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Electron Diffraction Patterns from Montmorillonite

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Electron diffraction spot patterns have been obtained from monocrystalline silicate sheets or aggregates of sheets of the clay mineral montmorillonite by the use of electron micro-probe methods. Such patterns usually show six-fold symmetry instead of the two-fold symmetry which might be expected from the accepted layer structure, and have intensity distributions which cannot be reasonably explained in terms of any feasible model under normal diffraction conditions.

It is shown that the observed symmetry and intensity distributions can be explained by assuming the crystal sheets to be appreciably bent within coherently diffracting regions of the specimen, a supposition clearly supported by electron microscope evidence. Most spot patterns may then be attributed to bent layers having the structure previously proposed from X-ray diffraction data, with the tetrahedral oxygen atoms rotated from their positions in the 'idealized' structure by a plausible amount.

Other patterns, obtained only after treatment of the montmorillonite with an organic additive, gave *a*- and *b*-axes two per cent greater and a different intensity distribution corresponding to silicate layers less bent and having the idealized structure with no rotation of the tetrahedral oxygen groups. The origin of these patterns is not yet clear.

No information was gained as to the ordering of absorbed organic molecules relative to the silicate sheets.

1. Introduction

The state of knowledge regarding the structure of the clay mineral, montmorillonite, is well summarized in the book edited by Brindley (1951). From the evidence of X-ray diffraction, chemical analysis and chemical reactions it has been shown that the mineral has a layer structure with a high degree of disorder in the spatial relationship between the component silicate layers, and a provisional structure of the individual layers has been proposed and is generally accepted as being in agreement with most observations.

The X-ray powder patterns consist of fairly sharp $00l$ reflections and broad hk bands, the inner edges of which correspond to the positions of $hk0$ rings for an ordered structure. From the minimum spacing found from the $00l$ lines, obtained from dehydrated material, the layer thickness is found and from the hk bands the b-axis dimension is obtained. The structure of the layers can be seen to approximate to that of the layers occurring in mica, pyrophillite, vermiculite and similar clay minerals. Fig. 1 shows two projections of the proposed structure. This is an idealized structure in that it has been assumed that the octahedral and tetrahedral oxygen groups about the metal atoms are regular and undistorted so that the layer has its maximum symmetry. The X-ray diffraction evidence is insufficient to allow any discussion of details of the structure, such as the possibility of a rotation of the outer oxygen tetrahedra and accompanying distortions of the octahedra which have been observed in the structures of the better ordered clay minerals including dickite (Newnham & Brindley, 1956) and

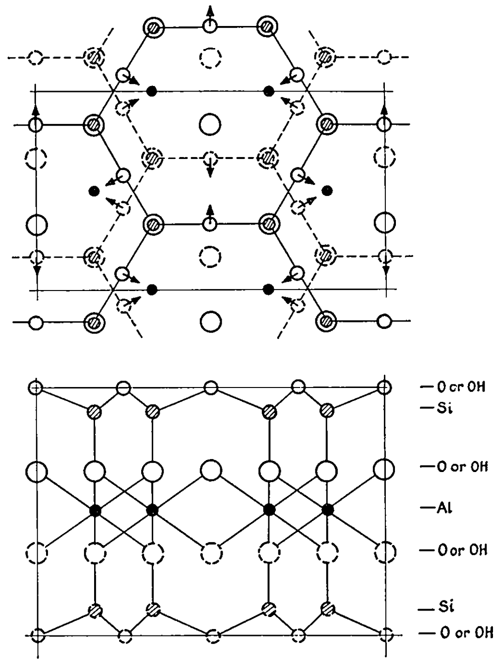

Fig. 1. Two projections of the accepted structure of montmorillonite in the undistorted form. The arrows indicate the distortions of the tetrahedral oxygen layers which may be expected by analogy with the structures of other clay minerals.

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vermiculite (Mathieson & Walker, 1954). The arrows in Fig. 1(*a*) indicate the way in which the tetrahedra oxygen atoms would be moved to produce such a distortion.

Zvyargin & Pinsker (1949) studied montmorillonite by the 'oblique texture' electron diffraction method, using oriented polycrystalline specimens. They did not find it possible to make any deductions as to the details of the layer structure but did find that, in at least some of their specimens considerable interlayer ordering existed and they were able to deduce a layer sequence giving a unit cell with dimensions,

$$a=5{\cdot}17\pm0{\cdot}02,\ b=8{\cdot}94\pm0{\cdot}02,\ c=9{\cdot}95\pm0{\cdot}06\ \text{Å};\quad \beta=99^\circ\ 54'\pm30',$$

and a space group $C^3_{2h}=C2/m$.

The possibility of obtaining more information on the structure of the silicate layers seemed to arise when it was found that extensive single-crystal spot patterns could be obtained from montmorillonite samples by use of the electron micro-probe diffraction techniques developed in this laboratory (Cowley, 1953). It soon became evident, however, that the interpretation of these single crystal patterns was not straightforward. Not only the relative intensities of the spots but also the symmetries of the patterns were at variance with those calculated from the accepted structure or any reasonable modification of it. Whereas the structure shown in Fig. 1 has only 2-fold axes and should give only a two-fold symmetry in the *hk*0 spot pattern, the *hk*0 spot patterns observed usually had hexagonal symmetry, apart from inconsistent minor variations which could be attributed to slight tilts of the specimen.

