

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 23

DECEMBER, 1938

No. 12, Part 1

CRYSTAL STRUCTURE OF VERMICULITES AND MIXED VERMICULITE-CHLORITES

STERLING B. HENDRICKS AND MERRILL E. JEFFERSON,
*U. S. Bureau of Chemistry and Soils,
Washington, D. C.*

In studying the structure of hydrates related to the clay minerals it was a matter of some importance to reexamine the vermiculites. Gruner¹ using x -ray powder diffraction data showed that these minerals are formed of silicate layers, similar to those of talc,² with water molecules introduced between the layers. Such a structure accounts for the behavior of the vermiculites upon heating, and while the following work introduces essential revision in detail, this feature remains unchanged.

EXPERIMENTAL PROCEDURE AND SOURCE OF MATERIALS

Dr. C. S. Ross of the U. S. Geological Survey kindly gave us several analyzed samples of vermiculite. The two used for the larger part of this work were Specimen #3 and #5 as described by C. S. Ross, E. V. Shannon, and F. A. Gonyer.³ Both were clear yellowish green varieties free from apparent impurities between the cleavage planes.

Single crystals suitable for study by x -ray diffraction methods were cut from large plates. After cutting, the crystals were compressed with moderate force in order to align the plates which were very flexible and easily distorted. These were used to obtain Weissenberg goniometer and rotating crystal photographs about the a and b axes. Lattice dimensions obtained from these photographs and from measurements of d (001) against (00 l) of β Al_2O_3 as reference are:

$$\begin{array}{ll} d(001) = 28.80 \pm .10 \text{ \AA} & c = 28.85 \pm .10 \text{ \AA} \\ d(100) = 5.32 \pm .05 \text{ \AA} & b = 9.18 \pm .05 \text{ \AA} \\ & a = 5.33 \pm .05 \text{ \AA} \\ & \beta = 93^\circ 15' \pm 15' \end{array}$$

The monoclinic angle β was estimated on equatorial zone Weissenberg photographs about the b axis. More accurate values were obtained from

¹ Gruner, J. W., *Am. Mineral.*, vol. 19, pp. 557-575, 1934.

² Pauling, Linus, *Proc. Nat. Acad. Sci.*, vol. 16, pp. 123-129, 1930.

³ *Econ. Geol.*, vol. 23, p. 536, 1928.

the measured spacings of (20 26) and (20 $\overline{26}$). Values of a , b , and c are essentially in agreement with those found by Gruner, while β is about 4° smaller. The two samples gave values that checked closely.

Intensities of the 8th to 28th orders of reflections of (001) or photographs of sample #5 made with $\text{FeK}\alpha$ -radiation were accurately measured by means of an integrating microphotometer, similar to the one described by B. W. Robinson.⁴ These were reduced to an absolute basis by comparison with the (004) reflection from a roughened face of NaCl on photographs taken with a reference x-ray goniometer, under conditions of reflection corresponding to a thick crystal completely covering the slit. Intensities of the 30th to 52nd orders of reflection from (001) were estimated by comparison with the 8th to 28th orders on photographs made with $\text{MoK}\alpha$ -radiation. Intensities of (00 l) reflections for $\text{CuK}\alpha$ -radiation from sample #3 were estimated to have the same relative values as the corresponding reflections of sample #5.

No correction was made for possible extinction in vermiculite since, as it will appear later, there was no entirely trustworthy method of calculating F values. Secondary extinction might be expected to be small for such poorly formed crystals. The linear absorption coefficient of vermiculite was taken as 120 cm.^{-1} for $\text{FeK}\alpha$ and 9.2 cm.^{-1} for $\text{MoK}\alpha$.

ELECTRONIC DISTRIBUTION NORMAL TO (001)

Integrated reflections and corresponding values of $F_{(00l)}$ for various orders of (001) are listed in Table 1. Probable signs of $F_{(00l)}$ given in the table were calculated on the basis of Gruner's structure with the further assumption that the water molecules are crystallographically equivalent and have $z = .208$. There is but little doubt, irrespective of poor absolute agreement between observed and calculated $F_{(00l)}$ values, that the signs are essentially correct since they chiefly are determined by the Mg and Si contributions.

