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X-ray studies of defects in clays

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Defects are any departures from the ideal well-ordered structure. Defects in clays can be classified in three categories: those affecting the layers themselves (*cis*- or *trans*-vacancies, rotation of tetrahedra, localization of the isomorphous substitutions, etc.); those specific to the interlamellar space (position of the cations and, for example, of the water molecules); and stacking faults (including a change in the nature of stacked layers). X-ray studies of clays usually involve the analysis of powder diagrams generally perturbed by a partial orientation of the particles in the powder. The paper will present a general approach to the determination of defects in clays with an indirect method of analysis. The intensities and shapes of the diffraction bands are calculated for model structures and are fitted to the experimental pattern. In such an approach the powder orientation, the shape and sizes of the coherent domains, the various backgrounds and perturbations due to the apparatus are taken into account.

1. Introduction

Defects can be defined as any departures from the ideal well-ordered structure. It is well known that the presence of structural faults in the clays modifies some of their properties and, consequently, their behaviour and use.

Defects in clays can be classified in three categories.

(1) Those affecting the layers themselves, such as: (i) localization of the octahedral vacancies in *cis*- or *trans*-positions; (ii) rotation of tetrahedra leading to a more or less important deformation of the 'hexagonal' cavities. This rotation depends, partly, on the interlamellar cation size.

(2) Those specific to the interlamellar space and corresponding with a modification of the positions of either cations or intercalated molecules or both. This kind of defect appears, for instance, when the number of energetically equivalent sites is higher than the number of cations or molecules in these sites.

(3) Stacking faults that concern either only the relative position of layers (translational or rotational stacking faults) or the kind of successive layers (mixed layer structures).

Lamellar silicates with irregular and disordered structures present a particle size range between 5 nm and 10 μm and only powders can be used for the X-ray diffraction studies.

To recognize the kind, the proportion and the distribution rule of structural defects in clays, the powder pattern analysis is always made with an indirect approach that consists of predicting the effect on the diffraction phenomenon of one given kind of fault. Brindley & Robinson (1946) have been the first to use such a way of research to interpret patterns of disordered kaolinites: to explain the simultaneous presence of hkl reflections (with $k = 3n$, n integer) and of (hk) bands (with $k \neq 3n$), these authors had suggested the existence of translational $\pm\frac{1}{3}\boldsymbol{b}$ stacking faults. Since these years, much work has been devoted to qualitative and then quantitative interpretation of the powder patterns of phyllosilicates that contain a large amount of structural defects. A good survey of these studies is given in the book edited by Brindley & Brown (1980). We shall just point out some fundamental works: those of Mering who was the first to explain, by means of a mathematical formalism, the main features of powder patterns of lamellar systems that contain different kinds of defects (Mering 1949). In the same way, MacEwan (MacEwen *et al.* 1961), Drits (Drits & Sakharov 1976) and Reynolds (1980) have given principles of calculation and interpretation of the $00l$ intensity distribution for the interstratified clay minerals.

All these studies were made on the basis of an indirect analysis of patterns consisting of devising a structural model adapted to each clay mineral studied. The model takes into account the presence of different kinds of defects with their abundances and the rule of their distribution. By starting from such a model, a synthetic pattern is calculated. Then, by modifying the values of characteristic parameters of the defects, the theoretical diagram is fitted with the experimental one, the agreement being obtained simultaneously for profiles and for intensities of the reflections.

Now such a method based on the model is fully developed, mainly in the Soviet and French laboratories of clay crystallography.

The following will be devoted to the description of modelling possibilities and to the power of this method for the determination of defects in clays.

2. Experimental conditions and principle of calculation

An effective modelling method requires, first of all, the recording of patterns in very rigorous experimental conditions in which all the functions that can perturb the diffraction phenomenon are controlled. Specifically, it is necessary to use monochromatic radiation, to have good precision in the intensity measurements and good angular resolution, to control the width of the beam and slits, the thickness of samples and the orientation of particles in the powders. Most of the disturbing functions can be minimized so as to give effects in patterns several times lower than those generated by defects. When such a function cannot be neglected, it is necessary to characterize its influence by introducing it to calculations. This is the case, for instance, with the residual orientation of particles in powder. The orientation distribution is experimentally determined from the $00l$ reflections (Taylor & Norrish 1966; De Courville *et al.* 1979). Calculations show that orientation influences relative intensities of reflections as well as their profiles (Plançon & Tchoubar 1977; Plançon 1980). Figure 1 illustrates this phenomenon for a partly disordered kaolinite (Plançon 1980). Curves correspond to the (02, 11) and (20, 13) domains. For random orientation, the calculated diagram is represented by the dashed line, while the solid line is obtained with the particle orientation given in figure 2.