Two explanations of these results seemed possible. Either the layer structure is very different from that deduced from the X-ray diffraction evidence, or else the intensities were affected by the special conditions of the diffraction experiments. The latter proved to be the case. In the present paper we describe our experiments on montmorillonite, on various complexes of montmorillonite with organic molecules and on vermiculite which was used for purposes of comparison, show how our observations can be explained by taking into account the nature of the specimens, and indicates the extent of the structural information which may readily be derived from our patterns. The theoretical consideration of the diffraction problem, and the wider implications for X-ray and electron diffraction work on such specimens are included in another paper (Cowley, 1961).

2. Experimental

The montmorillonite used in most of the experiments was from a standard sample, A.P.I. number H26, from Clay Spur, Wyoming. Other samples, including one from Little Rock, Arkansas (H28) and a bentonite from New South Wales, gave similar results. Specimens were prepared by dispersing the material in water, allowing it to settle for a few hours or days and then taking a drop from the upper part of the suspension and allowing it to evaporate on a supporting film of collodion or carbon.

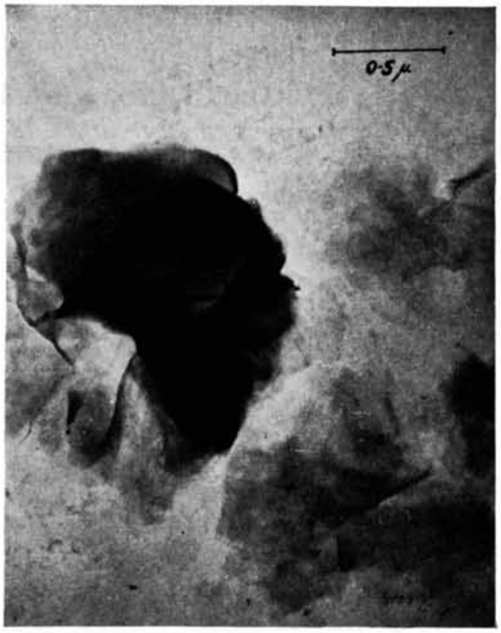
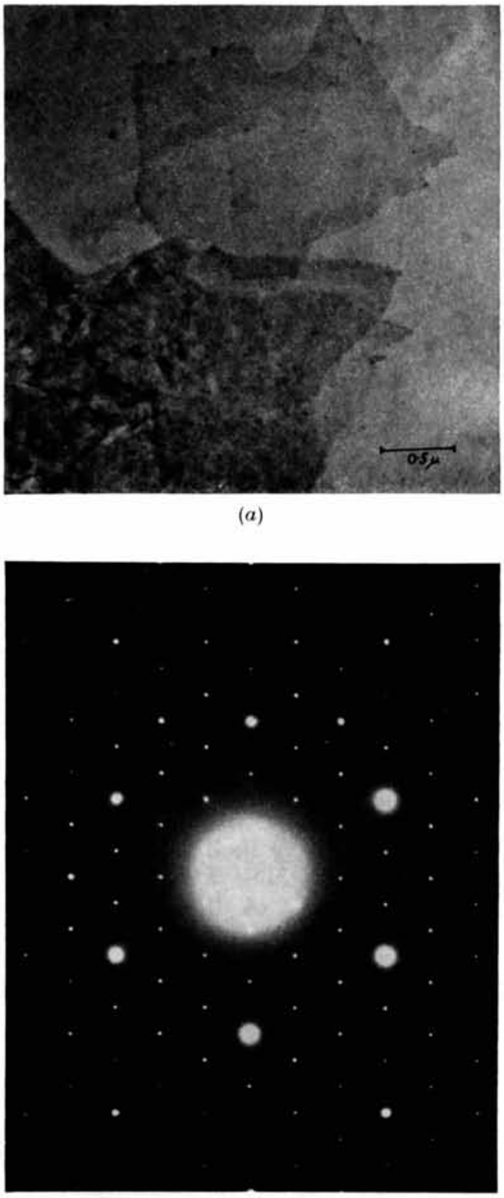


Fig. 2. Electron micrograph of montmorillonite particles, showing thin portions, and a much thicker aggregate.

Complexes with various organic molecules were formed, by first treating the montmorillonite with very dilute hydrochloric acid and then shaking it, and allowing it to stand in contact, with a solution of the organic compound in water or some other suitable solvent. The organic compounds used included aniline, α-naphthylamine, *o*-phenyline diamine, methylene blue, *o*-bromoaniline and 2,4,6-tribromo aniline. It has been shown, for example by Hendricks (1941) that such compounds form stable inter-layer complexes with montmorillonite.

Vermiculite in a state of dispersion comparable with that of montmorillonite was prepared by a method of Dr G. F. Walker (private communication). Lithium ions were first substituted for the normal interlayer metal ions of a well crystallized vermiculite by interaction with lithium chloride solution. The crystals could then be made to expand by the interlayer absorption of water molecules until the spacing between silicate layers was of the order of hundreds of Ångströms. This swollen material was mascerated and dispersed in water and samples were taken from the upper portions of the suspension after allowing the coarser material to settle.

Electron micrographs and selected area diffraction patterns were obtained from some specimens using the Siemens Elmiskop I. Micrographs such as Fig. 2 reveal that the montmorillonite crystals are very thin, often



(a)

(b)

Fig. 3. (a) Electron micrograph of portion of a vermiculite specimen showing very thin flat crystal plates, and (b) a selected area diffraction pattern from such thin crystals.

apparently no more than one silicate layer thick, and are folded and bent and often clumped together to form irregular aggregates. Selected area diffraction patterns sometimes showed almost continuous rings but more often arced patterns, indicating that the many crystal sheets contributing to the pattern tended to have parallel orientation. Occasionally extensive thin regions gave spot patterns similar to Fig. 4. The intensity distributions in these spot and arc patterns were similar. The vermiculite crystals, although of the same order of thickness appeared to be larger and flatter as shown in Fig. 3(a). The selected area diffraction patterns, such as Fig. 3(b) were sharper and more extensive, indicating a higher degree of order.

