

X-RAY DIFFRACTION BAND PROFILES OF MONTMORILLONITE—INFLUENCE OF HYDRATION AND OF THE EXCHANGEABLE CATIONS

by

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ABSTRACT

PREVIOUS studies of diffraction band profiles of montmorillonite are extended to the 13, 20 band which, for reasons discussed, is more sensitive to structural details than the diffraction bands considered previously. Hydration of Na-montmorillonite produces appreciable sharpening of this band, indicating, contrary to previous results, that the water layers have at least a partially ordered arrangement. For Cs-montmorillonite, the single water layer hydrate shows only a small sharpening of the band profile, possibly attributable to the water layer, but which clearly indicates that the Cs ions cannot be significantly displaced from their positions in the anhydrous material. For Ba-montmorillonite, the two-layer hydrate shows a small broadening of the diffraction band, which is possibly the result of a partial ordering of the water layers together with a movement of the Ba ions away from the hexagonal holes.

INTRODUCTION

THE present contribution extends earlier studies by Longuet-Escard, Mering, and Brindley (1960, 1961), hereafter referred to as $I(a)$, $I(b)$, in which the hk diffraction bands of montmorillonite were utilized to obtain information regarding the organization of the water molecules and exchangeable cations in the hydrated forms of the mineral. Alternative methods of studying the structure of montmorillonite are principally (a) analysis of $00l$ X-ray reflections from ordered aggregates to establish z parameters of atoms, and (b) electron diffraction methods which are restricted to anhydrous forms of the mineral. These methods are discussed and compared by Mering and Oberlin (1967).

Since the hk diffraction bands arise from continuous intensity distributions along hk lines in reciprocal space, it would appear that measurements of their intensity profiles would give directly the variation of $|F_{hk}|^2$ with Z .*

* Z signifies a coordinate in reciprocal space, z in crystal space.

This is not the case, however, because the reciprocal lattice "rods" are diffused normal to the Z direction by the small extent of the montmorillonite crystals in the (001) plane. An additional problem is that each observed band is a composite band arising from several sets of hk values produced by the pseudo-hexagonal character of the structure. Consequently a trial-and-error method is necessary in which band profiles calculated from assumed models are compared with experimental data.

The method of calculation used in the present work combines the numerical integration method developed by Brindley and Mering (1951) (referred to as II hereafter), with the earlier analysis of Warren (1941). The numerical integration method furnishes more accurate calculations for the low-angle terminations of the diffraction bands, Warren's analytical method is more convenient and is sufficiently accurate at the higher angles for each band.

It was pointed out earlier (Ia, b, II) that diffraction band profiles obtained from randomly oriented powder samples vary according to the variation of $\sum |F|^2$ with Z , and can be classified as follows:

Bands of Type I.—When $\sum |F|^2$ varies slowly with Z , the band has a sharp low-angle termination and falls off gradually to higher angles. The Warren analysis is applicable to these bands over their entire range with little error. The profile of the band is not sensitive to structural details, but is dependent on crystal size, with smaller crystals giving more diffuse bands. Estimates of crystal size can be made most reliably from these bands.

Bands of Type II.—These correspond to a rapid decrease of $\sum |F|^2$ with Z , and require the numerical integration method described in II. It appears that only the 06, 33 band is of this type.

Bands of Type III.—These correspond to a rapid increase of $\sum |F|^2$ with Z , and the numerical integration method is necessary at the lower angles. Since the rapid change of $\sum |F|^2$ with Z depends on the structure of the mineral, bands of this type are sensitive to structure. They are less suitable than bands of Type I for determining crystal size. The band profiles depend particularly on the values of $\sum |F|^2$ in the region of small Z values.

Previous studies (Ia, b) considered the bands (i) 11, 02; (ii) 22, 04; (iii) 31, 15, 24; (iv) 35, 17, 42 for montmorillonites saturated with the cations Na, Ba, Cs, and in various stages of hydration. The present study extends the analysis to the band 13, 20 for the same montmorillonite (from Camp-Berteau, Morocco) saturated with Na, Ba, and Cs, and in various hydration states. This band is of Type III and therefore provides a sensitive indication of changes in the organization of the exchangeable cations with hydration and of the organization of the water molecules relative to the silicate layer. The method suffers, however, from the indirect approach (trial-and-error method) of studying the structural details.