As for the mathematical formalism that describes the diffraction phenomenon, it varies with authors. Nevertheless it seems that the most powerful is the matrix notation. It was introduced for lamellar systems by Hendricks & Teller in 1942. Since then, several papers have developed analogous formalisms adapted to the complexity of the structural model considered or to the kind of reflections studied (Kakinoki & Komura 1952; Drits & Sakharov 1976; Plançon & Tchoubar 1976, 1977; Plançon 1981; Sakharov *et al.* 1982*a*, *b*).

In the general case, for a powder with particle orientation, various thicknesses of coherent domains, where each stack contains, simultaneously or not, (i) layers of different kinds, and (ii) different translations or rotations between these layers (with or without correlations between the defects), the intensity diffracted at the 2θ angle by an hk rod is given by:

$$I_{hk}(s) = \frac{1}{s\Omega\sigma}\sum_{M}\alpha(M)\int \bar{N}(\phi)\ \mathrm{trace\ Re}\,\{[F]\,[W]\,[R(M)]\}\ T(X)\ \mathrm{d}\phi,$$

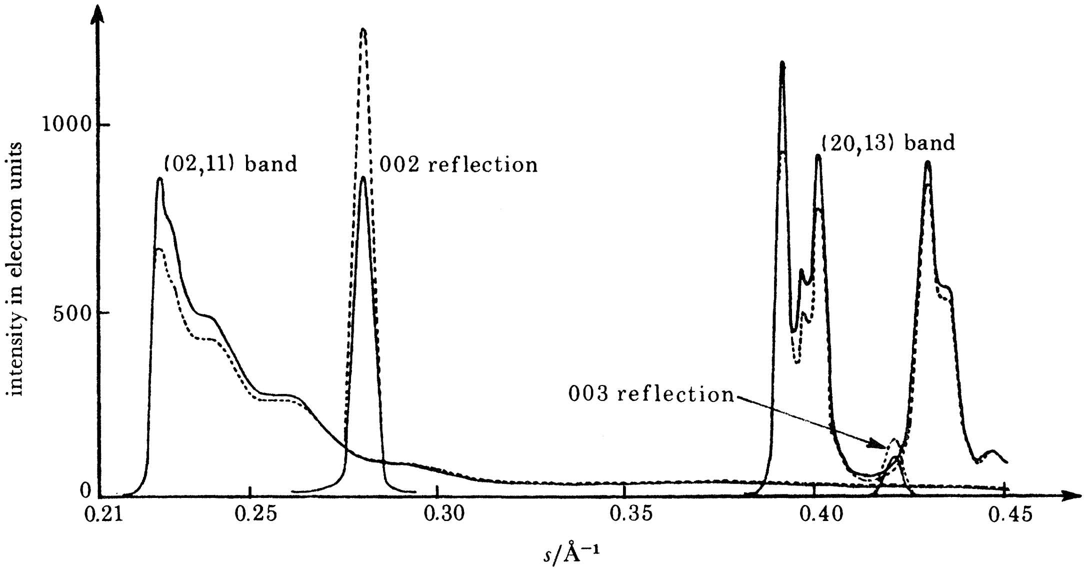

Figure 1. Effect of particle orientation on the X-ray intensities in the case of symmetric transmission; dashed line: sample with random particle orientation; solid line: sample with particle orientation corresponding to figure 2.

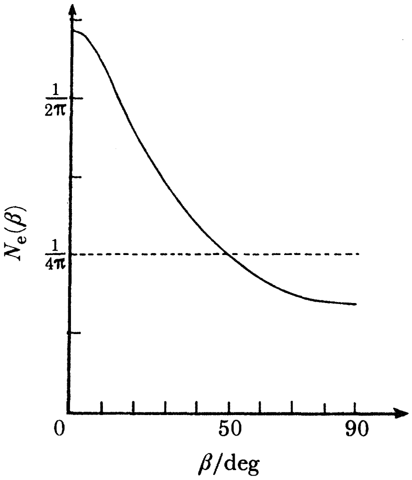

Figure 2. Orientation function that defines the orientation of particles in the powder.

where $s = 2 \sin \theta/\lambda$ is the modulus of the scattering vector; Ω is the area of the $(\boldsymbol{a}, \boldsymbol{b})$ unit cell; σ is the area of the coherent interferential domain in the $(\boldsymbol{a}, \boldsymbol{b})$ plane; $\alpha(M)$ is the statistical weight distribution of the stackings with M layers; ϕ is the angle between the scattering vector and a plane normal to the *hk* rod. Summation ϕ expresses a powder pattern calculation and the integration includes the effect usually described by the Lorentz factor; $\bar{N}(\phi)$ is the proportion of particles in powder which participate in diffraction at the chosen 2θ angle. $\bar{N}(\phi)$ is obtained from the experimental orientation function (De Courville *et al.* 1979; Plançon & Tchoubar 1977; Plançon 1980); $T(X)$ is a function characteristic of the shape and sizes of the coherent interferential domain. It has been introduced in the powder integration by Brindley & Mering