Distribution of electrons⁵ normal to (001) is given by

$$\begin{aligned} \rho(z) &= \frac{1}{d} \sum_{-\infty}^{\infty} F_n \exp(-2\pi i n z) \\ &= \frac{1}{d} [F_0 + 2F_2 \cos 4\pi z + 2F_4 \cos 8\pi z + \dots] \end{aligned}$$

where $d = d_{(001)}$, z is the coordinate in the c direction, F_0 is the total number of electrons in the unit of structure, assumed to be 976, and $\rho(z)$ is

⁴ *J. Sci. Instrum.*, vol. 10, p. 233-242, 1933.

⁵ Compton, A. H., and Allison, S. L.: *X-Rays in Theory and Experiment*, p. 460, 2nd edition, *New York*, 1935.

TABLE 1. INTEGRATED REFLECTIONS AND CALCULATED F VALUES FOR (001) REFLECTIONS OF VERMICULITE, SAMPLE #5

Order	Integrated Reflection $\times 10^6$	Absolute F		
		Observed	Probable sign	Calculated
2	vs FeK α		+	256
4	vw			10
6	ms			68
8	62.0	161	+	145
10	80.0	222	+	304
12	3.6	54	-	97
14	11.0	106	-	105
16	3.2	62	-	92
18	3.2	67	+	106
20	12.0	137	+	198
22	2.7	65	+	100
24	6.9	97	+	158
26	0.3	18	+	50
28	7.5	69	+	84
30	2.4 MoK α	51	+	88
32	4.8	76	+	110
34	2.4	56	+	100
36	0.0	00		
38	0.5	28	-	64
52	1.0	48	+	145

the electron density at (z). Calculated values for the summation, omitting F_4 , F_6 , F_{36} , F_{38} , and F_{52} are shown in Fig. 1.

The electron distribution from 0.0 to 4.0 \AA resembles that found for muscovite⁶ which also contains pyrophyllite-talc-like layers. An attempt was made to separate the distribution into several parts as shown in Fig. 1 by the dotted curve. Even though such a procedure is somewhat arbitrary it should lead to approximate values for the number of electrons associated with each peak. Results of this analysis are shown in Table 2.

Since individual peaks such as those at .000 and .038 of Fig. 1 are quite sharp the contributing atoms must be practically coplanar. Thus it follows that the talc layer, $(\text{OH})_2\text{Mg}_3\text{Si}_4\text{O}_{10}$, must closely approach the ideal structure put forward by Pauling. The peak at $z = .208$ which corresponds to the water molecules between the pyrophyllite layers is also quite sharp. It would seem that the water molecules could not deviate by more than .2 \AA from a plane and that they are probably coplanar. Moreover, there are two or more water molecules in each layer, and two such layers are present between each talc layer.

⁶ Jackson, W. W., and West, J., *Zeits. Krist.*, vol. 76, p. 215, 1930.

TABLE 2. ANALYSIS OF ELECTRON DISTRIBUTION NORMAL TO (001), SAMPLE #5

Coordinate	Probable Constituent	Total number of electrons	Number of electrons per atom
.000	5.5 Mg ⁺² , .5 Fe ⁺³	124	11.7
.038	3 O ⁻² , 3(OH) ⁻	63	10.5
.095	Al ⁺³ , 3 Si ⁺⁴	41	10.2
.115	6 O ⁻²	55	9.2
.208	2 H ₂ O, 1.4(OH) ⁻	28	8.2
.250	0.7 Ni ⁺²	11	16

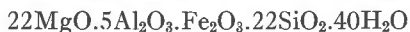
While the peak at .000 corresponding to the positions of the atoms with octahedral coordination is considerably greater than that at .095, which is formed by Al⁺³ and Si⁺⁴ in tetrahedral coordination, it is not sufficiently large to accommodate much replacement of Mg⁺² by heavier atoms. It will later be shown that such replacement is also inconsistent with the chemical analysis. A Fourier analysis usually gives some spurious features and the small peaks near $z = .15$ and $z = .18$ are probably of this type. However, the peak at $z = .25$ is somewhat larger indicating that a few atoms might be in that position. This would be expected for a chlorite which is formed by combination of brucite-like layers with pyrophyllite-talc layers. Sample #5 is then probably a mixed chlorite-vermiculite, being predominantly vermiculite with about one layer of chlorite for seven layers of vermiculite.