The purified mineral, Na-saturated, was dispersed in water and treated five or more times with N solutions of CsCl or BaCl₂ with intermediate washings with water and a final washing with alcohol. Diffraction measurements were made with CuK α radiation, using a focusing Guinier-type trans-

mission camera with crystal-monochromatized radiation and random powder samples. Graphical estimations of background scattering were made.

RESULTS AND DISCUSSION

Calculated 13, 20 Band Profiles for Anhydrous Montmorillonites

Figure 1 shows the calculated variation of $\sum |F|^2$ with Z for anhydrous "H", Na, Ba, and Cs-montmorillonites based on the z parameters of the structure obtained by Pezerat and Mering (1954, 1958) and with the assumption that the exchangeable cations are distributed statistically over the pseudo-hexagonal "holes" of the Si—O layer surfaces and enter these holes within the limits imposed by the structure and the ionic radii. The use of the ideal Hofmann model for calculating $|F|^2$ values is questionable and some of the finer points which arise later may be related to the use of this ideal layer structure model without allowance for the twist and tilt of the Si—O tetrahedra and the modifications of the Al—O octahedra indicated by recent structure analyses of layer silicates. The 13, 20 band is probably the most sensitive to small adjustments of the structural model. The z parameters used for the exchangeable cations are as follows: $z(\text{Na})=4.15$, $z(\text{Cs})=4.70$, $z(\text{Ba})=4.26 \text{ \AA}$ measured from $z=0$ for the octahedral cations.

The curve labeled "H" montmorillonite corresponds to the 2:1 aluminosilicate layer without interlayer cations. The addition of the interlayer Na ions modifies the $\sum |F|^2$ curve only very slightly. The curve for Na also represents well enough the curve for Ca-montmorillonite, for although $f(\text{Ca}) \simeq 2f(\text{Na})$, there are half as many Ca^{2+} ions as Na^+ ions. With Ba and Cs ions, however, the $|F|^2$ curves are considerably changed.

Figure 2 shows the 13, 20 band profiles calculated principally by the numerical integration method (II) for the anhydrous montmorillonites containing Cs, Ba, and light cations. The curves are scaled to the same maximum height and are displaced laterally so as to pass through the same point at $(I_{\text{max}}/2)$. These intensity distributions cannot be calculated without knowing also the diffusion of the reciprocal rods normal to Z , i.e. without knowing also the size and shape of the diffracting crystals. It suffices to use one size-shape parameter, namely L , the diameter of the equivalent circular disc.* A value $L=100 \text{ \AA}$ has been used based on the earlier work (Ib, especially p. 26), but in fact the calculated band profile for *this particular band* is not sensitive to the precise value chosen for L within a range from 100-500 \AA .

Observed 13, 20 Bands for Anhydrous Montmorillonites

Figure 3 shows the observed intensity profiles scaled to the same height and intersecting at $(I_{\text{max}}/2)$ as in Fig. 2. Comparison of the observed with the calculated data shows a satisfactory general agreement in that there is much the same change in going from the Cs, to the Ba, to the light cation curve in the two figures. The shapes of the observed and calculated curves

* The crystals being pseudo-hexagonal in form, this is a reasonable assumption.