(1951); $[F]$, $[W]$, $[R(M)]$ are three square matrices describing the structural model itself and Re means real part of their product; $[F]$ is the matrix characterizing the layer kinds; each ij matrix element is equal to $F_i^* F_j$, product of the structure factor F_j of the j-type layer by the conjugate structure factor F_i^* of the i-type layer; $[W]$ is the matrix that takes into account the abundance of each layer kind; $[R(M)]$ is the matrix that expresses the interference phenomenon between the waves scattered by the different layers of a stacking. This matrix takes into account the relative positions of layers, the kind and rate of stacking faults and their distribution.

The complexity of these matrices varies with the choice of the structural model, but the $I_{hk}(s)$ relation permits calculation of all kinds of powder patterns observed with clay minerals, even if more or less long range correlations exist either between layers or between defects or both (Plançon 1981).

The principle of defect determination by fitting of theoretical and experimental patterns leads immediately to a question: is it possible to obtain practically the same calculated diagram, starting from several absolutely different models?

For the purpose of answering the question, a systematic analysis, based on the crystallochemical viewpoint of the relationship between structural characteristics and diffraction patterns, has been made for the dioctahedral phyllosilicates (Drits *et al.* 1983). This study has shown that each kind of fault and structural characteristic leads to specific features in definite parts of the patterns and is insensitive in others.

A general approach to defect and fine structure determination for a given clay should include:

(1) successive consideration of all models which are crystallochemically possible;

(2) calculation, in all accessible domains of the reciprocal space, of intensity distribution and profile variation, obtained by changing only one parameter at a time that defines one type of structural feature (e.g. cation distribution in individual layers, nature of stacking faults, etc.);

(3) Systematic analysis of the calculated diffraction patterns to establish the diffraction criteria which will help to interpret the experimental data;

(4) Agreement of experimental and calculated diffraction patterns, to obtain the values of all parameters characteristic of the defects and fine structure of the studied mineral.

Such an approach will be illustrated by some examples.

3. Examples of X-ray studies of defects in clays

(*a*) *Specific modifications in intensity distribution correlated with the kind of stacking faults*

The more frequently imagined and crystallochemically possible stacking faults are:

(i) arbitrary translations or rotations of layers in their plane (probability of observing such a fault between two adjacent layers is p_A).

(ii) faults which we will name 'partly defined faults', in contrast to the arbitrary ones: they correspond to ± 120° or n 60° rotations of successive layers or to $-\frac{1}{3}n\boldsymbol{a} \pm \frac{1}{3}m\boldsymbol{b}$ translations (with $n = 0$ or 1, $m = 0$ or 1).

If the structural model contains only arbitrary stacking faults, calculations show, as is well known, an evolution of the pattern to a superposition of two-dimensional (hk) bands when p_A increases. In contrast, the presence of only 'partly defined' faults does not modify identically all the (hk) domains and moreover each kind of these faults can be identified.

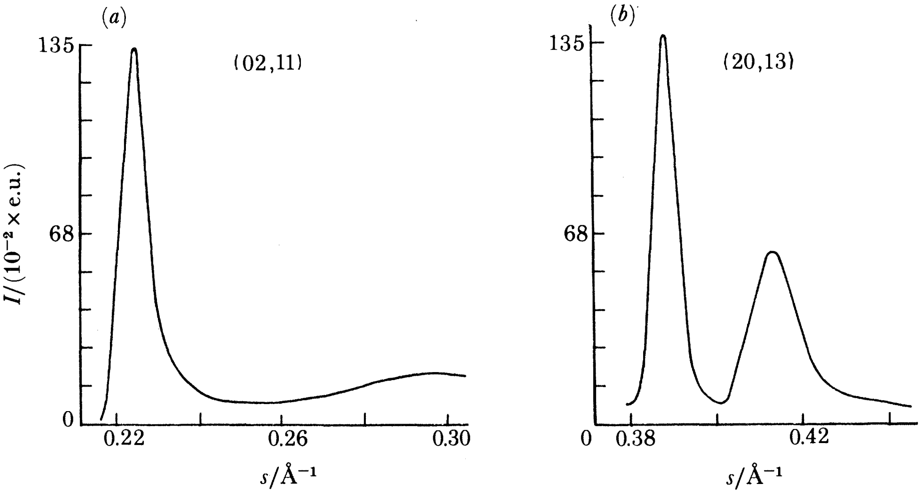

Figure 3. Calculated profiles for a *cis*-vacant dioctahedral smectite containing $\pm n\,60°$ rotational stacking faults ($p_r = 0.67$). (*a*) (02, 11) band; (*b*) (20, 13) band.