Most of the electron diffraction patterns were obtained using an instrument with an accelerating voltage of 50 kV. and camera length of about 25 cm. The diameter of the electron beam at the specimen level was of the order of $\frac{1}{2}\mu$.

Rough estimates of spot intensities were made by visual estimation. Since the stability of the specimens and of the instrumental settings were usually not sufficient to allow multiple exposures of the spot patterns, the intensity scale was established by taking multiple exposures of spot patterns obtained from ZnO smoke crystals under comparable conditions.

3. Results

The spot patterns obtained from montmorillonite samples, with or without the organic compounds, could be grouped into three distinct types. Intermediate type patterns were very rare. These three types have been labelled, arbitrarily, *A*, *B* and *C*. In each case no consistent deviation from hexagonal symmetry could be observed, all deviations being attributable to specimen tilting. The individual characteristics of the various types are as follows:

Type A

A typical pattern is shown in Fig. 4. Relative to the other patterns, the outstanding differences are that the 130,020 reflections are relatively strong and that the third-order reflections do not dominate the pattern.

This pattern was obtained from occasional parts of all montmorillonite specimens, with or without organic additives. The arc patterns obtained from less well

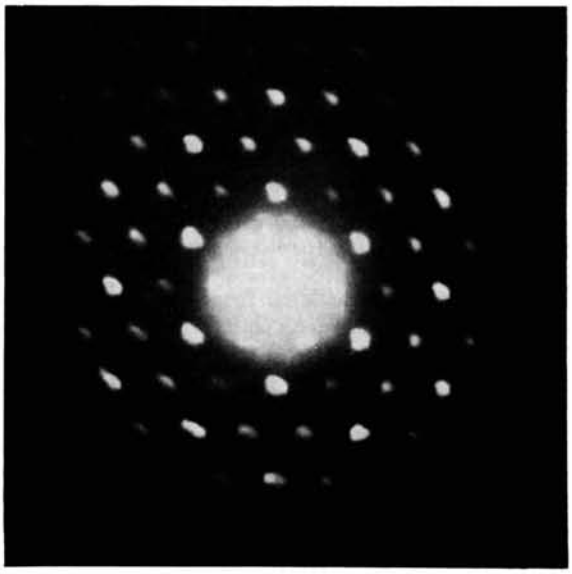


Fig. 4. Electron diffraction spot pattern of type *A* from a single montmorillonite 'crystal'.

oriented parts of the specimens had the same characteristic intensity distribution, as also have most arc patterns obtained from montmorillonite by other authors (e.g. Morita & Nishida, 1958).

The observed relative intensities are listed in Table 1.

The patterns of this type were also consistent in the values of the lattice constants derived from them. Thus from the eleven most extensive single crystal patterns of this type the d-values for the 110,020 reflections had an average value of $4{\cdot}44 \pm 0{\cdot}03$ Å. The uncertainty corresponds approximately to the probable experimental error. This value agrees well with the value $d_{110} = 4{\cdot}46 \pm 0{\cdot}02$ Å derived from ten ring patterns, some of which were obtained from material with organic additives and some from untreated material.

Type B

These spot patterns were usually sharper and more extensive than those of type A and had a distinctive intensity distribution, an outstanding feature of which is that all third-order spots are strong. An example is shown in Fig. 5.

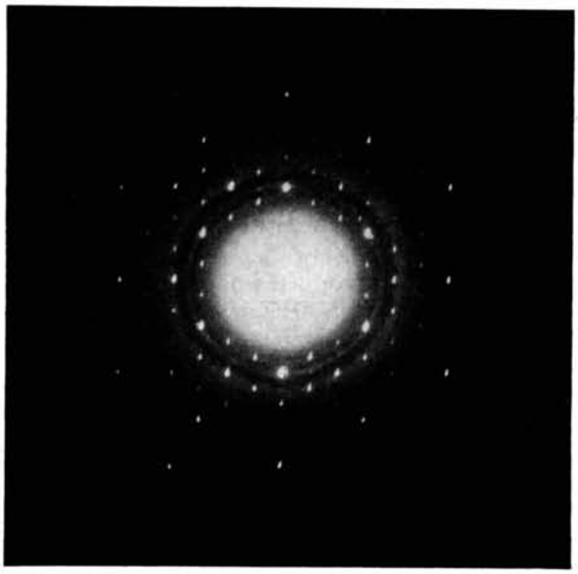


Fig. 5. Electron diffraction spot pattern of type B, from montmorillonite plus an organic additive.

This pattern was obtained from occasional parts of montmorillonite specimens but *only* when organic additives were present. No arc patterns with this intensity distribution were found. The relative intensities are listed in Table 1.

All patterns of this type had dimensions appreciably different from those of type A. For nine good patterns the average value for the d-values of the 110,020 reflections was $4{\cdot}55 \pm 0{\cdot}03$ Å, i.e. more than 2% greater than for type A or for the ring patterns.

This type of pattern was also given by the carbon–montmorillonite complex obtained by Dr G. F. Walker by heating a montmorillonite complex with organic material.