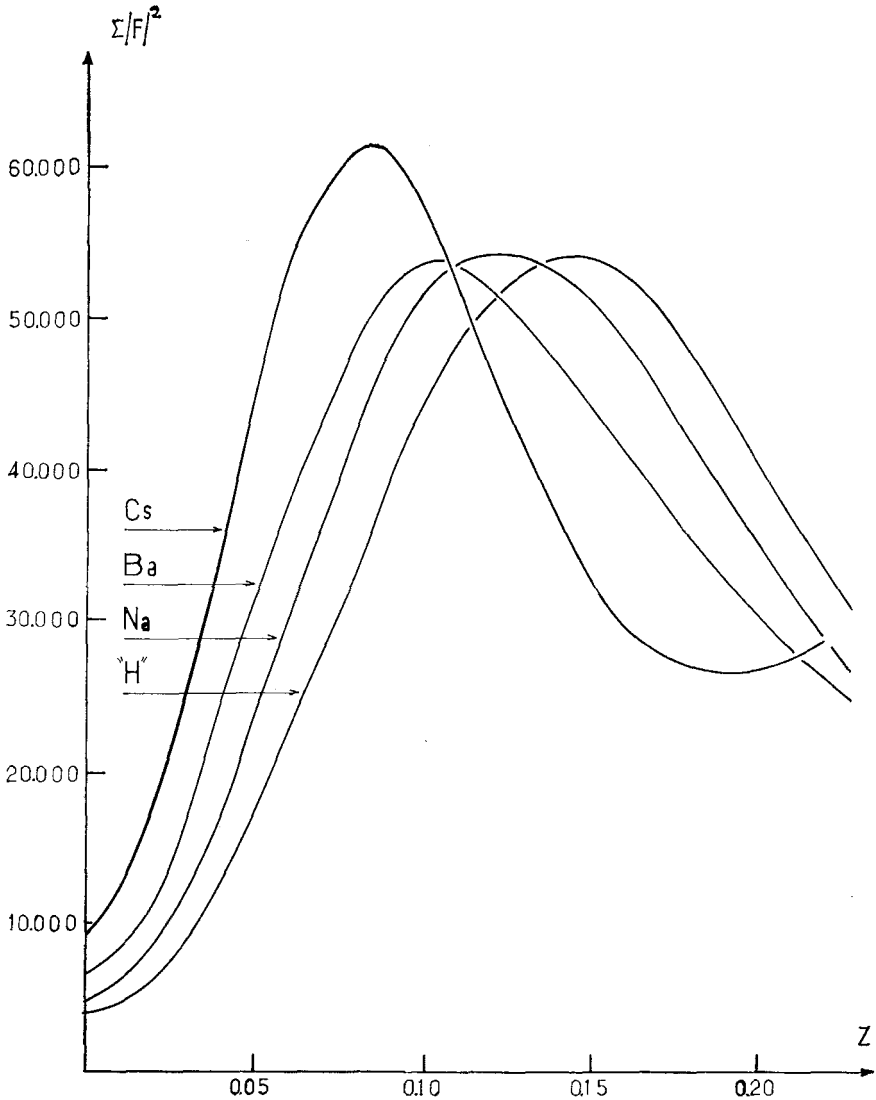


FIG. 1. Calculated values of $\Sigma |F|^2$ versus Z (in \AA^{-1}) for the 13, 20 bands of anhydrous montmorillonites saturated with various cations.

are not precisely the same, and most importantly the experimental profiles are all significantly sharper than the calculated profiles. This difference is not attributable to the assumed crystal size but most probably arises from the particular atomic parameters assumed in determining the $|F|^2$ curves.

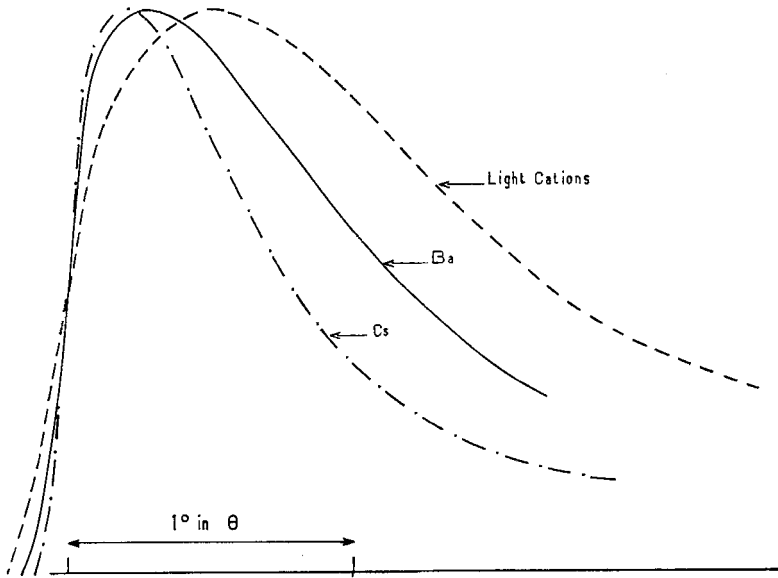


FIG. 2. Calculated intensity distributions in the 13, 20 bands of anhydrous montmorillonites saturated with various cations.