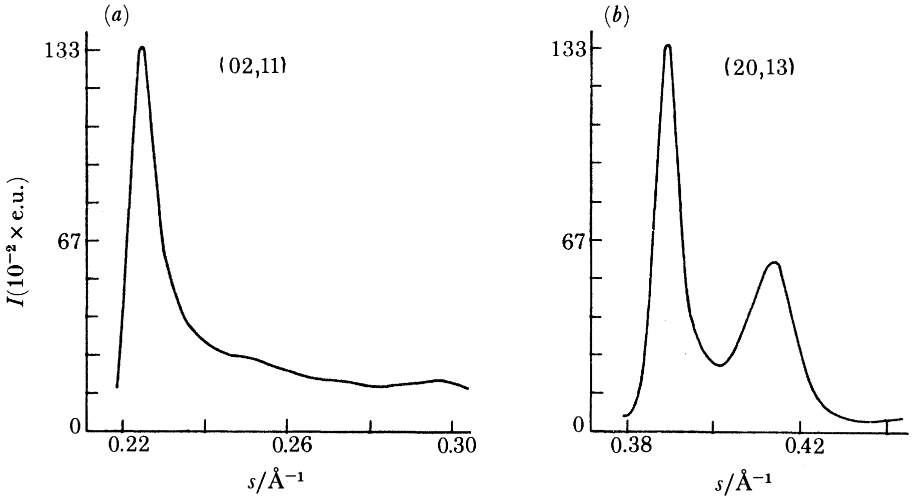

Figure 4. Calculated profiles for a *cis*-vacant dioctahedral smectite containing $-\frac{1}{3}na \pm \frac{1}{3}mb$ ($n = 0$ or 1, $m = 0$ or 1) translational stacking faults ($p_t = 0.67$). (*a*) (02, 11) band; (*b*) (20, 13) band.

For instance it is also well known that ± 120° faults can be easily distinguished from the $\pm\frac{1}{3}\boldsymbol{b}$ translations on the basis of the (20, 13) domain which is strongly modified only in the case of rotational faults.

The distinction is not so evident in the case of n 60° and $(-\frac{1}{3}na \pm \frac{1}{3}mb)$ faults. Figures 3 and 4 correspond to a dioctahedral smectite with *cis*-vacant positions and containing a probability p_R or p_T, equal to 0.67 of observing a stacking fault between adjacent layers (Drits *et al.* 1984). A superficial qualitative examination seems to reveal a strict analogy between the patterns calculated in the (02, 11) and (20, 13) domains respectively: for the two types of faults, there exists only one modulation at $s \approx 0.415$ Å^{-1}† on the two (20, 13) bands, and the two (02, 11) bands present a strong tendency to a two-dimensional structure. But in fact a quantitative comparison of the two patterns shows that the (20, 13) band corresponding to n 60° faults has,

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† 1 Å = 10^{-10} m = 0.1 nm.

at $s \approx 0.40$ Å^{-1}, a minimum more clearly pronounced. In the same way, for the translational faults, the (02, 11) band presents an almost regular decrease of the intensity between $s \approx 0.23$ Å^{-1} and $s \approx 0.30$ Å^{-1}, while in the case of n 60° faults a minimum at $s \approx 0.25$ Å^{-1} is visible as well as a modulation at $s \approx 0.30$ Å^{-1}.

(*b*) *Determination of defects inside the layers*

Clays defects inside layers usually concern modifications of a part of the atomic positions in the unit cell or modifications of the kind of cations. Because of the weakness of the X-ray atomic scattering power, it is often difficult to detect these categories of defects in the pattern of a natural untreated clay. Such a sample generally contains a large amount of stacking faults which gives a more important intensity modification than defects inside the layers. To reveal these defects it is necessary to minimize the effects of stacking faults by reorganizing the stack. Two ways permit one to obtain better ordering in the layer stackings: by K-saturation and several wetting and drying cycles (Mamy & Gaultier 1976) or, more simply, by Cs-saturation (Besson *et al.* 1983).