Table 1. *Comparison of observed and calculated intensities for the Type A and Type B hk spot patterns from montmorillonite*

	Type A		Type B		
	I_o	I_c	I_o	I_c (Bent)	I_c (Unbent)
0,2; 1,1	150	160	(∼50)	(210)	(148)
2,0; 1,3	110	85	32	47	16
0,4; 2,2	10	16	12	19	13
2,4; 1,5; 3,1	25	20	24	32	25
0,6; 3,3	90	75	140	160	201
4,0; 2,6	47	43	80	92	38
4,2; 1,7; 3,5	25	17	24	16	11
0,8; 4,4	4	5	20	10	5
2,8; 3,7; 5,1	2	3	5	8	7
4,6; 1,9; 5,3	5	15	6	8	2
0,10; 5,5	2	2	4	5	5
6,0; 3,9	5	12	48	30	47
2,10; 4,8; 6,2	2	2	4	6	2
6,4; 1,11; 5,7	2	3	6	5	4
0,12; 6,6	4	4	32	24	77
4,10; 3,11; 7,1	1	1	5	3	2
2,12; 5,9; 7,3	2	4	6	6	1
6,8; 1,13; 7,5	2	1	5	4	2
8,0; 4,14	1	2	16	10	2
R factor	—	0·19	—	0·16	0·29

Type C

Patterns such as that in Fig. 6 were sometimes obtained. These are very limited and rather diffuse. The only spots of appreciable intensity are the 060,330 spots. The diffuseness of these patterns usually prevented any accurate measure of d-values.

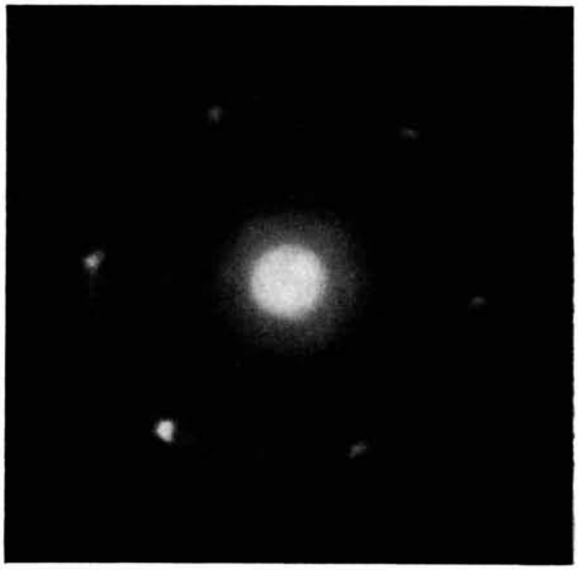


Fig. 6. Electron diffraction spot pattern of type C from montmorillonite.

The patterns obtained from vermiculite were usually much sharper and more extensive than either A or B

with intensities agreeing with neither but closer to B (Fig. 3(*b*)). In one or two cases, however, patterns with intensity distributions close to that of type A were observed from vermiculite specimens.

In an initial attempt at structure analysis from a pattern of type B it was assumed that the apparent hexagonal symmetry was a result of disorder in which different parts of one crystal flake, or separate parallel crystals, have orientations 60 or 120 degrees apart in the a–b plane. Reasonable agreement between observed intensities and intensities calculated on this assumption could not be obtained except by postulating a distortion of the silicate layer very different from that expected by analogy with clay minerals of known structure. The reliability index, R, as usually defined, could be reduced to 0·20 by postulating an unlikely form of distortion in which the top and bottom layer of tetrahedral oxygen atoms were translated bodily in opposite directions by about $\frac{1}{2}$ Å, thus 'shearing' the silicate layer in a most unnatural fashion.

Since vermiculite, of which the structure is known, was also found to give a variety of intensity distributions, some approaching that of type A, the idea of direct structural interpretations of the intensity distributions was discarded. The experimental evidence was then reexamined. It was seen that the Patterson projections obtained from the type A and B $hk0$ spot patterns (reproduced as Figs. 7(*a*) and 8(*a*) respectively) contained significant information. In each case the peaks corresponding to vectors between atoms in the bottom tetrahedral layer and atoms in the top tetrahedral layer (or vice versa) of the silicate sheets were missing. Thus, in Fig. 8(*a*) peaks occur at positions such as those marked X corresponding to the oxygen–oxygen vectors within either the top or bottom oxygen layers, if the structure of Fig. 1 with no distortion is assumed, but no peaks occur at the positions marked Y corresponding to oxygen–oxygen vectors between top and bottom oxygen layers. Similarly in Fig. 7(*a*) if it is assumed that there is a rotation of the triangular groups of oxygen atoms in the tetrahedral layers the peaks due to oxygen–oxygen vectors within the oxygen layers come at the positions marked X, but there are no peaks at positions such as those marked Y which correspond to oxygen–oxygen vectors between top and bottom layers.

