified parameters	Difference
200	100.69	100.82	0.13
400	6.58	6.75	0.17
600	7.64	8.43	0.79
800	5.99	7.48	1.49
10.00	21.19	22.01	0.82
12.00	9.85	10.16	0.31
14.00	29.34	31.17	1.83
		Sum 186.82	5.54
		Ratio of sums 2.97/100	

able material for the observation of *h*00 intensities which depend on the x coordinates alone. Unfortunately only 200 was observable with Mo radiation, all higher orders to 1400, the last within range, being below the limit of detectability because of unfavorable influence of the L. & P. and "temperature" factors. With copper radiation only three orders of *h*00 are within range. With 200 just fully blackened on the film, 400 is not detectable and 600 is barely discernible. This agrees with the intensity observations of Hendricks which are compared below with the calculated intensities, absorption and "temperature" corrections being omitted and the calculated intensity for 200 taken arbitrarily as 100:—

	200	400	600
$I_{obs.}$ Hendricks (1939, Table II)	vs	a	vw
$I_{calc.}$ Hendricks' parameters	100	0.16	0.31
$I_{calc.}$ modified parameters	100	0.17	0.38

It is customary to test parameters by means of a "reliability index" derived from the observed and calculated structure factors. Table 4 shows the structure factors of even orders of $h00$ up to $h=14$ for the single layer mica structure with Hendricks' parameters and with the modified parameters. The "ratio of sums" given at the foot of the table has the form of a "reliability index." Its value is much lower than is generally obtained in even the most precise crystal structure determinations.