Accurate structure factors cannot be calculated for a mixed layer crystal since the distribution of the chlorite layers is not known. Calculated $F_{(00l)}$ values of Table 1 are for an assumed $(\text{OH})_2\text{Mg}_3\text{Si}_4\text{O}_{10}\cdot 4\text{H}_2\text{O}$ structure. Lack of closer agreement between observed and calculated absolute values arises in part from the mixed chlorite structure, but it chiefly seems to be due to the ignoring of extinction and the temperature factor.

Appearance of a moderately intense (00 52) reflection further serves to verify the atomic distribution along the normal to (001). All the atoms of the pyrophyllite layer give their maximum contributions to this reflection as also do any possible atoms with $z = .25$. The water molecules also give a positive contribution of $0.4 n f \text{H}_2\text{O}$ to the structure where n is the number of water molecules in the unit of structure. This reflection was omitted from the Fourier analysis, since it could only cause a high frequency variation in the curve which would be enhanced by omission of other reflections, that although unobserved still might have moderate $F_{(00l)}$ values.

COMPOSITIONS OF THE VERMICULITES

Gruner⁷ has tabulated the analyses of a number of vermiculites and has shown that their average composition can be represented as



which is similar to that found by Ross and Shannon.⁸ In this formula Fe^{+2} , Ni^{+2} , and Ca^{+2} are considered as replacing Mg^{+2} . A true vermiculite is entirely free of potassium, and when potassium is present the resulting mineral is one in which mica layers are present, as Gruner has shown.

Since vermiculites consist of interleaved talc and water layers their compositions can be discussed on the basis of the talc formula, $(\text{OH})_2\text{Mg}_3\text{Si}_4\text{O}_{10}$, with isomorphous replacements. The fundamental structural principle is that only Al^{+3} and Si^{+4} ions have tetrahedral coordination, there being four such positions, all of which must be filled, for each twelve oxygen and hydroxyl ions. Positions with octahedral coordination, later referred to as Σ octahedral, can be filled by Al^{+3} , Fe^{+3} , Ti^{+4} , Mg^{+2} , Ca^{+2} , Li^+ , Na^+ , Ni^{+2} , Fe^{+2} and they are limited to three for every four tetrahedral positions. As Al^{+3} replaces Si^{+4} in tetrahedral positions, O^{-2} can be replaced by $(\text{OH})^-$.

Gruner's average formula reduces to



However, if each analysis is considered separately 2.75 it immediately appears that in five of the seven samples, including sample #5, Σ octahedral is greater than three, as can be seen in Table 3. In some sam-

TABLE 3. MOLECULAR COMPOSITIONS OF SOME VERMICULITES

	1 ¹	2	3	4	5	6	7	#3	#5
Σ Al and Si	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Mg	2.82	2.44	2.46	2.70	2.09	2.84	2.07	2.49	2.82
Fe^{+3}	0.24	0.45	0.27	0.68	0.15	0.16	0.16	0.29	0.20
Fe^{+2}	0.04	0.01	0.04	0.05	0.06	0.03	0.03	0.09	0.05
Ca	0.01	0.16	0.00	0.03	0.00	0.02	0.03	0.01	0.05
Ni	0.02				0.13	0.21	1.16	0.13	0.45
Σ Mg to Ni	3.13	3.06	2.77	3.46	2.43	3.26	3.45	3.01	3.57
Color	Clear pale yellow	Golden yellow	Yellow brown	Yellow brown	Green yellow	Green yellow	Apple green	Yellow green	Clear yellow green

¹ Samples 1 to 7 are listed by Gruner (*loc. cit.*), #3 and #5 by Ross, Shannon, and Gonyer (*loc. cit.*).

⁷ Gruner, J. W., *loc. cit.*

⁸ *Am. Mineral.*, vol. 11, p. 92, 1926.

ples, particularly 4, it is probable that impurities between the vermiculite plates enhance Σ octahedral, but this cannot possibly be the case for clear varieties such as 7 and #5.

A logical explanation for the apparent surplus of atoms with octahedral coordination is that they are partially present in brucite-like layers, $R_3^{+2}(\text{OH})_6$, between the talc layers thus forming a chlorite-like structure, as also is indicated by the Fourier analysis and permitted by the observed densities. There is no reason why Σ octahedral cannot be less than three for a true vermiculite and for such samples it is possible that part of the aluminum has octahedral coordination.