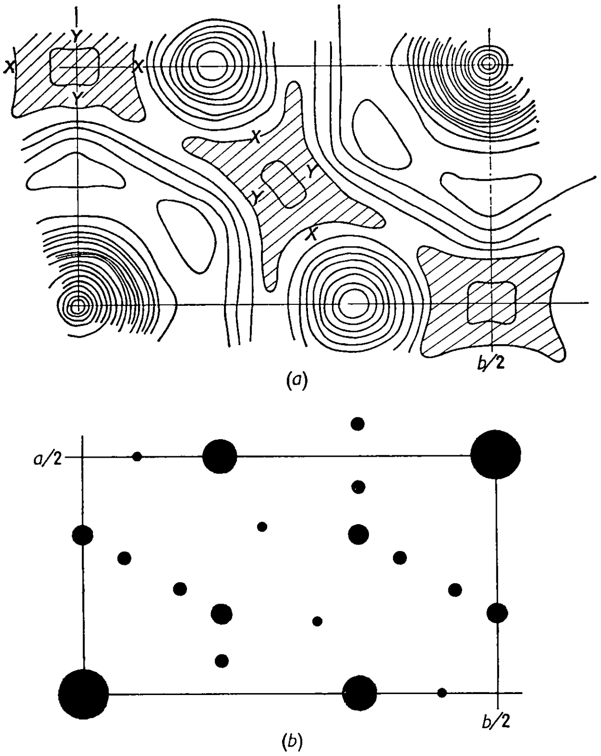


Fig. 7. (*a*) Patterson function calculated from the intensities of a type A spot pattern. (*b*) Theoretical Patterson function (diagrammatic) calculated for $z_0 = 2$–3 Å and distorted tetrahedral oxygen layers.

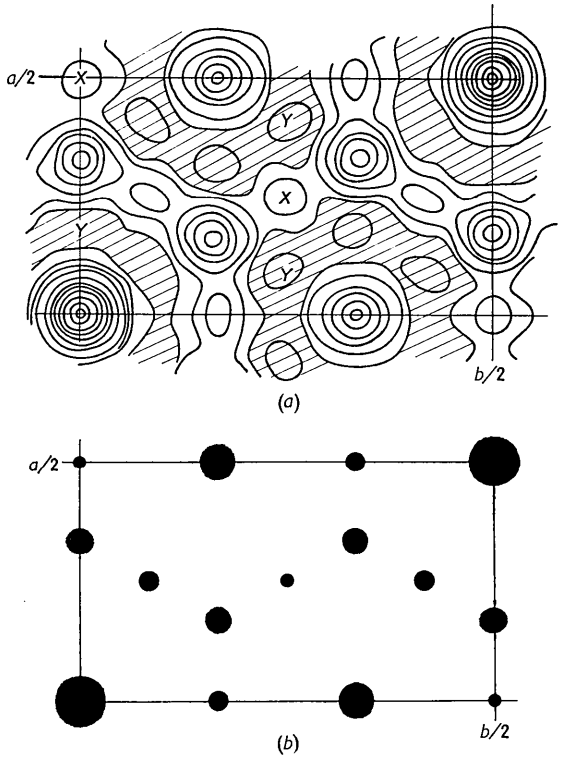


Fig. 8. (*a*) Patterson function calculated from the intensities of a type B spot pattern. (*b*) Theoretical Patterson function (diagrammatic) calculated for $z_0 = 4$–5 Å with undistorted tetrahedral oxygen layers.

It was realized that the absence of peaks corresponding to vectors with z components greater than a certain value could be the result of the bending of the crystals which is apparent in the electron micrograph, Fig. 2.

4. Diffraction from bent crystals

In a separate paper (Cowley, 1961) the problem of diffraction from a bent crystal is treated by a new method providing expressions for the diffraction intensities, which, although admittedly involving considerable approximations, are relatively simple and probably adequate for comparison with the limited diffraction data available on specimens of the type being considered here. It is assumed that the spread of orientations due to bending within a coherently diffracting region of the specimen is such that the Patterson peaks are spread along arcs according to a Gaussian distribution function

$$q_i(p/r_i) = (\pi^{-\frac{1}{2}}\sigma/r_i)\exp\left(-\sigma^2p^2/r_i^2\right), \qquad (1)$$

where r_i is the magnitude of the vector $\mathbf{r}_i$ from the origin to the Patterson peak, p measures the distance along the arc and σ is a constant specifying the width of the distribution, i.e. the average amount of bending.

If the electron beam is in the direction of the z axis and such bending takes place about the x and y axes, the intensities of the $hk0$ spots are then given by

$$I(\mathbf{s}) = \sum_i W_i(\mathbf{s})\exp\{2\pi i\mathbf{r}_i.\mathbf{s}\} \times\exp\{(-\pi^2/\sigma^2)(s^2z_i^2)\}, \qquad (2)$$

where the function $W_i(\mathbf{s})$ is the Fourier transform of the ith Patterson peak which has a z coordinate, z_i, and $\mathbf{s}$ is the reciprocal space vector of magnitude s.

The equation (2) implies that the contribution of a Patterson peak to the intensity of a reflection decreases as the z-component of the corresponding vector increases. As an approximation we may assume that the contribution of the Patterson peak is zero if the z coordinate exceeds a certain value z_0 given by the width of the Gaussian distribution in (2), i.e.

$$z_0 = \sigma/\pi s\,. \qquad (3)$$

Thus if two atoms are separated in the z-direction by more than a distance z_0 we may consider that they diffract incoherently. It is shown that for materials such as montmorillonite in which the bending can be 10 to 20 degrees within a coherently diffracting region of the specimen, the value of z_0 is of the order of 1–5 Å for a reflection with $s = 1$ Å^{-1}. For such reflections, then, it is not to be expected that the whole of the silicate layer in montmorillonite will diffract coherently, and peaks corresponding to vectors from atoms on the top of the layer to atoms on the bottom will not appear in the Patterson map.