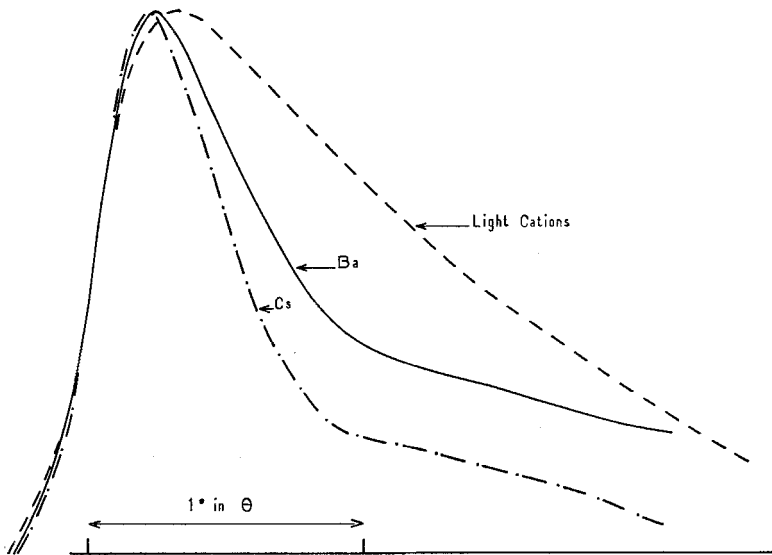


FIG. 3. Observed intensity distributions in the 13, 20 bands of anhydrous montmorillonites saturated with various cations.

The ideal layer structure model is such that $\sum |F|^2$ for the 13, 20 bands is always close to zero in the region of $Z=0$, (see Fig. 1); any less ideal arrangement of the atoms is likely to modify these curves quite considerably at small Z values and therefore to modify also the form of the calculated profiles.

It will be assumed at present that the agreement between Figs. 2 and 3 is sufficiently close to justify extending the discussion to the hydrated forms of the mineral.

Hydrated Na-Montmorillonites

Figure 4 shows the observed intensity profiles for Na-montmorillonites with zero, two, and three layers of water molecules. The diffraction bands sharpen with addition of water. These results differ from those previously

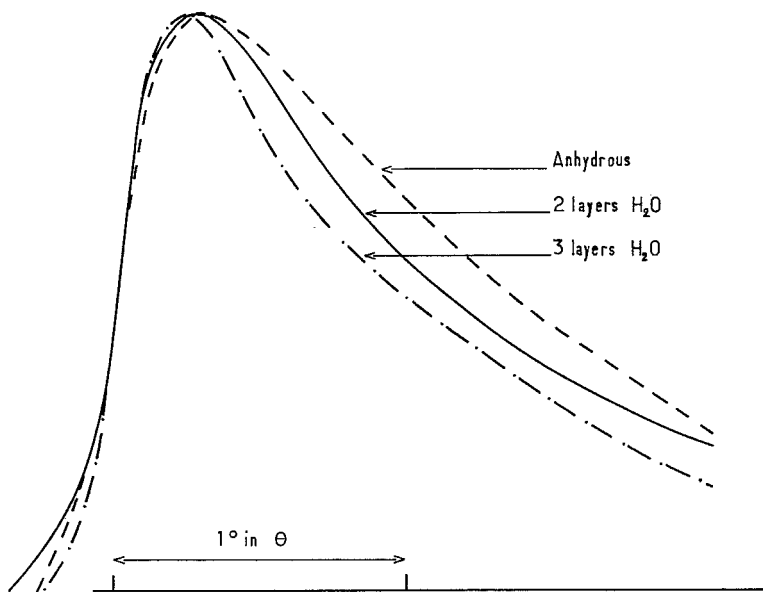


FIG. 4. Effect of hydration on the observed 13, 20 bands of Na-montmorillonite.

reported (*Ib*, p. 24) in which hydration of Na-montmorillonite produced no change in band profile, and which led to the conclusion that the hydration water of Na-montmorillonite behaved like a two-dimensional liquid. This conclusion needs reconsideration.

