

X-ray Diffraction by a Randomly Interstratified Clay Mineral

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Preheated lithium montmorillonite when treated with glycerol shows random interstratification effects which appear to follow those predicted by the Hendricks & Teller treatment for a two-component system of 9.4 and 17.7 kX. repeat distances.

Introduction

The frequent occurrence of partially ordered layer lattices in clays makes it desirable that their X-ray diffraction patterns should be easily and surely interpreted. Hendricks & Teller (1942) have derived formulae giving the interference functions for a variety of different types of disorder. Although MacEwan (1949) and Brown & MacEwan (1950) have calculated from the Hendricks & Teller formulae the diffraction effects to be expected from the random interstratification of pairs of spacings likely to occur in soil clays, there has been no detailed experimental demonstration that the predicted effects do indeed occur.

Dehydration studies on montmorillonite by Greene-Kelly (1952) showed that lithium montmorillonite, when dehydrated by moderate heating, had a greatly reduced rate of uptake of glycerol, and the resultant material gave X-ray diffraction photographs closely similar to those to be expected for a two-component randomly interstratified system. Such a system would be suitable for detailed investigation, and the usefulness of the Hendricks & Teller treatment could be tested by comparing the calculated diffraction effects with those obtained experimentally.

Experimental methods

Oriented aggregates (Nagelschmidt, 1941) of lithium montmorillonite were prepared from a very fine fraction of Wyoming bentonite. These aggregates, provided that they were not heated above 100° C., gave a rational series of orders corresponding to $d(001)$ of 17.7 kX. when soaked in glycerol. If the aggregates were preheated to 190° C., they gave a rational series of orders corresponding to $d(001)$ of 9.4 kX. and the same pattern persisted after prolonged exposure of the specimen to moist air. The immersion of the flakes in warm glycerol resulted in a slow and random penetration of the individual crystallites, the X-ray photographs showing in consequence a non-rational series of $(00l)$ reflexions. The rate of penetration could be increased by increasing the temperature of the glycerol. At room temperature the rate of penetration was very slow and the specimens showed no change during photography. A series of photographs was obtained

for different immersion times in glycerol and the photographs were assumed to represent the effect of the random interstratification of spacings of 9.4 and 17.7 kX. in varying proportions. The final photograph, obtained after several weeks' immersion of an aggregate in glycerol at 100° C., still showed a non-rational series of reflexions. To cover the gap between this specimen and the unheated sample, lower pre-heating temperatures were tried but it became evident that the system had become more complex with contributions from a spacing of about 14 kX. For this reason no further specimens were prepared, since most of the changes predicted by the Hendricks & Teller treatment had already taken place.

Interpretation of photographs

Hendricks & Teller (1942), in the second section of their paper, considered the case where a finite number of phase shifts exists between layers and they have derived the interference function for mixed structures based on the following assumptions:

1. That all the layers have the same structure factor.
2. That the crystallites are of infinite extent.
3. That the succession of phase changes is completely random.

Of these the first and second are obviously impossible in practice. The first assumption is equivalent to assuming that the identical layers are separated by different distances but with no interlayer material to support these separations. However, if the layers themselves consist of relatively heavy atoms which are separated by material of lower scattering power, a formula based on the assumption that the layers have the same scattering power should be fairly accurate. Hendricks & Teller (1942) and Méring (1949) have both dealt with the case where the layers have different structure factors, but the additional complication of the calculations did not seem justified. The second assumption, that the crystallites are of infinite extent, would have the effect of making calculated diffraction maxima sharper than those from smaller crystallites. Méring (1949) has shown that the same type of diffractions are obtained with finite

crystallites but that the diffraction maxima are broader the smaller the number of unit layers in each crystallite.

In our calculations the Hendricks-Teller formula for infinite crystallites was used. This formula gives infinite values for the intensities of some of the peaks and hence, to give a better representation of what is obtained on the diffraction pattern, the intensity in these regions was averaged over a small range. It is only in the region of a sharp peak that this gives an appreciable change in the shape of the curve.