As a very rough approximation we may say that most of the detail of a Patterson map from $hk0$ spot patterns, such as those of Figs. 4 and 5, comes from reflections with d-values between 1 and 2·5 Å, so that we may take an average value for s equal to about 1·5 Å and assume a constant z_0 value. It is then possible to calculate the weights and positions of Patterson peaks for various models of the silicate structure and for various values of z_0. Such calculations resulted in the theoretical Patterson projections shown in Figs. 7(*b*) and 8(*b*). The agreement with the observed Patterson projections is good in each case. For Fig. 7, corresponding to patterns of type A, it was assumed that the tetrahedral oxygen layers were distorted as shown by the arrows in Fig. 1(*b*), with a rotation of the oxygen triangles through about 10° and the value assumed for z_0 was 2–3 Å, so that each layer of metal atoms diffracted coherently with the adjacent oxygen atoms but not with the neighboring metal atom layers. For Fig. 8, corresponding to patterns of type B, no distortion of the tetrahedral oxygen layers was assumed and the value chosen for z_0 was 4–5 Å, so that, for example adjacent layers of metal atoms diffracted coherently but the two tetrahedral layers did not diffract coherently.

Encouraged by the agreement between theoretical and observed Patterson projections we have made calculations of the intensities to be expected under comparable experimental conditions but without the assumption of a constant z_0 value. Firstly for each reflection the intensity was calculated for $z_0 \approx 1$ Å (all sets of atoms with the same z parameter diffracting as if independent of other sets), for $z_0 \approx 2$–3 Å (the tetrahedral and octahedral layers diffracting independently), and for $z_0 \approx 9$ Å (the whole silicate layer diffracting coherently). By interpolation, the intensity for each reflection was deduced for the z_0 value obtained from (3) for a given σ value and the appropriate s value. Reasonable agreement with the observed intensities was obtained by making the same assumptions as to distortions of the silicate layers as above, and assuming for type A patterns a value of σ equal to 2·1, corresponding to an average bending of 50°($\pm$25°) within the coherently diffraction region (probably a few hundred Å diameter), and for type B patterns a value of σ equal to 5·8, or an average bending of 20°. The observed and calculated intensities are compared in Table 1, which also contains the intensities which would be given by flat crystals, one silicate layer thick, averaged to give hexagonal symmetry. For type A patterns the reliability index R is 0·19 for the assumed bending. Type B patterns are obviously closer to the pattern to be expected from unbent crystals, but R is 0·29 for flat crystals and 0·16 with bending. The 110,020 reflections have been omitted from these calculations. For these the observed intensity is uncertain because of the high background scattering intensity, and the lack of accurate atomic scattering factors in this region makes the calculated intensities unreliable.

5. Patterns from polycrystalline material

Because the ring patterns from polycrystalline materials gave lattice constants in agreement with those for type A patterns and the arc patterns from oriented aggregates of crystals gave a similar intensity distribution, it seems probable that the bulk of the montmorillonite samples consists of material with much the same structure and degree of bending as that deduced from type A patterns. An attempt was therefore made to detect the influence of bending on the intensities from polycrystalline specimens. Since specimens with random orientation could not be obtained the methods used for halloysite (Cowley, 1961) could not be employed, and so 'oblique texture' patterns given by crystals lying almost flat on a supporting film were used. With the film tilted at about 30° to the incident beam, the patterns consisted of continuous ellipses (Fig. 9) with variations of intensity due to the variation of scattering power along the *hkl* lines in the reciprocal lattice and variations of width due to the appreciable spread of orientations of the crystals about the mean orientation. The intensity profile of any one ellipse measured along any radial line will be determined by a distribution function, $D(l)$, giving the number of crystals producing diffraction spots at each scattering angle (and so at each l value), and the function $P(l)$ giving the scattering power for each l value for a single crystal.

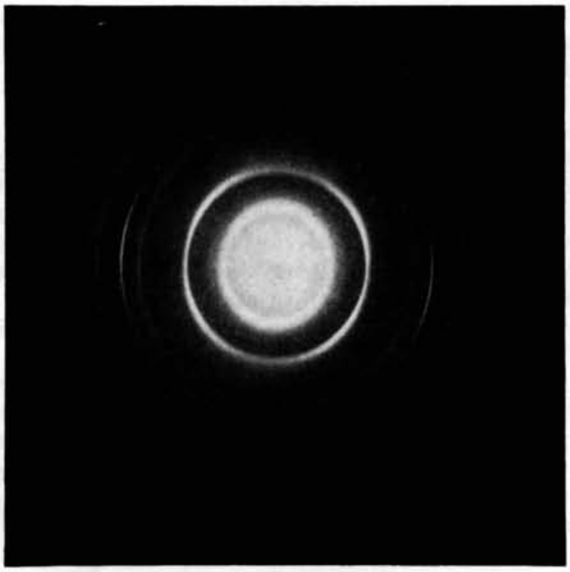


Fig. 9. Elliptical ring pattern obtained from montmorillonite crystals oriented on a supporting film tilted through 30°.

As in the case of halloysite, the scattering power for the average of the $11l$ and $02l$ reciprocal lattice lines is very nearly independent of the amount of bending of the crystals. It decreases slowly and uniformly with l whether the crystals are flat or severely bent. The profile of the 11,02 band should therefore be independent of the amount of bending. From the observed profile it is possible to calculate an intensity function $I(l)$ by using the formula due to Warren (1941) in the form appropriate to electrons.

Using the subscript 1 in reference to the 11,02 band, we then have that

$$I_1(l) = D_1(l) \,.\, P_1(l) \,. \tag{4}$$

Since $I_1(l)$ can be determined by experiment from the band profile, and $P_1(l)$ is independent of bending and can be calculated, it is possible to deduce the distribution function $D_1(l)$.