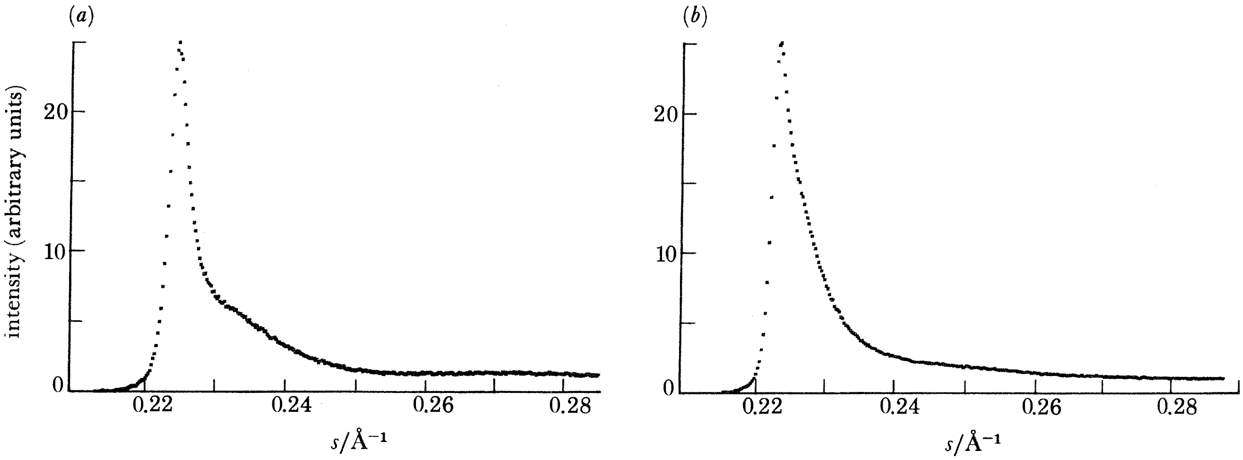

FIGURE 5. Experimental (02, 11) band profiles of anhydrous Na-beidellites. (*a*) Black Jack Mine beidellite; (*b*) Rupsroth beidellite.

If we plan to determine, for example, the nature of octahedral vacancies in a dioctahedral smectite, the analysis of the Na-saturated mineral does not lead to a conclusion. Figure 5 shows the experimental (02, 11) bands of the Black Jack Mine Na-beidellite (figure 5*a*) and of the Rupsroth Na-beidellite (figure 5*b*) in the anhydrous state: the (02, 11) bands are very similar (slight differences are localized in a part of the pattern sensitive to the nature of stacking faults) and do not permit any statement about octahedral vacancy positions. But calculations of the diffraction (02, 11) domain for a model of anhydrous Cs-beidellite leads to very different patterns whether vacancies are in *trans*-positions (figure 6*a*) or in *cis*-positions (figure 6*b*), or are statistically distributed between all octahedral sites (figure 6*c*). Comparing these theoretical patterns with the experimental ones obtained from Black Jack Mine and Rupsroth anhydrous Cs-beidellites (figures 7*a* and *b*), it can be concluded, without any ambiguity and even on the basis of only qualitative examination, that the Black Jack Mine beidellite has *trans*-vacant octahedral sheets while these sheets are *cis*-vacant in the Rupsroth beidellite (Besson 1980; Besson *et al.* 1983). A quantitative study, with agreement of intensities and profiles between

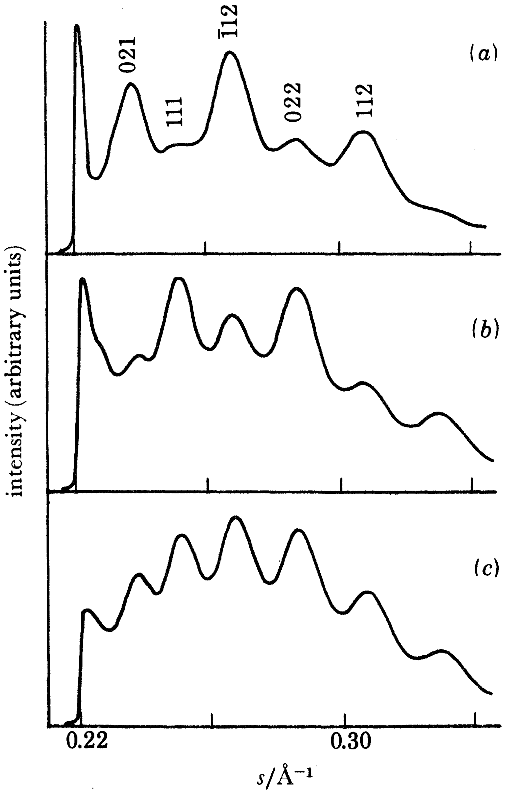

Figure 6. Calculated (02, 11) band profiles of anhydrous Cs-beidellite with three different positions of the octahedral vacancies. (*a*) Vacant *trans*-positions; (*b*) vacant *cis*-positions; (*c*) statistical distribution of vacancies between all the octahedral sites.