Hendricks & Teller's formula gives only that part of the total interference function which is conditioned by the distribution of the layers. The total scattered intensity is given by

$$I = F_i^2 \mathcal{E} \left[\frac{2p(1-p) \sin^2 \pi(d_2 - d_1)/d'}{1 - 2p(1-p) \sin^2 \pi(d_2 - d_1)/d' - p \cos 2\pi d_1/d' - (1-p) \cos 2\pi d_2/d'} \right],$$

where p is the proportion (expressed as a decimal fraction) of expanded layers and $(1-p)$ is the proportion of unexpanded layers,

d' is the apparent spacing as measured from the film (the term apparent spacing is used since d' , being a continuous variable, does not necessarily represent any interplanar spacing in the crystal),

d_1 is the higher interlayer spacing, d_2 is the lower interlayer spacing.

$\mathcal{E} = (1 + \cos^2 2\theta)/\sin 2\theta$ is a factor which is a function of angle of diffraction and in this case included the polarization and Lorentz effects only. No correction was applied for temperature effects, absorption by the specimen and orientation of the crystallites in the flake.

F_i , the layer structure factor, is given by

$$F_i = \sum_r n_r f_a^r \cos 2\pi Z_r / d',$$

where n_r = number of atoms of type r ,

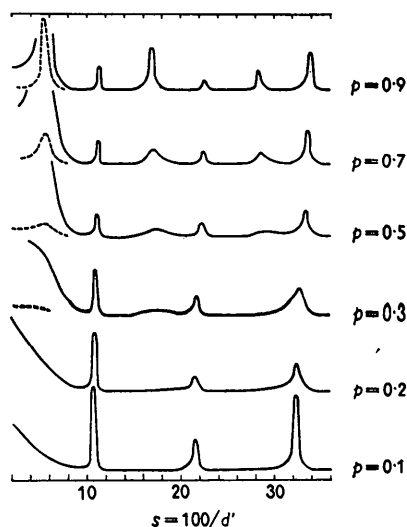


Fig. 1. Variation of total scattered intensity with p . The broken line in Fig. 1 and Fig. 3 denotes intensity reduced by a factor of 10.

f_a^r = atomic scattering factor for atoms of type r (these were obtained from James & Brindley (1931) and were modified assuming 50% ionization),

Z_r = co-ordinate of ions of type r in a direction perpendicular to the layers, the origin being the plane of the octahedrally coordinated ions.

A muscovite structure (Jackson & West, 1930) without interlayer cations was assumed for the layers of montmorillonite.

The calculated curves shown in Fig. 1 give the variations of the total scattered intensity with p . The intensity was calculated at intervals of 0.5 in $s = 100/d'$, except in the region of a peak where calculations were made at intervals of 0.1 in s . The intensity distribution is plotted on an arbitrary scale

which is constant for all curves and covers a range of apparent spacing from 50 to 2.78 kX. Fig. 2 shows the variation in the position of the peaks of important

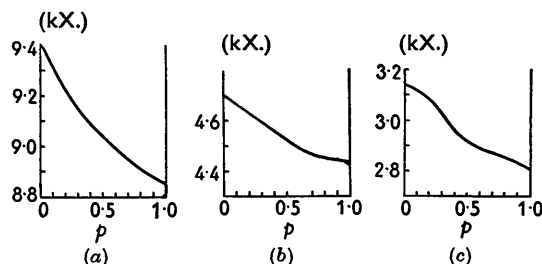


Fig. 2. Variation in the position of the peaks of important maxima with p .

maxima with p . These curves are derived from those shown in Fig. 1.