The orientational distribution function relating to the 131,201 average line, $D_2(l)$, will be the same as $D_1(l)$, except for a change in scale: thus

$$D_2(l) = D_1(l/3^{\frac{1}{2}}) \,.$$

If, then, the intensity function $I_2(l)$ is deduced from the 13,20 band profile, measured along the same radial line as the 11,02 band profile, it is possible to deduce $P_2(l)$ from the relation

$$\begin{aligned} P_2(l) &= I_2(l)/D_2(l) \\ &= I_2(l) \,.\, P_1(l/3^{\frac{1}{2}})/I_1(l/3^{\frac{1}{2}}) \,. \end{aligned} \tag{5}$$

A comparison of $P_2(l)$ so determined with values of $P_2(l)$ values calculated under various assumptions of bending thus gives an indication of the average state of bending in the polycrystalline samples.

Values of the function $P_2(l)$ were deduced from two measured band intensity profiles, one measured along the minor axis and one along the major axis of the ellipses for a tilting angle of about 30°. For the measurements along the minor axis the orientation distribution function, deduced from the 11,02 ellipse profile, was centred on the zero tilt orientation. For measurements along the major axis it was centred on a tilt of 30°. The two distributions overlapped considerably so that values for the function $P_2(l)$ could be deduced for l values from zero up to that corresponding to a tilt of about 40° or more.

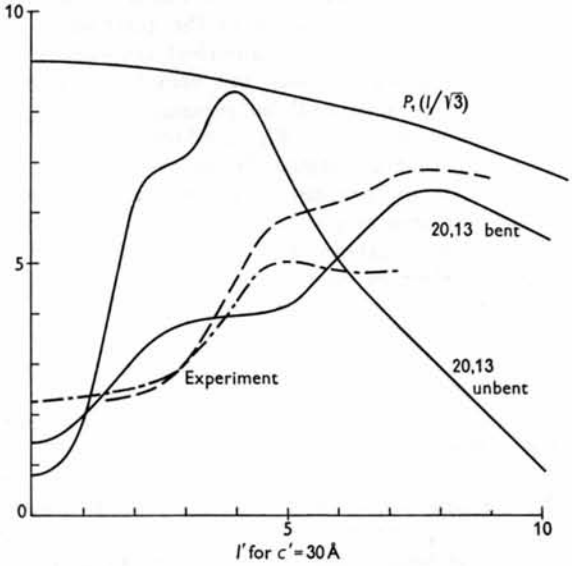


Fig. 10. The averaged distribution of scattering power for the $13l$, $20l$ reciprocal lattice lines. The experimental curves deduced from measurements of the pattern, Fig. 9, are compared with theoretical curves calculated for bent and unbent crystals.

The two experimental determinations of $P_2(l)$ are shown in Fig. 10, compared with the theoretical values calculated for an unbent silicate layer and also for a layer bent so that only atoms less than about 3 Å apart in the beam direction diffract coherently. It is apparent that the experimentally deduced curves are significantly different from that for unbent crystals, but not very different from that for the bent crystals. For comparison it may be noted that for single crystal patterns of type *A* the bending assumed to calculate I_c of Table 1 corresponds to coherent diffraction from atoms not more than 2–3 Å apart in the beam direction.

Although the accuracy of the experimental method in this case is not great, the agreement in the general form and trend of the two independent experimental curves suggests that the results are at least approximately correct. It is therefore concluded that the intensities of the 'oblique texture' patterns obtained from oriented crystals are, in this case, considerably influenced by bending of the silicate layers, and that any attempt to deduce structural information from such patterns must fail unless the bending is taken into account.

6. Discussion

Patterns of type *C*, described above, cannot be derived by making assumptions concerning the bending of single silicate layers. Calculations show, however, that, if one assumes some ordering between adjacent silicate layers the third order spots, such as the 060 and 330 may become very strong relative to all other spots. In order to explain the diffuseness of the spots, the rapid decrease in intensity with diffracting angle, and the near-hexagonal symmetry of the intensities it is necessary to postulate very imperfect crystals with a disorder in their orientations, but very little bending. Such conditions may well be present in aggregates such as the one shown in Fig. 2 where many silicate layers lie together in clumps. It may well be that the parallel orientation prevents appreciable bending over a considerable area and also results in a local ordering between adjacent layers. It is also possible that the diffuseness arises in part from variations in lattice dimensions accompanying variations in the composition of the contributing silicate layers.

The pattern *A* seems to be the pattern to be associated with the bulk of the material in a well dispersed sample of montmorillonite after drying in the vacuum of the diffraction camera. What can be deduced concerning the layer structure after allowance is made for the bending of the crystals seems to indicate that the structure postulated from the X-ray diffraction evidence is at least roughly correct, and that there is a distortion of the tetrahedral oxygen layers such as might be expected by analogy with the known clay mineral structures, although the amount of the distortion cannot be determined with any accuracy.

The fact that the crystals giving pattern *B* have lattice constants in the plane of the layer about 2% greater than those giving pattern *A* is well established. The conclusion that for these crystals there is very little or no distortion of the tetrahedral oxygen layers is less definite, although the occurrence of the larger values for the lattice constants suggests that this could feasibly be correct. The rotation of the triangular oxygen groups in the tetrahedral layers is generally considered to be the means whereby the dimensions of the tetrahedral layer may be contracted to comply more nearly with those favoured by the octahedral layer. An increase in the unit cell dimensions would mean that less distortion is required. The smaller degree of bending for these crystals seems reasonably well established.