ATOMIC DISTRIBUTION IN THE a AND b DIRECTIONS

Attention is now turned to the manner in which the talc-like layers are superimposed in the vermiculites. With Gruner it is found that reflections from (hkl) are present only if $(h+k)$ is even, and from $(h0l)$ if h and l are even. The space group, therefore, either must be $C2/c - C_{2h}^6$ or $Cc - C_s^4$, the former being assumed by Gruner.

TABLE 4. ATOMIC COORDINATES OF SOME POSSIBLE VERMICULITE STRUCTURES REFERRED TO GENERAL POSITIONS OF SPACE GROUP Cc

Atom	$x2'$	$x2$	$y = Y +$	z
Mg	0	0	0	0
Mg	0	0	1/3	0
Mg	0	0	2/3	0
(OH)	-.154	.180	1/2	.04
(OH)	.154	-.180	5/6	-.04
O	-.154	.180	5/6	.04
O	.154	-.180	1/2	-.04
O	-.154	.180	1/6	.04
O	.154	-.180	1/6	-.04
O	.117	-.048	3/4	.115
O	-.117	.048	7/12	-.115
O	-.382	.452	3/4	.115
O	.382	-.452	7/12	-.115
O	-.132	.202	0	.115
O	.132	-.202	1/3	-.115
Si	-.138	.196	5/6	.095
Si	.138	-.196	1/2	-.095
Si	.362	-.304	2/3	.095
Si	-.362	.304	2/3	-.095

Possible methods of superimposing talc-like layers are the same as those previously described for talc,⁹ and for the sake of brevity it will be

⁹ Hendricks, S. B., *Zeits. Krist.*, vol. A(99), pp. 264-274, 1938.

assumed that the other work is at hand. Atomic coordinates for structures 2 and 2' are given in Table 4. For these the $(\text{OH})_2\text{Mg}_3\text{Si}_4\text{O}_{10}$ layer has a center of symmetry and if the space group is $C2/c$, the translation Y is zero. Structures 2 and 2' differ in that the upper $(\text{Si}_2\text{O}_5)_x$ sheet of an $(\text{OH})_2\text{Mg}_3\text{Si}_4\text{O}_{10}$ layer is shifted by $+x$ or $-x$ with respect to the lower $(\text{Si}_2\text{O}_5)_x$ sheet. Gruner's structure corresponds to 2' when his coordinates are referred to the correct monoclinic angle β . Structures 1 and 1' are obtained if the centers of symmetry are between the silicate layers.

Reference to Table 5 shows that structures 1, 1', and 2' cannot possibly explain the observed intensities. Structure amplitudes were calculated, ignoring possible contributions of water molecules and chlorite layers. These structures, however, are safely eliminated even allowing for a maximum detrimental effect of the omitted atoms. Agreement between observed and calculated intensities for structure 2 is entirely satisfactory as can be seen in Tables 5 and 6. The structure can be accepted with confidence and only the possible arrangement along the y axis remains to be considered.

TABLE 5. CALCULATED $F/8$ VALUES OF SOME $(h0l)$ REFLECTIONS FOR POSSIBLE VERMICULITE STRUCTURES, $\text{CuK}\alpha$
Values considered to be impossible are indicated by asterisks.

Plane	Observed Intensity Sample #5	Structure			
		1'	1	Gruner 2'	2
200	vw	-6	6	6	-6
202	ms	39	2*	24	-12
20 $\bar{2}$	ms	15	35	-11	14
204	vw	-4	12*	35*	-4
20 $\bar{4}$	s	31	-13	-13	30
206	m	13	-4*	28	15
20 $\bar{6}$	vs	-7*	23	4*	37

Weissenberg goniometer photographs show that (hkl) reflections are diffuse unless k is a multiple of three. This is illustrated by the photographs of the equatorial zone and the first layer line about the a axis reproduced in Fig. 2. If k is a multiple of three the reflections are sharp and have intensities that can only be explained if the translation Y of Table 4 is a multiple of $1/6$. It also is observed as was the case for talc that (hkl) reflections with $k=3n$ and l odd are absent which also requires $Y=n/6$.