The variables of the diffraction patterns which were compared with the calculated curves were the position, intensity and shape of the maxima. The positions of these maxima were found by the direct measurement of their apparent spacings, and their intensities and shapes were obtained from microphotometer traces. A linear relation between blackening and intensity was assumed. This is practically true except for strong reflexions. In order to compare

Table 1

Photo-graph	Spacing of 9 kX. line (kX.)	p	Calculated spacings (kX.)	Observed spacings (kX.)
1	9.25	0.18	4.67	4.63
			3.09	3.08
			4.60	4.57
2	9.20	0.26	3.07	3.04
			18.52*	†
			5.72*	5.65
3	9.08	0.48	4.52	4.52
			3.45*	3.42
			3.015	3.02

† Much central scatter.

the calculated with the experimental curves it is necessary to know the value of p for the state of the specimen when each photograph was taken. Since the positions of the diffraction maxima move as p changes, it is possible to estimate p for any photograph from the positions of any of the maxima. From the curve shown in Fig. 2(a) the value of p corresponding to each photograph was obtained from the measured apparent spacings of the reflexion in the region of 9 kX. Using this p value the calculated

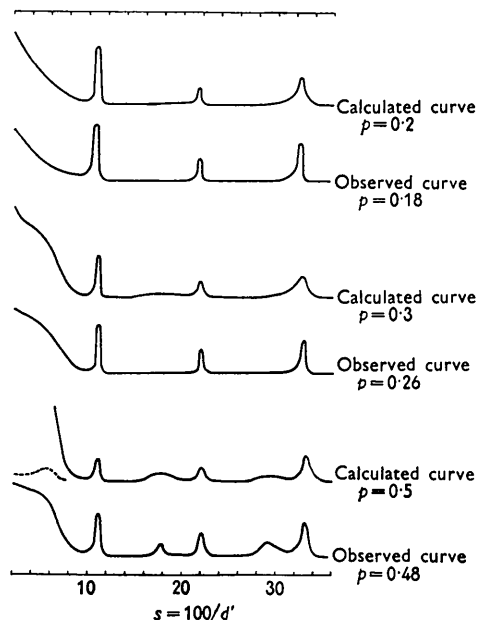


Fig. 3. Experimental microphotometer traces and calculated intensities of the diffraction maxima.

spacings of the other diffraction maxima were read off from Fig. 2(b) and (c), and Table 1 shows that agreement is good between these values and the observed values.

The spacings in Table 1 marked with an asterisk are for $p = 0.5$ as they cannot be obtained from Fig. 1 or 2 for $p = 0.48$.

Fig. 3 shows the experimental microphotometer traces after subtraction of background and calculated intensities of the diffraction maxima. The experimental traces for photographs 1, 2 and 3 are compared with the calculated intensity distribution curves for $p = 0.2$, $p = 0.3$ and $p = 0.5$ already shown in Fig. 1. Here again agreement is good.

The material used for the third photograph appears to have a p value of about 0.5, i.e. half the layers can be expanded by glycerol. It is interesting to note that pyridine sorption measurements on samples of lithium montmorillonite heated to 190° C. showed about half the uptake of unheated samples.

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A Hexagonal Modification of a Salt of Millon's Base

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A hexagonal modification of Hg_2NBr has an Hg_2N^+ framework based upon the idealized tridymite (SiO_2) structure, with Br^- in the interstices. The unit-cell dimensions are $a = 6.65$ and $c = 11.26$ Å. The deviation of the axial ratio $c/a = 1.693$ from the ideal value of 1.633 is probably related to the slightly greater stability of this hexagonal modification as compared with the cubic form in which the Hg_2N^+ framework is based upon the cristobalite structure. The Hg-N bond distance is 2.06 Å.

A correction of 1.6% in the lattice constants of the HgNH_2Br structure is given.

An interesting analogy exists between the idealized SiO_2 structures and the Hg_2N^+ framework in Millon's base and its salts. In the cubic modification (Lipscomb, 1951a) the Hg_2N^+ framework has the idealized cristobalite structure. In the hexagonal modification described here a similarly idealized tridymite structure

exists for Hg_2N^+ in which Si is replaced by N, thus forming regular tetrahedral bonds and Hg replaces O, forming linear bonds at 180° angles. The bromide ions fit into the interstices of this framework, as described below.

This study is part of a more general program of