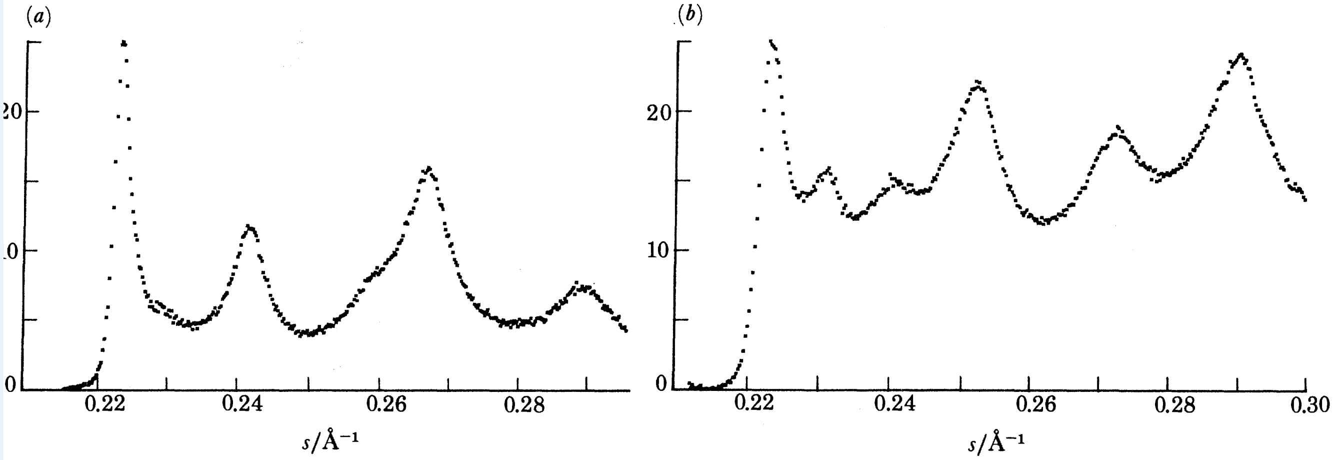

Figure 7. Experimental (02, 11) band profiles of anhydrous Cs-beidellites. (*a*) Black Jack Mine beidellite; (*b*) Rupsroth beidellite.

calculated and experimental patterns, shows that the presence of faults in the octahedral vacancies positions cannot be detected if the proportion of defects is less than 10% (because of the existence of residual stacking faults).

(*c*) *Distribution of atoms and molecules in the interlamellar spaces*

This problem will be illustrated by work of Ben Brahim *et al.* (1984) concerning the X-ray study of the two-water-layer homogeneous hydration state of the Rupsroth Na-beidellite.

Three different categories of sites are proposed in the literature for water molecules in the two layer homogeneous state of hydrated clays. The water position projections on the (***a***, ***b***) plane are given in figure 8*a*: we distinguish (i) sites projected near the basal oxygens of the layer (A_1 sites), (ii) those projected close to the tetrahedral cations (B sites), and (iii) those neighbouring to the centre of the 'hexagonal' cavities (C sites).

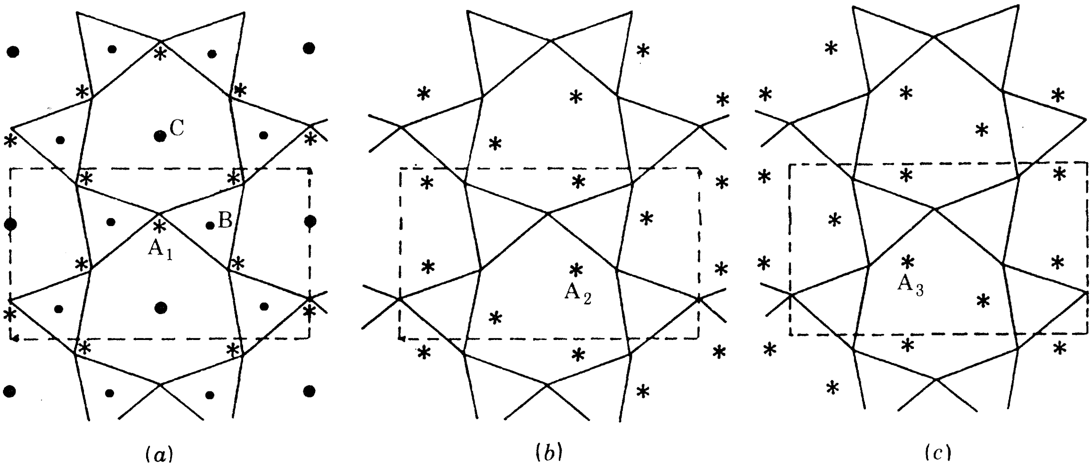

FIGURE 8. Projection, on the (***a***, ***b***) plane, of possible water molecules sites in a two-water-layer hydration state of smectite. (*a*) First possibility with three types (A_1, B, C) of water positions. (*b*) and (*c*). Enantiomorphic distributions (A_2 and A_3) of the A sites, obtained by changing *y*-coordinates of A_1 sites into $y \pm \frac{1}{3}$.