TABLE 6. CALCULATED F/8 VALUES* AND ESTIMATED INTENSITIES FOR SOME (*h0l*) REFLECTIONS OF VERMICULITE, CuK STRUCTURE 2, SAMPLE #5

<i>l/h</i>	2	4	6	2	4	6
0	vw -6	mw 13	mw 19			
2	ms 14	mw -13	m 24	ms -12	m-ms 37	vwv 7
4	s 30	m -13	w 16	vw -4	m 24	vwv 1
6	vs 37	w 9	0 5	m 15	0 2	vwv 2
8	m 16	m 23	0 0	ms 18	vw 5	w 10
10	ms 10	w -12	vw	w 8	mw 17	vw
12	ms 15	0 -5	w	w 2	m 26	0
14	s-ms 27	0 4	vw	m 18	w 13	w
16	m-ms 23	mw 23	0	m-ms 30	0 -5	
18	0 0	mw 29		ms 30	0 -4	
20	w	mw		w	0	
22	vw	vw		0	vwv	
24	w	0		0	vwv	
26	mw	0		mw	vwv	
28	0	w		mw		
30	vw	w		0		

* Water molecules between layers were ignored in obtaining the calculated values.

TABLE 7. CALCULATED F/8 VALUES AND ESTIMATED INTENSITIES FOR SOME (*0kl*) REFLECTIONS OF VERMICULITE, CuK α STRUCTURE 2, SAMPLE #5

<i>l/h</i>	2*	4*	6	8*	10*	12 β^2
0	ms } ¹	mw } ¹	vs 35	vw } ¹	w } ¹	m 22
2			ms 25			mw 14
4	w	w	m 11			0 2
6	m	mw	0 0	0	0	0 -3
8	mw	vw	w 5	0	0	w 8
10	0	mw-w	m 15	0	0	
12	0	0	mw 11	0	0	
14	0	w	0 -3	0	0	
16	0	0	w -9			
18	0	0	0 2			
20	0	0	w-mw 23			
22	0	0	mw-m 28			
24	0	0	mw 13			

* Reflections having these indices are lengthened and diffuse.

¹ These reflections are not sufficiently resolved for estimation of separate intensities.

² Intensities estimated for CuK β line, all others are for CuK α .

Attempts to explain (02*l*) and (04*l*) intensities with a particular value of *n* were unsuccessful and there can be no doubt but that the vermiculites have the type of random structure along the *b* axis found for dickite,¹⁰ talc,⁹ and pyrophyllite.⁹ This is a structure in which the various talc-like layers of the vermiculite structure would have random shifts of *n*/6 along the *b* axis. Such a structure should only give weak (*hkl*) reflections with *k* ≠ 3*n*, as was observed to be the case. However, the reason