A change in the band profile with hydration implies either a movement of the exchangeable cations, and/or a significant degree of organization of the water molecules; this organization may be with respect to the silicate layer

surfaces, or among the water molecules themselves without respect to the silicate layer surfaces.

Since the Na ions contribute very little to the total scattering (see Fig. 1), the possibility that the variation in profile shown in Fig. 4 arises from their displacement can be excluded. One cannot, however, exclude the possibility of Na ion displacement, nor can one prove it from the diffraction band profiles. On the basis of one-dimensional Fourier syntheses, Pezerat and Mering (1958) concluded that during hydration of Na-montmorillonite, the Na ions are displaced very little from their positions adjacent to the silicate layer surfaces.

One is left with the conclusion that the hydration water has some degree of organization but whether this is with respect to, or independently of, the silicate layer surface is difficult to ascertain. It is regarded as certain that the previous conclusion that the water resembles a two-dimensional liquid needs modification, and is now seen as having been based on those diffraction bands which are less sensitive to structural details.

Hydrated Cs-Montmorillonite

Only a single layer of water can be introduced into Cs-montmorillonite. The diffraction profile, Fig. 5, is sharpened slightly by the introduction of water, which is consistent with the behavior of Na-montmorillonite. There

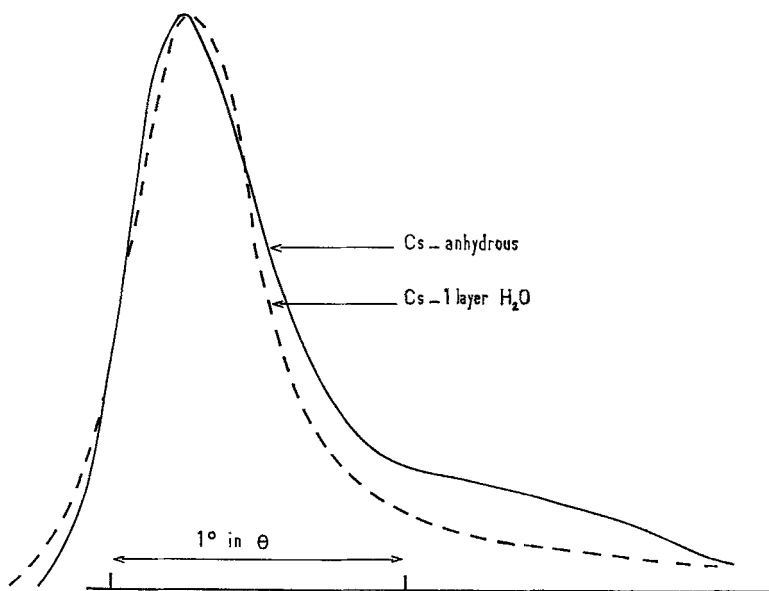


FIG. 5. Effect of hydration on the observed 13, 20 bands of Cs-montmorillonite.

is no large change in the band profile such as would arise if the Cs ions became randomly distributed; Fig. 2 indicates the big difference which would occur if the Cs ions moved from the "hexagonal" holes and took up less organized positions such that they no longer contributed to the coherent scattering. The present evidence supports the previous conclusion that the Cs ions remain attached to the silicate surfaces and are distributed over the "hexagonal" holes.