Seeing that the two B and C site categories can be deduced from one another by changing their *y*-coordinates into $y \pm \frac{1}{3}$, the authors have imagined a simultaneous identical modification of the *y*-coordinates of the A_1 sites, leading to two enantiomorphic A_2 and A_3 site distributions (see figure 8*b* and *c*).

Theoretical pattern calculations have led to the following conclusions.

(1) The (20, 13) domain does not permit one to distinguish A_1, A_2, A_3 sites from one another, or B sites from C sites. In this diffraction domain, profiles and intensities of reflections are sentitive only to the ratio $(A_1+A_2+A_3)/(B+C)$, $(A_1+A_2+A_3)$ and $(B+C)$ being the total quantity of water molecules in the A and $(B+C)$ sites.

(2) The (02, 11) domain varies with the B/C ratio, but it is also absolutely insensitive to the sharing of water molecules between the different A site types.

(3) On the other hand the (04, 22) domain shows important differences depending on whether A_1 or A_2 sites are occupied (but patterns are identical for the two enantiomorphic A_2 or A_3 situations).

The comparison of the calculated and experimental X-ray data, in the (04, 22) domain,

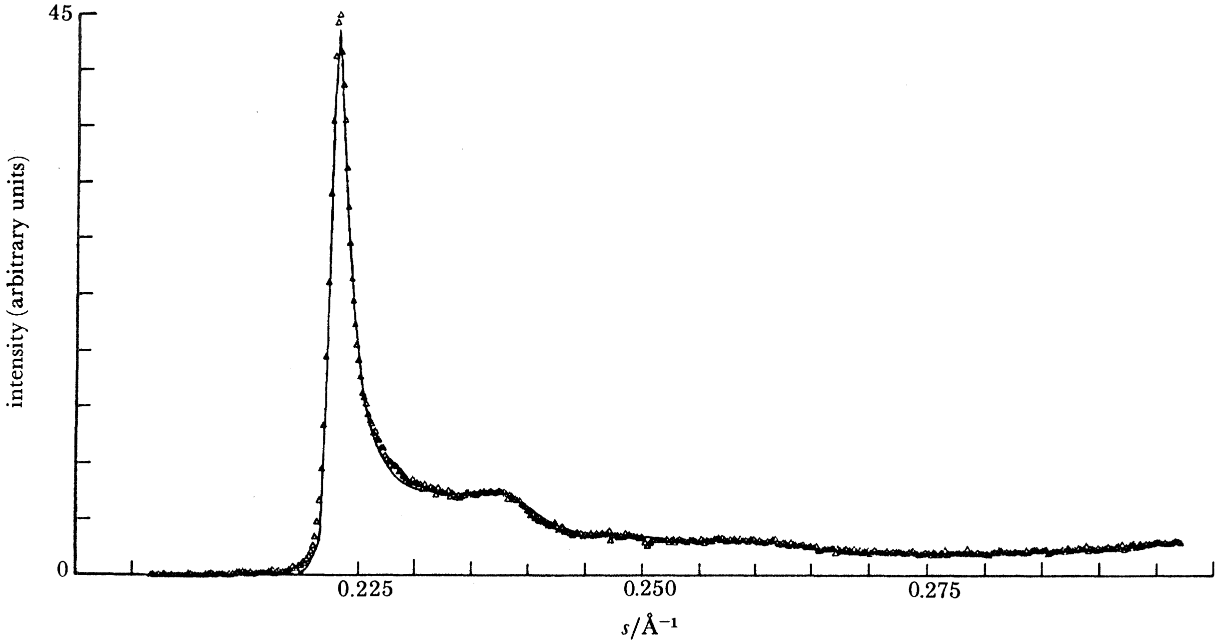

FIGURE 9. Two-water-layer Na-beidellite: agreement between the calculated and experimental patterns in the (02, 11) domain.