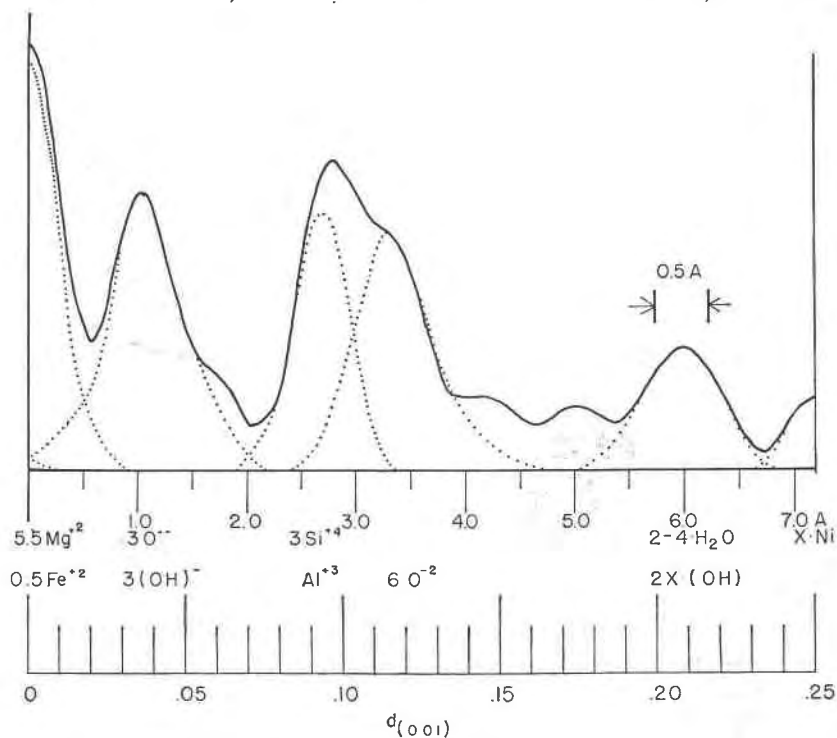


FIG. 1. Electronic distribution normal to (001) of vermiculite. This particular crystal contains some chlorite layers.

for the diffuseness of these reflections is not very apparent although it is quite probably related to the random structure. A possible reason is that the absence of a regular periodicity in the structure for these planes is equivalent to a reduction of the lattice thickness. However, the consequences of an irregular structure have not been carefully thought through.

Atomic positions in neighboring silicate layers of a unit of structure have coordinates required by space group $Cc-C_s^4$. However, the positions along the *b* axis are not the same from one unit of structure to another and thus the space group is only a pseudo one.

¹⁰ Hendricks, S. B., *Am. Mineral.*, vol. 23, pp. 295-302, 1938.

DISCUSSION

Consideration of possible arrangements of water molecules in the a and b directions is deferred to the following paper. They have but small effect on the intensities of (hkl) reflections and thus cannot be located by strict argument.

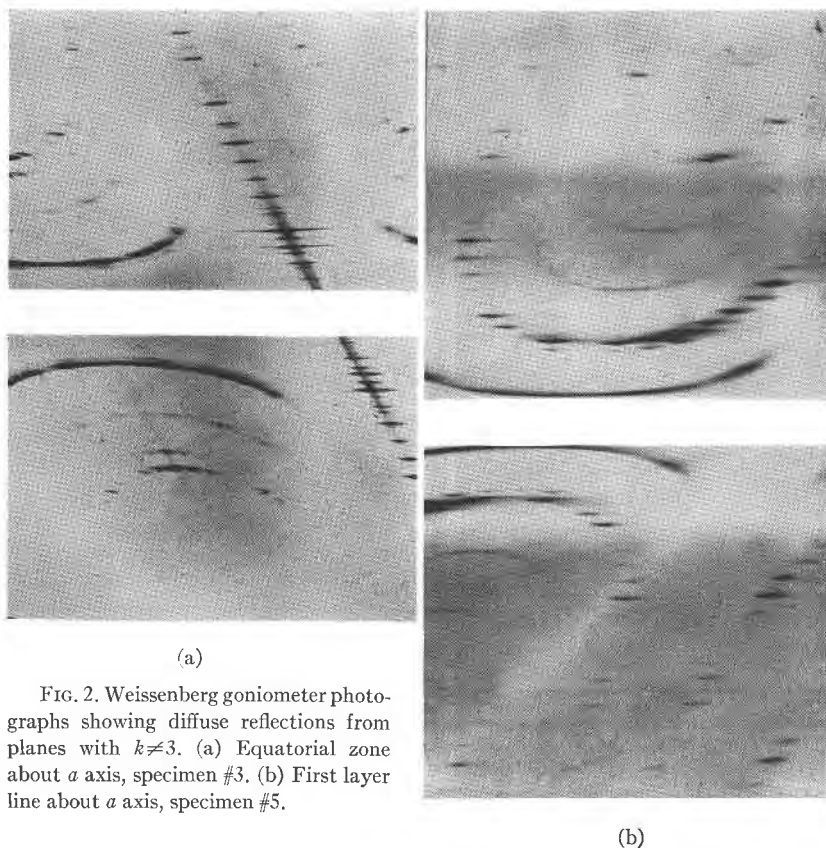


FIG. 2. Weissenberg goniometer photographs showing diffuse reflections from planes with $k \neq 3$. (a) Equatorial zone about a axis, specimen #3. (b) First layer line about a axis, specimen #5.