Several explanations are possible for the occurrence of the crystals giving patterns of type *B*. Firstly one may suppose that these crystals have a different composition from the bulk of the sample and hence a different lattice constant. The fact that these patterns were obtained only from specimens containing organic additives must then be attributed either to chance or else to some unknown physical factor involved in the specimen preparation which is operative when organic compounds are present.

Secondly one may suppose that the absorption of organic molecules on selected sites between the tetrahedral oxygen atoms bounding the silicate layer modifies the charge distribution in such a way that the distortion of the oxygen layers decreases and the lattice constant increases, and that the presence of the organic molecules stiffens the layers so that the bending decreases. The crystals giving patterns of type *B* would thus be those for which the absorption of organic molecules was most favoured.

If we combine the less unlikely features of these two explanations we arrive at a third and possibly better explanation: namely, that a small proportion of the crystals have a different composition and a different lattice constant from that of the bulk of the sample and that the organic molecules are absorbed preferentially on these particular crystals. The presence of the organic molecules tends to stiffen the crystal sheets and so reduces the amount of bending in them and consequently produces the characteristic intensity distribution of patterns of type *B*. In the absence of the organic molecules these crystal layers are just as crumpled as the rest, or more so, and so give no very distinctive pattern.

At present it is not possible to confirm or refute any of these suggestions. To do so would require a more detailed examination, preferably with careful selected area diffraction and electron microscope study of samples with organic additives.

At no stage in the present experiments was there any definite evidence of diffraction effects which could be attributed to the organic molecules which are presumably absorbed on and between the montmorillonite silicate layers. This would suggest that the molecules are not absorbed in any ordered array. It may be that a particular active group of the molecule is attached preferably at some particular site such as, for example, the centre of the hexagonal 'holes' in the tetrahedral oxygen layers. This would cause a slight modification of the spot pattern intensities, but such a modification would probably not be of the same order as that due to the bending of the crystals. It seems probable that single crystal patterns may offer a means of studying the absorption of organic molecules on clay minerals but only if the absorbing material is in the form of flat undistorted silicate layer sheets.

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Short Communications

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Kristalldaten von Stickstoffselenid (Selenstickstoff) $[NSe]_x$.

Von Hartmut Bärnighausen, Tassilo von Volkmann und Jochen Jander, *Anorganische Abteilung des Chemischen Laboratoriums der Universität Freiburg/i.Br., Deutschland*

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Im Anschluss an präparative Untersuchungen zur Chemie des Stickstoffselenids, in deren Verlauf Jander & Doetsch (1960) erstmals ein *kristallisiertes* Präparat der Bruttozusammensetzung (NSe) darstellen konnten, haben wir mit der röntgenographischen Kristallstrukturaufklärung dieser Verbindung begonnen. Neben dem Molekulargewicht, das sich mit Hilfe anderer physikalisch-chemischer Methoden auf Grund der besonderen Eigenschaften des Stickstoffselenids nicht ermitteln liess, interessiert der sterische Bau des Moleküls und gegebenenfalls die strukturchemische Verwandtschaft mit Tetrastickstofftetrasulfid N_4S_4, dessen monokline Kristallstruktur von Clark (1952) aufgeklärt wurde.

Stickstoffselenid kristallisiert vorzugsweise in langgestreckten, zum Teil aber auch gedrungenen, roten Blättchen, die stets nach der Längsrichtung (c-Achse) verzwillingt sind. Durch leichten Druck auf die gut sichtbare Verwachsungsnaht lassen sich die Zwillinge trennen.

Zur Bestimmung der Kristalldaten fertigten wir mit Cu $K\alpha$-Strahlung Drehkristalldiagramme und Weissenbergaufnahmen bis zur dritten Schichtlinie sowohl von einem Zwillingskristall als auch von einem Einkristallsplitter bei Drehung um die c-Achse an. Es ergab sich trikline Symmetrie mit den Zelldimensionen

$$a=6{,}47\pm0{,}01,\ b=6{,}85\pm0{,}01,\ c=6{,}85\pm0{,}04\ \text{Å};$$
$$\alpha=90{,}5\pm0{,}0^\circ,\ \beta=100{,}4\pm0{,}1^\circ,\ \gamma=100{,}4\pm0{,}1^\circ.$$

c wurde aus den Schichtlinienabständen der Drehkristalldiagramme ermittelt. Nach der Bestimmung von a^*, b^* und γ^* auf einer Weissenbergaufnahme des Äquators bei Anwendung des Eichverfahrens von Christ (1956) wurde zur genauen Berechnung der übrigen Konstanten die Tatsache benutzt, dass auf der Weissenbergaufnahme der 3. Schichtlinie des Zwillingskristalls die beiden Interferenzmuster des Zwillings nahezu aufeinanderfallen.

Unter Annahme von 8 Formeleinheiten (NSe) in der Elementarzelle ($V=293$ Å^3) stimmt die Röntgendichte 4,22 g.cm.$^{-3}$ gut mit der von Jander & Doetsch (1960) pyknometrisch ermittelten Dichte 4,2 g.cm.$^{-3}$ überein. Die Entscheidung zwischen den beiden möglichen Raumgruppen $P1$ und $P\bar{1}$ kann gegenwärtig noch nicht getroffen werden, obgleich die zentrosymmetrische Raumgruppe mit 2 Molekülen 'N_4Se_4' naheliegt. Wir haben die vollständige Aufklärung der Struktur in Angriff genommen.

Der Deutschen Forschungsgemeinschaft danken wir für die Mittel zur Beschaffung eines Weissenberggoniometers.

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