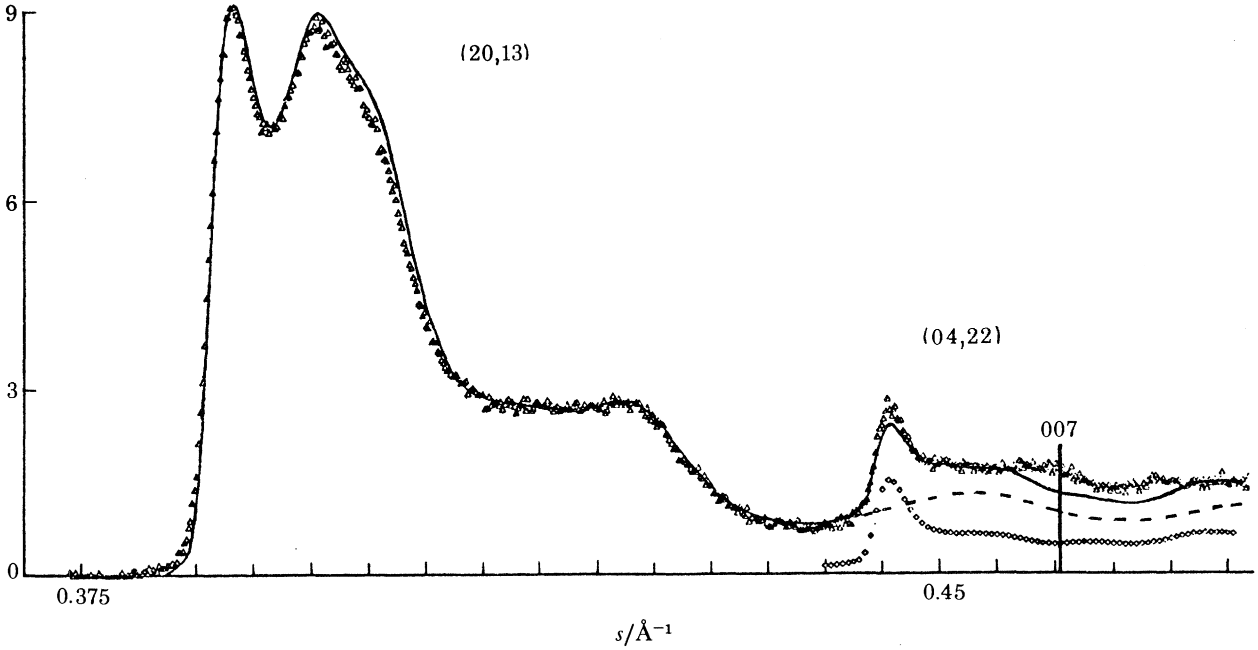

FIGURE 10. Two-water-layer Na-beidellite: agreement between the calculated and experimental patterns in the (20, 13) and (04, 22) domains.

leads to the conclusion that A_1 sites are vacant and A_2 (or A_3) sites are occupied; but simultaneous A_2 and A_3 occupations in the same water sheet is excluded.

The number of water molecules per unit cell and their *z*-coordinates are defined from the comparison of ratios I_{001}/I_{003} and I_{001}/I_{005} (Ben Brahim *et al.* 1983). And finally proportions of water molecules distributed between the B, C and A_2 (or A_3) sites are determined by fitting the profiles and intensities of the calculated pattern with the experimental one, simultaneously in the (02, 11), (20, 13) and (04, 22) diffraction domains.

Final agreement is given in figures 9 and 10 where calculated curves are full lines and experimental intensities, point by point, are represented by triangles. Figure 9 corresponds to the (02, 11) band and figure 10 to the (20, 13) and (04, 22) bands; the curve represented by squares is the calculated (04, 22) band before superposition of the (20, 13) band tail (dashed line). The agreement is obtained with the following structural characteristics:

(i) Probability of arbitrary stacking faults: $p_A = 0.74$;

(ii) *z*-coordinates of water molecules: $z = \pm 6.3$ Å (origin at the centre of the octahedral sheet);

(iii) total number of water molecules per unit cell: 10.8;

(iv) number of water molecules in A_2 (or A_3) sites: 7.5; in B sites: 2.6; in C sites: 0.7.

4. CONCLUSIONS

The modelling method is the only way that permits the interpretation of an important part of the problem connected with determination of defects in clays by X-ray powder pattern studies. It is effective even if the experimental pattern is reduced to successive poorly modulated (*hk*) bands. However, to find the concentration and nature of principal defects in each clay, it is necessary, in all cases (i) to obtain 'good' experimental patterns (that is, to control experimental conditions exactly); and (ii) to fit the calculated diagrams with the experimental ones quantitatively, not only on the basis of profile agreement but also by comparing the intensity values. Obviously, the better the ordering of each stacking, the more precise the solution will be.

It is also necessary to emphasize that imagining a model that contains structural defects does not mean making an arbitrary choice between an infinity of possibilities. In practice, this choice must always be controlled by crystallochemical considerations. It also depends on the set of data described in the literature obtained by means of different, not only diffractometric, techniques. In such conditions, the choice is considerably reduced and only a few models must be tested.

Finally it can be noted that it is always better not to limit a determination of defects to the X-ray pattern analysis only. It is preferable to associate other complementary techniques such as electron microscopy, electron and neutron diffraction, and different spectroscopic methods.

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