The muscovite, revised vermiculite, talc, pyrophyllite, and possibly the chlorite structures have the same type of relative shift of the $(\text{Si}_2\text{O}_5)_x$ sheets of the silicate layers. Oxygen atoms in the upper part of one talc-like layer and the bottom of another have nearly the same arrangement in projection on (001) for vermiculites and talc, even though they are separated by 7.8 and 2.8 Å, respectively, in the two structures along the normal to (001). Figure 3 of the previous paper⁹ on talc thus holds approximately for vermiculite, the relative shifts of the hexagons along the a axis being -0.21 \AA and $+0.07 \text{ \AA}$, respectively. This figure also shows

the probable translations of talc layers along the b axis of the vermiculite structure.

Random structures of the type found in dickite, pyrophyllite, talc, and the vermiculites possibly are present also in related minerals, such as the chlorites. However, before a general conclusion can be reached each case must be examined on the basis of as extensive data as can be obtained. Micas and brittle micas would not be expected to have such random structures, since the alkali or alkaline earth ions have twelve fold coordination which can only be met by one particular shift of the layers. The stability of the single configuration is enhanced by the electrostatic attraction due to the ions between the layers.

Chrysotile¹¹ also has some random type of structure along the b axis which requires further study. A closely analogous situation has been found for several compounds that form liquid crystals,¹² including parazoxyanisole, p-azoxyphenetol, cholesteryl chloride, and cholesteryl bromide. In these compounds, according to Bernal and Crowfoot, the diffuse reflections are from planes that are normal to the characteristic long direction of the molecules along which apparently there is some freedom of translation in the lattice.

It is not surprising to find that vermiculites form mixed structures with the chlorites and micas. In fact, any mixture of mica, vermiculite, chlorite, pyrophyllite, stilpnomelane (provided this is not a mixed structure) and talc layers would not be unreasonable. The list also might include kaolin and hydrated kaolin layers. The presence of vermiculite layers in macroscopic crystals can best be recognized by a swelling produced upon heating, which also might be applied to microscopic crystals. Mixed vermiculite-chlorites need not have Σ octahedral greater than three, and thus might be very difficult to recognize.

The intermingling of mica, pyrophyllite, talc, kaolin, or hydrate kaolin layers with vermiculite should greatly alter the (001) reflections. If the mixing is a random one the resulting effect would be similar to that discussed for montmorillonite in the following paper. This probably is the case for the mixed vermiculite-micas studied by Gruner, a condition which he rather recognized. Minerals of this type apparently are quite common in soils and Dr. Drosdoff of these laboratories has isolated several specimens. A sample of jefferisite from Brandon Quarry, the type locality, gave the usual vermiculite diffraction pattern which indicates that it is either a vermiculite or vermiculite-chlorite. Gruner previously had described similar material as vermiculite-mica, so it is apparent that considerable variation can be expected even in a restricted locality.

¹¹ Warren, B. E., and Bragg, W. L., *Zeits. Krist.*, vol. 76, pp. 201-210, 1930.

¹² Bernal, J. D., and Crowfoot, D., *Trans. Faraday Soc.*, vol. 29, pp. 1032-1049, 1933.

SUMMARY

The crystal structure of vermiculites has been determined by use of *x*-ray diffraction data from single crystals. Lattice dimensions for the unit of structure are: $a = 5.33\text{\AA}$, $b = 9.18\text{\AA}$, $c = 28.85\text{\AA}$, and $\beta = 93^\circ 15'$. A Fourier analysis of the $(00l)$ reflections leading to the electron distribution normal to (001) verifies the structure previously advanced by Gruner insofar as it requires interleaving of layers containing water molecules with silicate layers similar to those of talc.

Vermiculites have the same type of shifts in the *a* direction as found in muscovite, talc, and pyrophyllite. They resemble the last two minerals and dickite in having a partially random superposition of structural layers along the *b* axis.

Many of the minerals previously described as vermiculites are mixed vermiculite-chlorites similar to the mixed vermiculite-micas described by Gruner.

NOTE. In carrying out the above analysis no attention was given to alternative choices of the *c* axis and it was assumed that the angle β as given by Gruner was somewhat in error due to the inherent difficulty of interpreting powder diffraction data. Actually the only difference is in the choice of the *c* axis and his structure corresponds to 2 above, instead of 2', and the shift in the structure is different from that of mica. The index transformations are:

$$-h = h', k = k', l = h' + l'$$

where the primes refer to the axes used by Gruner.