Hydrated Ba-Montmorillonite

The change in band profile produced by introduction of two water layers (Fig. 6) is rather small, but is mainly in the direction of giving a more diffuse

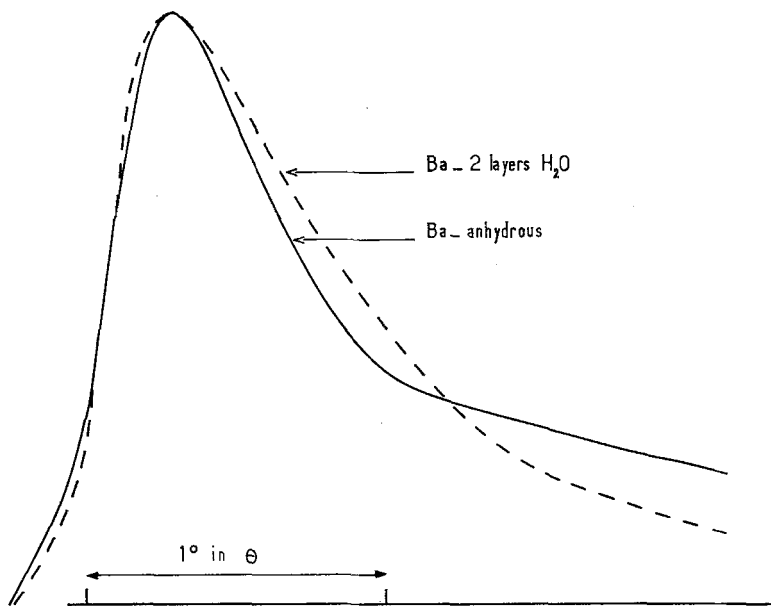


FIG. 6. Effect of hydration on the observed 13, 20 bands of Ba-montmorillonite.

band. In other words, the effect is contrary to that observed with Na-montmorillonite and to a lesser extent with Cs-montmorillonite. As with Cs-montmorillonite, the heavy Ba ions (though half as numerous) must play an important part in the total scattering. The broadening of the band points to the Ba ions taking up less specific sites with respect to the silicate layers, particularly if the broadened band is judged with respect to a sharpened band provided by partially organized water molecules.

The general conclusion regarding the Ba ions, therefore, is in the same

direction as that previously given (*Ib*, p. 26), namely that hydration causes the Ba ions to leave their statistically ordered positions in the "hexagonal" holes.

CONCLUSIONS

The 13, 20 diffraction profiles of montmorillonite are more sensitive to structural changes than the other two-dimensional profiles previously studied (*Ia*, *b*). This sensitivity is related to the rapid rise of $\sum |F|^2$ as Z increases (*cf.* Fig. 1).

Conclusions regarding the organization of water molecules and exchangeable cations in the hydrated forms must be stated more cautiously than in the previous discussion (*Ib*). The conclusion which stands out most firmly is that the Cs⁺ ions are not dissociated in the single layer hydrate. As before (*Ib*), it is tentatively assumed that other monovalent ions, such as Na⁺, will remain associated with the silicate layers, but the contribution of Na ions to the total scattering is so small that it is doubtful if this question can ever be categorically settled from considerations of band profiles.

The previous conclusion that the water layers resemble a two-dimensional liquid is not upheld. It appears that the water layers are organized sufficiently to modify the sensitive 13, 20 diffraction profiles. This organization of the water molecules is concerned with their parameters with respect to the *a*- and *b*-axes; their arrangement in layers, i.e. with respect to the *c*-axis, also is involved but is not the main consideration.

Turning finally to the case of Ba-montmorillonite, one would expect that if the two-layer hydrate is organized to the same extent as the two-layer Na hydrate, there would be a distinct sharpening of the profile. On the contrary, a broadening is observed which is quite appreciable particularly if considered with respect to a sharpened profile due to hydration. This broadening points to a dissociation of the Ba cations from the hexagonal holes, which agrees with the previous conclusions. The behavior of Ca-montmorillonite or of Mg-montmorillonite is of considerable interest, but these small divalent cations, which are half as numerous as monovalent ions, contribute little to the total scattering and there is little chance of seeing their behavior from changes in the band profiles. Results for these forms of montmorillonite would be of interest mainly in relation to the organization of the water molecules.

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